

Synthesis, characterization and modeling of sodium titanate nanostructures for energy storage applications

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RESUMEN

En esta tesis se presenta un estudio completo de las propiedades físicas de titanatos de sodio e hidrógeno nanoestructurados sintetizados por el método hidrotermal, con posibles aplicaciones en el diseño de dispositivos para almacenamiento de energía. Estos compuestos presentan un gran número de aplicaciones, dentro de las que destacan la conversión de energía fotovoltaica, aplicaciones biomédicas, sistemas de catálisis, prototipos de purificación de agua y aire, sensores de humedad y almacenamiento de energía. Esta última aplicación ha tenido un reciente impulso al aparecer como una alternativa prometedora a las tecnologías basadas en litio, por los aspectos colaterales que trae aparejado (ej. costo económico e implicacias ambientales). Una señal de este impulso es el ranking publicado por IUPAC en el año 2023 sobre las diez tecnologías emergentes más relevantes del año 2022, en donde las Baterías de Ión Sodio (SIB) se encuentran listadas.

El método hidrotermal se presenta como un método económico, robusto y fácilmente escalable para sintetizar nanoestrucrturas de titanatos, y es el método de síntesis elegido en el presente proyecto de tesis. Se exploraron diferentes condiciones de síntesis, tales como: temperatura del reactor, tiempo de reacción y pH de reacción. De este modo se obtuvieron diferentes materiales con diferentes carácterísticas, entre ellas morfológicas: nanorods, nanopartículas y nanotubos, siendo estos últimos la morfología predominante en las condiciones estudiadas. Sobre los materiales preparados se estudiaron sus carácterísticas estructurales, variaciones morfológicas, propiedades vibracionales, propiedades ópticas, propiedades de transporte eléctricas y su comportamiento con la variación de la temperatura.

Los nanotubos de titanatos, ya sean de sodio o de hidrógeno, muestran una morfología laminar consistente de láminas que se estabilizan mediante mecanismos de enrollamiento. Esto implica una gran dificultad a la hora de tratar de comprender las propiedades estructurales de las muestras, habiendo aún al día de hoy un amplio debate sobre las fases cristalinas que conforman las estructuras cristalinas que hacen a estos nanotubos. Técnicas basadas en absorción de rayos X y difracción de rayos X, permitieron determinar posibles entornos locales y órden de largo alcance del titanio y posibles fases presentes en las muestras en los sistemas de titanatos. Estas contribuciones fueron empleadas para interpretar los datos, obteniendo la fase trititanato $(Na_xH_{(2-x)}Ti_3O_7 \cdot nH_2O)$, con diferentes proporciones de Na/H como una de las mas viables en estas muestras. Simulaciones computacionales basadas en métodos por *Primeros Principios* fueron realizadas teniendo en cuenta la fase tri-titanatos $(Na_xH_{(2-x)}Ti_3O_7)$ y la hexa-titanatos $(Na_xH_{(2-x)}Ti_6O_{13})$ sugeridos por estudios de difracción luego de un proceso de calentamiento y calcinación. En todos los casos se observa que es posible la coexistencia de ambas fases, así como la presencia de agua estructural en los espacios interlaminares y también la presencia de agua de hidratación.

Al estudiar las propiedades electrónicas se observó una fuerte dependencia de las mismas con las proporciones de Na/H. Se evidencian procesos de transporte electrónico a frecuencias intermedias, inexistentes en muestras con baja proporción de Na/H. De la interpretación de los resultados de las medidas de transporte eléctrico pudimos inferir la presencia de al menos dos procesos de conducción intrae inter-grano con tiempos característicos del órden de μs y ms respectivamente. El tercer proceso se oberva en muestras sometidas a temperaturas altas y tiempos prolongados de síntesis, mostrando tiempos carácteristicos del órden de los ms. Las medidas de absorción óptica también muestran la presencia de estados de impureza electrónico, sobre todo en aquellas muestras con mezclas de proporciones Na/H marcadas. Tanto la temperatura como el tiempo de síntesis influyen en la obtención de mezclas, mientras que el pH acentúa esta característica. En particular, emplear concentraciones de soda diferentes a 10 M marca procesos nuevos en las propiedades electrónicas y genera dobletes en las medidas estructurales. Además, el efecto del pH en la síntesis muestra una interesante influencia sobre las propiedades ópticas, permitiendo la sintonización de la energía de banda prohibida (band-gap) y la aparición de estados de defectos electrónicos. Por último, las propiedades de transporte eléctrico de las muestras fueron estudiadas en función de la temperatura en un posible rango de operación de una batería real. Se observó un marcado proceso de deshidratación de las muestras, con una variación importante de sus propiedades de transporte eléctrico, evidenciando el rol de la presencia de agua superficial y estructural. Se vió además que este proceso es reversible si las muestras son expuestas a la humedad ambiente. Una vez alcanzada la deshidratación, las propiedades eléctricas se estabilizan en el ciclo de temperatura, presentando una histéresis térmica. Sin embargo, las propiedades ópticas mantienen modificaciones luego del ciclado.

En síntesis, esta tesis presenta un estudio experimental detallado sobre nanotubos de titanatos de sodio e hidrógeno sintetizados por el método hidrotermal. El trabajo aporta información relevante sobre posibles fases estructurales que componente las muestras, ofreciendo además un estudio mediante simulación computacional que ayudan a comprender las carácterísticas estructurales, electrónicas y vibracionales de las fases potencialmente presente en las muestras. Se analizan las propiedades estructurales y electrónicas a temperatura ambiente y con el cambio de la temperatura.

Palabras claves:

Nanoestructuras de titanatos, Cálculo por DFT, Propiedades estructurales, Propiedades ópticas, Propiedades eléctricas con temperatura.

ABSTRACT

This thesis encompasses a comprehensive exploration into the physical attributes of nanostructured sodium and hydrogen titanates, fabricated via the hydrothermal method, with a specific focus on their utility within energy storage applications. Nanostructured sodium titanates exhibit a great variety of applications like photovoltaic energy conversion, biomedical domains, catalytic systems, water and air purification prototypes, humidity sensing mechanisms, and energy storage. Notably, the latter has emerged as a promising alternative to expensive and contaminant lithium-based technologies. A sign of this, is the inclusion of Sodium Ion Batteries (SIB) in the IUPA's 2023 ranking of the ten most pertinent emerging technologies of 2022.

The synthesis of titanate nanostructures is facilitated through various techniques, and among them, the hydrothermal approach stands out as an economical, robust, and easily scalable method. This method was employed in this study for synthesizing the materials under investigation. Different synthesis conditions were explored: reactor temperature, reaction time and pH of the reaction solution. That led to obtain different morphologies: nanorods, nanoparticles and nanotubes, the latter being the predominant morphology in the studied conditions. The crystalline structures, morphology coexistence, vibrational modes, optical properties, electrical properties and their behavior with temperature were studied on the resulting products in order to provide better understanding of the material.

Sodium/hidrogen titantes nanotubes show a lamellar morphology consisting of coiled sheets. This implies a great difficulty in trying to understand the structural properties of the samples, and it is still under debate which phases conform the structures. X-ray diffraction techniques were used to determine possible local environments of the titanium and possible structural phases present in the samples. These contributions were used to interpret the data, obtaining the trititanate phase $(Na_xH_{(2-x)}Ti_3O_7 \cdot nH_2O)$, with different ratios of Na/H as one of the most viable in these samples. First Principles calculations were performed taking into account the trititnates $(Na_xH_{(2-x)}Ti_3O_7)$ and hexatitanates phase $(Na_xH_{(2-x)}Ti_6O_{13})$ suggested by diffraction studies after an annealing process. In all cases it is observed that the presence of both phases, as well as structural water and water of hydration,

is viable.

Electrical impedance with frequency (EIS) measurements showcased intermediate processes previously absent in samples with low proportion Na/H mixing. Interpretation of the EIS outcomes revealed the existence of at least two distinct intraand intergrain conduction processes with characteristic times on the order of μs y ms respectively. The third process is marked in samples with high temperatures and long synthesis times and its time constant is on the order of ms. Furthermore, absorption measurements indicated the emergence of new edges in samples exhibiting pronounced Na/H mixtures. Both temperature and synthesis time influence the obtaining of proportion mixtures, while pH accentuates this feature. Moreover, the effect of the pH during synthesis shows an interesting influence on the optical properties, allowing bandgap tuning and modifying the presence of defects.

Finally, a comprehensive study of the samples electrical properties was conducted in relation to temperature variations across a possible operational range of a battery. A notable dehydration process was identified, inducing significant shifts in electrical properties, exposing the presence of surface and structural water, and it was seen that this process is reversible if the samples are exposed to atomospheric humidity. Optical measurements exhibits several variations after the temperature cycle.

In sum, this thesis offers a meticulous experimental exploration into nanotubes of sodium and hydrogen titanates, synthesized using the hydrothermal method. The work not only provides crucial insights into the potential structural phases existing within the samples but also undertakes theoretical simulations of some of these structural phases. The findings concerning the electronic properties of the samples at room temperature are detailed, along with an analysis of their electronic behavior in response to temperature variations. These novel measurements carry significant importance due to their novelty and direct relevance to energy storage applications.

Keywords:

Titanate nanoestructures, DFT calculation, Structural properties, Optical properties, Electrical properties with temperature.

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Chapter 1

Introduction

Due to the energy requirements of today's society, there is a general debate about the increase in energy demand and the impact that this increase may have on the environment [1, 2]. Naturally, this topic has captured the interest of researchers in science and engineering. Fossil fuels are the most used energy resource worldwide, but they have certain disadvantages such as resource depletion, environmental pollution and political problems surrounding the production of these fuels. These difficulties have led to the rapid emergence of various intermittent and less polluting renewable energy sources, such as wind, solar and hydropower energy [3]. Due to the characteristics of electricity generation from the aforementioned sources, energy production tends to present temporary peaks and an inhomogeneous spatial distribution [2]. As a result, energy production does not meet energy demand in time and place. Thus, an additional challenge arises: the storage of the energy produced for later extraction and use.

To integrate these renewable energies into the power grid, a large-scale energy storage system is essential. Among the various energy storage technologies, electrochemical batteries are a promising large-scale approach because of their flexibility, high energy conversion efficiency and easy maintenance [3]. It is therefore necessary to devote efforts to understand, improve and develop technologies capable of storing the energy produced. Storage devices have their own requirements that must be met in order to operate. They must be safe, with high energy density, with slow aging in the charge and discharge cycle, and spatially adequate for their use. These characteristics do not seem to be sufficient, adding to the needs of diminish costs of production and maintenance, and reduce environmental impact [2–4].

Lithium-Ion Battery (LIB) have largely satisfied the requirements of safety, high

energy density, and slow aging. They have been extensively used to store energy in mobile devices since SONY first marketed them in the early 1990s [1, 3, 5]. The introduction of LIBs into the automotive market in the 2000s as a battery for electric and hybrid vehicles aims to reduce dependence on fossil fuels. Since then, LIB technology has been developed and improved. As an example of this, the 2019 Nobel Prize in Chemistry was awarded jointly to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino in recognition of their pioneering work on the essential intercalation electrode materials (two different electrodes composed of materials with lithium insertion) for LIB.

It is important to note that LIBs technologies have revolutionized our daily lives although they have two major disadvantages. Lithium is an expensive and scarcity resource. Few countries in the world have natural lithium deposits [6] and most of the lithium used comes from these natural sources. As this mineral is not an infinite resource, efforts have been made to recycle it in order to avoid resource lackness in the near future. Although these recycling proposals have yielded good results in terms of efficiency, quality and profitability, there are currently no clear policies in this regard [6]. The growing demand for lithium associated with new large-scale applications is expected to increase the price of lithium, also affecting resources. According to estimations on lithium consumption in the first decade of the 21st century and projections of resource use, it is estimated that the resource will be depleted just after the half of the 21st century [3]. In this sense, the scientific community is devoting efforts to the study of alternatives for energy storage.

An economically and environmentally friendlier alternative to LIBs are Sodium-Ion Battery (SIBs) [1, 2, 7]. As LIBs, SIBs consist of two different electrodes composed of materials with sodium insertion, avoiding the use of sodium in its metallic form. It is worth mentioning that sodium is the fourth most abundant element on earth, which makes it inexpensive and accessible [3]. While SIBs technology emerged in parallel with LIBs, it lower energy density and the lack of available negative electrodes (anodes) make that the majority of research and development efforts were directed towards advancing LIB technology. However, this focus on LIBs has left numerous inquiries and challenges pertaining to SIBs unanswered [1].

As it was mentioned before, we are currently facing the need to explore alternative technologies to lithium in order to store energy. In this sense, in the year 2023, the IUPAC (*International Union of Pure and Applied Chemistry*) published its ranking of the ten emerging technologies in chemistry in the year 2022, where SIBs is listed. This reaffirms the idea of the importance of studying new systems that can be used in the construction of sodium-based energy storage devices.

After lithium (Li), sodium (Na) is the second smallest and lightest alkali metal in the periodic table, with both elements sharing several chemical properties. The elemental disparities between sodium and lithium are rooted in their atomic attributes. Notably, sodium possesses a threefold greater atomic weight compared to lithium. Additionally, there exists a distinction in the ionic radius, with Na^+ having a larger ionic radius in comparison to Li^+ . When contemplating energy density, a noteworthy observation arises when juxtaposing negative electrodes made of metallic sodium and metallic lithium. In this scenario, the energy density linked to sodium is notably lower to that of lithium, primarily due to the standard electrochemical potential discrepancy between Na^+/Na and Li^+/Li , wherein the former exhibits a 0.34 V higher potential [4].

A disadvantage for sodium, in terms of operational safety, is the lower melting temperature of metallic Na (97,7°C) in comparison with metallic Li (180,5°C) when Na/Li is used as the negative electrode respectively. Finally, as the size of Na^+ ions is greater than the Li^+ ions, the host electrode materials must have a sufficiently large interstitial space to accommodate sodium ions and allow for rapid reversible insertion and removal [4]. It follows from the above that a crucial element in the design of SIBs, and one that requires in-depth study, is the construction of the anode. Different compounds have been proposed that can serve as anode construction materials. Among them are: carbonaceous composites, alloy materials, metal oxides based on conversion reactions and titanium based composites [1, 4].

Among carbon compounds, graphite, which is widely used in commercial LIBs, fails to intercalate Na^+ ions effectively. However, expanded graphite with an interlayer spacing of 4.3 Å has a better performance in sodium storage. This is presented as a new alternative for adapting graphite to SIBs. In addition, disordered carbon with large interlayer spacing is also presented as a good alternative. Despite this, the specific capacitance of carbonaceous materials is generally low (below 300 mA $h g^{-1}$) [1]. Furthermore, these compounds have presented significant safety issues during the charging process. However, carbonaceous materials continue to represent a challenge and are an area of study and development for the manufacture of SIBs anodes.

Alloy materials have reached an extremely high capacity, especially for phosphorus allotropes (theoretical capacity of 2600 $mA \ h \ g^{-1}$) [1]. However, these materials present a high volumetric expansion during sodiation/desodiation. This constant change in its mechanical properties during cycling presents an obstacle for their use in SIB-type devices. The current problem is to design micro- or nanostructures to decrease the volumetric expansion while maintaining the efficiency [4].

Despite metal oxides (like Co, Fe) in lithium cells show a good device performance, sodium storage performance is far from satisfactory presenting low capacity and reduced cycling level. In addition, they have high activation barrier and large potential hysteresis, presenting then bad electrical characteristics to be used as a storage device. Even so, it is necessary to continue investing efforts in their study, mainly in those materials composed of iron or manganese since they are very abundant elements in nature [1].

Titanium-based composites, are characterized by excellent cyclic stability and low structural stress, which is crucial for long service life [1] and a high storage capacity of 335 $mA h g^{-1}$ [8]. Thus, titanium-based compounds appear to be a promising material for anode construction. They also have a wide range of applications in the energy and environmental fields. Due to their lamellar crystalline structure, titanium oxides are used for photocatalysis (photon-mediated decomposition of water) and as electrolytes in adsorbent fuel cells. In addition, due to their high ion exchange, intercalation power and adsorption capacity, they are used in dye-sensitized solar cells (DSSCs) and for humidity control in the manufacture of humidity sensors [9].

Sodium titanate nanostructures have been extensively studied, showing good results as anode materials for SIBs [10–13]. However, their fundamental properties are still under study [14–19]. In this thesis, the relation between different synthetic routes to obtain sodium titanate nanostructures and their fundamental physical properties will be explored. In particular, special attention will be paid in the electronic and structural properties, the latter being a topic of wide discussion in the literature. These studies will contribute not only to the understanding of nanostructured sodium titanates with application to energy storage, but also, they may be useful in some of the other applications mentioned before as humidity sensors, for example [9, 17].

The objective of this thesis is to synthesize and study the fundamental properties from a physical approach of sodium titanate nanostructures with possible applications in batteries. The aim is to identified the structures obtained by different synthesis route and to related them with the structural, morphological, vibrational and electronic properties of the system. For this purpose, several experimental techniques applied in solid state physics are used together with a theoretical study focused on simulations based on *First Principles*.

By means of the hydrothermal synthesis method, tubular titanate nanostructures are synthesized, as indicated in the literature (see Chapter 2 and 3). The synthesis conditions (time, temperature and pH) are varied to analyze their influence on the obtained morphologies and physical properties. The results of exploring these synthesis conditions and their experimental characterization are shown in the Chapters 3 and 4. Furthermore, some initial phases are suggested and, particularly in Chapter 4, the presences of Na/H ions in different proportions in a tri-titanate phase is explored. Following a exhaustive experimental characterization, the research endeavors progress to the exploration of diverse phases constituting the samples. While these investigations are grounded in experimental measurements, their potentiality is amplified through theoretical simulations, elucidating the properties of select phases within the samples. This results are shown in Chapter 5. The identification of these phases stems from the results of Chapter 6 and an annealing process applied to the samples. Concluding this step, the examination of sample properties under the rigors of temperature cycling forms a pivotal component of the study. The electrical temperature dependence study is presented in Chapter 6, including the effect of humidity in the electrical response.

This thesis work is organized as compilation of articles published in peerreviewed scientific journals. The original papers can be found in Chapters 3 to 6 of this manuscript [20–23]. The articles are not presented in chronological order but are arranged in such a way as to be useful for the development of the thesis. Chapter 2 contains the transversal theoretical basis necessary to understand all the techniques used in the articles. In addition, where required, each technique will contain detailed information on the data collection or analysis process. Chapters 3 to 6 includes a brief introduction to each work (article) at the beginning. Finally, the thesis in summarized in the conclusion Chapter 7 bringing together the most relevant results and contributions in the field.

Chapter 2

Literature Review

This chapter will provide an overview of the fundamental techniques employed in this work, starting with the synthesis methods for sodium titanates. Subsequently, we will describe the specific synthesis approach used in this research. Afterward, the theoretical basis of the experimental characterization techniques and first principle calculations will be presented.

2.1. Titanium Oxides and Titanates

Titanium dioxide (TiO_2) can occur in nature in four most common polymorphs [24]. All the structures show a distorted geometry of the octahedron TiO_6 where titanium is coordinated with six oxygens as shown in Figure 2.1. *Rutile* has a tetragonal crystalline system structure where the octahedrons share sides and is considered the most stable structure in non-nanoscale conditions, in normal conditions of temperature and pressure. On the other hand, *anatase* and *brookite* are the most stable in nanostructured form. In the tetragonal crystalline system structure of anatase the octahedra share edges while in brookite, which has a rhombohedral crystalline system structure, the octahedra share both edges and sides. The fourth structure of TiO_2 , a monoclinic one, is called $TiO_2(B)$. Compared to other phases of TiO_2 , $TiO_2(B)$ has a lower atomic density, which contributes to its ability to withstand high temperatures. Macroscopic (bulk) structures of titanium oxides are shown in Figure 2.1.

As mentioned above, titanium oxide is only composed of titanium atoms and oxygen atoms. On the other hand, titanates are the corresponding salts of titanium oxide. Depending on the cation of the salt, titanates have different names. In particular, sodium titanate is the salt containing sodium and acid titanate is the one that has protons as an intercalated cation in the structure of titanium oxide. Sometimes samples have mixed structures where both sodium and hydrogen are present in the sample, calling them hydrated sodium titanates.

Indeed, the macroscopic structures of titanates introduced earlier provide a foundational understanding of the material's crystallographic arrangements. However, it is crucial to recognize that the materials investigated in this thesis exist as nanostructures, which significantly impacts their properties and behavior. Therefore, a brief description of these nanostructures is essential.



Figure 2.1: Crystal structures of TiO_2 ; Rutile, Anatase, $TiO_2(B)$ and Brookite.

2.1.1. Nanostructured Titanates

It is well known that when the size of the material becomes smaller and smaller, down to the nanometer scale, new physical and chemical properties emerge. In this thesis we would use the conventional definition of nanoscale to refer to lengths between 1 and 100 nm [25]. As a result, a material is nanoestructured if at least one dimension length is between 1 and 100 nm. One of the most significant characteristic properties of semiconductors in nanoscale is the conduction process involving electrons and holes. This phenomenon is highly relevant due to its impact on the electronic behavior of semiconductor nanostructures. Quantum confinement plays a crucial role in governing the movement of charge carriers within these nanostructures. In structures like nanotubes, as their size decrease the aspect ratio increases dramatically, leading to enhanced interactions with the environment, particularly at

the surface or interface. This unique combination of quantum effects and increased surface area makes nanostructured semiconductors, such as TiO_2 , particularly appealing for a wide range of applications in various devices [16]. Thus, it is of interest to explore the applications of TiO_2 in nanostructures.

In particular, both titanium oxide and titanate nanostructures can be classified by their geometry into 0D, 1D, 2D and 3D materials, depending on the relationship between the dimensions in the three spatial directions. Each group of nanostructured materials exhibits distinct characteristics, offering a diverse range of potential applications. Moreover, specific synthesis methods have been identified to promote the growth of particular structures over others [9, 17]. The different types of general morphologies that can be obtained from titanium oxide are exemplified in Figure 2.2.



Figure 2.2: Different morphologies for nanostructured titanium oxides and titanates. A-Quantum dots, B- Nanofibers, C- Nanowires, D and H- Nanotubes, E- Nanorods, F-Nanosheets, G- Nanoflowers, I- Nanolayers. Images reproduced with permission from [17] Licence *Creative Commons CC-BY-NC-ND*

2.1.1.1. 0D Structures

The 0D structures are either nanoparticles or quantum dots, preferably spherical or cubic with a diameter of nanometric dimensions (< 100 nm for nanoparticles and size below the Bohr radius of its exciton for quantum dots) [9, 17]. Unlike other morphologies, zero-dimensional (0D) nanoparticles have emerged in the scientific literature only in the last few decades, mainly due to the inherent challenges associated with controlled synthesis methods. They are mostly used as precursor for hierarchical 3D structures. Quantum dots exhibit distinct chemical and physical properties compared to bulk materials. These unique properties make quantum dots valuable as decorative elements, enriching the design of various technologies. Their surface properties play a crucial role in enhancing the functionality of different applications, including fuel cells, solar cells, antibacterial surfaces, and photocatalysis [17].

2.1.1.2. 1D Structures

Within the category of one-dimensional (1D) nanostructures, there are various types, including nanofibers, nanowires, nanorods, and nanotubes. Despite all being tubular in shape, they have distinct differences in their diameter-to-length ratio and density. These variations in their geometries and properties make each type of 1D nanostructure suitable for specific application.

Nanotubes were the first nanostructures synthesized using a simple method developed by Kasuga [26], which will be discussed in more detail in the next section. However, structures such as nanofibers have only been synthesized in the 21st century. Nanofibers are characterized by their elongated shape and extremely small diameter, which contributes to their high flexibility. This flexibility is a desirable property when aiming to incorporate functionality into various applications. Due to their unique geometry and properties, nanofibers are often used in conjunction with other materials, especially metal oxides [17]. This coupling allows for the synergistic combination of their distinct characteristics, resulting in enhanced performance and tailored functionalities.

By using nanofibers in combination with other structures, researchers can create advanced materials and devices with a wide range of applications, including sensors, filters, energy storage systems, and biomedical devices [17]. The versatility and compatibility of nanofibers make them essential building blocks for cutting-edge technologies. Indeed, one of the highly valuable properties of these 1D nanos-

tructures, such as titanate nanofibers, is their exceptional thermal stability. During the calcination process, where the material is heated to high temperatures, titanate nanofibers demonstrate remarkable resistance to structural changes. Despite undergoing calcination at temperatures of up to about 1000 °C, the crystalline structure of the nanofibers remains unaffected [17]. This thermal stability is crucial for various applications where high-temperature processing is required, ensuring that the unique morphology and properties of the nanofibers are preserved.

Nanowires, like nanorods, are cylindrical structures with a circular base [27]. The primary distinction between them is that nanowires have a higher aspect ratio than nanorods, meaning they are longer and more slender. Both nanowires and nanorods differ from nanotubes as they lack a layered internal structure. Instead, their composition is solid throughout. Nanowires are often found alongside nanotubes in samples fabricated at temperatures above $400 \, ^{\circ}C$. Despite their solid structure, they still exhibit good thermal stability, withstanding temperatures of up to $600 \, ^{\circ}C$ [28]. This thermal stability is slightly lower than that of nanofibers but still considerable. Nanowire arrays have found practical use in dye-sensitized solar cells (DSSCs) and demonstrate good photoconversion efficiency when exposed to white light illumination [29]. Additionally, these structures display excellent compatibility with carbonaceous materials, which enhances their potential for various applications [17]. Overall, nanowires represent a promising category of nanostructures with diverse applications, and their unique properties make them valuable components in cutting-edge technologies.

On the other hand, nanorods are of great value since they can be synthesized by various methods and in large quantities [17]. Their morphological characteristics were described in the previous paragraphs. Similar to nanotubes, nanorods have a great potential to be used as a matrix for decorating with nanoparticles of different materials [30, 31]. Their main applications are in photoelectric energy conversion and photocatalysis [32–34].

Nanotubes have cylindrical geometries with hollow cavities along the central axis, usually with a characteristic morphology that consists on multi-layered walls, coiled in concentric circles as shown in Figure 2.3 [17]. The aspect ratio of nanotubes ranges from tens to hundreds. Typically, nanotubes tend to be straight structures, with a relatively constant diameter. Their high aspect ratio, high ion exchange and photocatalytic ability present them as strong candidates in applications such as photocatalytics, photoelectrochemistry, biomedicine, energy storage and energy conversion [35]. Although these structures were the first to be obtained in the 1990s,



Figure 2.3: HRTEM image of a Tubular structure of sodium titanate obtained by hydrothermal method.

the synthesis method provided inhomogeneous and disordered structures. Sophisticated methods now exist for the synthesis of titanium oxide and titanate tubular structures, which control the number of layers, lengths, diameter and intercalations with other materials [36–40].

An essential consideration to bear in mind is the complex coiled sheet structure of nanotubes, which possess challenges in modeling their internal atomic arrangements. As a result, determining the precise crystalline structure of titanate nanotubes remains a difficult task. The small crystal size in these nanostructures leads to broadened peaks in X-ray diffraction patterns, making it challenging to discern distinct features. Due to the broadening of peaks, multiple crystal structures can be encompassed within the width of the peaks, leading to uncertainties and difficulties in accurately determining the true structure [9].

Furthermore, the proposed crystal structures by the scientific community often exhibit significant similarities in terms of atomic positions, further complicating the analysis. These similarities can mask crucial details within the experimental data, making it difficult to distinguish between different structures. To overcome these challenges, various advanced characterization techniques are employed, such as electron microscopy, spectroscopy, and computational simulations, to gain deeper insights into the internal structures of titanate nanotubes. By combining multiple approaches, a comprehensive understanding of these intriguing nanostructures and a refination of the models to capture the atomic arrangements within the nanotubes are obtained.

Despite the complexities involved, the pursuit of unraveling the true crystallo-

graphic phase or structure of titanate nanotubes remains a subject of active investigation within the scientific community. Furthermore, the determination of a single phase containing only sodium or acid titanates in nanotubes is not yet conclusively established [14]. Instead, there are possibilities of mixed phases, wherein various compositions and arrangements of sodium and acid titanates may coexist within the nanotube structures. According to Esteves et. al. [14], through a combination of experimental measurements and theoretical simulations, they argue that the predominant phase in these structures is of the form $[Ti_2O_5]$. Their findings align with the results presented in Chapter 3 of this thesis, supporting the prevalence of the $[Ti_2O_5]$ phase in titanate nanotubes.

However, preliminary fitting on the x-Ray Powder Diffraction (XRPD) patterns show that this type of Ti-O coordination do not reproduce the experimental XRPD obtained. On the other hand, Morgado et al. [41, 42] propose a different perspective, suggesting that the most common phase is of the $[Ti_3O_7]$ tri-titanato type. Their study is based on thermal decomposition studies of the structures, enabling them to infer the original phase or phases present in the nanotubes. Chapter 4 models the diffractograms from the different sodium and hydrogen tri-titanates phases proposed by Morgado et. al. Fitting the experimental XRPD data we established ratios of the hydrogen phase to the sodium phase in the different samples.

Additionally, another possible phase is of the form $[Ti_6O_{13}]$ (hexa-titanate) [43– 45]. This phase appears at high temperatures, when the structures are subjected to annealing. However, there are no studies that evaluate its presence at low temperature. In Chapter 5 we show the results of calculating by *First Principles* the properties of this phase, and thus evaluate the feasibility of its presence in the samples. These contrasting findings highlight the complexity of characterizing the crystal structures of titanate nanotubes, as different techniques and interpretations may lead to diverse conclusions. It is essential to recognize the ongoing nature of this research, as the debate continues to evolve with new experimental data, improved simulations, and refined characterization techniques. This thesis work contributes to this discussion aiming to provide valuable insights and a deeper understanding of the predominant phases in titanate nanotubes.

2.1.1.3. 2D Structures

Nanosheets or nanoflakes are two possible structures in which titanium oxides or titanates are presented in two dimensional systems. Nanoflakes are irregular platelike form two-dimensional nanostructures. Recent studies have shown that flakelike structures have excellent surface properties. This has led to TiO_2 nanoflakes being used as semiconductors for environmental and energy applications [17]. When TiO_2 nanoflakes are decorated with uniform tungsten oxide clusters, their photoelectrochemical properties are improved promoting their use in the purification of contaminated water.

Nanosheets, on the other hand, are two-dimensional nanostructures with a thickness ranging from 1 to 100 nm. Nanosheets of TiO_2 can be synthesized as an intermediate product for nanotube formation by hydrothermal method, or by proton titanate stripping with single layered structure [46, 47]. Also, synthesis routes can be designed to obtain well-defined sheet characteristics [17]. Porous TiO_2 nanolayers have shown a remarkable enhancement of photoreactivity against some compounds compared to non-laminated structures [48]. The enhanced photocatalytic activity is explained due to the increased surface area and improved light collection caused by multi-reflection of incident light between the layers. Potential applications are also focused on water purification and treatment.

2.1.1.4. Hierarchical 3D structures

Three-dimensional hierarchical titanate structures have been a challenge for several years due to the complexity of the synthesis [9]. These structures have captivated many researchers because of their exceptional and unusual properties, and their potential applications in the fields of energy and environmental applications.

In particular, the first 3D titanate structures were nanoflowers which have the advantages over traditional nanoparticle catalysts because they have better UV absorption, easy recovery after reactions and better charge separation. Characteristics such as porosity, high specific surface area, adequate refractive index and high photocatalytic efficiency make nanoflowers suitable for several applications such as air purification, environmental management, sterilization and many energy storage and convertion applications. Moreover, the self-assembly of different titanium nanostructures (nanowires, nanoparticles, nanosheets) lead to the formation of hierarchical nanoflower-like structures. In general, the formation and migration of phototransporters occur efficiently in such a material, which enhances the adsorption of reagents on the surface. Therefore, and due to their high specific surface area, nanoflowers usually have a higher photocatalytic efficiency [17].

In addition to flower-like structures, hollow spheres are taking an increasingly

relevant role in research for the design of efficient photocatalysts [49]. Porous, hollow TiO_2 structures have large surface areas along with abundant active reaction sites, a shorter diffusion distance of photogenerated charge carriers, and greater access to reagents through the porous shells [50]. Precise control of the structure and other properties are the key factors to develop better hollow photocatalysts. On top of the microspheres, dendritic structures (Figure 2.4) can be included to further improve their properties and can be applied in solar cells, catalysis and water pufication [51, 52].



Figure 2.4: Different 3D dendritic structures obtained on porous spheres. A- Hollow sphere, B- Rod-like dendrites, C- Nanofiber-like dendrites, D- Nanowire-like dendrites. Images reproduced with permission from [17] Licence *Creative Commons CC-BY-NC-ND*

2.2. Synthesis of sodium titanate nanostructures

As mentioned in Chapter 1, titanates in their nanostructured form are presented as an alternative for the fabrication of anodes in batteries. In particular, different nanostructures of sodium titanates are being studied for application in SIB [18]. Three main techniques are used for the production of titanium oxide and sodium titanate nanotubes [15]: chemical synthesis with template, electrochemical synthesis and alkaline hydrothermal synthesis.

The first group includes synthesis techniques using matrices in which the desired compound is deposited. In this way, nanostructures with defined and wellcontrolled morphologies and dimensions are achieved. On the downside, this method tends to destroy the matrix in each synthesis process, making it expensive and difficult to scale up to mass production.

Electrochemical synthesis for obtaining titanium oxide nanotubes was developed from titanium anodizing. This method makes it possible to obtain thin films of titanium oxides, which has the advantage of rendering the nanostructures immobile. On the other hand, the dimensions are usually quite large (diameters of 50 nm and lengths of 300 nm) compared to other synthesis methods.

Finally, the hydrothermal method offers the possibility of synthesize titanium oxide nanotubes from any of the three polymorphs of titanium oxide (anatase, rutile and brookite) by reacting them at high temperature and pressure in an alkaline solution. The hydrothermal method has the advantage of being easily scalable to large productions, economical and simple to perform but has the disadvantage of its variability in the result of the product obtained. In addition, because it is synthesized in an aqueous medium, it is expected that the structure of the final product contains water either superficial or interstitial.

In this thesis the nanostructures were obtained by alkaline hydrothermal synthesis under endogenous pressure. The steps of the synthesis will be detailed in the next sections.

2.2.1. Alkaline hydrothermal synthesis under endogenous pressure

Alkaline hydrothermal synthesis to obtain titanium oxide nanostructures was developed by Kassuga [26]. He proposed the production of TiO_2 nanotubes using the rutile polymorph as a precursor. From Kasuga's original method, alternatives have been derived to obtain titanate nanostructures. In particular, in this work we use the technique explored in [53] for the synthesis of sodium titanate nanotubes. The first step of the synthesis is performed in a hydrothermal reactor or autoclave (see Figure 2.5). An autoclave is a metal vessel designed to facilitate heat exchange between the surrounding environment and the chemical reaction occurring within. Autoclaves can be either hermetic, enabling reactions under endogenous pressure, or equipped with an injection valve to increase the pressure within the vessel. The simplest autoclaves consist of two main components: an outer hermetic vessel and an inner vessel (Figure 2.5 A). The hermetic outer vessel provides a sealed environment to ensure containment and safety during the reaction. Inside the outer vessel,

the inner Teflon vessel serves as the reaction chamber, accommodating the chemical components and maintaining a controlled environment for the reaction to occur. Autoclaves are commonly used in various chemical and materials synthesis processes, allowing to conduct reactions at specific temperatures and pressures. The design and configuration of autoclaves can vary based on the intended applications, with more sophisticated models incorporating additional features such as pressure control systems and temperature regulation mechanisms. For example, an agitation system to homogenize the temperature during reaction could be added, as it is shown in Figure 2.5 B. The latter set up was employed in this work.



Figure 2.5: Autoclaves for hydrothermal synthesis: A) Simple autoclave without internal temperature control and stirring (left) and with components (right), B) Autoclave with temperature control and stirring.

In the hydrothermal method to synthesize nanostructured titanates, there are four key variables that determine the outcome of the product obtained: the reaction time (t_s) , the reaction temperature (T_s) , the reaction pressure (determined by the fill factor, that means the percentage of solution relative to the total volume of the reaction vessel) and the pH of the reaction medium. In a previous thesis [53] an exhaustive study of the optimal conditions for titanium nanoestructures was done. In the present work, the starting point was the conditions established in [53] for obtaining nanotubes. In this work the reactor fill factor was kept constant at a value of 75 % of the total reactor capacity. The other variables were modified as indicated in the Table 2.1 where the nomenclature of the samples used coincides with the nomenclature used in the articles presented in Chapters 3 to 6.

Table 2.1: Hydrothermal synthesis parameters for each sample. T_s synthesis temperature, t_s synthesis time, Rev stirring rate, $[OH]^-$ molar concentration of NaOH. A mass of TiO_2 of about 1.18g was used for all samples.

Sample	$T_{s}\left(^{\circ}C ight)$	$t_{s}\left(h ight)$	$Rev\left(r/m ight)$	[OH](M)	Morphology
M1	145	48	120	10	Nanotubes
M2	145	72	150	10	Nanotubes and nanoparticles
M3, S1: 10M	125	96	150	10	Nanotubes
M4, S2: 10M	105	96	150	10	Nanotubes
M5	105	144	150	10	Nanorods
S2:9M	105	96	140	9	Nanotubes
S2:11M	105	96	150	11	Nanotubes
S1:9M	125	96	140	9	Nanotubes and nanorods
S1:11M	125	96	150	11	Nanotubes and nanorods

In all syntheses, 1.18 g of commercial TiO_2 in its anatase polymorph (Sigma-Aldrich Laboratory ID: 799289, External ID: 232033 ALDRICH) is used as the precursor for the nanostructures. This TiO_2 is dissolved in sodium hydroxide (NaOH) to obtain a fill factor of 75 %. A reaction temperature sweep is performed ranging from 48 h for the shortest syntheses to 144 h for the longest ones. In addition, three temperature values are explored: 105°C, 125°C and 145°C. Since the syntheses with higher temperature resulted in more inhomogeneous samples, it was decided to set the reaction time condition at 96 h and the temperature at 105°C and 125°C to explore the effect of pH on the reaction. The NaOH concentrations were varied from 9*M* to 11*M*, as indicated in Table 2.1, to study the influence of the synthesis pH on the properties of the obtained structures.

The synthesis process is carried out using stirring. Although the agitation should have been always the same, since it was not intended to study its influence on the synthesis, due to difficulties in the stability of the experimental set up not all samples were synthesized with the same agitation conditions. As previously reported [54–56], for temperatures above $100 \,^{\circ}C$ the safety mechanism of the autoclave detects overheating, triggering an alarm and shutting down the process. This can be avoided if the stirring speed is properly regulated. In particular, in our case this agitation speed ranged between 120 rev/min and 150 rev/min. As described in the references [57] and [58] both the diameter and the length of nanotubes synthesized by the hydrothermal method increase if the stirring speed increases. However, if the variations are in a narrow range of speed (as in our case) the morphological properties will not be significantly modified.



Figure 2.6: Washing process. On the left is the solid resulting from the reaction, after being separated from the alkaline supernatant and placed in water. On the right the sample in the washing process using 400 mL of distilled water at a temperature of 42 $^{\circ}C$ and a stirring speed of 450 rpm.

After the completion of the reaction, it is essential to allow the solution to cool down gradually. Once cooled, any excess alkaline solution should be promptly discarded to prevent undesired reactions. Rinsing the sample with water is necessary to remove any residual alkaline solution and by-products from the reaction. Preventing the formation of carbonates from CO_2 in the air is crucial as they can interfere with the desired properties and characteristics of the final product. Proper handling and washing of the sample after the reaction help to ensure the purity and quality of the resulting material. Figure 2.6 shows the solid resulting from the reaction (without the alkaline supernatant) in distilled water.

The solid will be washed for 24 h in distilled water with agitation (between 300 and 600 rev/min) to remove the sodium hidroxide that may have remained on the surface of the nanostructures. Then, the washing water is separated from the solid by a centrifugation process (5 minutes at 450 rev/min) where the water is discarded and the solid is reserved for subsequent drying. Drying is done in air for at least 12 h at a temperature not exceeding 80 °C to avoid degradation of the structures. Finally, the dried solid is ground to obtain a fine powder. Generally, before fin-

ishing the synthesis process, a routine control is performed using X-ray diffraction (XRPD) technique. Then, it is possible to control the formation of sodium carbonates from insufficient washing. In case of finding traces of carbonates in the diffraction pattern, the washing process must be repeated, this time rising the temperature. The solid is then placed again in 400 mL of distilled water, washed with agitation during 24 h but the plate is regulated to maintain a temperature between 40 °C and 50 °C, favoring the dissolution of the carbonates in the water.

2.3. Experimental characterization techniques.

This section introduces the fundamental theoretical bases necessary to understand the experimental techniques used in the different works. The techniques cover morphological, vibrational, structural, electrical and optical characterization. In each subsection at least one technique is briefly described including, where appropriate, details of the experimental setup.

2.3.1. X-Ray diffraction

X-ray diffraction (XRPD) is a well-established non-destructive technique widely used for material characterization [59]. A crystal is a 3D atomic arrangement that present long-range positional order [60]. When matter (in this case a solid) interacts with radiation (for example in the form of X-rays) there is an attenuation of the reflected beam along the material resulting in an attenuated signal at the exit of the material. The complex interactions that can occur are usually classified into two types: absorption (photoelectric effect) or deflection [61, 62]. The deflection can occur elastically conserving energy or inelastically losing energy. The latter interaction is known as the Compton effect. When performing an X-ray diffraction measurement, it is of interest to detect the intensity of the electrons in the elastic deflection, and this interaction is called scattering [61]. The model used to approach this study considered atoms as coherent sources whose radiation can interfere. Since the model for understanding the X-ray diffraction phenomenon involves the interaction of a large number of point sources, it is necessary to first recall the result of calculating the scattering due to a single point charge.

For a free charge at the origin of coordinates experiencing an interaction with an unpolarized plane wave propagating in x-axis direction of intensity I_o , a sinusoidal acceleration of the charge will be observed. We want to study the shape of this ra-



Figure 2.7: A- Classical scattering for an unpolarized primary beam by a single free electron. *Image extracted from* [63]. B- Schematic illustration of the scattering vector \vec{q} as a function of the incident \vec{k} and diffracted $\vec{k'}$ wave vectors.

diation at a point **P** in the XY plane located at a distance **R** from the point charge forming an angle ϕ with x-axis. Because the radiation is not polarized, the electric field can take any orientation in the YZ plane, so we will study one direction, E_O with components E_{OY} and E_{OZ} and then average in all directions (Figure 2.7 A). Because the charge experiences an interaction with a sinusoidal field, it will be accelerated ($a_Y = \frac{eE_{OY}}{m} sen(2\pi\nu t)$, with e the electron charge, m the electron mass and ν the incident field frequency) and therefore emits radiation. The amplitude of the radiation field generated by the oscillating charge (E), the amplitude of the incident field (E_O) and the total field at the observation point (P) can then be calculated as the sum of the two previous ones. Furthermore, assuming that the incident field has equal probability of taking any orientation in the YZ plane, the following result is obtained for the total field at the point **P**:

$$\langle E^2 \rangle = \langle E_o^2 \rangle \frac{e^4}{c^4 m^2 R^2} \left(\frac{1 + \cos^2(\phi)}{2} \right) \tag{2.1}$$

From the relationship between the (observable) intensity (energy per unit area per unit time) and the amplitude of a sinusoidal variable field $(I = \frac{c^2}{8\pi^2} \langle E^2 \rangle)$ we obtain the Thompson scattering equation [61, 62]:

$$\langle I \rangle = \langle I_o \rangle \frac{e^4}{c^4 m^2 R^2} \left(\frac{1 + \cos^2(\phi)}{2} \right)$$
(2.2)

The factor $\frac{1+\cos^2(\phi)}{2}$ is called the polarization factor. This equation contains two relevant information to be highlighted, fundamental for diffraction. The first is that the intensity scattered from an unpolarized beam depends on the scattering angle. This information is contained in the polarization factor. The second refers to the characteristics of the scattering charges. The scattered intensity is proportional to q^4/m^2 , which implies that for diffraction theory only the electrons contribution is relevant.

The above development for a single electron as a scattering center can be generalized to understand the behavior of a sample characterized by its electron density $\rho(\vec{r})$ [62]. Generally, the long-range positional order present in crystalline materials can be inferred from the existence of Bragg peaks in the Fourier spectrum of the solid [60]. For instance, X-ray diffraction is used for examining and characterizing the position of atoms, their arrangement in each unit cell, and for quantifying spacing between the atomic planes. To better understand these statements, it is useful to introduce some definitions that lead to a more explicit exposition of the relationship between interatomic planes, incident radiation and diffracted radiation.

A crystalline structure is composed of a grouping of structures (ions, atoms or molecules) that repeat periodically in three dimensions. The unit cell is defined as the repeating pattern or motif that, when translated, can reconstruct the entire crystal lattice. The translation vector that constructs such a lattice is of the form

$$\vec{R}_l = u\vec{a} + v\vec{b} + w\vec{c} \tag{2.3}$$

where (u, v, w) are integers and $\vec{a}, \vec{b}, \vec{c}$ are the non-coplanar lattice axes. In addition to the description by means of a direct lattice basis, crystals can be studied on the reciprocal space. A vector \vec{G} of the reciprocal lattice satisfies the relation $\vec{G} \cdot \vec{R_l} = 2\pi p$ where $\vec{G_{hkl}} = h\vec{a^*} + k\vec{b^*} + l\vec{c^*}$, $(h \ k \ l \ integers)$ and p an integer. The reciprocal basis $\vec{a^*}, \vec{b^*}, \vec{c^*}$ is formed by three vectors called reciprocal axes and each of them are, by construction, perpendicular to the plane defined by two of the vectors of the direct lattice.

Additionally, the diffraction condition for the \vec{G} occurs when $\vec{G} = \vec{k} - \vec{k'} = \vec{q}$ with \vec{q} called the transference vector, \vec{k} the incident wave vector and $\vec{k'}$ the diffracted wave vector (see Figure 2.7 B). The reciprocal lattice helps to index any families of lattice planes, where the aforementioned Miller indices $(h \ k \ l)$ are used.

Due to the translational symmetry of the crystal, every plane passing through three nodes of the direct lattice belongs to a family of equidistant planes whose mutual distances are called interplanar spacing. The interplanar spacing d_{hkl} is the distance between two consecutive planes of the index family $(h \ k \ l)$ and can be expressed as $d_{hkl} = 2\pi/|G_{hkl}|$.

A useful result derived from the study of the diffraction amplitud is the Laue's condition: $\vec{q} \cdot \vec{R}_l = 2n\pi$ with *n* integer and for all *l*. Using the diffraction condition and the definition for \vec{G} , Laue condition may be interpreted as the moment transferred to a crystalline lattice that equals a vector of the reciprocal lattice. Graphically, the spots present in a Laue diffractogram correspond to the reflections produced by a set of crystallographic planes. If we consider the particular case where the vector \vec{q} is always perpendicular to a family of lattice planes of indices $(h \ k \ l)$, we are in a type of geometry named as Bragg-Brentano [62] (Figure 2.8).



Figure 2.8: X-ray diffraction measurement in Bragg-Brentano geometry.

This type of configuration is one of the most common in diffractometers, and in particular is used in the measurements of this thesis. It is possible to see that in this configuration Bragg's law is fulfilled. For this we must remember that the vector \vec{q} in Figure 2.8 can be written in terms of a vector of the reciprocal basis as $\vec{q} = n\vec{G}_{hkl}$ with n an integer and $|G_{hkl}| = 2\pi/d_{hkl}$. As a result, $q = |\vec{q}|$ takes the form:

$$q = \frac{2\pi n}{d_{hkl}} \tag{2.4}$$

Relating q with k (the incident wave vector) we have $q = 2k \sin \theta$ resulting in Braggs law if $k = \frac{2\pi}{\lambda}$:

$$k\sin\theta = n\frac{\pi}{d_{hkl}} \to 2d_{hkl}\sin\theta = n\lambda$$
 (2.5)

In the previous development an infinite crystal was always assumed. This assumption is very restrictive and in particular does not suit the samples studied in this thesis, which are made up of nanostructures. For these cases, what in an infinite crystal is observed as a Bragg peak will now be transformed into a Fraunhofer type interference pattern. The relationship that explains this behavior is the Scherrer formula [64] which is written in angular terms as [61]:

$$\delta \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{Nd} \Longrightarrow 2\delta\theta = \delta(2\theta) = \frac{\lambda}{\cos \theta Nd}$$
(2.6)

The peaks centered on each Bragg condition will then have a width (δ) inversely proportional to the sample size (Nd, with N the number of unit cell and d distance between planes) in the direction normal to the diffracting planes. By measuring the width of the peaks one can then estimate the coherence length, a result that is used in some of the works presented in this thesis. Due to the nanometric nature of the samples, the X-ray patterns in the present thesis are often broadened and of weak signals, requiring long data collection times.

In [9] different phases with their diffraction planes are reported showing different indexations and interplanar distances. They are compiled in Table 2.2. In the following chapters (3 to 6), XRPD patterns are used to identify interplanar distance and coherent length of the different plane reflections. In Chapter 3, the interplanar distances and crystalline coherence are analyzed. In Chapter 4 this pattern is assigned to a tritatanate phase that can have two possible interplanar distances due to the presence of both Na or H, for which the peaks are fitted with two contributions. Furthermore, the presence of structural water is suggested, which explains larger interlayer distances than those reported. In Chapter 6 this water is confirmed by observing the changes with temperature. Additionally, in Chapter 5, the proposed phase is evaluated, plus a hexa-titanate phase, by computational calculations, as the constituent phases of these samples.

In addition to using X-ray diffraction measurements in the Bragg-Brentano configuration, this thesis also employs the low-angle configuration. This technique is called Small Angle X-ray Scattering (SAXS) and is used to obtain surface or size information for nanometric structures. SAXS provides detailed physical and surface information for a scale between 1 and 100 nm allowing to characterize average particle sizes when density contrast is sufficient [65]. In a SAXS experiment, the sample is exposed to X-rays of a specific wavelength, which scatter elastically be-
Table 2.2: Comparison of Structural Parameters of the Titanate Nanotubes (Å). a) JCPDS 47-0561 monoclinic; lattice constants a = 16.023 Å, b = 3.749 Å, c = 9.191 Å, and β = 101.45°. b) JCPDS 36-0655 monoclinic; a = 18.77 Å, b = 3.75 Å, c = 11.62 Å, and β = 104.6°. c) JCPDS 47-0124 orthorhombic; a = 18.03 Å, b = 3.783 Å, and c = 2.998 Å. [9]

$H_2Ti_3O_7^a$		H_2Ti_40	$O_9.H_2O^b$	$H_2Ti_2O_5.H_2O^c$			
d	hkl	d	hkl	d	hkl		
7.87	200	9.05	200	9.04	200		
3.65	110	3.67	110	3.696	110		
3.05	310	3.185	310	3.204	310		
2.67	31-2	2.668	21-3	2.684	301		
2.37	11-3	2.298	21-4	2.306	501		
1.88	020	1.876	020	1.893	020		

tween $2\theta = 0^{\circ}$ and 5° to produce a spatially averaged intensity distribution. SAXS measurements to obtain surface area and sample size information can be found in the paper presented in the Chapter 3.

In each chapter, in the methodology section, details of the equipment and measurement settings are given.

2.3.2. Raman Spectroscopy

Raman spectroscopy and Confocal Raman microscopy techniques are routine techniques commonly available in materials science and engineering laboratories [66]. The former is an structural technique that allows the local study of the vibrational modes present in the sample. This information can be used to identify the presence of compounds, contaminants or to compare samples with similar compositions. The second technique presents a mode mapping that can be translated into an approximate compositional image of the vibrational modes of the sample. It serves to identify regions with higher or lower concentration of some components or phases, mainly in heterogeneous samples. In particular, in this thesis work, both are used as head techniques to deepen the knowledge of samples structure.

In addition, the Raman wavenumber (or frequencies) modes can be contrasted with the DFT calculation results for different stoichiometries phases. For this reason a presentation of the basis of Raman spectroscopy will be made in the following paragraphs.

In a simple way, the Raman effect can be described as the inelastic scattering of light by matter. Rayleigh scattering arises from transitions that begin and end at the same vibrational energy level while Stokes Raman scattering arises from transitions that begin at the vibrational energy level of the ground state and end at a higher vibrational energy level. On the other hand, anti-Stokes Raman scattering, which is less likely than Stokes and therefore less intense, involves a transition from a higher vibrational energy level to a lower one. The energy gained by the molecule in Stokes scattering appears as vibrational energy and when a molecule has excess vibrational energy above the ground state, it is this energy which is lost to the anti-Stokes scattered photons [66].

From a classical approach to the phenomenon of radiation-matter interaction, it is possible to think (as was done in the previous section) of a sinusoidal oscillating external field ϵ (Equation 2.7) interacting with a set of atoms or molecules.

$$\epsilon = \epsilon_o \cos 2\pi \nu_o t \tag{2.7}$$

with ϵ_o the equilibrium field strength and ν_o the frequency of the radiation. This interaction generates a small displacement of the electron cloud with respect to the nucleus, inducing a dipole moment (μ_i) proportional to the incident field [66]. If the field is oscillating, so will be the induced dipole. This induced dipole will emit or scatter radiation of frequency ν_o (Rayleigh scattering). In the particular case of a diatomic molecule vibrating with a frequency ν_v , we can express its vibration by a coordinate q_v which variate as a sine function with frequency ν_v . In turn, this vibration will induce small changes in polarizability (α) can be written as [66]:

$$\alpha = \alpha_o + \left(\frac{\partial \alpha}{\partial q_v}\right)_o q_v \tag{2.8}$$

Finally, and recalling that the frequency of the field is ν_o it is possible to write the induced dipole moment (μ_i) in its classical form for a diatomic molecule interacting with an external field:

$$\mu_i = \alpha_o \epsilon_o \cos 2\pi \nu_o t + \left(\frac{\partial \alpha}{\partial q_v}\right)_o \frac{\epsilon_o q_v}{2} \left[\cos 2\pi (\nu_o + \nu_v)t + \cos 2\pi (\nu_o - \nu_v)t\right]$$
(2.9)

The first term in Equation 2.9 describes the Rayleigh scattering and the remaining terms describe the Stokes and the anti-Stokes Raman scatters. Light will be scattered with frequencies:

$$\nu_{scat} = \nu_o \qquad Rayleigh \ Scattering$$

$$\nu_{scat} = \nu_o \pm \nu_v \qquad Raman \quad Scattering$$
(2.10)

From Equation 2.9 it can be observed that the polarizability of the molecule must change during a vibration if that vibration is to be Raman active.

One last feature to mention about Raman spectroscopy refers to the spectral shape. The spectral pattern is characterized by the energy or frequency shifts mentioned above. In general, absolute intensities are not easy to know, so we usually work in terms of relative intensities. In addition, for crystalline solids, the spectral bands are usually narrow and sharp, with broadenings mostly coming from the inharmonicities of the molecular vibrations. Other factors that can alter the width of the bands are defects (vacancies or impurities) or that the material is amorphous (short range of periodicity in the crystal lattice) [67]. In our case, the material under study is not amorphous but nanostructured. Therefore, the number of unit cell in each direction is highly reduced from a bulk.

Finally, the above theory can be applied not only to understand Raman spectra but also Confocal Raman Microscopy. This technique is employed in several works presented in Chapters 3, 4 and 6. With this technique a significant improvement in both the contrast and the spatial resolution may be obtained, in comparison with conventional microscopy, when a point source is focused at the diffraction limit onto the specimen, while the enlarged image of the illuminated spot is analyzed through a pinhole diaphragm. Unlike a conventional microscope, where the entire field is illuminated, the confocal system measures simultaneously the intensity of the light reflected or transmitted by a very small area of sample. A reconstruction of a two-dimensional image is performed via numerical data treatment of the photoelectric signals resulting from a sequential analysis by an XY-raster scanning of the sample field [67]. An example of an image taken by confocal raman microscopy on sample S2 : 11M where four spectra are observed at different points of the image is shown in Figure 2.9.

Raman spectra for nanostructured titantes are usually characterized for a series of raman active bands. Around 900 cm^{-1} the peak is considered to be ascribed to Ti - O stretching involving non-bridging oxygen atoms [56, 68–75]. The region between 670 cm^{-1} and 280 cm^{-1} are related to different Ti - O - Ti stretching modes of titanate nanotubes. At low frequencies a mixture of peaks usually appears, these peaks are assigned to lattice modes $(Na^+ - O - Ti)$ [76] or can be associated with the Ti - O - Ti vibrational modes in the $[TiO_5]$ layer. Additionally, the Raman spectra could showed the presence of peaks at ~ 1100 cm^{-1} , related to CO_3^{-2} anion [77], probably formed with CO_2 from the air as can be seen from Figure 2.9 in the blue curve.



Figure 2.9: A-Conforcal Raman microscopy for sample S2:11M and B- the spectra in different zones marked in the image with colours. The difference in the Raman spectra for the different zones is observed, denoting the presence of zones with different vibrational responses and therefore different compositions (black curve).

2.3.3. X-Ray Absorption Spectroscopy: EXAFS and XANES

X-ray absorption spectroscopy (XAS) is an essential tool for studying the structure of atomic energy levels [78], providing valuable information on the oxidation state, coordination environment and bonding characteristics of specific elements in a sample in a short range approach. Since 1952, with the discovery of synchrotron radiation, this technique has become increasingly important. With the possibility of having tunable X-ray sources, the capabilities of this technique are magnified. Different contributions in the understanding and interpetation of the collected spectra have allowed XAS techniques to evolve from a spectroscopic tool to a structural technique [79].

The total X-ray absorption spectrum can be divided into two regions: the Extended X-ray Absorption Fine Structure (EXAFS) that allows to quantify interatomic distances, near-neighbor coordination numbers and lattice dynamics. X-ray Absorption Near Edge Structure (XANES), on the other hand, gives information on valence state, energy bandwidth and bond angles.

The configurations for data acquisition can vary between transmission, fluores-

cence, energy dispersion and reflectance. In Figure 2.10 a transmission detection scheme is presented, since it was the arrangement used in this work. For this type of measurements, the sample requires some preparation to prevent exceeding the absorption threshold. Therefore, the sample is suspended in alcohol and progressively deposited on a Millipore membrane, so as to adjust the thickness to have a total absorption around 1.25.



Figure 2.10: Schematic of the experimental setup for the transmission configuration of EXAFS and XANES measurements.

Figure 2.11 shows the normalized X-ray absorption cross section as a function of energy. There, the near-edge and extended absorption regions are indicated. The absorption cross section (probability of an absorption process), $\mu(E) \cdot x$, is obtained by measuring the attenuation that X-rays experience when passing through a sample of thickness x, as indicated in Equation 2.11, where I_0 and I_1 (Figure 2.10) represent the intensity of the incident and transmitted beam by the sample.



Figure 2.11: Normalized X-ray absorption cross section as a function of energy for a TiO_2 Anatase sample indicating EXAFS and XANES regions. Measurements taken using the facilities of the Brazilian Synchrotron Light Laboratory (LNLS), beamline XAFS1.

$$\frac{I_1}{I_0} = \exp\{-\mu(E) \cdot x\}$$

$$ln \frac{I_0}{I_1} = \mu(E) \cdot x$$
(2.11)

Each of the regions will be described below.

2.3.3.1. XANES

The X-ray absorption process results from the excitation of an inner-level electron to a higher energy level by an incident photon. Since it involves an electronic transition, it can be represented by a transition matrix element that couples the initial state $\langle i |$ to the final state $|f\rangle$:

$$\mu(E) = |\langle i | \vec{\epsilon} \cdot \vec{r} | f \rangle|^2 \tag{2.12}$$

Where $\vec{\epsilon}$ is the electric field polarization vector of the photon, and \vec{r} is the position vector of the photoelectron. Since the operator coupling the two states is a dipole, the selection rules apply and thus determine the allowed final states for a given initial state. For example, when an electron in the 1s level is excited, the empty p level of lower energy will be occupied, the process being called K-edge absorption. The empty energy levels above the Fermi level in a compound are sensitive to the nature of the chemical bond and its valence. Changes observed in absorption can be quantitatively related to the valence state of the absorbing atom, and such measurements can then be used to determine the valence of a given atom. Due to the atomic nature, this type of experiment requires well-defined and tunable X-rays over a wide range of energies. This is only possible using synchrotron light

2.3.3.2. EXAFS

Extended absorption spectroscopy of the fine structure is an interference effect caused by the interaction of photoelectrons from the inner levels of the nucleus stripped by resonant radiation, and backscattered electrons from neighboring atoms, modulating the wave function of the final state of the absorbing atom. This interference is related to the radial distribution function around the central absorbing atom. To address the problem it is possible to use the plane wave formalism to describe the electrons and as a result to describe also the oscillatory part of the absorption coefficient $\chi(k)$ for the fine structure as follows:

$$\chi(k) = \sum_{j=\text{atoms}} \frac{N_j S_0^2 f_j(k)}{kR_j^2} e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda_j(k)} \sin(2kR_j + \delta_j(k))$$
(2.13)

Where N_j represents the number of neighbors, R_j the distance between neighbors, σ_j^2 the disorder in the neighboring atoms, $f_j(k)$ the backscattering amplitude, S_0^2 the total attenuation factor, $\delta_j(k)$ the phase factor and the mean free path of the photoelectron λ_j . All these factors depend on the wave vector $k = 2\pi/\lambda$. The exponential term takes into account the distortion of the interatomic distance due to static and thermal disorder. It is related to the Debye-Waller factor of X-ray scattering [79]. The Equation 2.13 allows the numerical determination of the local structural parameters N_j , R_j , and σ_j^2 knowing the scattering amplitude $F_j(k)$ and phase $\delta_j(k)$ for a small number (typically 1 to 10) of shells or paths. In practice, in order to apply this equation it is necessary to assume a certain starting structure for the sample, thus choosing the number of paths in which the adjustment is to be made to obtain the distances between atoms of interest. In this thesis it is proved the Ti - O pentacoordination.

EXAFS and XANES measurements must be acquired in a laboratory using synchrotron light. While small equipments are available, it does not achieve the range of accuracy and versatility that synchrotron installations have. In particular, this measurements used facilities of the Brazilian Synchrotron Light Laboratory (LNLS), part of the Brazilian Center for Research in Energy and Materials (CN-PEM), a private non-profit organization under the supervision of the Brazilian Ministry for Science, Technology, and Innovations (MCTI). The XAFS1 beamline staff is acknowledged for the assistance during the experiments. This technique was only used in two samples in Chapter 3, due to the possibility of accessing the synchrotron during the work period.

2.3.4. Electron microscopy techniques: TEM, HRTEM, Electron diffraction and EDS.

Electron microscopy is a valuable tool used for high-resolution imaging in a variety of applications, including material science, physics, chemistry, biomedical research and technology [80]. Electron microscopes can capture images at a much higher resolution than optical microscopes (nm vs μm respectively), providing information that would otherwise be unattainable. The electron microscopes work

by accelerating a focused stream of electrons in vacuum toward a sample. The interactions between the electron beam and the sample create an image, similar to the way optical microscopes use light to capture images. The image created reveals details of a sample's surface or internal composition, depending on the type of electron microscope used [80–82]. Transmission electron microscopy (TEM) gives information about the internal characteristics of the sample. When the microscope is operated in its classical mode (not in high resolution) it is used to quantify the morphologies present in the samples as well as to determine morphological distances. In this particular work, the structures obtained were nanorods, nanotubes and nanoparticles, as it was mentioned in Table 2.1. By means of the *Digital Micrograph* software the morphology and average characteristic distance (diameter and length) were obtained. Figure 2.12 shows some of the morphologies obtained in three of the synthesized samples.



Figure 2.12: TEM images exemplifying different stuctures obtained during the synthesis. A-S2:9M showing tubular structures, B- Uncoiled sheet for M3 and C- S1:9M nanorods.

Furthermore, if the microscope works in the high resolution mode (HRTEM), where the magnification is higher (0.1 *nm* resolution), atomic arrangement could be detected. The difference between the images obtained in both modes is illustrated in Figure 2.13, where A shows a normal mode micrography and B exhibits an image in HRTEM mode. In addition, the procedure for establishing the interplanar distance using HRTEM images is also illustrated in Figure 2.13 C and D. First of all, an area where the atomic arrangement is clearly visible must be selected from the image using the *Digital Micrograph* software. Then, a direction is selected (see colored

lines in the insets of Figure 2.13 C) to generate a profile of intensities, where the white zones (presence of atoms) are given as peaks in the profile, and the dark zones represent the absence of atoms and are valleys on the intensity graph (Figure 2.13 C). By measuring the distance between maximum, it is possible to obtain the approximate interplanar separation.



Figure 2.13: Microscopy images: A- low and B- high magnification extracted from [9]. Inset in A shows diffraction electron image for a periodic arrangement. C- HR-TEM for M2 sample and the areas of study of the atomic planes indicated in colors. D- Intensities on the lines marked on the HR-TEM image, indicating the appearance and absence of atoms. Interplanar distances are obtained from this information.

Another way to study the interplanar distances is by using electron diffraction. The electron beam interacts with the sample in a very specific way when the atoms are arranged in a periodic order. As was introduced in the XRPD section (2.3.1), in microscopy it is useful to work with Miller indices ($h \ k \ l$) and the interplanar distance, d_{hkl} , where the Bragg's diffraction law (Equation 2.3.1) is also valid. In TEM, $\lambda \ll d_{hkl}$, so an electron beam will only be diffracted from lattice planes which are almost parallel to the electron beam. This factor makes the geometry of electron diffraction patterns much simpler than that of X-ray diffraction patterns. However, the accuracy of a structural analysis performed via electron diffraction is rather limited by the relatively small values of the Bragg angles [80].

In the case of our samlpes, their nanostructured character makes sometimes difficult to interpret the pattern. In the context of crystalline materials, electron diffraction patterns typically exhibit a central maximum resulting from the electron beam passing entirely through the sample. This central maximum is accompanied by higher-order maxima that correspond to the lattice structure, as illustrated in Figure 2.13 A (inset). However, in the case of nanostructured samples, the resulting diffraction patterns resemble those of polycrystalline materials. These patterns, as it is exemplify in Figure 2.14, consist of concentric circles, where the distance from the center of the pattern to these circles can be correlated with the interplanar distance within the crystal lattice. This characteristic pattern allows researchers to analyze the structural features of the nanostructured material, even though the presence of multiple orientations within the polycrystalline sample may result in a more complex diffraction pattern.



Figure 2.14: Selected Area Electron Diffraction (SAED) image for M2. Scale line equivalence: $5 nm^{-1}$

Finally, Energy Dispersive X-Ray Spectroscopy (EDS) is an analytical technique that enables the elemental analysis of materials. A sample excited by an energy source, in our case an electron microscope, dissipates some of the absorbed energy by ejecting a core-shell electron. A higher energy outer-shell electron then proceeds to fill its place, releasing the difference in energy as an X-ray that has a characteristic spectrum based on its atom of origin. This allows for the compositional analysis of the sample. The position of the peaks in the spectrum identifies the element, whereas the intensity of the signal corresponds to its concentration. However, to precisely quantify the amount of each element it is necessary to calibrate the measurement setup. In our work, we have not collected calibrated measurements so the error in the estimates will be around 15 % [83].

We use the relative amplitudes to establish a criterion for the concentration of

sodium in the samples, as will be presented later in Chapter 4. To make this estimation, we proceed as follows: with the EDS data, the peaks corresponding to sodium (see Figure 2.15) are selected and the area under the curve for these peaks is estimated. Then, the same procedure is performed for the oxygen and titanium peaks and the *sodium*/(*sodium* + *titanium* + *oxygen*) ratio is calculated. This gives a measure of the relative amount of sodium in the sample.

It should be noted that some samples have peaks that do not correspond to any of these three elements, due to impurities in the synthesis process or even to the way they are measured. Furthermore, some overlapping between different elements can be observed. It should also be noted that this uncalibrated technique presents important differences between light and heavier elements [83]. For this reason, it was decided to make the sodium ratio with respect to the total expected elements present in the sample (without considering hydrogens, since they are invisible for this technique) and not with respect to titanium or oxygen separately. Details of the EDS and HRTEM techniques are presented in Chapters 3 and 4.



Figure 2.15: EDS measurements for A- S1 : 10M and B- S2 : 9M. It can be observed (A, red zone) the overlapping of some elements. The porcentages are obtained by estimation without calibration, and some trace elements are present.

2.3.5. Electronic properties

Three techniques are presented in this thesis to study the electronic properties of samples. The first technique studies the frequency response of the sample to a sinusoidal excitation by means of electrochemical impedance spectroscopy (EIS). This technique explores the electrical response at different frequencies for a given temperature (room temperature). The second technique measures the evolution of the impedance of the sample, excited with a fixed frequency signal, as the temperature is varied over a possible operative range (assuming that the application is a battery, this temperature range goes from $-30 \,^{\circ}C$ to $50 \,^{\circ}C$ aproximately). Finally, the optical properties of the samples are probed by analyzing the optical absorption and photoluminescence at room temperature, before and after submitting the sample to a temperature cycle.

2.3.5.1. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a technique that uses a small sinusoidal potential (V_{AC}) wave applied as a stimulus, which may also be accompanied by a DC component or bias. As a result, the current response of the system contains an AC component (I_{AC}), with a phase that is generally shifted with respect to the phase of the potential [84]. Both, the phase and modulus of the V_{AC} and I_{AC} are tretaed as the phase and modulus of a complex number, named \tilde{E} and \tilde{j} , and the ratio gives the complex impedance Z ($\tilde{Z} = \tilde{E}/\tilde{j}$). From this relation, information of the kinetics of the system can be obtained.

On the experimental setup, point contacts of silver paint are made at both sides of a compacted samples forming a pellet (0.18 g of sample, at 4 kN for 30 s, see Figure 2.16). Then, the sample with the contacts is placed between two conductive plates (electrodes) which are in turn connected to a function generator capable of adding an offset DC potential to its sinusoidal signal ($V_{AC} + V_{DC}$ called disturbance). The system is in turn connected to a current-voltage converter and a frequency analyzer in order to detect the sample response (I_{AC}). The measurement setup detects not only the amplitude but also the phase of the AC signal of both the disturbance and the response. The measurement is repeated for different frequency and DC values. Once these frequency components have been separated, the final measurement is obtained, which is the reason for the name of the technique (spectroscopy in the sense of frequency spectrum, in this case of an electrical response).

One possible way to interpet the obtained data is by associating the obtained results with the behavior of some circuit with known elements (resistors, capacitors, constant phase elements, among others). These equivalent circuits are then physically interpreted, either by their characteristic response times or by their macro-



Figure 2.16: Pellets prepared by compacting powdered samples in a hydraulic press at 4 kN for 30 s.

scopic properties in the conduction processes. There are some physical processes that can be modeled by simple electrical elements. Such is the case of a membrane or interphase that can be modeled as a capacitor [84]. The concept of interface is more adapted to this work, where we have interfaces between structures and then between clusters. Figure 2.17 illustrates the equivalent circuit that explains the interface model. Additionally, there are other simple elements that have known impedances and represent known phenomena (e.g., diffusion or attenuation) listed in Table 2.3.

In general, real phenomena are usually more complex than a single interface or diffuser, so several elements must be included to explain the behavior of the whole system. This causes the equivalent circuits to increase in complexity due to the increase in the number of fitting parameters. Even so, it should always be sought to find the equivalent circuit that best explains the behavior of the system and that contains a number of elements that can be associated to physical processes that are likely to occur in the system.



Figure 2.17: Double-walled model representing an interface or double membrane. A-Schematic of the interface as a capacitor including the Faradic current (j_f) and displacement current (j_d) , σ represents the charge. B- Schematic of the equivalent circuit for this model with the Faradic impedance Z_f and C_{dl} the membrane capacitance.

In addition to the widely known elements that can make up a circuit (resistors, capacitors and inductors) there are other types of elements that are convenient to introduce when working in EIS. An important element used in this work is the Constant Phase Element (CPE). This element is similar to a capacitor but its phase does not change in quadrature but can vary any angle from 0° to 180° , and its is not an ideal element as it is usually used to explain deviations to ideal models [85]. Like capacitors, it is often used in circuits in conjunction with resistors.

Before continuing it is useful to introduce the concept of Nyquist graphs. These graphs, which consist of plotting the frequency evolution of the imaginary part of the impedance against the real part of the impedance, give a simple and quick way to identify the predominant processes in the system and therefore associate an equivalent circuit to it. Some examples of Nyquist diagrams are shown in Figure 2.18. There, it is observed that for a 2RC circuit (paralell RC in series with a R, Figure 2.18 A) representing a simple electron transfer, the shape of the graph is a half arc. In this case the behavior at low and high frequencies is similar, having a maximum response at the midpoint of the radius of the circumference. Moreover, in the case of a 2RCPE circuit (Figure 2.18 C), the semicircle is off center and flattened [84, 85].

On the other hand, for processes involving diffusion, where a new Warbug element (CPE with a constant phase of 45°) or 2R2C (RC serie with C paralell and in serie with a R, Figure 2.18 B) element is introduced, the arc is present but as frequencies increase the arc opens in the form of a monotonically increasing straight line. The slope of the straight line will depend on the element used.

Table 2.3: Impedance for some common electrical elements. i is the imaginary unit, R the resistance, C the capacitance, L the inductance, Y_{CPE} the equivalent to C but in a CPE and n a value from 0 to 1 that defines the phase shift in a CPE.

Element	Impedance (Z)
Resistance	R
Capacitor	$1/i\omega C$
Inductor	$i\omega L$
Constant phase element	$1/(i\omega Y_{CPE})^n$

Once the EIS measurement has been obtained, the equivalent circuit or circuits that better model the behavior of the system must be identified. After selecting the system, the data can be adjusted (in this thesis work is done with Gamry Echem Analyst Software) to obtain the values of the model's characteristic parameters. With



Figure 2.18: Nyquist plot and equivalent circuit for: Electron transfer reaction for A- 2RC and C- 2RCPE and Difussion process as B- 2R2C and D-2RCZw. Z_W represents the Warburg element modulus impedance.

these values it is then possible to obtain the characteristic times of the equivalent circuits, representing another way to approach the problem. As an example, and because it is used later in Chapters 3 and 4, we will introduce now the the time constant for a RCPE circuit (R in parallel with a CPE). In analogy with a RC circuit (which has a time constant of the product $\tau = RC$), the characteristic time for a RCPE circuit takes the form $RY_{CPE}^{1/n}$. Its physical interpretation is that this time is associated to a charge mobility time (lifetime) inside the grain or a dielectric relaxation time. During the thesis this type of physical interpretations are made, linking lifetimes with possible physical processes occurring in the samples and studying the behavior with the applied DC voltage [86–91].

It is important to mention that the electrical measurements depend on the distance between the electrodes, which in this case is associated with the thickness of the sample. While the pressing pressure and mass were kept constant for the pellet, the compaction of each sample is different. This results in pellets of different thicknesses. Therefore, the values should be analyzed considering this variable characteristic in the samples.

2.3.5.2. Temperature-dependent electrical impedance (Z(T))

After probing the electrical response of the samples as a function of frequency, and identifying the processes present in the conduction along with the association of an equivalent circuit to explain them, we move on to the study of the impedance properties with temperature. These measurements are performed in two frequency bands (high and low) where different behaviors of the system were previously identified. The behavior of the system at low frequencies is mostly resistive and as the frequency increases the system response becomes more capacitive.



Figure 2.19: Representation of the circuit setup for Z(T) measurements.

Temperature measurements are performed inside a closed cycle cryostat (CRY-ODINE), where a vacuum was made from atmospheric pressure to 10^{-4} mbar with a HiCube pump. This equipment allows going to very low temperatures but measurements were made between 240 K and 325 K. This temperature range, in addition to being a possible operating range, was selected because no appreciable changes were observed below 240 K.

For the calculation of the impedances and the study of their variation with temperature in different samples, the arrangement of the contacts in the samples is crucial. The contacts are made with silver paint but this time on the same side of the pellet. These contacts are soldered with thin copper wires (0.1 mm diameter) connected in series to a resistor (R_0) and a function generator (*TEKTRONIC AFG* 3021B) as shown in Figure 2.19. As the geometry of the contacts in the sample is not reproducible the analysis focused on the dependence with temperature and not in the specific value of the impedance Z. The sample is excited by means of a sinusoidal signal with a fixed frequency (10 Hz and 20 kHz). The sample response signal V_2 is collected and amplified by a lock-in amplifier (SR 530) in the configuration shown in Figure 2.19. Another lock-in amplifier is used for register the reference resistance V_1 and both lock-in are connected sharing references with the function generator. In this configuration the impedance can be calculated as follows:

$$V_{1} - R_{0}I = 0 \quad \rightarrow \quad I = \frac{V_{1}}{R_{0}} = \frac{V_{1R} + iV_{1I}}{R_{0}}$$

$$V_{2} = V_{2R} + iV_{2I} = Z_{eq}I = Z_{eq}\frac{V_{1R} + iV_{1I}}{R_{0}}$$

$$Z_{eq} = R_{0}\frac{V_{2R} + iV_{2I}}{V_{1R} + iV_{1I}}$$
(2.14)

Where the subscripts $_R$ and $_I$ represents real and imaginary part respectively and I represents the current. By studying the evolution of the modulus and phase of the impedance calculated by Equation 2.14, changes in the electrical behavior of the samples can be observed. These effects are studied in Chapters 4 and 6. Finally, it is worth mentioning that no previous reports on this kind of measurements were found in literature.

2.3.6. Optical properties: Absorption and photoluminescence

Optical properties are an important part of the study of the electronic properties of a given material. Like Raman measurements, these techniques not only provide valuable information from an experimental point of view, but also properties that are easily comparable with results from theoretical simulations. In fact, this relationship is studied in Chapter 5 of this thesis. Within the optical properties, absorption and photoluminescence are the two properties explored.

Absorption is obtained indirectly by light transmission measurements on the sample. An experimental setup containing a solar simulator lamp is used. Due to the position of the absorption edge for our samples (around 3 - 4 eV), a 1000 W Xe lamp (Oriel 6271) with a broad spectrum and emission in the area of interest was used. This lamp exhibits the spectrum shown in Figure 2.20. Below 300 nm the lamp shows almost no emission, between 300 nm and 400 nm, an important energy range to study the samples, the lamp shows stable emission. After 400 nm the absorption peaks of the gas that composes the lamp are observed, and then a flat area above 500 nm is found where the spectrum has an anomalous behavior. Both, the region without emission and the region with peaks, is outside the region of interest. Due to the high emitting power of the lamp, an absorption filter is used to attenuate the light reaching the sample to avoid damage and saturation in the spectrometer (*OO FLAME*).

The samples, which are measured in pellets prepared under conditions similar



Figure 2.20: Spectrum of the 1000 W Xe lamp (Oriel 6271) showing the range of interest for the optical measurements in this work.

to those used for EIS measurements (Figure 2.16), are held in a glass that is placed at the entrance of an integrating sphere (see Figure 2.21). The sphere is connected to a spectrometer where the transmitted signal is detected. In order to analyze the data it is necessary to take a reference spectrum containing only the light from the lamp with the filter. The ratio of the input light (I_o) (the signal collected without the sample) to the transmitted light (I) gives the absorption by the sample (Equation 2.11). Explicitly, considering that the absorption is determined by the Lambert-Beer Law, the absorption coefficient α can be calculated as a function of the transmitance $T_d = I/I_o$ as $\alpha = -log(T_d)$ [92].



Figure 2.21: Schematic of the experimental setup for transmission measurements. F: Filter, S: Sample, IE: Integrating sphere, OF: Optical Fiber, Spectro: Spectrophotometer.

Let's see a brief development of the optical properties in order to understand the data analysis performed. From a semiclassical approach to the interaction of light with the material, a classical field with angular frecuency ω and amplitude $E(\omega)$ is assumed interacting with an atomic system modeled with the quantum formalism. The probability of occurrence of an atomic transition from a state $|i\rangle$ to a state $\langle f|$,

 P_{if} , can be obtained by the Fermi's Golden Rule as [93]:

$$P_{if} = \frac{2\pi}{\hbar} \left(\frac{e}{m\omega}\right) \left|\frac{E(\omega)}{2}\right|^2 \sum_{k_v,k_c} |B_{if}|^2 \delta(E_c(\vec{k_c}) - E_v(\vec{k_v}) - \hbar\omega)$$
$$\sum_{k_v,k_c} |B_{if}|^2 \delta(E_c(\vec{k_c}) - E_v(\vec{k_v}) - \hbar\omega) = \frac{2}{(2\pi)^3} \int d^3k \delta(E_c(\vec{k_c}) - E_v(\vec{k_v}) - \hbar\omega) = n_{cr}$$
(2.15)

Where B_{if} is a probability amplitude and it is supposed to be constant, and n_{cv} is the combined state density. The *c* and *v* subscripts correspond to the conduction and valence states, respectively. This combined density of states can be calculated for each system. In particular, there are two common models that define two particular types of transitions. Both will be developed below as they are used in the following chapters. Before developing these particular cases, it remains to relate the transition probability described in Equation 2.15 to the power loss (*R*) in the transition, and to the absorption coefficient [93]:

$$R = \hbar \omega P_{if}$$

$$R = \frac{c}{n} \alpha I_o \qquad (2.16)$$

with c the speed of light in vacuum and n the refractive index.

With these relation in mind it is possible to move on to the study of two particularly relevant cases, direct and indirect transitions. In direct transitions the quantity of momentum of the photon is conserved, so that the condition $\vec{k_v} = \vec{k_c} = \vec{k}$ is satisfied (Figure 2.22 A). If the material under study is a semiconductor with a bandgap of energy E_g and if the bands are parabolic, the energies of the electrons in each band will be [93]:

$$E_{c}(\vec{k}) = E_{g} + \frac{\hbar^{2} \vec{k_{c}}^{2}}{2m_{c}^{*}}$$

$$E_{v}(\vec{k}) = -\frac{\hbar^{2} \vec{k_{v}}^{2}}{2m_{v}^{*}}$$
(2.17)

With these expressions for E_c and E_v it is possible to calculate the combined density of states n_{cv} by means of Equation 2.15. Defining the reduced effective

mass as $1/m^* = 1/m_c^* + 1/m_v^*$ we obtain:

$$n_{cv} = \frac{4\pi}{(2\pi)^3} \left(\frac{2m^*}{\hbar^2}\right) (\hbar\omega - E_g)^{1/2}$$
(2.18)

Therefore, the absorption coefficient for a direct semiconductor has the following dependence whit E_g and $h\omega$:

$$\alpha \propto \frac{(\hbar\omega - E_g)^{1/2}}{\hbar\omega}$$
(2.19)



Figure 2.22: Schematic representation of the band structure for the A-Direct and B- Indirect electronic transitions with two possible transitions.

This relationship for the absorption of a direct edge will be used on the experimental data to obtain direct gap values in the samples.

A similar reasoning can be made for the study of indirect transitions. These transitions are characterized by having the maximum of the valence band at a different wave vector value than the minimum of the conduction band (Figure 2.22 B). Unlike direct transitions, in this case the photon momentum will no longer be sufficient to maintain the conservation of electronic momentum. Therefore, the transitions will have to be mediated by the emission or absorption of a phonon [93].

This phonon will have a momentum $\vec{k_P}$ end energy $E_p = \hbar \omega_p$ which balances the initial and final state. Therefore, the conservation of energy will also be modified. The schematic in Figure 2.22 B shows the two processes by which the absorption of a photon occurs. In the first one, a photon of energy $\hbar \omega_1$ is absorbed. Since the wave vectors of the initial and final states are different, the system must emit a phonon of energy $\hbar \omega_p$, which carries away the excess energy and contributes to the conservation of momentum. In the second process, the photon having energy $\hbar\omega_2$ is absorbed, so a phonon of energy $\hbar\omega_p$ must be absorbed. These two possible processes can be written, in terms of energy conservation, as [93]:

$$\hbar\omega = E_c(k) - E_v(k) \pm E_p \tag{2.20}$$

For this type of transition, the expressions for the joint density of states cannot be obtained with the expression described in Equation 2.18, but must appeal to higher developments of Fermi's Golden Rule [93]. As a result of this operation, the following expressions for the valence and conduction bands are obtained ([93]):

$$n_{cvv} \propto \begin{cases} (-E_v)^{1/2} \ if \ E_v < 0 \\ 0 \ if \ E_v > 0 \end{cases}$$
(2.21)

$$n_{cvc} \propto \begin{cases} (E_c - E_g)^{1/2} \ if \ E_c > E_g \\ 0 \ if \ E_c < E_g \end{cases}$$
(2.22)

Being the transition rates:

$$R \propto \begin{cases} \frac{(\hbar\omega E_p - E_g)^2}{\hbar^2 \omega^2} & if \ \hbar\omega > E_g \pm E_p \\ 0 & else \end{cases}$$
(2.23)

The absorption coefficient will be the sum of the emission absorption coefficient α_e and the photon absorption coefficient α_a .

$$\alpha = \alpha_a + \alpha_e \tag{2.24}$$

$$\alpha_a \propto \frac{(\hbar\omega + E_p - E_g)^2}{\hbar\omega}$$

$$\alpha_e \propto \frac{(\hbar\omega - E_p - E_g)^2}{\hbar\omega}$$
(2.25)

Up to this point it has been assumed that a material either has a direct edge or an indirect edge. In general, in non-crystalline or composite materials the band structure is complex and it is possible to detect the presence of a mixture of both direct and indirect edges (Figure 2.23) [14, 94]. Such is the case of the samples under study in this thesis. In several of the samples, the absorption profiles show a step-like behavior. This leads to the assumption that both types edges must be present in the samples. To perform the fits, it is useful to introduce Tauc plots as $h\nu$ vs $(\alpha h\nu)^n$ with n = 1/2 for an indirect absorption and n = 2 for a direct one. In our data, in addition to removing the background assuming an indirect edge, a direct fit is made on the Tauc plot (n = 2), and this component is subtracted from the data to make the subsequent indirect fit. In this way, at least two gap values corresponding to a direct and an indirect fit are obtained. The adjustment process is explained in detail in Chapter 3 and it is applied to Chapters 3 to 6.



Figure 2.23: Bands structure obtained by DFT calculation TiO_2 . Extracted from [94] with the x axis the atomic orbitals as defined in [95].

In addition to the radiation absorption processes experienced by the sample, emission processes can be studied. Photoluminescence, as well as electroluminescence and thermoluminescence, belong to the group of emission processes. We will focus on the photoluminescence that is the optical radiation emitted by a physical system resulting from its excitation to a nonequilibrium state by irradiation with light [96]. There are three different types of processes that can be associated with photoluminescence emission: the creation of electron-hole pairs (e - h) by the absorption of the exciting light; radiative recombination of e - h, which represents the reverse process of optical absorption; and the recombination radiation escaping from the sample [96].

For radiative recombination of e - h, recombination rates can be obtained from the Fermi's Golden rule, using an approach similar to the one used in the study of optical absorption ($\alpha(\omega)$). The relation between the absorption coefficient and the recombination rate of the e - h pair can be obtained (van Roosbroeck-Shockley relation) if the system is assumed to be in thermal equilibrium and studied according to the *detailed balance* assumptions. A detailed development of this model is presented in [93], where some central conclusions are remarked:

- The intensity of the optical emission will be proportional to the rate of recombination of the carriers.
- The optical emission will not be sensitive to the differences between the parabolic band model and the actual shape of the band structure. Therefore, for the study of the optical emission it will be sufficient to model the shape of the bands as if they were parabolic bands.
- This model is particularly useful when there is no theory or model available to explain the shape of photoluminescence spectra.

It may be interesting to study the possible shapes of the emission spectra, in order to properly select the models for fitting them. For the case of transitions between discrete levels the emission spectrum will have discrete lines positioned at the energies corresponding to that transition. However, experimentally it is observed that in a solid these lines present a broadening in energies [93]. This spectral broadening can be represented by a line function $f(\hbar\omega)$. The probability that the recombination of an e - h pair occurs by emitting a photon whose energy is between $\hbar\omega$ and $\hbar(\omega + d\omega)$ is associated with the quantity $f(\hbar\omega)d\omega$ and satisfies the normalization condition [93].

In the case of atomic systems, it is simple to understand the mechanisms of spectral line broadening (Doppler effect, collisions and lifetime of carriers [93, 97]). For semiconductors the origin of the broadening becomes more complex. For example, small distortions in the crystal lattice will introduce changes in the electronic structure and energy levels. Furthermore, electrons and holes interact with other charge carriers or phonons changing their energy. In addition, the presence of isotopes of the atoms will generate differences in energy levels. As a result of these processes, there will not be a single characteristic frequency for each transition [93].

This variety of phenomena leads to a classification of possible broadening. If the broadening occurs for all transitions with the same center frequency and with the same broadening mechanism, we have the case of homogeneous broadening. For these cases, the emission spectrum will be a Lorentzian curve. However, if the frequencies of the resonances are different or the broadening mechanism is different, we have the so-called inhomogeneous boradening. In this case, different Lorentzian curves centered at different frequency values may be considered. The values for this main frequency (resonance frequency) will be given by a Gaussian distribution of values. Therefore, the emission spectrum may be represented by a Voigth curve (the convolution between a Lorentzian and a Gaussian functions), which in the par-

ticular case where the width of the Gaussian curve is much larger than that of the Lorentzian curve, the spectrum will be Gaussian [93]:

$$f_{hom}(\hbar\omega) = \frac{2\Delta\omega}{2\pi[(\omega - \omega_o)^2 + \Delta\omega^2]} \quad homogeneous$$

$$f_{inhom}(\hbar\omega) = \frac{1}{\sqrt{2\pi\Delta\omega}} e^{-\left(\frac{\omega - \omega_o}{2\Delta\omega}\right)^2} \quad inhomogeneous$$
(2.26)

Where ω_o is the resonance frequency and $\Delta \omega$ is the curve broadening.

Finally, it is worth mentioning that in the presence of defects in the crystal lattice (either in the inner or at surface level) discrete energy levels will appear in the interior of the forbidden band. This will promote the appearance of emission signals specific to each type of defect. In the following chapters we will see an interpretation of the photoluminescence signals of the samples in relation to some possible defects present in their structures, such as oxygen vacancies, distortion in the tetrahedron Ti - O and OH group defects. The principal component in PL emission in pure samples are: in the 2.5-3.1 eV region due to oxygen vacancies defects [98], 2.4-2.7eV are ascribed to sallow defects like monoionized oxygen vacancies [99] or electronic transition associated with the $[TiO_6]$ octahedron [100, 101], higher energy emission (2.8-3.1 eV) with deep defects like double-ionized oxygen vacancies [102] and finally the emission at approximately 2.1 eV could be related to OH group defects [98].



Figure 2.24: Two possible setups for photoluminescence measurements. A- Retrodispersive collection configuration and B- Transmission configuration. S: Sample, OF: Optical Fiber, Spectro: Spectrophotometer.

The experimental measurements for photoluminescence were carried out in the pressed samples (pellets) as shown in Figure 2.24. The excitation light selected was

a LED (with narrow emission in the vicinity of 300 nm) whose emission energy was higher than the absorption edge energy. This ensured that the sample was excited to states with possible emission. Measurements were recorded in both backscattering and transmission (Figure 2.24 A and B respectively), and the data were collected with an optical fiber connected to a spectrometer. At all times we tried to minimize the excitation light that was captured by the detector, since its intensity is much higher than that of the photoluminescence signal. The measurements were done at room temperature.

2.4. Theoretical approach: Density Functional Theory

The physical and chemical properties of a compound are governed by what happens at the molecular or atomic level. Understanding the structure, therefore, at a deep level can help predict the behavior of a certain material and can even be used to improve its design. It is well known that the study of matter at the atomic level is highly complex, due to the number of variables involved in the development of the theory. Even so, there are methods to approach the problem. In this section we will present the basis of the Density Functional Theory (DFT) approach, a method that involves certain approximations to solve the quantum mechanical equations that describe the structure of matter.

2.4.1. Quantum mechanical description of matter

As has already been mentioned in previous sections, matter is formed by a more or less ordered set of atoms and the properties of such matter will depend on the arrangement of these atoms. In general, the physical variable of interest for studying atomic behavior is energy. In particular, the energy of an atom can be modified as a function of its environment, i.e. the atoms surrounding it. To make a detailed study of the physical properties of matter, we must define the positions of the atomic ensemble that constitute it. To do this, one can use the Born-Oppenheimer approach, which proposes to consider atoms as a fixed set of nucleus and a set of moving electrons [103]. The problem is then reduced to studying the motion of electrons around a certain position (given by the atomic nuclei) and then to minimize the energy of the set of moving electrons subjected to a field generated by the atomic nuclei of the lattice [104]. This lower energy state is known as the fundamental or ground state of the system, and is the starting point for studying the variations in the properties of the system if perturbations are made to the positions of the atoms. The energy of the ground state, E_o , can be written as a function of the positions of the nuclei, $\vec{R_i}$, taking the name of *Adiabatic Potential Surface* $E(\vec{R_i})$.

To know the possible energies for a certain physical system approached from quantum mechanics, it is necessary to raise the problem starting with the Schrödinger equation in its non-relativistic form [104]:

$$H\Psi = E\Psi \tag{2.27}$$

Where H represents the Hamiltonian describing the system, E the energy eigenstates corresponding to the Hamiltonian and Ψ the wave function of the system. When we focus on the electrons that conform the system, the Hamiltonian is composed of three contributions: the Hamiltonian representing the motion of the eletrons of mass m associated to a kinetic term; the contribution due to the interaction between the electrons, $U(\vec{r_i}, \vec{r_j})$; and the potential due to the interaction with the nuclei, $V(\vec{r_i})$. Writing it in its explicit form [104]:

$$\left[\frac{h^2}{2m}\sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N \sum_{j(2.28)$$

In this equation Ψ represents the wave function for the electrons, while E is the energy of the fundamental state of the system. This energy is independent of time, so the Equation 2.28 is stationary. It is important to emphasize at this point that the Equation 2.28 depends on 3N variables. In order to reduce the complexity of the system to be solved, it is possible to work on the Hartree-Fock approximation [105, 106] which proposes to represent the electronic wave function as the product of N individual wave functions ($\Psi_1(\vec{r})$):

$$\Psi(\vec{r_1}, ..., \vec{r_N}) \sim \Psi_1(\vec{r_1}) \Psi_2(\vec{r_2}) ... \Psi_N(\vec{r_N})$$
(2.29)

At this point of the theory it is necessary to establish which is the physical observable under study. It is useful to know what is the probability of finding N electrons positioned in the coordinates $\vec{r_1}, \vec{r_2}, ..., \vec{r_N}$. This information is given by the electron density $(n(\vec{r}))$, where the Pauli exclusion principle must be taken into account considering the electron spin [104]:

$$n(\vec{r}) = 2\sum_{i} \Psi_{i}^{*}(\vec{r})\Psi_{i}(\vec{r})$$
(2.30)

The electronic density represented by the Equation 2.30 is a function of three variables, in contrast to the dependence on 3N variables of the density of states (Equation 2.28). This fact is very beneficial, since the electron density will be the basis for solving the initial problem described in Equation 2.28.

In the framework of the DFT, it is possible to find the ground state energy by studying an electron density functional¹ to solve the Schrödinger equation. To make sense of this statement it is necessary to know two mathematical theorems that make possible the study by DFT of a problem such as the one posted in this section. The first theorem, proved by Hohenberg and Kohn [107] states that:

The wave function corresponding to the ground state obtained by the Schrödinger equation is a unique functional of the electron density $(n(\vec{r}))$.

The implication of this theorem is that it is possible to determine all the properties of the ground state only by determining the electron density of the fundamental state. In particular, the Energy (E) is defined as a functional of the electron density $(E[n(\vec{r})])$.

In addition to the existence of this density of states, it is necessary to know what its form is like. For this, a second theorem is proposed and proved by Hohenberg and Kohn [107], which states:

The electron density that minimizes the energy of the total functional is the real electron density corresponding to the complete solution of the Schrödinger equation.

In practice, this variational principle is employed with approximate forms of the functional. A suggested form to describe electron density is to write the functional in terms of the individual wave functions for the electrons, $\Psi_i(\vec{r})$ (see Equation 2.30) [108]. This functional is composed of a first term (E_o), corresponding to a functional containing the information of kinetic energy and Coulombic interactions corresponding to electron-nucleus, electron-electron, nucleus-nucleus (E_{ion}). An additional term (E_{XC}) containing information on the other quantum mechanical effects not included above, must also be included. This term is called the exchange

¹A function that takes real values in a vector space, usually a function space.

and correlation term and has the following form [104]:

$$E\left[\Psi_{i}\right] = \frac{h^{2}}{m} \sum_{i} \int \Psi_{i}^{*} \nabla^{2} \Psi_{i} d^{3}r + \int V(\vec{r}) n(\vec{r}) d^{3}r + \frac{e^{2}}{2} \iint \frac{n(\vec{r}) n(\vec{r'})}{|\vec{r} - \vec{r'}|} d^{3}r d^{3}r' + E_{ion} + E_{XC}$$
(2.31)

$$E\left[\Psi_{i}\right] = E_{o}\left[\Psi_{i}\right] + E_{XC}\left[\Psi_{i}\right]$$

$$(2.32)$$

To solve the problem it is necessary to find the electron density that minimizes the total functional. Kohn and Sham [109] propose that in order to find such a density, one must solve a set of equations involving the individual electron wavefunctions, $\Psi_i(\vec{r})$. The proposed equations are similar to the Schrödinger equation, but with the particularity that they are simpler because they are equations for single particles [104]:

$$\left[\frac{h^2}{2m}\nabla^2 + V(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r})\right]\Psi_i = E_i\Psi_i$$
(2.33)

The solutions $\Psi_i(\vec{r})$ of this equation represent wave functions of individual electrons, depending only on three variables given by the coordinates of the spatial position. Recalling, the potential $V(\vec{r})$ contemplates the interaction between the electron and the ensemble of nuclei. A new potential is introduced, $V_H(\vec{r})$ called the Hartree potential, which describes the Coulomb repulsion between the electron under consideration and the total electron density defined by the total number of electrons in the system [104]:

$$V_H(\vec{r}) = e^2 \int \frac{n(r')}{|\vec{r} - \vec{r'}|} d^3r'$$
(2.34)

_

Looking carefully at the Hartee term it can be inferred that it contemplates the interaction of the electron with itself. In the Equation 2.33 the electron under study is part of the total electron density, as can be seen explicitly in Equation 2.34. This problem is overcome by the V_{XC} potential which takes into account the exchange and correlation effects in the single particle equations. It is possible to mathematically write the relationship between the exchange and correlation potential, V_{XC} , the exchange and correlation energy, E_{XC} , and the electron density, $n(\vec{r})$:

$$V_{XC}(\vec{r}) = \frac{\delta E_{XC}(\vec{r})}{\delta n(\vec{r})}$$
(2.35)

Where δ represents the functional derivative. At this point it is evident that the

problem to be solved is circular, so the methods used are iterative. To recall, if one wants to solve the Kohn and Sham equations it is necessary to know the Hartree potential. Defining the Hartree potential requires knowing the electron density which is defined by the wave functions of individual electrons, solutions of the Kohn and Sham equations. This algorithm represents a self-consistent method of solving the equations.

2.4.2. Correlation and exchange functional

From the previous paragraphs we may be left with the idea that the problem of finding the ground state of the Schrödinger equation describing the system is completely solved. However, when we revisit the method proposed by Kohn, Hohenberg and Sham we see the necessity of defining the exchange and correlation functional (E_{XC} [{ Ψ_i }]) in the Kohn-Sham equations. Although the exact form of this exchange and correlation functional is unknown, it is possible to write it exactly for the particular case of a homogeneous electron gas, where the electronic density is constant. Although this situation is not the one we are interested in solving when studying a set of bound atoms, it can serve as a starting point for using the Kohn-Sham equation. The exchange and correlation potential at each position is set as the exchange and correlation potential of the uniform gas at that position:

$$V_{XC}(\vec{r}) = V_{XC}^{gas}[n(\vec{r})]$$
(2.36)

This approach is called the Local Density Approximation (LDA) and while it can solve the Kohn and Sham equations, it does not solve the exact equation of the problem because it does not use the exact exchange and correlation potential. There are other ways of approaching the problem outside the LDA framework. Here we will mention those that were employed in the thesis work, thus leaving out a large number of approximations for the functional.

There is a class of approximations where local electron density and electron density gradient information is employed. This group is called the Generalized Gradient Approximation (GGA). In particular, when working with GGA it is necessary to establish how the information extracted from the gradient is used in the calculation. In this work the PBE (Perdew-Burke-Ernzerhof [110]) functional is used.

In addition, hybrid functionals can be introduced. These functionals combine

exact information from the exchange function (by Hartree-Fock theory) supplemented with information from other sources (e.g., empirical). In this thesis we explore the hybrid functional HSE06 belonging to the HSE (Heyd-Scuseria-Ernzerhof [111]) family. Generally, hybrid functionals are more computationally expensive but they present more accurate results in terms of electronic properties, reflected in gap values, for example.

The DFT calculations are presented in Chapter 5 of this thesis and although it can be implemented with different codes, in our case VASP code was used [112]. There, the atoms positions in the unit cell are optimized for different possible phases of bulk titanates, the vibrational modes are tested and the electronic properties obtained are studied. The usefulness of using the hybrid functional HSE06 for the calculation of gap values is explored, comparing them with the results obtained from the calculations with PBE and with some experimantal data. The details of the methodology used to obtain the structural, vibrational and optical properties of the selected structures can be found in the introduction of Chapter 5 and in the corresponding article.

Chapter 3

The effect of morphology on the optical and electrical properties of sodium titanate nanostructures

One of the objectives of this thesis work is to synthesize one-dimensional (1D) nanostructures of sodium titanates, in particular with high aspect ratio, for example nanotube structures. This chapter presents the results of investigating various conditions, during hydrothermal synthesis, to achieve this type of nanostructure. Initially, the study builds upon synthesis conditions explored in [53], where tubular nanostructures were successfully obtained. From these trigger conditions, the focus is on exploring the effects of varying the reaction time and synthesis temperature.

The experimental exploration of these variations yields not only tubular nanostructures but also nanorods and nanoparticles, leading to mixtures of different morphologies. To comprehensively characterize each sample, a diverse set of experimental techniques mentioned in Chapter 2 were utilized.

This work serves as a critical starting point for the exploration of different nanostructures and their properties, with potential applications in energy storage. It represents the initial efforts in understanding the obtained structures or phases. Moreover, it marks the beginning of an extensive exploration for the optimization of the materials using several experimental techniques. The results obtained from these techniques are then combined to deepen the understanding of each sample and its unique properties. Appendix A details some of the results and includes extra information published as the Supplementary Material of the article.

The morphologies present in the samples and their structural characteristics

were initially studied using simple and high-resolution transmission electron microscopy (TEM and HRTEM) on the electron microscope (JEOL JEM 2100) at CURE in Rocha, Uruguay. These microscopy techniques provided valuable information about the shapes and sizes of the nanostructures. To further investigate the structural properties, electron diffraction were conducted on the same electron microscope.

Additionally, X-ray powder diffraction (XRPD) measurements were carried out using the Rigaku Ultima IV diffractometer at the Faculty of Chemistry, UdelaR. Complementary small-angle X-ray scattering measurements in grazing incidence configuration (GI-SAXS) were also performed, allowing for the quantification of the average size and shape of the nanostructures. To study the local environments of titanium in the samples, a subset of samples was subjected to fine structure analysis using extended X-ray absorption spectroscopy (XANES and EXAFS). By means of the Athena and Artemis software, the data was analyzed. These measurements were conducted at the XAFS1 beamline at the National Synchrotron Light Laboratory (LNLS) in Campinas, Brazil. The vibrational modes of the samples were determined using Raman spectroscopy, carried out with the confocal Raman microscope (WITEC Alpha 300RA) at the Pando Technological Pole.

Turning to the electronic properties, the frequency response of the samples was characterized using electrochemical impedance spectroscopy (EIS). Data processing was performed using Echem Analyst software from Gamry. This allowed for an understanding of the electrical behavior of the nanostructures. Moreover, the optical properties of the samples, including absorption and photoluminescence, were investigated. This involved studying the absorption profile, edge, and bandgap energy values, as well as examining the relationship between defects and the position of photoluminescence emissions. The experimental set-up for data collection was designed specifically for these samples as explained in the previous chapter. Optical measurements were performed at the Optical Properties Laboratory of the Solid State Group at the Engineering Faculty, UdelaR.

Correlating the results from the different techniques, the study gained valuable insights into the structural and electronic properties of the synthesized nanostructures. This detailed characterization smooth the way for potential applications of these materials in energy storage and other fields.

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The effect of morphology on the optical and electrical properties of sodium titanate nanostructures



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ABSTRACT

Sodium based titanate nanostructures (NaTNT) are promising materials for energy storage and photoelectrode applications. We present an experimental work describing the structural, morphological and electronic properties of hydrothermally synthesized NaTNT, evaluating different synthesis conditions (synthesis temperature and time). We found a clear dependence between the synthesis condition and the observed, morphological, electrical and optical features. Increasing synthesis time and decreasing temperature allow the nanotubes to be filled. Local and extended structural analysis, and Raman spectroscopy, supported the samples stoichiometry with a pentacoordinated Ti-O polyhedral. Electrochemical impedance spectroscopy analysis revealed a predominant two-transport mechanism; however, a third process was observed for two samples with particular morphology (nanorods and nanoparticles co-existing with nanotubes). Finally, the influence on the optical properties of the structural and morphological characteristic is determined and discussed. We found a reduction of the gap energies when compared with anatase. Additionally, from the photoluminescence response we suggest different kind of defects must be present in the samples. This work presents a very complete set of experimental tools for the analysis of NaTNT, showing how the synthesis conditions allow tuning the electrical and optical responses of NaTNT for energy storage and photoelectrode applications.

1. Introduction

Lithium-ion batteries (LIB) are commonly used on several technologies and their use is constantly increasing [1,2]. In search of costeffective systems that increase electronic mobility and power, sodiumion batteries (SIB) are proposed as a possible substitute for LIB [3-5]. While the technologies for both types of batteries are similar, the materials used for each one requires significantly different properties. In particular, the biggest challenge lies in the manufacture of the anode [6-8]. Titanates are a promising alternative for the preparation of anodes for SIB [9]. In particular, we study nanostructured sodium titanates for this purpose. However, the specific atomic arrangement that conforms the nanostructures continues under study [10]. There is a wide variety of works in bibliography, referring to the actual formation mechanism and structural properties of titanates with high aspect ratio [11,12]. Nevertheless, no concluding information is reported, being essential to provide further evidence for the understanding of the physical properties of the obtained nanostructures and correlate them with the structure and the morphology of the samples. This is crucial for

the understanding of the behavior of sodium-based nanostructures for energy storage applications [10].

A controlled synthesis, evaluating different conditions, accompanied with a very complete set of tools for a detailed experimental approach, allows a deep structurally characterization of the samples considered in this work. This is done by means of X-ray Powder Diffraction (XRD), Grazing Incidence Small Angle X-ray Scattering (GI-SAXS), Extended Xray Absorption Fine Structure (EXAFS), High-resolution TEM (HRTEM) and Raman Spectroscopy. With this approach it is possible to shed light on the crystalline structure of these kind of materials and thus further correlate it with the electrical and optical properties. This work presents a thorough experimental characterization employing a complete set of experimental tools, showing how the synthesis conditions allow tuning the electric and optical response of nanostructured Na-titanates for energy storage and photoelectrode applications.

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Full Length Article





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2. Methods and materials

2.1. Synthesis of NaTNT

Sodium titanate nanostructures (NaTNT) were prepared by hydrothermal means under endogenous pressure, using approximately 1.18 g of commercial TiO_2 anatase nanopowder provided by Sigma–Aldrich (ID: 799289, External ID: 232033_ALDRICH). The powder was dispersed in 75 mL of NaOH with 10 molL⁻¹ concentration in a Teflon-lined autoclave with a fill factor of 3/4 under simultaneous magnetic stirring.

To evaluate the effect of synthesis conditions on the obtained nanostructures the temperature reactor (T_s) was varied between 105 °C and 145 °C, and the synthesis time (t_s) was also varied from 48 h to 144 h. The main objective was to study the morphology and the physical properties of the obtained samples as a function of T_s and t_s . As the physical properties of the samples depend on its morphology, we aim to control/predict the different types of morphologies obtained (nanorods and nanotubes) during the synthesis process as a function of these two parameters (T_s and t_s). We suspect that a lower temperature and a longer reaction time could allow the nanotubes to be filled and thus obtain nanorods. The appearance of nanoparticles was not expected in the choice of parameters. Our samples were prepared with a stirring rate between 120 rev/min and 150 rev/min. References [13,14] prove that the length and diameter of the nanotubes increase with the stirring rate, but the narrow variation of this parameter would not affect the morphology itself. However, its variation was necessary for a proper operation of our synthesis set up [11,15,16]. Afterwards, the solid was separated through a centrifugation process, and washed during two days, with 400 ml distilled water. Finally dried for 24 h at 80 °C. The synthesis conditions are summarized in Table 1.

2.2. Characterization techniques

For structural characterization X-ray powder diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer operating with CuK_{α} radiation, taking diffractograms in the range of $2\theta = 5.00 - 80.00^{\circ}$ with a 2θ steps of 0.02° and a 60 s integration time per step. Confocal Raman spectroscopy was performed using WITec Alpha 300-RA confocal Raman spectrometer, operating with $\lambda = 532$ nm laser wavelength. The laser power was adjusted to ~ 30 mW and Raman spectra were obtained by averaging a set of 100 spectra of 0.25 s integration time.

Extended X-ray Absorption Fine Structure (XANES and EXAFS) studies over M1 and M2 samples were made in the XAFS1 beam line, at the National Laboratory of Synchrotron Light (LNLS), Campinas Brazil. This technique allows us to further characterize the local structural environment of the two selected samples (M1 and M2). The study was performed at the titanium K-edge (4966 eV [17]) in the range 4850 to 5696 eV, using a Si(111) crystal monochromator. All the spectra were collected at room temperature in transmission setup. The sample preparation involved the suspension of the powdered samples in 2-propanol, to later be deposited on Millipore membranes. The thickness was adjusted to obtain a total absorption of 1.5. As a reference we measured

Table 1

Hydrothermal synthesis parameters. T_s synthesis temperature, t_s synthesis time and *Rev* stirring rate. For all the samples NaOH (10 M, fill factor 3/4) was used as a solvent.

	Anatase (g)	T_s (°C)	t_s (h)	$\textit{Rev}\left(r/m\right)$	Morphologie obteained*
M 1	1.1900	145	48	120	Nanotube
M2	1.1853	145	72	150	Nanotube & nanoparticle
М3	1.1656	125	96	150	Nanotube
<i>M</i> 4	1.1715	105	96	150	Nanotube
M5	1.1560	105	144	150	Nanorod

See Table 2 for more details.

different oxidation states for titanium, TiO_2 and metallic foil. The data reduction process was performed with the Demeter Suite.

The morphology of NaTNT samples was studied by transmission electron microscopy (TEM) and electron diffraction, obtained using a JEOL JEM 2100 with 100 kV acceleration voltage. The samples were dispersed in ethanol and dropped onto a carbon film supported by a copper grid. Also, high resolution images (HRTEM) were done to obtain the lattice parameters. For better quantification of the mean size and shape of the nanostructures, Grazing Incidence Small angle X-ray scattering (GI-SAXS) measurement were made, also using a Rigaku Ultima IV diffractometer with CuK_{α} radiation, working with 40 kV and 30 mA radiation in the q = 0.15 nm⁻¹ 4.50 nm⁻¹range.

Electrical characterization consists on Impedance spectroscopy (EIS) measurements, performed on pressed pellets at room temperature using a Gamry Reference 3000 impedance analyzer in the 1 Hz-1 MHz frequency range with a 10 mV AC amplitude, and DC amplitude from 0 V to 4 V. Silver blocking electrodes were deposited on both sides of the pellets, then the pellets were placed between two copper plates. Data processing was performed using Echem Analyst software from Gamry.

Finally, optical characterization was carried through transmittance and photoluminescence (PL) measurements in the UV-Visible spectrum. Direct transmittance was measured exiting the pressed pellets with a 1000 W Xe lamp (Oriel 6271). The sample was fixed before the input of an OceanOptics (OO) FOIS - 1 integrating sphere coupled to an OO FLAME (S-UV-vis-ES) spectrometer and a 100 µm core diameter fiber acting as input slit. The direct and indirect band gap values were calculated by means of Tauc's plot. PL was measured using a 300 nm wavelength diode (Thorlabs M300L4) to illuminate the samples. The PL emission was collected in diffuse transmission configuration to avoid detecting the excitation diode light. The light was collected on a 200 μm core diameter optical fiber and sent to an OO FLAME spectrometer. The properties obtained for anatase (20 nm diameter) were used to identify the changes produced using the different preparation conditions. All the measurements were performed at room temperature. As mentioned, for Raman, Electrochemical impedance and transmission measurements the powder samples were pressed into pellets (diameter = 1.2 cm, thickness = 0.15 cm) at \sim 40 kN pressure for 10 min.

3. Results and discussion

3.1. Structural characterization

X-ray diffraction (XRD) patterns obtained for all samples are shown in Fig. 1a. In general, all the samples (NaTNT) present a very similar pattern, showing the presence of diffraction peaks at approximately $2\theta \sim 9.40^{\circ}$, and a series of doublet at $2\theta \sim 24.36^{\circ}$, $2\theta \sim 28.46^{\circ}$, $2\theta \sim 48.30^{\circ}$, and $2\theta \sim 61.60^{\circ}$. These features are similar as those observed for other titanate nanotubes that were synthesized by hydrothermal methods reported in literature [11,18-20]. The first peak at $2\theta \sim 9.40^\circ$ may be ascribed to the reflections of planes perpendicular to the radial direction of the nanotubes (lower crystallinity) associated to the distances between [TiO₅] layers. For M1, M3 and M4 samples, this peak corresponds to an interplanar distance of 9.3-9.5 Å. However, for M2 we obtained 8.82 Å and 10.03 Å for M5. Also, sample M4 presents half of FWHM than the rest of the samples, indicating a larger wall size. The thinner peak at $2\theta \sim 48.30^{\circ}$, is narrow and intense, probably corresponding to planes that are perpendicular to axial (or growth) direction (higher crystallinity) [11]. Contrary to the first peak all the samples present this peak in the same position, correlating to an interplane distance of 1.88 (1) Å. The FWHM of these peaks (between 0.76° and 0.64°) indicate that the coherence in the axial direction is very similar in all the samples and close to 13 nm. This peak may correspond to the second reflection of 24.36° peak, and like the latter, it usually has a shoulder to its right. For the case of sample M2 and M4, the shoulder appears more intense and shifted to 25.34°, this could correspond to (1 0 1) anatase

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Fig. 1. a) X-ray scans and b) Raman spectra for NaTNT samples. The dashed lines indicate the peaks referred in the text, and the dotted lines correspond to anatase peaks.

reflection. Finally, a doublet at $2\theta \sim 28.46^{\circ} - 29.12^{\circ}$ is present, according to distances of 3.05 Å and 3.11 Å. The first peak is usually the most intense of the pair, except in sample M4 where this relationship is reversed. The last two interplanar distances are observed for all the samples in HRTEM. The most relevant interplane distances are summarized in Table 2.

Raman spectra obtained in the $100 - 1600 \text{ cm}^{-1}$ range for all samples are displayed in Fig. 1b. All the samples present the same structure, with a series of well-defined peaks around 910 cm⁻¹, 667 cm⁻¹, 450 cm⁻¹ and 280 cm⁻¹. The first one, is considered to be ascribed to Ti - Ostretching involving non-bridging oxygen atoms [11,18-25], the last three are related to different Ti - O - Ti stretching modes of titanate nanotubes. A mixture of peaks is present in the region between 90 cm⁻¹ and 220 cm^{-1} , in all the cases peaks in 192 cm^{-1} and 155 cm^{-1} appear to stand out. These peaks are assigned to lattice modes $(Na^+ - O - Ti)$ [26] or can be associated with the Ti - O - Ti vibrational modes in the $[TiO_5]$ layer. Once again, for M2 and M5, the peak at 192 cm⁻¹ appears shifted to lower and higher frequencies respectively. The pronounced peak at 150 cm⁻¹ for M2, corresponds with anatase, for which a Raman image analysis revealed 96% NaTNT phase, and 4% anatase phase. This is also congruent with the presence of the peak at $2\theta \sim 25.32^{\circ}$ in the X ray diffraction pattern. Additionally, the Raman spectra showed the presence of peaks at $\sim 1080 \text{ cm}^{-1}$ for most of the samples, related to CO_2^{-2} anion [27], probably formed with CO_2 from the air.

We performed X-ray Absorption Fine Structure spectroscopy (EXAFS and XANES) studies on the LNLS beamline XAFS1, over M1 and M2 samples, in order to get more insights in the local structure of the obtained titanate nanotubes. In the case of the X-ray Absorption spectroscopy, we started analyzing the near-edge region (XANES). When comparing the data sets with the other reference materials, shown in Fig. 2a, we observed that the oxidation state of titanium corresponds to Ti^{+4} , being pretty similar for M1, M2, TiO_2 (anatase) and $SrTiO_3$. As expected by symmetry, samples M1 and M2 present the pre-edge peaks: A1, A2 and A3 [28], similarly to the ones observed for anatase and rutile TiO_2 samples. Differences in the relative intensities can be related to changes in the $Ti |1s\rangle \rightarrow |3d\rangle$ transitions, maybe due to further changes in the dipole located at 4971 eV (A2 peak).

In the case of EXAFS, data reduction and fitting procedure were performed using Demeter suite [17]. For this, we prepare an input file considering the bulk $Na_2Ti_2O_5.nH_2O$ model, as the one chosen in [10]. Due to the fact that the structure presents different non-equivalent crystallographic positions for the *Ti* atoms, we considered the "aggregate" and "fuzzy degeneracy" options in order to statically describe all the titanium atoms environment. According to this the path finder routine is run for each in-equivalent *Ti* atom position, and then, all of them are merged together, weighted by the fractional population of the site in the unit cell. Finally, the check for fuzzy degeneracy is performed. This procedure allowed us to statistically describe this complex structure, studied and analyzed at the local level. The same model was utilized for both samples, that were further refined in the Artemis suite, working with the oscillation part of the absorption spectra $\chi(k)$ (the fine structure) [17]:

$$\chi(k) = \sum_{j=\text{atoms}} \frac{N_j s_0^2 f_j(k)}{kR_j^2} e^{-2k^2 \sigma_j^2} e^{-2r/\lambda(k)} \sin(2kR_j + \delta_j(k))$$
(1)

Table 2

Relevant parameters obtained from TEM, XRD and SAXS analysis. D_{ext} is the mean diameter from TEM images, and the error is evaluated as the mean standard deviation. Plane distances *ED* were obtained from electron diffraction and *XRD* from X ray diffraction pattern (for each pair in XRD we report the most intense distance). R_{1g} and R_{2g} gyration sizes, G_1 and G_2 amplitudes and P_1 and P_2 exponents for the two structural level considered. D_1 and $k = 8C_V$ are the correlation length and packing factor.

	D _{ext} (nm)	Planes Distances ED (Å)	Planes Distances XRD (Å)	R _{1g} (nm)	G_1	D ₁ (nm)	C _V	<i>P</i> ₁	R _{2g} (nm)	<i>G</i> ₂	<i>P</i> ₂
M 1	43.4 (1.5)	2.7, 3.7, 6.6, 7.6, 10.0	1.89, 2.64, 3.11, 3.64, 9.36	11.36	3.00	63.2	0.75	2.23	32.4	0.35	0.20
M2	79.1 (2.6)	1.9, 2.7, 3.1, 3.7, 4.8	1.88, 2.32, 3.11, 3.65, 8.91	10.62	2.89	60.6	0.75	2.93	49.3	0.005	1.27
	9.9 (0.2)	1.9, 3.5									
МЗ	41.7 (1.1)	1.9, 3.1, 3.7	1.88, 2.31, 3.11, 3.67, 9.25	11.35	2.99	62.6	0.75	2.66	26.8	0.25	0.45
<i>M</i> 4	17.9 (1.6)	3.3, 5.2, 6.8	1.88, 2.59, 3.04, 3.55, 9.51	11.35	3.03	63.1	0.75	2.24	41.7	0.15	0.74
M5	46.1 (3.1)	1.9, 3.1	1.89, 2.38, 3.16, 3.62, 10.03	11.29	3.07	63.1	0.75	1.92	27.4	0.42	0.30



Fig. 2. a) XANES spectra plotted as normalized $x\mu(E)$ for: M1, M2 and TiO_2 (anatase) as reference with a zoom in the pre-edge zone. EXAFS fitting real space $|\chi(R)|$ for b) M1 and c) M2 samples, and d) sketch of the bulk $Na_2Ti_2O_5$. $n(H_2O)$ presenting the selected paths.

Which depends on: N_j the number of neighbors, R_j distance between them, the disorder in the neighbor atom σ_j^2 , the backscattering amplitude $f_j(k)$, the total attenuation factor S_0^2 , the phase factor $\delta_j(k)$ and the mean-free-path of the photo-electron λ_j , all of them depending of the wavevector $k = 2\pi/\lambda$. The fitted results for the real space $|\chi(R)|$ are shown in Fig. 2b and c, meanwhile the real part of $|\chi(k)|$ is presented in the Supplementary Material. A sketched of the bulk considered for the fitting is display in Fig. 2d.

According to the initial model, the fitting is composed by six singlescattering paths Ti \rightarrow O \rightarrow Ti, with Ti-O distances obtained ranging from 1.76 to 2.32 Å, totaling a number of five (N = 5) oxygen atom neighbors. Additionally, we included two Ti \rightarrow Ti \rightarrow Ti single scattering paths in order to complete the selected region for the fitting. According to the fitting results we get the final Ti-Ti distances ranging from 2.96 to 3.23 Å for both samples. All the distances resulting from the fitting are reported in the Supplementary Material along with the fitting statistical parameters. In order to stabilize the refinement, fittings were performed with fixed $\sigma_j^2 = 0.001 A^2$, initially estimated from a first shell fitting. It provides the ratio of 14:7 of independent data to fitting variables $N_{indep} : N_{var}$. Some problems arise in the case of M2, that can be observed particularly in the fitting region of ~ 2.6 Å. This issues can be attributed to the presence of small amounts of anatase as confirmed by XRD. Nevertheless, the trends are conclusive in having a pentacoordinated TiO polyhedral, with a very reasonable agreement with the model based on $Na_2Ti_2O_5.nH_2O$. This is a very relevant result that confirms the local environment of the titanium atoms, and that therefore the "building block" of the NaTNT nanotubes is five-coordinated Ti-O units, as previously demonstrated by XRD [10].

Summarizing, structural characterization (XRD, Raman Spectroscopy and EXAFS-XANES) confirm the five-coordinated *Ti-O* units. It was found differences in XRD pattern and Raman spectrum for samples M2 and M5. The observed shifts were associated with different interplanar distances between [*TiO*₅] planes, and in some cases the presence of a small amount of anatase crystalline phase.

3.2. Morphological characterization

The TEM images depicted in Fig. 3 confirmed the presence of nanoparticles and tubular nanostructures. In Fig. 4 we show high resolution image and their corresponding electron diffraction pattern in the insets. M2 and M5 exhibit peculiar morphologies, in particular M2 shows a co-existence of nanotubes and nanoparticles, with a mean diameter of about 10 nm. Electron diffraction was carried out on isolated nanoparticles areas, finding a polycrystalline behavior with interplanar distances of 1.88 Å and 3.49 Å. For the M5 synthesis condition, the nanotubes became nanorods. The mean nanotube diameter, nanoparticle size and the interplane distance obtained from HRTEM and


Fig. 3. Transmission electron microscopy (TEM) images for M1 to M5 samples. $M2_S$ refers to sphere zones and $M2_T$ refers to tube zones both presented in M2.

electron diffraction are listed in Table 2. The mean diameter is around 42 nm, which decrease to 18 nm for M4, and increase up to 80 nm for M2.

For a better determination of the characteristic distance in all the samples we performed small angle X-ray scattering (SAXS) measurement. The SAXS method allows us to evaluate the size of small particles or modulation of the electronic density in the scale range from several nm to 100 nm, by analyzing the scattered intensity of X-rays in small angular range from about 0.1 to 5.0 degrees. The scattering intensity produced by this type of morphology can be described by a semiempirical equation, written in Eq. (2), proposed by Beaucage et al. [29–31]. The unified equation describes a material over a wide range of sizes in terms of structural levels. One structural level pertains to a Guinier regime describing an average structural size, and a power-law regime describing the mass- or surface-fractal scaling for that structural level. We consider two structural levels, and a correlation scattering factor for the smaller level, taking into account a weakly correlated system.

$$I(q) = G_{1} \frac{e^{-\frac{R_{1g}^{2}q^{2}}{3}} + \frac{81}{50R_{1g}^{4}} \left(\left(erf\left(\frac{qR_{1g}}{\sqrt{6}}\right) \right)^{3} \right)^{P_{1}}}{1 + \frac{8C_{v}(3sin(qD_{1}) - qd_{1}cos(qD_{1}))}{(qd)^{3}}} + G_{2} \left[e^{-\frac{R_{2g}^{2}q^{2}}{3}} + \frac{81}{50R_{2g}^{4}} \left(\left(erf\left(\frac{qR_{2g}}{\sqrt{6}}\right) \right)^{3} \right)^{P_{2}} e^{-\frac{R_{1g}^{2}q^{2}}{3}} \right]$$

$$(2)$$

The parameters R_{1g}, G_1 and P_1 describe the size, amplitude and

exponent of smaller structural level, and R_{2g} , G_2 and P_2 the same for the next structural level. The parameters D_1 and $k = 8C_V$ are the correlation length (i. e. average distance for structural correlations) and the packing factor characterizing the correlation between the two structural levels respectively. Although the model considers spherical media, it allows to obtain a notion of the characteristic distances. Fig. 5 shows all the SAXS measurement, and in the Figure inset an example of the fitting obtained with Eq. (2) for M4 is presented. All the fittings are display in the Supplementary Material. For the fitting procedure we used a minimal square methodology with weightier function. The fitted parameters are also summarized in Table 2.

If we observe all the superimposed measurements in Fig. 5, it is clear that in the region of low q all the samples present the same behavior with the exception of M2, where a different morphology was identified. The gyration radius (R_{1g}) are about 11.3 nm for M1, M3, M4 and M5 and 10.6 nm for M2. Also, the drop to large q is very similar, denoted by a correlation length (D_1) around 63 nm and a P_1 exponent between 2 and 3. According to [32] scattering from cylindrical symmetrical structure it expected to produce a P = 3 dependence in the Porod regime. Furthermore, values of $P_1 = 1.8$, 2.0 and 2.5 were assigned to multi-particle diffusion limited aggregate [33], lineal ideal polymer and swollen branched polymer [34], diffusion limited aggregate [35] and percolation cluster [36]. Generally, 4 > P > 3 is expected for surface fractals, P < 3 for mass fractals and P > 4 for diffuse interfaces [37–40]. Therefore, we are in presence of mass fractal and the fractal dimension is $D_m = P$. Once again, the correlation length D_1 is smaller for M2 (\sim 60 nm). This could be a product of different packing or cluster formation involving particles instead of tubes. The packing factor $k = 8C_V$ describes the degree of correlation. For a perfect three-dimensional crystal one yields



Fig. 4. High resolution transmission electron microscopy (HRTEM) images for M1 to M5 samples, and electron diffraction pattern in the inset of the figures.



Fig. 5. Small angle X-ray scattering curves (log(I) vs log(q)) for M1 to M5. Inset: experimental data (square point) and fitted curve with Eq. (2) (solid line) for M4.

 $k_{max} = 5.92$, while for a perfect two-dimensional crystal $k_{max} = 6.24$ is obtained [31,41]. We restrained the fitting to the maximum k possible at six, all the fitting falls in the maximum value allowed. The most notorious differences are in the second gyration radium and the exponent P_2 . This is also observed in Fig. 5, where the slope of the high q region differed between samples. The ratio R_{2g}/R_{1g} is very similar for M1, M3 and M5, but it increases for M4 and M2. One interpretation is a higher ratio L/R of the tubes in agreement with the TEM pictures. Also, P_2 is smaller than 1, between 1/5 and 3/4, and 5/4 for M2. Thin rods are one-

dimensional objects, so a power law of -1 is expected between the average length of the rods and the average radius of the rods [30,42].

Morphological analysis reveals the presence of two kinds of morphologies. The first one, presented in sample M2, is a mixture of nanoparticles and nanotubes. Its structure was locally seen in TEM images and was then confirmed by SAXS in bulk. The second morphology is conformed by cylindrical structures. TEM images exhibit rod structures for M5 (lowest synthesis temperature, longest time). On the contrary, samples M2, M3 and M4 show tubular structures with different characteristic length. Furthermore, SAXS results are in concordance with TEM images.

3.3. Optical characterizations

Optical behavior of titanates have been extensively studied, usually attributed to an indirect semiconductor behaviour [43,44]. It has been proposed that reducing anatase dimensions to nano scales allow direct band transitions to appear [45]. They argue that there are no size quantization effects in anatase titanates with dimensions larger than 10 nm.

Optical measurements were performed detecting direct transmittance (T_d) and photoluminescense (PL) at room temperature. Considering that the absorption is determined by the Lambert–Beer Law, the absorption coefficient α can be calculated as $\alpha = -log(T_d)$ [46]. The PL and α measurements are shown in Fig. 6 for all the samples and the precursor anatase. It can be observed the differences in energy existing in emission processes and absorption ones. It can be seen that absorption involves high energy transition, while PL is observed for energies below the onset of the absorption spectra. When the sample interacts with



Fig. 6. Room temperature Absorption coefficient and Photoluminescence measurements (excitation diode 300 nm).

light, some well defined energy levels are excited. However, the excited state does not necessarily decay in a radiative way. Furthermore, its decay consists of a sequence of phononic energy transfer through the lattice, combined with a radiative low energy process. That low energy decay is seen as a PL signal.

For all the samples we considered two different bandgap edges on the absorption coefficient results, since the fitting using only one edge do not explained the overall behaviour. For the estimation of the indirect and direc gap, we analyzed Tauc plots to determine direct ($h\nu$ vs ($\alpha h\nu$)²) and indirect ($h\nu$ vs ($\alpha h\nu$)^{1/2}) gap energy respectively [47,46]. Also the Urbach Tail effect was studied. This soft increment in the absorption coefficient, observed for energies bellow the bandgap, was fitted using an exponential function $\alpha = \alpha_0 exp(E/E_U)$ to obtained the Urbach Energy E_U [48–51]. This parameter has been associated with the lattice disorder present in the sample.

For each sample, we first determined the experimental absorption coefficient (α_{exp}). Then a background absorption modeled as an indirect transition was considered. From an indirect Tauc Plot calculated using

 α_{exp} , we performed a linear fitting in the low $h\nu$ region. The absorption coefficient α_{bkg} obtained from this linear fitting was subtracted from α_{exp} (Fig. 7a), labeling the new data as α_{AD} . Following, we constructed an indirect Tauc plot ($h\nu$ vs $(\alpha_{AD}h\nu)^{1/2}$), which was used to calculate the value of the indirect gap energy (Fig. 7b). Employing the fitting information and inverting Tauc relation we obtained α_{Ind} . The latter was subtracted to the α_{AD} ($\alpha_{Dir} = \alpha_{AD} - \alpha_{Ind}$), for the construction of the direct Tauc plot $(h\nu \text{ vs } (\alpha_{Dir}h\nu)^2)$. By means of a linear fitting we found the gap energy value corresponding to the direct transition (Fig. 7c). Finally, Urbach Energy was calculated linearizing the absorption coefficient data (α_{AD}) in the region below the indirect bandgap, employing the expression shown in the paragraph above for Urbach Tail (Fig. 7d). The methodology explained before has already been used to determined the optical properties of a wide variety of structures [52,53]. In Fig. 7e we show the complete measurement with the three fittings performed. The results for Energy gap E_g applying this methodology are summarized in Table 3.

The band gap energies obtained as a function of sample number are shown in Fig. 8. Additionally, characteristic dimensions for each sample are shown in Table 2. Analyzing the dimensions and the indirect gap energy obtained for each sample, it is clearly visible that they do not exhibit quantum confinement behavior. It can also be observed that our nanostructure dimensions exceed the limit expected for quantum confinement as reported for anatase polymorph [45], suggesting that no

Table 3

Optical Parameters: E_{gD} direct gap, E_{gI} indirect gap, E_U Urbach energy, E_{PI} energy peak position for the four peaks (i = 1,2,3 and 4) presented in the PL specta.

	E _{gD} (eV)	E _{gI} (eV)	<i>E_U</i> (eV)	<i>E</i> _{<i>P</i>1} (eV)	<i>E</i> _{P2} (eV)	<i>E</i> _{P3} (eV)	<i>E</i> _{P4} (eV)
Anatase	3.05	2.88	0.035	2.356	2.554	2.791	2.992
	(12)	(4)	(5)	(17)	(5)	(4)	(3)
M1	2.99	2.60	0.086	2.222	2.479	2.773	2.933
	(6)	(4)	(3)	(8)	(4)	(8)	(10)
M2	3.04	2.76	0.072	2.371	2.549	2.791	2.972
	(2)	(2)	(2)	(15)	(5)	(4)	(4)
M3	3.22	2.57	0.222	2.358	2.529	2.795	3.002
	(7)	(6)	(6)	(12)	(4)	(4)	(5)
<i>M</i> 4	3.11	2.55	0.151	2.280	2.515	2.810	2.988
	(5)	(2)	(5)	(10)	(3)	(4)	(4)
M5	3.09	2.54	0.162	2.361	2.550	2.808	2.987
	(1)	(4)	(2)	(17)	(5)	(4)	(1)



Fig. 7. a) Direct transmittance with the Absorption coefficient (α) determinations, b) indirect tauc gap fitting (Tauc Plot: $h\nu$ vs $(\alpha h\nu)^{1/2}$), c) direct tauc fitting (Tauc Plot $h\nu$ vs $(\alpha h\nu)^2$, d) linear fitting for Urbach determination and e) final result of the analyzed curve. The sample selected for the example was M2.



Fig. 8. Indirect and direct band gap energy for each sample (left), and Urbach energy (right). The Urbach energy is in accordance with the tendency of the indirect band gap energy.

quantum effect is presented in our anatase reference. Based on that, we analyze the indirect tauc plot for each sample. We found values between 2.54 eV and 2.76 eV, resulting in smaller values than the one experimentally obtained for anatase. It suggests that the inclusion of sodium on the samples tends to diminish the energy gap for the indirect transition. Meanwhile, the direct band gap energy is mostly constant (considering the experimental error) and it matches with anatase direct energy gap. It suggests that the same electronically allowed direct transition is present among the samples (probably $X1a \rightarrow X1b$, X edge of the Brillouin zone from the valence band to conduction band [45]).

Urbach tail was also studied in the absorptance spectrum. Urbach energy (E_U) refers to the width of the Urbach tail of localized defect states in the band gap. As indirect transition predominates in our samples, we can relate its behavior with the E_U tendency. From Fig. 8 it is evident that an increase in E_U results in a decrease in E_{gl} . Lets now analyze the PL spectra, displayed also in Fig. 6. All the samples exhibit a broad PL emission and can be fitted by the sum of four Lorentz functions, more details of this can be found in the Supplementary Material. All the samples present the same shape except for M1 where the peak with higher intensity emission shifts from ~ 2.8 eV to ~ 2.3 eV. A broader peak in the region of 3.0 eV is observed for M3, in accordance with the Urbach tail that suggests M3 has more interband defects. It has been reported in literature [48] that the PL emission corresponding to energies around 3.1 eV, 2.7 eV and 2.5 eV in anatase nanostructures ascribed to oxygen vacancies defects. Furthermore, emissions around 2.1 eV are related to OH group defects. We found a redshift with respect to absoption edge in all the samples (reported in Table 3 FWHM around 0.20-0.30 eV, with no appreciable dependence between samples (see Supplementary Material).

To summarize, the band gap energies were obtained from the measured absorptance signal. After a rigorous data analysis, we found lower indirect transition energies for the samples than those found for anatase reference. We also found that the highest band gap energy of the prepared samples appears in the nanoparticle-nanotubes mixture. We observe no difference between the behaviour of the nanotubes and nanorods samples. Urbach tail and PL signal confirms the presence of defects mostly associated with oxygen vacancies and OH group defects.

3.4. Impedance spectroscopy

The Impedance spectroscopy (IS) measurement is an AC electric technique to monitor the carrier response under the oscillating voltage as a function of frequency. It is useful to study the dynamics of charge carriers. Since IS deals with retarded electrical responses of carriers through the sample, it can display the carrier accumulation processes at the grain interfaces and carrier diffusion through the sample. Therefore, IS has shown to be a valuable tool to study recombination loss and carrier mobility as well as to separate the grain and grain boundary (GB) effects. It is highly desirable to perform IS measurement to analyze the effect of modified morphology on the electrical processes. It can directly display the dynamics of carriers and also provide information about how

the carrier diffusion and recombination evolves. Recent studies focused on the interface modification in order to facilitate effective charge extraction and improve overall photovoltaic performance [54–56].

Fig. 9 shows the impedance spectroscopy data displayed as Nyquist plots (left) and phase-frequency plot (right), with two applied DC voltage: 1.0 V and 3.0 V, for all the samples. In all cases, the IS spectra in the complex impedance plane displays a small semi-circle at higher frequency and a large semi-circle at low frequency. The latter is presented as a straight line for low DC applied voltage, and a complete arc develops as voltage increases. Several models have been proved for the explanation of the electrical behavior [57-61]. Depressed semi-arc is usually modelled with a parallel Resistance-Capacitor (RC) or parallel Resistance-Constant Phase Element (R-CPE) circuit. To fit our IS spectra we proposed a model that adds two contributions of parallel resistance (R) and constant phase element (CPE), schematized in the inset of Fig. 9. The high frequency arc is labelled as R_1 -*CPE*₁ and can be attributed to the bulk zone. Additionally, the low frequency arc, denominated R_2 -*CPE*₂, can be associated with the grain boundary or depletion zone in the pellet. The selected model is in agreement with previous reports [61-67].

According to the responses observed in Fig. 9, we can classify the samples mainly into two groups. One group is formed by samples M1, M3 and M4, and the other by M2 and M5, justified in the two observed behaviors of curve phase-frequency. Fig. 10 shows the impedance modulus, phase and imaginary part as a function of frequency varying the applied DC voltage, only for M1 and M2 (representing each set of samples). The rest of the measurements are display in the Supplementary Material. The samples M1, M3 and M4, present very similar shapes in the Nyquist plot, with a R_1 value of about 20 k Ω and without a clear dependence on DC Bias. A decrease of one magnitude order (respect to zero bias) in the impedance modulus was observed at low frequencies (f < 10 Hz) for a DC applied voltage above Vdc = 2.0 - 2.5 V. In addition, the phase-versus-frequency plots show the same trend: at low frequency, when increasing DC bias, the phase decrease from -75° to -10° in the region of 10–103 Hz. This is probably an effect of increasing the charge carrier mobility due to the applied DC voltage. Additionally, for voltage applied higher than 2.0 V and decreasing frequency, the phase exhibits a transition from a capacitive-like behavior (phase proximal to -90°) to a resistive one (phase proximal to zero degrees). For M2 and M5 samples, special behavior is observed. A small decrease in impedance modulus is presented when applying voltage for M2, and hardly noticeable for M5. In the phase and imaginary impedance plot (third column in Fig. 10), a peak for intermediate frequencies is resolved for applied voltage higher than 2.0 V. We will address a possible explanation shortly.

Another possible approach, mentioned at the beginning of the section, is to interpret each *R*-*CPE* parallel elements as two main retarded AC responses in the sample both related to two characteristic times. The time obtained from R_1 -*CPE*₁, can be associated to a charge mobility time (lifetime) inside the grain, and it can be calculated as $t_1 = R_1 CPE_1^{1/n_1}$



Fig. 9. Impedance spectroscopy data displayed as Nyquist plots (left) and phase vs log(f) (right), with an applied DC voltages of 1.0 V (top) and 3.0 V (bottom), for NaTNT samples.



Fig. 10. Impedance modulus (left column), phase (middle column) and imaginary part (right column) versus frequency at Vdc = 0-4 V for M1 and M2, as examples to illustrate the two types of observed behavior.

(where the impedance for *CPE* element is defined as $Z_{CPE} = 1/(CPE\omega)^n$). The second time (t_2), could be related to a dielectric relaxation time [68]. It could be explained as a diffusion time in the intergrain or a recombination time, favored by the carrier accumulation processes at the grain interfaces. For that reason, it is expected to decrease when charge carrier concentration increases [69,70]. Fig. 11 displays the separated R_1 and R_2 contribution to the resistance, and t_1 and t_2 calculated from the fittings, as a function of the applied DC voltage.

For the samples M1, M3 and M4 the R_2 -*CPE*₂ contribution governs the electrical behavior for lower V where R_2 is more than two orders of magnitude higher than R_1 (no bias applied). When increasing V the R_1 -*CPE*₁ becomes the more relevant carrier mechanism. The major decrease in the second contribution to the resistance is an evidence of the carrier injection process at this applied DC voltage [63,64,70]. It suggests that when increasing applied voltage, the accumulated charge carriers in the intergrain became able to overcome the potential at the grain boundary. Therefore, the application of DC bias enables the accumulation of charge carriers to become mobile, and makes the electron hopping easier through the nanotubes [68]. A linear relation of log(R) vs log(V) is expected on the basis of the space-charge-limited current (SCLC) theory. The slope of the relation (-m), gives information about the trap distribution of charge carriers [71,72]. In our case we obtained values of m = 8.4, 5.7, 5.1 and 3.5 for M1, M3, M4, and M2 respectively (calculated in the range of 1.5 V–3.5 V, as shown in Fig. 11c). This result supports the idea that the charge carriers follow the SCLC theory with exponential trap distribution (m > 2). Above 3.0 V, the second arc is completely depleted and R_2 is constant.

In general, the electron lifetime (t_1) is independent of the DC voltage, as can be seen in the high frequency peak observed in the imaginary impedance (Fig. 10). The peaks observed in the imaginary part correspond to relaxation processes [57], and its frequencies are related to the inverse of the corresponding relaxation times. In the third column of Fig. 10 (and Supplementary Material), we can observe that all samples present a peak or a shoulder proximally to 250 kHz ($\sim 1 \mu$ s), according



Fig. 11. Equivalent circuit fitting parameters: (a) $log(R_1)$, (b) $log(R_2$ (c) $log(R_2)$ vs Log(V) with linear regression, (d) t_1 and (e) t_2 as a function of DC voltage.

to the results in Fig. 11d, and similar to other reports [57,68]. In all cases, the intergrain associated time t_2 is higher than t_1 (for low voltage reach more than seconds), which indicates a lower mobility in the depletion zone, according with carrier accumulation. For M1, M3 and M4 samples, this time strongly decreases with an apparent exponential decay, similarly to other reports [57,68]. For the second group (M2 and M5), the resistance R_1 or R_2 present a different trend with Voltage. For M5, R_1 and R_2 appears to be constant with DC Bias, for the case of M2, R_2 present similar behavior to the first group (with m = 3.5), but the resistance associated to R_1 -CPE₁ presents a small decrease with the increase in voltage. In this case, we also plot the first resistance in the plot corresponding to R_2 . Furthermore, when we look at phase or imaginary impedance plot in the range of milliseconds, we find a third characteristic time to emerge and domain the spectra. If we look at the case Z_{imag} (f) for M1, this peak is also present but its shape is very little pronounced. These results indicate the existence of a third electrical response in the samples M2 and M5. We think that the electrical phenomenal representing R_1 for M2 is not the same as the rest of the samples, this is even clearer observing that the corresponding t_1 is two orders higher than the others ones. The latter is also plotted in the $log(t_2)$ graph. For M2, the R₁-CPE₁ circuit is modeling the new peak emerging at intermediate frequencies. For M5, this happens with the second R_2 -CPE₂, explaining why R_2 and t_2 are constant above 1.5 V. Both samples have a common characteristic: they present a mix in the morphology. For M2 nanotubes and nanoparticles with characteristic size for 100 nm and 10 nm are observed. Additionally, nanorods were obtained in M5, having a mean diameter of 45 nm and length of 700 nm. The different morphology could affect the intergrain. Also, this could imply a second characteristic length for the carrier diffusion, and could result in a second lifetime.

As mentioned at the beginning of the section, EIS is a desirable technique to analyze the impact of modified morphology on the electrical processes. All the samples present at least two processes related with the grain and grain boundary mobility, modeled by a two R –*CPE* or two characteristics times. The time t_1 , related with the grain lifetime is around microsecond and nearly voltage independent. Meanwhile, the time t_2 associated with the intergrain decreases with DC voltage expected due to the charge mobility enhancement. This also causes R_2 to decrease with DC voltage, allowing us to clearly observe the transport process in the grains (R_1). For the samples where the intergrain con-

stants were obtained, the slope -m shows that the charge carriers follow the SCLC theory with exponential trap distribution (m > 2). Finally, when a mixed morphology is presented, such M2 and M5, a third process is observed (around ms). This third time could be associated with a different boundary time (for example nanotube-nanoparticle or nanoparticle-nanoparticle) or to a probably new characteristic length.

4. Conclusions

We present the dependence on the synthesis conditions of the structural, morphological, electrical and optical features, for sodium titanate nanostructures. We found that depending on the time and temperature of the hydrothermal synthesis, nanotubes, nanorods and nanoparticles were obtained. We inferred that solid structures are obtained for soft synthesis conditions (low temperature, long times). On the contrary, mixed morphologies appear when we apply higher temperature for a long time. The samples stoichiometry was confirmed to be a pentacoordinated Ti-O polyhedral by local and extended structure analysis, and Raman spectroscopy. The samples exhibit two major transport mechanisms, determined by Electrochemical impedance spectroscopy analysis. However, a third process was observed in both the nanorod sample and the mixed nanotube-nanoparticle sample. Optical measurements revealed a lower band edge energy for the samples compared with the anatase precursor. Finally, the photoluminescence response varies among the samples. We suggest that the cause of this variation is due to the amount and kind of defects presented on each sample. To sum up, this work presents an exhaustive set of experimental tools for the analysis of the tunability of the electrical and optical response of nanostructured Na-titanates with synthesis conditions.

CRediT authorship contribution statement

Lucia Amy: Data curation, Formal analysis, Methodology, Investigation, Visualization, Writing - original draft, Conceptualization. Sofia Favre: Formal analysis, Data curation, Methodology, Visualization, Writing - original draft, Writing - review & editing, Conceptualization. Daniel L. Gau: Investigation, Writing - review & editing. Ricardo Faccio: Conceptualization, Formal analysis, Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apsusc.2021.149610.

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Chapter 4

Structural, optical, and electrical properties of proton intercalation H^+/Na^+ phases in nanostructured titanates induced by pH during hydrothermal synthesis.

In the previous chapter, we presented a study investigating the relation between specific synthesis conditions and the resulting morphologies of the material. This study explored various properties of the material, and the information obtained will be essential in proposing different phases for the samples. Specifically, it provides support for the stoichiometry samples consisting of pentacoordinated Ti - O polyhedra. Additionally, an electrical analysis highlights a prevailing dual transport mechanism, which may diversify into multiple mechanisms when different morphologies are combined. Furthermore, a reduction in bandgap energies is observed when compared to anatase.

In this new chapter, we describe a variant of the synthesis method previously explored. For this experiment, we fixed the reaction time and two temperatures, t =96 h and $T = 105 \,^{\circ}C$ (called SERIES 2) and $T = 125 \,^{\circ}C$ (called SERIES 1), while varying the concentration of the aqueous solution of sodium hydroxide from 9 to 11 M. This variation in pH appears to have a significant impact on proton exchange within the material's structure. We check into a structural study of some possible phases that could constitute the material (H^+/Na^+) mixture in a trititanate phase) and analyze how different H^+/Na^+ concentration affect the electronic properties at room temperature. Additionally, EIS measurements exhibits a third process well marked for samples with higher mixed sodium and hydrogen phases.

Moreover, we extend our investigation to explore the electrical response of the sample with temperature, in a temperature range similar to a possible operating condition, assuming the material could serve as an anode for energy storage. This exploration will provide information into its potential applications in practical energy storage devices.

This work holds particular significance as it serves as an extension of the first article while also paving the way for other potential future research paths. Firstly, it offers an opportunity to pause and consider the possible phases that constitute the material and explore them by *ab-initio* theoretical calculations. This will lead to Chapter 5. Secondly, it provides the basis for further exploration of the properties exhibited by the samples under varying temperature conditions such as the effect of surface and structural water, and the influence of moisture on it permorfance (Chapter 6).

In this chapter, the XRPD and Raman techniques are employed to study the morphology, TEM, HRTEM and EDS for structural analysis, and EIS, absorption, and photoluminescence are used similarly to the previous chapter. In particular, one of the strengths of this work is that a more comprehensive analysis of the XRPD patterns is performed. Additionally, the initial electrical measurements as a function of temperature are conducted, with an experimental setup specifically designed for their execution.

As mentioned early, this work expands the results of the first article. Based on a detailed structural analysis, new phases possibly present in the samples are proposed $((Na, H)_2Ti_3O_7 \cdot nH_2O)$. Taking into account this phase mixture, the analysis of the electrical and optical results is addressed. It was found that pH can be a variable to consider if tuning the energy gap is desired together with the Na/H proportion. Moreover, by varying the temperature, the impedance of the samples changes by 20%, exhibiting thermal irreversibility during the cycle (thermal hysteresis). Additionally, it enriches the understanding of the material's behavior and properties under different conditions. Appendix B details some extra results about structural, optical and stoichiometrical properties that were published as Supplementary Material of the article.

Before proceeding with the paper, it is important to acknowledge a consistent error that occurred throughout the work. Specifically, SERIES 1 was defined with the lowest temperature $(105 \circ C)$, and SERIES 2 was assigned to the highest temperature $(125 \circ C)$. This mix-up in temperature designations has been identified, and it is essential to interchange the temperatures to accurately represent the samples comprising each group. It is crucial to emphasize that this error does not impact the validity of the results and the conclusions presented in the manuscript. The journal has already been informed about the oversight, and necessary corrective measures were taken as can be seen in the corrigendum at the end of the Chapter.

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Structural, optical, and electrical properties of proton intercalation H^+/Na^+ phases in nanostructured titanates induced by pH during hydrothermal synthesis

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ABSTRACT

Keywords: Sodium titanate nanotubes Confocal Raman spectroscopy HRTEM Optical characterization Temperature dependence electrical measurement In search of a promising alternative to manufacture anodes for sodium-ion batteries, a study of the pH variation during hydrothermal synthesis of nanostructures of sodium titanate is presented. In particular, structural, optical and electrical properties of these materials are assessed when varying the pH for two different synthesis conditions. A mixture of phases was found, in agreement with $(Na, H)_2 Ti_3 O_7 \cdot nH_2 O$, and its cause is attributed to the proton(H^+)/sodium(Na^+) exchange and the intercalation of structural water. Also, changes in the morphology of the structural phases were observed, for example the phase with lower interlaminal distance appears to be nanorods, instead of nanotubes. The relative weight between phases and the direct band gap can be tuned by controlling synthesis conditions, in particular pH conditions. An enhancement of new processes in the electrical response and the suppression or enhancement of some defect due to the mixture of phase is also discussed. Additionally, the changes in electrical properties over a possible operation temperature range of a potential device, between -30 °C and 50 °C is reported. It was found that the changes in impedance in the proposed temperature range are of the order of 25 % of the modulus. This work shows how the final Na^+ content in the sample alters its optical and electrical properties, which are determinant in its performance as an anode.

1. Introduction

An extensive study of nanostructured titanates has been performed over the last two decades for many novel applications in various fields such as catalysis, photocatalysis, electrocatalysis lithium batteries, hydrogen storage and solar-cell technologies [1-3]. In particular, these materials are proposed for the manufacture of anodes in sodium-ion batteries (SIB) [4-7], being these a promising alternative to Lithiumion batteries (LIB) [8,9]. The former presents some advantages such as high mobility, lower cost and being environmentally friendly [8-12]. Furthermore, the nanostructured aspect is essential to promote the Na-ion diffusion and enhance the electrochemical activity of titaniumbased anodes [13]. Despite the huge variety of studies concerning the formation mechanism in the high aspect ratio titanates and their physical properties (crystal structure, morphology, electrical and optical behavior), sodium titanates are still under debate [1-3,8,14-20]. This is why it is essential to understand the properties of sodium-ion titanates nanostructures (NaTNT) and their behavior as a component for an energy storage device. Several structures have been proposed for this titanates, for example [18,21] show strong evidence that NaTNT actually

possesses a trititanate structure with a general formula $Na_xH_{2-x}Ti_3O_7 \cdot nH_2O$, where *x* and *n* depend on the degree of sodium proton exchange during the washing procedure after hydrothermal synthesis [18,22,23]. The structural water and adsorbed surface water content is inherent to this type of synthesis [24], involving low temperature reactions in aqueous medium.

In a previous work [25], sodium-based titanates were synthesized using a hydrothermal method varying the reactor's temperature and time between 105 and 145 °C and from 48 h to 144 h. The physical properties of the system were analyzed through morphological, optical, and electrical measurements. For two particular conditions (105 °C and 125 °C at 96 h.) different structures evidenced through X-ray diffraction appear to resolve, probably a mixed phase. In the present work, the sodium concentration (pH) during the hydrothermal synthesis was modified in the two synthesis routes mentioned above (105 °C and 125 °C). The scope of this work is to vary the sodium content and examine its influence on the structural, optical and electric properties under these two conditions. Sodium content

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Table 1

Hydrothermal synthesis parameters, percentage of (H⁺) phase and content estimation of Na⁺ ions for the considered samples. Each sample was washed in 400 ml of distilled water.

	S1: 105 °C, 96 h., 150 rev/min			S2: 125 °C, 96 h., 150 rev/min			
[NaOH]	9M	10M	11M	9M	10M	11M	
"Green" phase (H+) (%)	45 (10)	51 (9)	41 (7)	38 (6)	34 (5)	64 (11)	
$Wt_{Na}/Wt_{(Na+Ti+O)}$ (%)	10 (1)	15 (2)	7.5 (7)	12 (4)	16 (1)	11 (2)	

(Na⁺) is taken as a new parameter that can help tuning the desirable properties for these materials. For example, the proportion of mixed phases, band gap, electronic defects, among others. Several structural techniques (X-ray Powder Diffraction, High-resolution microscopy, and Raman Spectroscopy) were used for the structural characterization. The results from the structural characterization were correlated with room temperature spectroscopy impedance, temperature dependence impedance and optical properties.

2. Methods and materials

2.1. Synthesis of NaTNT

The samples were grown by hydrothermal synthesis under endogenous pressure using Kasuga method [23], starting with 1.18 g of commercial TiO₂ anatase nanopowder precursor supplied by Sigma-Aldrich (ID: 799289, External ID: 232033_ALDRICH). The synthesis time (t_s) was 96 h., whereas two reactor temperatures (T_s) were used: 105 °C and 125 °C. A volume of 75 mL of NaOH (fill factor of 75 %) with three different molar concentrations (9, 10 and 11 mol L^{-1}) was used to dissolve the precursor in a Teflon-lined autoclave. During the hydrothermal synthesis the solution was magnetically stirred with a rate of 150 rev/min. Finally, a two days washing with distilled water and subsequent centrifugation process was needed to separate the solid from the residue. The solid was then dried for 24 h. at 80 °C resulting in NaTNT confirmed by morphological and structural techniques.

The 10M samples, which will be referred as references, were previously presented in [25], where different types of structures appear to emerge when varying T_s . The main scope of this work is to study the structure, morphology and physical properties of the samples obtained with the outlined method as a function of pH, for the two temperatures described above. The pH series are referenced as SERIES 1 and SERIES 2 for the lowest and highest temperatures, respectively. The synthesis conditions together with the nomenclature of samples are presented in Table 1.

2.2. Characterization techniques

The characterization of physical properties of the system was carried out applying a variety of techniques. For structural properties, Xray diffraction (XRPD), high-resolution electron microscopy (HRTEM), electron diffraction (ED), and confocal Raman microscopy were employed. XRPD was performed using a Rigaku Ultima IV diffractometer with CuK_{α} radiation. The 2θ angle was varied from 5.00° to 80.00° with a step of 0.02°, and an integration time of 60 s per step. The morphology of the samples, EDS spectra and the lattice parameters were obtained by HRTEM and ED (JEOL JEM 2100, 100 kV of acceleration), with a prior sample preparation on a carbon film supported by a copper grid. WITec Alpha 300-RA confocal Raman spectrometer with an excitation laser wavelength $\lambda = 532$ nm was used on pressed samples to obtain a 75×75 Raman Image. Afterwards, the average spectrum for this images was analyzed. For the estimation of sodium content, EDS spectra were used, from which only three elements (O, Ti, Na) were considered to estimate a total mass percent (% $Wt_{Na+O+Ti}$) used as a renormalization factor. With this renormalization factor the mass percentage of Na⁺ was calculated as: %Wt_{Na} / %Wt_(Na+Ti+O).

For Raman, Electrochemical impedance and optical measurement the powder samples were pressed into pellets at ~40 kN pressure for 30 s.



Fig. 1. Representation of the circuit setup.

Electrical characterization consists of Electrochemical Impedance Spectroscopy (EIS) measurements at room temperature and a study of the temperature dependency of the electrical impedance. In the first case Gamry Reference 3000 impedance analyzer, with Aluminium electrodes at both sides of the pellets, was used. The frequency was set between 1 Hz and 1 MHz with a 10 mV AC amplitude, and DC voltage was applied between 0 V and 4 V to evaluate the response in these conditions. Echem Analyst software from Gamry was used for data analysis.

Measurements of the dependence of the electrical impedance with the temperature were performed between 240 K and 325 K, in a closed cycle cryostat (CRYO Industries), with a temperature variation rate of 1.5 K/min regulated with a temperature controller (LAKESHORE 321). The circuit used for these measurements employs a Tektronix AFG3021B for the signal generation, and two Lock In Amplifiers SR 560 to determine the current and voltage in the sample. This circuit is depicted in Fig. 1. The sample was placed in series with a known resistance R_0 , and both were excited with a signal generator operating at 500 mV and two frequencies (10 Hz and 20 kHz). The electrical contacts in the samples were done with silver paste. The potential difference in both circuit elements (sample and R_0) was monitored with the two lock-in that share a phase and frequency reference with the source. The current intensity was then obtained by means of the voltage variation in the reference resistor R_0 (V_{1R} real and V_{1I} imaginary components); and the real and imaginary impedance components of the samples are derived using the voltage in the sample (V_{2R} real and V_{2I} imaginary components).

$$V_{1} - R_{0}I = 0 \quad \rightarrow \quad I = \frac{V_{1}}{R_{0}} = \frac{V_{1R} + jV_{1I}}{R_{0}}$$

$$V_{2} = V_{2R} + jV_{2I} = Z_{eq}I = Z_{eq}\frac{V_{1R} + jV_{1I}}{R_{0}}$$

$$Z_{eq} = R_{0}\frac{V_{2R} + jV_{2I}}{V_{1R} + jV_{1I}} \qquad (1)$$

Absorbance and photoluminescence measurements in the UV-Visible spectrum were carried out to study the optical behavior in the pressed samples. The measurement configuration consisted of an integrating sphere (OceanOptics (OO) FOIS - 1 coupled to a spectrometer (OO FLAME) and an input slit fiber (100 µm core diameter). The samples were placed before the integrating sphere and illuminated with a 1000 W Xe lamp (Oriel 6271) to measure direct transmittance. Before exiting the samples, the light was attenuated by a filter to protect them. The processing of the transmittance measurement allows



Fig. 2. (a) X-ray scans for NaTNT samples, the dotted lines indicate the peaks referred to in the text. (b) Diagram of the coiling sheet that the nanostructures form and its crystallographic directions.

to obtain the direct and indirect gap values, as will be detailed in Section 3.3. A 300 nm (~4 eV) wavelength diode was used to illuminate the samples during the photoluminescence (PL) measurements at room temperature. The thickness of the samples requires PL emission to be collected in a back scattering configuration. Finally, an optical fiber of 200 μ m core diameter was used to collect the PL emission and send it to the *OO* FLAME spectrometer. In most of the samples the excitation diode light was detected despite the set up design.

3. Results and discussion

3.1. Structural characterization

Fig. 2(a) shows the X-ray diffraction patterns for the six studied samples. All patterns have a similar structure between them and they also agree with what has been reported in the literature for other titanates nanotubes prepared by the hydrothermal method [15,26–28]. The diffraction peaks structure is conformed by peaks at approximately $2\theta \sim 9.25^{\circ}$ –9.45°, and a series of doublet at $2\theta \sim 24.36^{\circ}$ (interplanar distance of 3.66 Å and 3.54 Å), $2\theta \sim 28.46^{\circ}$ (interplanar distance of 3.16 Å and 3.04 Å), $2\theta \sim 48.3^{\circ}$, and $2\theta \sim 61.6^{\circ}$. Also, in Fig. 2(b) we outline the sheets coiling that the nanostructures form and the crystallographic directions based on [14,28]. Figs. 3–5 summarize the peaks interplanar distance deduced from the peak position and coherent length obtained from the Scherrer formula (for more details see Supplementary Material).

In the present work the lower angle peak $(2\theta \sim 9.25^{\circ} - 9.45^{\circ})$ is assigned to the $(2\ 0\ 0)$ reflection of a tri-titanate phase like $H_2Ti_3O_7$ or $Na_2Ti_3O_7$, corresponding to the radial direction of the nanotubes. This direction is expected to exhibit the lower crystallinity, consistent with broader peaks. The interplanar distance obtained correspond to the distances between $[TiO_5]$ layers. In a subset of the samples this peak is clearly asymmetric, suggesting the presence of more than one peak. Therefore the peak will be considered as the sum of two contributions (see Supplementary material), and, as a consequence, two mean peaks positions (9.6 Å and 8.7 Å) were found. The largest interplanar distance corresponds to an approximately constant coherence length around 5 nm. However, for the phase with the smallest interplanar distance this coherence, also of 5 nm in the majority of the samples, doubles for the S2:9M and 10M conditions. These coherence lengths are most likely associated with the wall size of the nanotubes. An isolated nanotube for S1:9M is shown in the Supplementary Material, where the wall size can be clearly seen, and is about 5 nm.

Considering the general formula $Na_xH_{2-x}Ti_3O_7 \cdot nH_2O$ proposed by several authors [19,21], the limits for the interlaminal distance between the bulk trititanates $H_2Ti_3O_7$ and $Na_2Ti_3O_7$ are d = 0.78 nm and d = 0.84 nm respectively. The higher *d* values obtained here (between 0.84 nm and 0.97 nm) confirm the presence of structural water. Therefore, the phase of smaller interplanar distance could be assigned with more relative weight of H⁺ phase, and the higher interplanar distance with a predominance of Na^+ (*x* in the general formula).

The peak at $2\theta \sim 48.30^{\circ}$ (interplanar distances of 1.88 Å) is outstanding for its narrowness and intensity. It is also presented in the same position for all the samples XRPD pattern. This peak is associated to (0 2 0) reflection corresponding to the growth direction (planes perpendicular to the axial directions), which presents a higher crystallinity [15,28]. The peak assignment is supported with HRTEM (See Supplementary Material), where the 1.88 Å distance corresponds to the plane perpendicular to the growth direction. The coherence distance in the axial direction is in the range of 10–13 nm in all samples, and it is smaller than the tube length observed by TEM images suggesting that the nanotube is polycrystalline. Furthermore, this peak has a shoulder at higher angle in all the samples, with a characteristic distance of 1.846 Å and a coherent length between 5 nm and 10 nm. Both *d* values are observed in electron diffraction images.

The doublets at $2\theta \sim 24.36^{\circ}$ and $2\theta \sim 28.46^{\circ}$, are probably ascribed to the (1 1 0) and (3 1 0) planes [28]. For the S2 conditions (125 °C, 96 h.), the higher angle peaks of each doublet (green curves in Fig. 4) are more resolved, with a smaller FWHM (full width half maximum) indicating a larger crystallinity. This can be seen in Fig. 4(b) and (d) where all the green curves present a maximum for S2 conditions. Also, the phase with smaller interplanar distance (probably H⁺), presents a higher intensity. This is consistent with a previous report [29] pointing out that the incorporation of sodium decreases crystallinity.

Additionally, for the S2 series the peaks around $2\theta \sim 34^{\circ}$ (interplanar distance of about 2.6 Å), $2\theta \sim 38^{\circ}$ (interplanar distance of about 2.3 Å), and 52.70° are more pronounced. This can also be seen in the S1 series for the highest NaOH concentration. In [28], is suggested that these two peaks could be associated with (3 0 1) and (5 0 1) for dititanate acid (H₂Ti₂O₅ · H₂O), (2 1 - 3) and (2 1 - 4) for tetratitanated acid (H₂Ti₄O₉ · H₂O), or (3 1 - 2) and (1 1 - 3) trititanate acid (H₂Ti₃O₇). In Fig. 5(a) and (b), the position and coherence length for these two



Fig. 3. (a) Interplanar distances and (b) coherent length for the contribution peak of [2 0 0] reflection; (c) interplanar distances and (d) coherent length for the [0 2 0] reflection. Blue point: greater interplanar distance and green point: smaller interplanar distance. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. (a) Interplanar distances and (b) coherent length for the contribution peak of [1 1 0] reflection; (c) Interplanar distances and (d) coherent length for the [3 1 0] reflection. Blue point: greater interplanar distance and green point: smaller interplanar distance. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

peaks are shown as a function of the synthesis condition; they present the same trend of the "green" phase.

The relative concentrations of the two phases was calculated using the sum of the peaks integrated intensities for each phase, according to $[Ph_2] = \sum I_{ph2}/(\sum I_{ph2} + \sum I_{ph1})$ [30], with I_{ph1} and I_{ph2} the integrated intensity of each peak associated to Phase 1 and Phase 2, respectively. This methodology is similar to the one used to determine the percentage of amorphous phase [31]. The results are shown in Fig. 5(c) and Table 1. A drop of 20% in the phase with the smallest interlaminal space can be observed, except in the most extreme conditions of temperature and pH.

These results suggest the presence of a mixture of two phases, probably with different ordering patterns between the layers, which leads to a change in *a*-axis from 17.4 Å to 19.2 Å. This difference may be a result of proton (H⁺)/sodium (Na⁺) exchange and/or structural water intercalation. The phase with lower interlaminal distance ("green phase") appears to be a nanorod, because their coherence length in the wall direction is similar to the corresponding diameter. The estimated

 Na^+ content normalized to the Na+Ti+O % mass is also shown in Table 1. As can be seen, there is an inverse correlation between the Na^+ content and the presence of Phase 2.

Average Raman spectra in the 50–1200 cm⁻¹ range for all samples are displayed in Fig. 6. Only in the case of S2:11M, Raman spectra showed the presence of bands located at ~1080 cm⁻¹ related to C–C–C bending modes probably formed with CO₂ from the air [32]. In all the samples, common characteristics are observed in the spectra. For example, all of them consist of a series of defined peaks at 910 cm⁻¹, 667 cm⁻¹, 450 cm⁻¹ and 276 cm⁻¹. The highest Raman shift peak (910 cm⁻¹) is associated to Ti–O stretching involving non-bridging oxygen atoms [15,26,27,33–37] or short Ti–O bonds in the distorted TiO₆ octahedron [1,38,39]. The last three are related to Ti–O–Ti stretching in the edge shearing TiO₆ unit [1,38,39]. In particular, the 667 cm⁻¹ mode is also reported as due to the Ti–O–H vibration [40–42]. In this case the mentioned peak is very similar in all the samples, appearing slightly finer for cases where the phase with the smallest interplanar distance is more crystalline (i.e. where there is less "green" phase).



Fig. 5. (a) Interplanar distances, (b) coherent length for interplanar distances of 2.3 Å and 2.6 Å and (c) percentage area of the "green" phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. Normalized average Raman spectra. The dashed lines indicate the peaks discuss in the text and the highlighted area referred to the following modes: B-D: stretching involving non-bridging oxygen atom or short Ti–O bonds in the distorted TiO_6 octahedron; S-E-S stretching in the edge shearing TiO_6 unit; F-M: Flexing mode. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The 276 cm⁻¹ mode is characteristic of Na-Ti-O bonds. For S2 condition a shoulder in the left of the 276 cm^{-1} mode is present. This could be related with a more pronounced differentiation between the $\mathrm{Na^{+}}$ and $\mathrm{H^{+}}$ phases, as it occurs in the XRPD pattern. Also for this series, a peak around 370 cm⁻¹ is present with a higher intensity. The intensity of this peak is, nonetheless, small and is not usually reported in the literature, but it can be observed in [42], where the modes below 400 cm⁻¹ are associated with Na–O. In [14] a simulation over Na₂Ti₂O₅ · nH₂O predicts a band around 350 cm⁻¹. However, another explanation is possible, similarly to the one proposed for the shoulder of 276 cm⁻¹: the phase with the highest crystallinity could be responsible for the resolution of this peak. The low Raman Shift region, between 90 cm⁻¹ and 220 cm⁻¹, presents a mixture of bands. However, a more pronounced effect is seen in S2 series where peaks in 192 cm⁻¹ and 155 cm⁻¹ have higher intensity. These peaks are usually ascribed to Na-O-Ti or Ti-O-Ti vibrational modes in the [TiO₆] layer [38,39,43].

Figs. 7 and 8 display the TEM and electron diffraction images for the two series, confirming tubular nanostructures, with average diameter of 26 nm for S1 and 14 nm for S2. This supports the idea that sample S2 probably has more content of nanorods because the mean diameter is close to the coherence length in the corresponding direction. Therefore,

based on the wall thickness deduced from the diffraction patterns and the mean diameter of the tube, we can classify the morphology in: nanotube (mean diameter higher than two times wall thickness) and nanorod (mean diameter lower than two times wall thickness). Due to the higher wall size in the Phase 2 (H predominance), nanorod are the more likely morphology. For example, S2:11M has the highest percentage of *H* phase and, therefore, it could be mainly constituted by nanorod. However, these differences are not clearly seen in the TEM images. Given the fact that *H* has a smaller size ion in comparison to Na⁺, its titanates could facilitate the tube coiling more easily.

Electron diffraction was carried out, finding interplanar distances from 1.80 Å to 3.72 Å (see Supplementary Material).

3.2. Electrical characterization

As mentioned in Section 2 two types of impedance measurements were performed. The first one was made to monitor the carrier response in a room-temperature impedance spectroscopy (RTEIS) setup. The second one studied the temperature dependence of impedance to evaluate the material performance over -30 °C and 50 °C range for two frequencies (10 Hz and 20 kHz).



Fig. 7. Transmission electron microscopy (TEM) images for (a) \$1:9M, (b) \$1:10M, (c) \$1:11M, (d) \$2:9M, (e) \$2:10M, and (f) \$2:11M.



Fig. 8. High resolution transmission electron microscopy (HRTEM) images for (a) S1:9M, (b) S1:10M, (c) S1:11M, (d) S2:9M, (e) S2:10M, and (f) S2:11M. Their corresponding electron diffraction images are displayed in the insets.

3.2.1. Room temperature impedance spectroscopy (RTEIS)

Impedance spectroscopy presented as a Nyquist plots is shown in Fig. 9(a) and (c) for 1.0 V and 3.0 V applied DC voltage, respectively. Phase-frequency plot for the same DC voltages are display in Fig. 9(b) and (d). Additionally, Fig. 10 shows the impedance's imaginary part as a function of frequency when varying the applied DC voltage, for the two series of samples.

The Nyquist plots for low applied DC voltage show two semi-arcs, a smaller one at higher frequency and a larger one at low frequency, in all the samples. In a subset of samples (corresponding to higher sodium hydroxide concentration: 11M NaOH) a middle frequency process appears or is more pronounced. This can also be observed in the imaginary impedance plot where some peaks are enhanced for intermediate frequencies. Furthermore, the arc or areas enclosed by the arcs are bigger than in the rest of the samples. No correlation was found with the morphology since it is similar to other samples. However, in Table 1 it is observed that these two samples have a lower Na weight (%Wt_{Na}) within its series, and in the case of S2:11M the content of the phase dominated by H⁺ is the highest. Therefore, these samples probably present a more marked mixture of phases which accentuates the intermediate process and more arcs are observed in the impedance measurements. The resistance of the process are similar, as can be seen in Fig. 11 when 3 processes are involved in the fitting.

When increasing the applied DC voltage, the high frequency arc is markedly reduced. Additionally, the phase at low frequency is diminished from a capacitive behavior (in the 40° - 80° range) to a resistive one with a phase close to zero. The DC voltage increases the charge carrier mobility, reducing the capacitive behavior. For S1:11M and S2:11M, at high frequencies there is still a capacitive behavior present.

In this work, the treatment explained in [25] to fit the RTEIS spectra is repeated. The authors in [25] propose a model circuit consisting of two elements in series, each of which is composed of a resistance (R) and a constant phase element (CPE) in parallel. The bulk zone is represented by the highest frequency arc, in this case called $R_1 - CPE_1$. A characteristic time, related to a charge mobility time (lifetime), can be obtained from this $R_1 - CPE_1$ parallel elements, through the following formula $t_1 = R_1 C P E_1^{1/n_1}$. Also, the low frequency arc labeled $R_2 - CPE_2$, can be related with the grain boundary or depletion zone. For this case, a characteristic time can also be defined (t_2 = $R_2 CPE_2^{1/n_2}$), related to recombination processes or diffusion time in the intergrain [44]. In some cases, like samples in 11M condition, a third process (R_m, CPE_m) needs to be included for a better representation of the curves. The fitting results for R_1 , R_2 (and R_m in some cases), and their characteristic times are schematized in Fig. 11. The $R_m - CPE_m$ process appears to be also related to the bulk zone, inferred from an absence of a marked change with DC voltage, probably due to the presence of other type of carrier.



Fig. 9. (a) Nyquist plots of Room temperature Impedance spectroscopy and (b) Phase-frequency plots for 1.0 V of applied DC voltage. (c) Nyquist plots of Room temperature Impedance spectroscopy and (d) Phase-frequency plots for 3.0 V of applied DC voltage. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. Impedance's imaginary part as a function of frequency varying the applied DC voltage for (a) S1:9M, (b) S1:10M, (c) S1:11M, (d) S2:9M, (e) S2:10M, (f) S2:11M. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

For low DC voltage, the contribution of the parallel element 2 is dominant. This changes at larger DC voltage when the $R_1 - CPE_1$ or even the $R_m - CPE_m$, overcame the contribution of the grain boundary process ($R_2 - CPE_2$). It has already been reported [44–47], that increasing the applied DC voltages allows the accumulation of charge at the grain boundary to overcome the potential barrier and act as an injection of mobile charge carriers, decreasing R_2 resistance, as was observed in the measurements. Although R_1 (and also R_m) seems to be higher for the case S2:11M in comparison to the remaining samples, it is an artifact produced by the difficulty in resolving middle and high frequency contributions. This can be better understood when the measurement is decomposed in the sum of three R - CPE (curve with triangles in Fig. 11(a), (b) and (e)), where it is clearly seen that R_1 and R_m remain mostly constant.

The appearance of the intermediate process is clearer when the characteristic times are analyzed. In general, in the process of lower frequency, the time is of the order of seconds, and decreases with increasing voltage. This time is related to diffusion or recombination process, which are favored by the processes of accumulation of carriers in the grain interfaces. As a result, the recombination time is expected



Fig. 11. Fitting results as a function of the applied DC voltages for (a) $Log(R_1)$, (b) $log(R_2)$, (c) t_1 , (d) $log(t_2)$ in series 1; and (e) $Log(R_1)$, (f) $log(R_2)$, (g) t_1 , (h) $log(t_2)$ in series 2.

to decrease when the concentration of charge carriers increases [47, 48].

The intermediate process times (of about 1 ms) and the high-frequency times (of about 1 μ s) are approximately constant with voltage. It is worth highlighting that for 11M in both series, the intermediate process is very strong and dominates the fittings. When NaOH concentration is increased during synthesis, the third electric process could be enhanced. Since the process appears to be a non-voltage dependent bulk process, it should respond to a carrier lifetime dependence. To account for this new bulk carrier mechanism one notices that the presence of more Na modifies the inter-laminar space. As a consequence, this may increase the conductivity properties of Na⁺ and H⁺ ions which could explain this non-voltage dependent process.

3.2.2. Z(T)

The electrical impedance of the samples as a function of temperature was estimated in the range between 240 K and 325 K. These range was chosen considering possible application of the material, ranging from low temperatures (-30 °C) to extreme heat (50 °C). The temperature was lowered from 290 K to 240 K, and then raised again to 325 K. As mentioned before, the measurement circuit is exemplified in Fig. 1, from which it is obtained the temperature dependent impedance Z(T). It is important to remember that the absolute values of Z depends on the contact geometry. Although an attempt was made to maintain a similar geometry in all the samples, it cannot be guaranteed that the geometric constant is the same since the electrical contacts were performed with silver paint and irregular samples.

In Figs. 12 and 13 the temperature dependence of *Z*'s modulus and phase is shown for 10 Hz and 20 kHz in both sets of samples. For the 10 Hz frequency, all the curves are similar, the impedances are about 15 M Ω , and they present a phase in the range of -60° to -70° , which means a strong capacitive behavior, in agreement with Fig. 9. The impedance increases when lowering the temperature but whose variations are smaller than 25%. For the S2 series, we can see that the phases have a maximum in the region between 0 °C and room temperature that can be related to the freezing of the interstitial water.

Assuming the samples as a parallel *RC* element (similar to the cases considered in the previous subsection), the characteristic times of the process that dominates at 10 Hz are in the region of 18–30 ms. The characteristic resistances and times correspond to the results of R_2 and t_m obtained from the EIS study.

In most of the samples (except S1:11M and S2:10M) when the frequency increases to 20 kHz, the sample loses the capacitive behavior and reduced its impedance modulus to a few k Ω and the characteristic time to 3–10 μ s. At this frequency the impedance modulus and the phase are almost constant for all the samples in the temperature range tested. This is again in agreement with EIS measurement at room

temperature. For S1:11M at 20 kHz there still remains a capacitive behavior and an intermediate resistance, consistent with the observed results in the EIS measurement (Fig. 9(d)). However, S2:10M results are not concordant with the EIS measurement. This sample was measured multiple times and the results remain unaltered.

Increasing the frequency reduces the capacitive effect and increases the conductance of the sample. Furthermore the effect of temperature in the impedance of the samples is small, and is further reduced when the frequency increase.

3.3. Optical characterization

As it was previously mentioned, the optical characterization consists of direct transmittance (T_d) and photoluminescence (PL) measurement at room temperature. The absorption coefficients, α , were calculated from T_d by means of the Lambert–Beer Law ($\alpha = -log(T_d)$) [49]. The α measurements for both sets of samples are shown in Fig. 14(b). The general behavior of the absorption coefficient is complex and cannot be explained by considering only one type of bandgap edge, therefore, at least two types of bandgap edges should be considered to fit the curves. The Tauc plots were analyzed to estimate the direct band gap (hv vs. $(\alpha hv)^2$) and the indirect band gap (hv vs. $(\alpha hv)^{1/2}$) energies [49,50]. The data analysis procedure is explained in detail in [25] and is commonly used in the determination of these properties [51,52]. An example for S1:11M is shown in Fig. 14(a) (all the fittings are presented in the Supplementary Material).

In Fig. 14(b) it is noticeable that the S2 set has a step-like shape. Despite the complete S2 set having the step around 3.0 eV, S2:9M and S2:11M exhibit remarkable differences on its length and slope. Additionally, the S2 samples can be well fitted by a direct and an indirect band gap (BG) in the 3.0 eV-3.3 eV region (see Fig. 15(a)). This double gap behavior and the step was also found in S1:11M (Fig. 14(a)). This behavior could indicate electronic transitions between the valence and conduction band of distinct crystalline phases in the material, which is in concordance with the XRPD analysis. Therefore, the band gap overlay could be attributed to the pronounced separation and higher crystallinity of one of the two phases present in these samples. Analyzing the S1 set it can be seen that increasing the pH on the sample synthesis changes the absorptance curve from a smooth one to a step like one. We can conclude that a higher relative concentration of the Na⁺ phases (increase the interlaminal distance) increases the step like behavior, resulting in the observation of more than one gap.

Indirect and direct BG energies are plotted in Fig. 15(a), where some tendencies are appreciable. Indirect band gap energies are minimized close to 2.3 eV for the 10M samples in both sets. In the case of the direct BG energies (between 3.0 and 3.4 eV), two different behaviors are observed. While the direct BG on the S1 set decreases when pH grows,



Fig. 12. Temperature dependence of the impedance's modulus for (a) S1 and (b) for S2 series; and impedance phase for (c) S1 and (d) S2 series at 10 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 13. Temperature dependence of impedance's modulus for (a) S1:9M, S1:10M, S2:9M, S2:11M and (b) S1:11M and S2:10M; (c) and (d) impedance's phase respectively at 20 kHz. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

S2 has an approximately constant value (near S1:11M). This fact could be related to the appearance of an overlay of two BG types in samples S1:11M and the S2 series around 3.0 eV, as was mentioned before. For S1:11M and S2:9M, two indirect band gaps are found around 2.3– 2.5 eV and 3.0–3.3 eV (see Supplementary Material). If the presence of the overlay BG is related to the formation of a new phase, the optical measurements should exhibit the phase mixing. However, is not possible to accurately distinguish these behaviors. Despite that, it could be stated that when the phase with the greatest distance between layers increases its relative concentration, the direct band gap decreases. Since the band gap obtained corresponds to energies in the visible region (above 410 nm) the materials may present photoactivity under visible irradiation.

Fig. 14. (a) Example of absorption coefficient with direct and indirect band gap fitting, (b) Superposition of the absorption coefficient for all the samples. (c) Example of a normalized PL spectra with a four Gaussian decomposition and (d) normalized PL spectra for all the sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 15. (a) Indirect and direct band gap energy vs. NaOH precursor molar concentration for both sets of samples. Higher energies correspond to direct BG (Square: S1, Triangles: S2), and Lower energies correspond to indirect BG (Dots: S1, Inverted triangle: S2). Peak area form PL signal vs. NaOH precursor molar concentration for (b) S1 and (c) S2 series.

Photoluminescence (PL) signal was measured in powdered samples by exciting them with a 300 nm LED source (approximately 4 eV) and the response was obtained by means of a spectrometer (OO FLAME spectrometer). Because the light source is higher in energy than the band gap energy (maximum at 3.4 eV) of the samples, the samples should be correctly excited by the LED. Fig. 14(d) shows the PL spectra for the six samples. All the samples present a broad spectrum in the 2.0–3.2 eV region, characteristic of multiphononic processes due to the high density of electronic states within the band gap region, most likely from defect centers. This is also influenced by structural disorder and mixed phases. Similar to the absorption measurements, PL signals show commonalities between S1:11M and S2:9-10M. To analyze the contribution of different defect centers, deconvolutions of the PL intensity was performed considering four Gaussian peaks. We also added a peak for the LED when required. An example is shown in Fig. 14(c).

The principal component in PL emission, in anatase nanostructures, at energies in the 2.5-3.1 eV region has been associated with oxygen vacancies defects [53]. Lower energy emission (2.4-2.7 eV) are ascribed to sallow defects like monoionized oxygen vacancies [54], and higher energy emission (2.8-3.1 eV) with deep defects like Doubleionized oxygen vacancies [55]. The emission at approximately 2.1 eV could be related to OH group defects [53]. Additionally, visible luminescence emission around 2.4 eV has been reported in titanium oxide and titanates, and it is described as an electronic transition associated with the [TiO₆] octahedron [56,57]. This emission has, therefore, a local character. As a result, any distortion in the octahedron environment may diminish the PL signal near 2.4 eV because of the absence of excited states inside the [TiO₆]. In [56] it is demonstrated that the presence of Na⁺ ions does not distort the octahedron, while the hydrogen proton does. Table 2 presents the position and percentage area of each PL peak for all the samples. Additionally, in Fig. 15(b) Table 2

Samples		E_{gD} (eV)	E_{gI} (eV)	Peak 1		Peak 2		Peak 3		Peak 3	
				E_{P1} (eV)	Area _{P1} (%)	E_{P2} (eV)	Area _{P2} (%)	$\overline{E_{P3}}$ (eV)	Area _{P3} (%)	E_{P4} (eV)	Area _{P4} (%)
Anatas	e	3.05 (12)	2.88 (4)	2.40 (1)	34 (1)	2.57 (5)	27 (1)	2.83 (4)	29 (2)	2.96 (5)	9.6 (3)
S1:	9M	3.35 (7)	2.89 (5)	2.3 (1)	47	2.52 (7)	12	2.76 (4)	5.2	2,94 (7)	21
	10M	3.24 (6)	2.18 (4)	-	-	2.5 (2)	41	2.8 (1)	35	2.99 (8)	24
	11M	3.11 (2)	2.28 (8)	2.2 (1)	15	2.5 (1)	36	2.80 (8)	26	3.01 (8)	22
S2:	9M	3.09 (6)	2.54 (3)	2.2 (2)	32	2.5 (1)	37	2.82 (7)	19	3.00 (5)	12
	10M	3.12 (11)	2.15 (1)	2.3 (1)	15	2.5 (1)	29	-	-	3.0 (2)	57
	11M	3.11 (2)	2.62 (3)	-	-	2.5 (1)	45	2.85 (7)	27	3.03 (7)	27

Band Gap energies, energy peak position and percentage area under the peak for the resolved PL spectra with four Gaussian functions.

and (c) the peak area dependence with NaOH content for each series of samples is plotted.

In the present work, the peaks in the energy region between 2.6 eV and 3.1 eV are assigned to oxygen vacancies, for energies ~2.5 eV electronic transitions associated with the $[\text{TiO}_6]$ octahedron are considered, and OH group defects are responsible for emission around ~2.2 eV. All the peaks present an almost constant position (see Table 2 and Fig. 7 in the Supplementary Material), with a maximum variation of 4%. However, the intensity of the peak changes drastically.

According to Fig. 15(b) and (c), the OH group defect decreases with NaOH content for both sets of samples. More precisely, the condition that minimizes the OH group contribution to the PL signal correlates with higher values of H-phase amount obtained from XRPD. In particular, the predominance of this peak for S1:9M is observed, and the absence of this peak in S1:10M and S2:11M is noticed. For the last ones a narrower PL spectrum is observed.

The peak around 2.5 eV appears with high intensity in all the samples, and it is approximately constant in S1:10-11M, S2:9-10M samples. As it was mentioned before, this emission has a local character associated with the octahedron [TiO₆]. The presence of hydrogen protons distorts the structure diminishing the 2.5 eV PL signal. This could be the case of S1:9M. Based on the previous discussion about OH defects, the S1:9M sample exhibits a strong presence of the peak related to OH group defects. It may suggest that octahedrons are conformed by H⁺ more than Na⁺.

Finally, the signals with energy higher than 2.5 eV, that correspond to oxygen vacancies, increases with Na content in both series.

In general, changing the pH modifies the amount of Na that enters the structure, and with it the relative proportion of the phases (H, Na) that formed the nanostructures. When more Na is achieved within the structure, the distance between the nanotubes sheets increases, facilitating the conduction of Na⁺ and H⁺ ions, increasing the medium and high frequency impedance processes. However, it does not appreciably change the behavior of the impedance with temperature. In addition, increasing sodium content, diminishes the contribution of the OH group defects and increases the oxygen vacancies, changing the optical properties. It also allows to regulate the band gap, depending on the condition. In summary, the synthesis condition together with the sodium content tuned by the NaOH concentration, influences the final phase, and the structural phase regulates optical and electrical properties that must be considered for applications.

4. Conclusions

The effect of NaOH concentration conducts to different physical properties in the studied systems. All the samples present a mixture of phases concordant with $(Na, H)_2Ti_3O_7 \cdot nH_2O$: for the extreme condition synthesis and lower NaOH concentration, the phase with lower interplanar distance (probably the H-phase) is more crystalline, and it is resolved from the higher interplanar distance phase (Na-phase). The last one is present in all the samples with lower crystallinity. All the samples present structural water, according to the interplanar distance obtained. Additionally, for the S2 series (higher temperature during the synthesis), according to XRPD data and mean diameter, the lower

interlaminal distance phase is probably a nanorod phase. The mixture of phases is reflected in the electrical and optical properties. In the first ones, all the samples present a middle frequency process that is enhanced for higher NaOH concentration. This middle process could be attributed to a bulk one, like the high frequency process. Neither of them are influenced by the application of voltage, with a characteristic time around 1 ms and 1 µs, respectively. One possible explanation for the middle process is that, besides the electron mobility (high frequency arc), there is also a H⁺ or Na⁺ proton mobility inside the bulk. These materials also present a mixture of energy band gaps, finding both direct and indirect behavior. For the S1 condition, the direct band gap can be tuned with the increase of NaOH concentration and make it comparable with the S2 condition. PL spectra confirms the presence of a mixture of phases. Finally, it is important to remark that the impedance response of the samples present a change of 25% in the temperature range of operation for low frequencies and is almost constant for high frequency. These systems could be of interest for applications, since the properties of the electrodes are dependent with the amount of Na-ions.

CRediT authorship contribution statement

Lucia Amy: Data curation, Formal analysis, Methodology, Investigation, Visualization, Writing – original draft, Conceptualization. Sofia Favre: Formal analysis, Data curation, Methodology, Visualization, Writing – original draft, Writing – review & editing, Conceptualization. Ricardo Faccio: Conceptualization, Formal analysis, Methodology, Data curation, Supervision, Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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Corrigendum to "Structural, optical, and electrical properties of proton intercalation H+/Na+ phases in nanostructured titanates induced by pH during hydrothermal synthesis" [Mater. Today Commun., vol. 33 (2022), 104908]

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The authors regret a mistake in the definition of the synthesis conditions. The synthesis temperature for Series S1 was erroneously listed as 105 °C, and for Series S2 as 125 °C. The correct information should be the inverse: Series S1:125 °C, and Series S2:105 °C. This error was made in Table 1, and is replicated in section 2.1 in lines 19–20, in section 3.1, fifth paragraph where the temperature associated with conditions S1 and S2 is repeated, and the same in section 4 when referring to S2 conditions, and finally in the title of Figure 12.

We assure that, despite this error, the scientific validity of our results and the conclusions presented in the manuscript remain unaffected.

The authors would like to apologise for any inconvenience caused.

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Chapter 5

Structural phases of sodium titanate nanotubes obtained in diferent synthesis conditions: A theoretical study

In the preceding articles, we presented results for structures obtained through various synthesis routes, with a particular focus on studying their structural properties with a proposed sodium/hydrogen trititanate initial structural phase incorporating structural water in the interlaminar space. The significance of investigating these properties stems from the lack of consensus within the scientific community regarding the structural phases present in titanate nanostructures.

Chapter 3 and 4 provided valuable information, offering indications of possible phases present in the nanoestructured sodium titanates. This chapter proposes a theoretical study based on residual structural phases resulting from high-temperature heating of a selection of the samples (reaching several hundred degrees Celsius, see Apendix C), made in the Functional Materials Department of Material Science, Saarland University, Germany. After this calcination process, an X-ray diffraction scan reveals that the samples show the coexistence (in different proportions) of hexa- and tri-titanates of sodium. Due to the high annealing temperatures applied, only sodium phases appear, but it cannot be ruled out that it initially phases incorporates H^+ . As it suggested in literature [41, 42], it is inferred that before the annealing process both hexa- $(Na_xH_{2-x}Ti_6O_{13})$ and tri- $(Na_xH_{2-x}Ti_3O_7)$ titanates of hydrogen and sodium phases may be presented. To study this possibilities we simulate the mentioned phases with x = 0, 1, 2. These phases are examined theoretically applying first-principles calculation, using the VASP code, and Debyer to simulate XRPD patterns from the atomic position information in all the structures. It is important to highlight that during the initial stages of the thesis, numerous phases described in existing literature, such as for example $Na_xH_{2-x}Ti_2O_5$ phase, were used for attempt to reproduce the XRPD patterns for the samples. Appendix C contains some examples of these outcomes, presented as supplementary material accompanying the paper featured within this chapter.

Figure 5.1: Scheme of a laminated tubular structure with the directions of principal axes (a radial, b longitudinal, c tangencial). A quarter of a tube is illustrated.

To substantiate the proposed structures, our validation process unfolds in the following manner: we commence by seeking an optimized geometry for a given atomic arrangement, originated from an initial crystallographic structure. Subsequently, we utilize this optimized geometry to conceptualize tubular nanostructures (rolled lamellar nanostructures) and then simulating the corresponding XRPD patterns. The tubular nanostructures are schematized in Figure 5.1. There it is shown that the lattice parameter a was repeated B1 times in the radial direction, lattice parameter b was repeated B2 times in the axial direction (tube length), and lattice parameter c was repeated in the tangential direction B3 times. The patterns were simulated for different values of $B = (B_1, B_2, B_3)$. These simulated patterns are subsequently juxtaposed with a selection of experimental measurements. It's important to note that the nanostructure model lies external to the simulation framework. Additionally, we meticulously examine the plausibility of the vibrational modes to validate the structures. We present Raman spectra simulation for bulk material, but

their alignment with the empirical data necessitates a more meticulous approach. This is due to the fact that these spectra are generated for bulk materials and not specifically tailored for nanostructures.

Furthermore, the chapter explores the use of both single (PBE) and hybrid (HSE06) functionals for calculating bandgap energies. Surprisingly, contrary to what might be expected for other types of structures, the hybrid functional does not demonstrate any improvement in the gap values. This unexpected result adds an interesting dimension to the study.

To validate the theoretical findings, numerical results are compared with experimental properties measured (XRPD pattern, Raman spectra and band gap energies) for the samples. This comparison enhances the reliability of the theoretical approach and sheds light on the agreement between theory and experiment.

We found compelling evidence sustaining the co existence of both sodium and hydrogen tri- and hexa-titanate phases. Moreover, indications point towards the presence of structural water. Including these waters could improve the correspondence between experimental and theoretical interplanar distances. It is remarkable that while this current study does not delve into this aspect, it emerges as a potential avenue for future exploration. Furthermore, nanostructures patter should continue to be adjusted to better represent experimental measurements. This refinement will allow to obtain a better quantification of the nanotube geometry and Na/H proportion, leading to a more accurate alignment of vibrational and optical properties with experimental measurements.

As it was another objective of the thesis, this chapter serves as a crucial step toward clarifying the phases present in these materials, contributing significantly to the current knowledge in the field. By employing theoretical simulations and carefully designed experiments, the study bridges the gap between theory and practice, advancing our comprehension of titanate nanostructures and their potential applications. **ORIGINAL PAPER**

Structural phases of sodium titanate nanotubes obtained in different synthesis conditions: A theoretical study

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Abstract

Sodium-based titanate nanotubes are promising materials for energy applications, declared as one of the ten emerging technologies in chemistry. However, their structural properties, the presence of structural water, and the emergence of mixed phases due to the interchange between H and Na, are strongly dependent on the synthesis conditions, being difficult to determine the internal structure of these materials. The present work is a theoretical approach based on ab initio calculations to understand the inner structure (building blocks) of the nanotubes. We use as possible models of crystalline structure: hexa $(Na_xH_{2-x}Ti_6O_{13})$ and tri $(Na_xH_{2-x}Ti_3O_7)$ titanates of hydrogen and sodium (x = 0, 1, 2), suggested by the results of an annealing process on real samples. We calculated the structural, vibrational and electronic properties of the systems under study, founding good agreement with the experiments, thus suggesting the possible coexistence of $Na_xH_{2-x}Ti_3O_7$ and $Na_xH_{2-x}Ti_6O_{13}$ phases in the nanostructured samples.

Introduction

Sodium ion-based technologies for device manufacture or energy storage applications are currently one of the most studied subjects [1]. In particular, nanostructured sodium titanates (NaTNT) are being analyzed as a promising material for the batteries anode development [2–6]. Due to the relevant application of these materials, it is important to have a precise characterization of them. So far there are many studies in the literature trying to elucidate the formation

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mechanisms and the structural phases of these compounds [1, 7-12]. One strategy is to simulate bulk initial structures, and then calculate the X-ray powder diffraction (XRPDs) for a slab or a rolled slab as a nanotube. With these simulated XRPD patterns, the goal is to fit the experimental diffraction patterns. If both agree, the initial structure can be validated [8].

In previous works [13, 14], we have synthesized this type of materials by the hydrothermal method, varying the synthesis conditions (reaction temperature, reaction time and pH of the medium where the reaction is carried out). Since the final structure influences the optical and electrical properties, it is important to have the former regulated and characterized, to apply these materials in useful devices. This motivates understanding which are the main structural blocks that could build these nanotubes. In [13, 14] we have found that there is not a single crystalline phase that can explain the whole XRPD patterns of these compounds and that the ratio between these phases is affected by the initial conditions of the synthesis. Phases such as di-titanates $Na_2Ti_2O_5$, $Na_2Ti_2O_2H_2O$ (with and without structural water) were analyzed theoretically, as they were suggested by extended X-ray absorption fine structure (EXAFS) experiments [13]. Still, it was not possible to reproduce the experimental diffraction patterns with the simulated ones (see Fig. 1 in Supplementary Material). We proposed that the phases of the compounds are probably tri-titanates of hydrogen and

sodium with structural water $Na_xH_{2-x}Ti_3O_7 \cdot nH_2O$ following Morgado analysis [10, 11, 14]. Once again, although the tri-titanate phases fit better than Ti_2O_5 phase, they fail to represent faithfully the XRPDs.

Continuing with the efforts of determining the main structural building blocks, we include an extra phase $Na_xH_{2-x}Ti_6O_{13}$. This phase, which was already suggested in the literature after studying the transformation of samples at high-temperature [15–17], was attributed to the transformation of the $Na_xH_{2-x}Ti_3O_7$ phase when all the structural water and *H* content evaporates.

In this work, we present First Principles based simulations carried out on $Na_xH_{2-x}Ti_3O_7$ and $Na_xH_{2-x}Ti_6O_{13}$ with x = 0, 1 and 2 for each phase. With the results of the simulations, the slab XRPD patterns and the bulk off-resonance Raman spectra are evaluated and compared with the experimental ones. The electronic properties are also studied from the density of the electronic states of the systems, from which the bandgap was estimated with two functional. Moreover, the optical absorbance was calculated and compared with experimental measurements.

Materials and methods

Computational method

The ab initio calculations based on density functional theory (DFT) [18, 19] were applied using the Vienna ab initio simulation package (VASP) [20]. This methodology utilizes plane waves as a basis set, with pseudopotentials, incorporating the projector augmented wave method [21]. The selected exchange-correlation functional corresponds to GGA in the Perdew-Burke-Ernzerohf (PBE) [22, 23] parametrization. The basis set was expanded up to an energy cut-off of 400 eV, and the Monkhorst-Pack grid was adjusted to a $4 \times 4 \times 2$. The initial structures were obtained from early reported sodium-based titanates of the following stoichiometry: $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$. In order to obtain the corresponding hydrogen-based titanates, we substituted the Na atoms with H atoms: $Na_xH_{2-x}Ti_3O_7$ and $Na_xH_{2-x}Ti_6O_{13}$ for x = 0, 1and 2. These initial structures, including unit cell parameters and atom positions, were fully relaxed with a force tolerance of 0.01 eV/Å and a stress tensor component lower than 1 kBar. Due to the limitations of conventional xc-functionals in DFT, after the full relaxation, we applied the HSE06 screened hybrid functional [24] to get a better description of energy bandgaps. In order to confirm the local stability of the obtained structural geometries, we proceed with the analysis of the phonon spectra utilizing density function perturbation theory (DFPT) [25-28] as implemented in the VASP code. Finally, we simulate the off-resonance Raman spectra of the studied titanates, applying the methodology reported

by Porezag et. al. [29], as implemented in the *vasp_raman*. *py* script (https://github.com/raman-sc/VASP/).

Sample preparation and structural characterization

Nanostructured titanates were synthesized by hydrothermal method under different temperatures, time and pH conditions as reported in [13, 14]. An exhaustive study of its structural, vibrational, and electronic properties has been also published in the previous references. In search of new possible phases that form the obtained nanostructures, an annealing process was performed in a selection of samples in vacuum at 800 °C, after which X-ray scans were performed with a PANanlytical X'Pert MPD X-ray diffractometer. The system was operated with Cu radiation at 40 kV and 40 mA, with a solid-state X-ray detector (PIXcel 1D). The measurements were done at room temperature, mounting a graded parabolic parallel beam X-Ray mirror for Cu-radiation in the incident path and parallel plate collimator in the diffracted path. The measurement range was from 5.00° to 80.00°, with a step size of 0.013° and a counting time of 4.4 s (detector in receiving slit mode).

The conditions for the X-ray diffraction measurement of the samples in the nanostructured state (prior to the annealing process), the Raman spectroscopy spectra and the absorbance coefficient were explained in [13, 14]. When comparing numerical results with experiments, the more relevant hydrothermal conditions are displayed, the rest can be found in the preceding references.

Results

Models: Na_xH_{2-x}T i₃O₇ and Na_xH_{2-x}T i₆O₁₃, x = 0,1 and 2

As mentioned in the "Sample preparation and structural characterization" section, a selection of the previously reported samples underwent an annealing process. The XRPDs after the annealing process are presented in Fig. 1a. The final phases were identified with sodium tri-titanates $Na_2Ti_3O_7$ and hexa-titanates $Na_2Ti_6O_{13}$, in different proportions depending on the synthesis condition. In the literature, the hexa-titanate phase usually appears as a derivative of the dehydrated tri-titanate phase [15–17]. However, there is no evidence to rule out the possibility that the hexa-titanate phase is prior to the annealing process. For this reason, six possible starting structures are simulated, taking $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ as the starting structures, and replacing Na with H, partially and totally. The models used are shown in Fig. 1b.

Fig. 1 a Standard $\theta - 2\theta$ XRPD scans for NaTNT samples after the annealing process at 800 °C; b Structural models for possible starting phases

Fig. 2 XRPD spectra for four samples (with the hydrothermal conditions in the figure), and simulated XRPD diffraction for the six building block considering a slab enrolled with a periodicity of 6a radial, 50b axial and 8c tangential

Structural properties: XRPD and Raman

Figure 2 shows the diffraction patterns for a selection of four samples manufactured by the hydrothermal method [14]

compared with the XRPD obtained for the six models considered. It is observed that the correspondence is not univocal, but this is to be expected since the simulated patterns correspond to slab enrolled with a certain periodicity, and the mixture of them was not evaluated. However, we found great similarities between the patterns. For example, the peaks at $2\theta \sim 9.5^{\circ}$ and $2\theta \sim 48 - 50^{\circ}$ appear in all cases. The position of the first one is associated to the distance between sheets and its width is related to the wall of the nanotube. The difference in positions can be explained with the lack of structural water in the theoretical models. This water would be located between sheets, increasing the radial lattice parameter, and thereby decreasing the position of the diffraction peak. This was confirmed by measuring the diffraction pattern under vacuum, where the elimination of water generates an appreciable shift of the mentioned peak (see Fig 4. in Supplementary Material). The peak at $2\theta \sim 48 - 50^{\circ}$ is obtained in the correct position. The presence of the both phases (tri and hexa) is necessary to explain the peaks doublets in the region between $2\theta \sim 23 - 30^\circ$, since a mixture of only H and Na in the same phase would not be enough to explain its separation.

Experimental and simulated Raman spectra are shown in Fig. 3, for the same samples and simulated structures. Again, similarities are observed between the simulated and experimental Raman bands, where the five most intense and relevant bands were identified. However, due to the

Fig. 3 Raman spectra for four selected samples (with the Hydrothermal conditions in the figure), simulated Raman spectra for the four building block considered in bulk

bulk character of the structure used to simulate the Raman spectra, peaks may change in wide and central peak positions. But taking those effects, and the tendency of DFT in underestimating the simulated frequencies, we can conclude that there is a reasonable agreement. Additionally, and in reference to the correct band's assignment when there is the presence of Na atoms, we can generally establish that regions between wave-number k = 0 to 350 cm^{-1} correspond to Na-Ti-O vibrations, then the regions between 350 and 1000 cm⁻¹ correspond to Ti–O vibrations and finally when there is hydrogen atoms present almost free O-H vibrations occur in the region of 3000 cm⁻¹. In the case of samples with Na atoms content, the strong signal locate between 800 and $1000 \,\mathrm{cm}^{-1}$, comes from the electronic polarizability effects of it cation in the Ti and O atoms close to the inter-lamella or channel cavities for tri- and hexa-titanates structures. When comparing with the experimental measurements, to explain the double peaks in the region $600-800 \,\mathrm{cm}^{-1}$, it again seems necessary to consider both types of phases.

Both structural characterizations were in support of a mixture of phases in the nanostructured samples.

Electronic properties

Electronic structure properties were calculated using conventional xc-functional GGA-PBE and with the HSE06 screened hybrid functional, in order to compare electronic structure results. The electronic density of states looks as expected, showing a semiconductor behavior with a clear separation of the valence—and conduction band with an energy gap around 3 eV. The valence band (BV) is mainly dominated by O-2p states, while Ti-3d states mainly contribute to the conduction band (CB). The contributions from H and Na states are totally negligible in the region of the Fermi levels, as expected. But their presence introduces changes in the total charge of Ti atoms, which establishes slight changes in the band positions and DOS changes, thus modifying the VB and CB indirectly. The DOS curves and bandsgaps values obtained from them are summarized in the Supplementary Material.

Tri-titanates present higher bandgaps in comparison to hexa-titanates, and an increase in bandgaps is observe when going from x = 0 to 2 for both phases. This trend, that was observed priory in the bibliography [11], it is further confirmed by DFT calculations. Here it is important to mention that besides the fact that GGA-PBE underestimates the bandgaps, the correct trend is recovered with this analysis. In order to improve the determination of this electronic structure–property, hybrid HSE06 was also applied, obtaining an overestimation of the bandgap values between 4.3 and 4.8 eV, with the same trends obtained for PBE-GGA. Furthermore, if we consider the hexa-titanate as the hightemperature structure of the tri-titanate, then the expected reduction of the bandgap is also recovered.

Figure 4 shows the calculated optical absorbance for the six structures, and two examples of experimentally measured absorbance. The shapes of optical absorbance spectra for both systems present similarities. It can be highlighted that experimental samples exhibit multiple bandgap edges in absorbance curves. The staggered form also appears in the calculated absorbance. This supports the presence of these phases.

Therefore, the main conclusion here is that conventional HSE06, in terms of relative weights of exchange and correlations, did not properly describe the energy bandgaps of tri and hexa-titanates. It requires further correction, but the single analysis made by GGA-PBE is sufficient to recover the trends and shapes of the optical absorbance properties.

Conclusion

We performed ab initio calculations in order to understand the inner structure of the titanate-based nanotubes, which will help to predict their structural, vibrational, and electronic structure properties. The potential crystalline structure models of hexa ($Na_xH_{2-x}Ti_6O_{13}$) and tri ($Na_xH_{2-x}Ti_3O_7$) titanates, including hydrogen and sodium, suggested by experimental results, demonstrated to be reasonable for the expected description. The calculated XRPD, Raman spectra and optical properties present good correspondence with the experimental data. To explain the peaks doublet that appears in the diffraction patterns for 2θ between 20 and 30°, it is

Fig. 4 Simulated absorbance for the structures based on a tri-titanates, b hexa-titanates, and c experimental measurements of absorbance for two synthesis conditions. The insets in the figure show the bandgaps values estimated by DOS and experimentally obtained

necessary to consider both (tri- and hexa- titanate) phases. On the other hand, the level of mixture between H and Na will help to better predict or explain the position of each contributing peaks. Furthermore, when the sample is synthesized at a higher temperature it appears to have a greater contribution from the hexa-titanate phase. Similarly, there are doublets in the case of Raman spectra that cannot be explained if we do not consider both phases, for example in the bands around the $600-800 \,\mathrm{cm}^{-1}$ region. This suggests the possible coexistence of these two phases prior to the high temperature annealing process. The bandgap calculations with the PBE functional underestimate the gap but allow to justify variations in the range of 2 to 3.3 eV, as observed in this type of structures. In summary, joint experimental and simulation procedures can give relevant responses to complex systems based on nanostructured systems. Next step would be to refine further the contribution of the different phases.

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Code availability Not applicable

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article. The authors have no financial or proprietary interests in any material discussed in this article.

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Chapter 6

Temperature cycling effect on structural, optical and electrical properties of nanostructured sodium titanates.

In the preceding chapters, significant effort has been dedicated to comprehending the internal structures and fundamental physical properties of nanostructured titanates, promoting the understanding of these materials. Building on this foundation, this chapter delves into the material's behavior under temperature cycling, studying the effect of temperature on the structural and electronic response before and after a temperature cycle. The cycle is performed between 240 and 325 K, choosing for the reason stated in Chapter 4, this range includes a possible ranges of operation when this material is tested in real energy storage devices. This study was further prompted by the disparities observed in the impedance measurements during the cooling and heating part of the curve (Z(T)).

To comprehensively address this, our approach encompassed the utilization of Z(T) technique with other characterization techniques. This involved tracking the variation of Z as a function of time when subjecting the samples to ambient humidity. Additionally, we conducted XRPD, Raman spectroscopy and optical measurements, both prior to and post-cycling, while also incorporating XRPD assessments across a temperature range from $30^{\circ}C$ to $180^{\circ}C$. Thermogravimetric methodologies were also employed. The thermogravimetric techniques are geared towards investigating phase transitions or dehydration within a defined temperature range. In our

specific context, these methods were employed to ascertain dehydration processes and quantifying the percentage of water loss. Thermogravimetric measurements were made at Centro Universitario de la Región Este - CURE, UdelaR, Uruguay.

This work not only leverages the knowledge acquired from previous research but also presents a novel perspective on the material potential applications in energy storage devices. By exploring its behavior under temperature changes, we aim to contribute for practical implementations and help unlocking the material's full potential in energy storage technologies.
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Temperature cycling effect on structural, optical and electrical properties of nanostructured sodium titanates



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ABSTRACT

Sodium titanates represent a promising alternative for the construction of anodes for sodium-ion batteries. To study the electrical response of nanostructured sodium titanate samples under plausible temperature conditions, we evaluate the electrical impedance in the range of temperatures from -30 °C to 50 °C, and the effect of consecutive temperature cycling. Strong changes in electrical properties are observed during the first temperature cycle, followed by a stabilization in the consecutive cycles. This behavior is reversible when the sample is exposed to external conditions and room temperature for less than an hour. Probably a structural and surface water removal and a surface water reabsorption occur, affecting the charge carriers and with it the impedance. Structurally, no differences are detected before and after the cycles, nor when evaluating only the vacuum process. However, when the optical properties are evaluated we find non-reversible changes after the temperature cycles. The optical behavior after the temperature cycling becomes uniform, the same type of electronic defects become predominant and similar direct and indirect band gap values are obtained, regardless of the starting synthesis condition. These results have significant implications for potential technological applications of these materials.

1. Introduction

Recently, nanostructured sodium titanates (NaTNT) have gained more interest for the manufacture of anodes in batteries based on Na ion [1–7]. However, the structure and the formations mechanisms of these compounds are still under debate, promoting the study of their physical properties for a deeper comprehension of the material. Various structures and forms of nanostructures titanates (3D nanoarrays, nanowires, hollow spheres, nanobelts, 3D microflowers 3D flower like nanotube among others [8]) have been designed, where the manufacturing method is usually based on a wet-chemistry process. In particular, the hydrothermal method [9] has been widely used for the synthesis of tubular nanostructures, which involve low temperature reactions in water medium. This process will inevitably introduce adsorbed water or structural water into these type of sodium titanate compounds [8]. Water in electrode materials can cause several problems like serious gassing behavior, swelling issues during charge-discharge cycling, instability against moisture and sensitivity to water molecules. These problems increase the cost of transportation and storage, and reduce the stability on the battery performance [10,11]. Moreover, both the larger ion Na⁺ and its smaller polarization produce that these materials present a more severe water sensitivity. In addition, a greater

difficulty arises in the case of nanostructures regarding water absorption due to the high surface area. Therefore, the effect of absorbed water and structural water should be further studied, in order to control the mentioned problems. There are studies of the effect of water by increasing the temperature up to 700–800 °C [8,9,12,13], but we found no studies, to the best of our knowledge, that analyze the effect of a probable operating temperature cycle in the absorbed water and with it how electronic behavior changes.

On the other hand, this type of materials present a global (re)adsorption of atmospheric water that could lead to some applications such as humidity sensing. However, at the same time, this surface-absorbed water changes the electrical properties, making it difficult to understand the charge carrier nature [7,14,15]. Therefore, the investigation on the influence of the presence of structural and surface water in the optical and electrical properties of NaTNT is of interest for a wide range of applications of these materials.

In a previous work [16] the influence of pH during hydrothermal synthesis for two temperatures synthesis was analyzed, and the first measurement of impedance as a function of temperature was presented. In this work we delve into the study of the influence of temperature cycling on the structural, optical and electrical properties. For this, we

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Table 1

Hydrothermal synthesis parameters with a volume of washing water of 400 ml per sample, and the (H^+) phase percent.

	S1: 125 °C	2, 96 h,	S2: 105 °C, 96 h,		
	150 rev/m	in	150 rev/min		
[<i>NaOH</i>]	10 M	11 M	9 M	10 M	
Phase (<i>H</i> ⁺) (%)	51 (9)	41 (7)	38 (6)	34 (5)	

study the electrical impedance during consecutive cycles in a temperature range between 240 K and 325 K. We analyze the changes in the structural and optical properties after the thermal cycle. To discern between the effects of temperature and vacuum (due to the setup of the measurement), the structural properties were also studied after keeping the sample under vacuum for certain time.

2. Methods and materials

2.1. Samples NaTNT preparation

The samples were synthesized using a modification of the hydrothermal method developed by Kasuga [17]. Hydrothermal growth, under magnetic stirring rate of 150 rev/min, is performed with commercial TiO₂ anatase nanopowder as a precursor supplied by Sigma-Aldrich (ID: 799289, External ID: 232033_ALDRICH) with a synthesis time (t_s) of 96 h. Two reactor temperatures (T_s) were used: 105 °C and 125 °C. A volume of 75 mL of NaOH (fill factor of 75%) with two different NaOH molar concentrations in the range of 9–11 molL⁻¹ was used to dissolve the precursor in a Teflon-lined autoclave. To complete the synthesis the samples are washed in sufficient volume of distilled water for two days. Finally, the sample is centrifuged to separate the solid from the washing water. The solid was then dried for 24 h at 80 °C resulting in NaTNT confirmed by morphological and structural techniques. The samples were named as Series 1 S1: 125 °C, 96 h, 150 rev/min.

The phase of the nanostructures was attributed to $Na_{2-x}H_xTi_3O_7.n$ H₂0. From the X-ray diffraction patterns the relative proportion between both phases was estimated. In the four selected samples the percentage of H⁺ phase varies in the range of 30% to 50% [16]. The nomenclature of the samples and the percentage content of phase H⁺ can be seen in Table 1.

2.2. Characterization techniques

The impedance measurements as a function of temperature were carried out as explained in Ref. [16]. It consists on measuring at two points with a Tektronix AFG3021B as a signal generator with 10 Hz and 500 mV, and two Lock In Amplifiers SR 560 for the voltage and current registration. The measurement was done inside a closed cycle cryostat (CRYODINE), where prior to the temperature variation a vacuum was made from atmospheric pressure to 1×10^{-4} mbar with a HiCube pump. Two rates of temperature variation were used (1.5 K/min and 0.7 K/min), regulated by a LAKESHORE 321 temperature controller. All measurements were made between 240 K and 325 K.

To study the structure before and after the cycle, powder diffractograms were made with Rigaku Miniflex 600-C X-ray diffractometer operating in a θ -2 θ Bragg–Brentano geometry. The latter uses a X-ray generator for Cu K α radiation, $\lambda = 1.5419$ Å, operating at 40 kV, 15 mA and utilizing a D/tex Ultra2 1D detector. The measurements were carried out in a scan mode over a 2 θ range from 3° to 90° with a step size of $2\Delta\theta = 0.02°$ with a velocity of 10°/min. All the diffractograms were made in a pressed pellet to be compared before and after the temperature cycle. For two of the samples, diffraction measurements were made at four temperatures 30, 80, 120 and 180 °C, to study the effect of the evaporation of structural or surface water. Measurements were performed in a 2θ range between 5 and 55°, with a stepsize of 0.013°, and counting time of 150 s, under vacuum conditions in a PANanlytical X'Pert MPD X-ray diffractometer, equipped with an Anton Paar HTK1200 high temperature chamber. The system was operated with Cu radiation at 40 kV and 40 mA, with a solid-state X-ray detector (PIXcel 1D, scanning mode). Temperature XRD were performed in the Chair of Functional Materials Department of Material Science, Saarland University, Germany. Raman spectroscopy images were taken using a WITec Alpha 300-RA confocal Raman spectrometer on a pressed S1:11M sample before and after temperature cycling. A $\lambda = 532$ nm excitation laser was used to collect a 75 × 75 Raman Image that was then averaged to obtain a representative Raman spectra.

Absorbance and photoluminescence (PL) measurements in the UV– Visible spectrum, before and after the temperature cycling, were performed at room temperature as an optical characterization. The details of the measurement were described elsewhere [16,18]. These measurements were also carried out on pressed pellets.

Finally, thermogravimetric analysis (TGA) was carried out under air from 25 to 600 $^{\circ}$ C with a heating rate of 5 $^{\circ}$ C/min using a Netzsch simultaneous thermal analysis (STA) 449F5 equipment.

3. Results and discussion

3.1. Electrical characterization

Previously in [16] the temperature dependence impedance (Z(T)), to evaluate the material performance over $-30\ ^\circ\mathrm{C}$ and 50 $^\circ\mathrm{C}$ range for two frequencies (10 Hz and 20 kHz), was studied. In the case of 20 kHz an almost constant behavior with temperature was observed. For 10 Hz, we find that the changes in impedance was less than 25%, and for the S2 series, a peak in the impedance phase was observed around 250 K-270 K. A possible second peak for temperature higher than 325 K was suggested. Increasing the frequency reduces the capacitive effect and increases the conductance of the sample. Furthermore, the effect of temperature in the impedance of the samples is smaller, and is further reduced when the frequency increases. The selection of 10 Hz frequency for the study of temperature cycles is based on the previous comments. On one hand, low frequency allows us to study phenomena more similar to a DC current, and the association with space charge polarizations, which occurs in insulating materials at grain boundaries. On the other hand, we have seen that larger frequencies tend to reduce the change with temperature, obtaining approximately constant responses in the selected temperature range. However, it should be noted that this choice only affects the electrical conduction results shown in this work, and not the optical and structural results, since the latter are supposed to only depend on the temperature cycles and the vacuum to which the samples are subjected.

It is important to remember that the absolute values of Z depends on the contact geometry. It can be notices that the curves during descending and increasing temperature were different, indicating some kind of hysteresis behavior. Both, the peak in the imaginary part and the presence of a hysteresis in a temperature scan can be related to the presence of absorbed surface water [14]. Furthermore, after undergoing a temperature cycle under vacuum, the electric response of the samples do not return to the same point.

To further study the influence of consecutive temperature cycles and the effect of vacuum, impedance measurements were made as a function of temperature in two consecutive cycles to study the change in electric behavior. This study was accompanied by structural and optical measurements of PL and absorbance, before and after the temperature cycles, shown in the next sections. Fig. 1 shows the Z(T)results for S1: 10M and 11M, and Fig. 2 for S2 for 9M and 10M, with a 1.5 K/min temperature rate. As can be seen, the results of the first cycle are quite different from the second cycle. The biggest change is observed between the first heating and the second cooling process. The impedance of the sample increases in the second cycle, but the phase of the sample remains approximately similar in almost all the samples.



Fig. 1. Temperature dependence during two consecutive cycles at 10 Hz of (a) impedance modulus and (b) phase for S1:10M and (c) impedance modulus and (d) phase for S1:11M.



Fig. 2. Temperature dependence during two consecutive cycles at 10 Hz of (a) impedance modulus and (b) phase for S2:9M and (c) impedance modulus and (d) phase for S2:10M.

If cycles continue, the results do not change appreciably, as shown in Fig. 3 for the case of S2:9M.

One possible explanation is that the vacuum experienced by the sample inside the cryostat and or the thermal cycle can alter the surface water content of the nanotubes, causing differences in the charge carriers available for conduction, thus changing the electrical behavior. It is known that the adsorption of atmospheric water on the surfaces of functional ceramics promotes proton/hydroxide conduction and generates additional charge carriers [7,14,15]. Therefore cooling down a sample in a vacuum atmosphere could minimize the content of surface water, or the freezing on structural interlaminar water, reducing the additional charge carrier, and thus increasing the impedance of the sample. This occur during the first temperature cycle, therefore the following cycles show less changes, because surface water has been already removed. However, structural water can still cause minor

hysteresis in the measurements, for example the observed peak in the impedance phase for S1:10M in Fig. 3 (b).

To evaluate the influence of the vacuum process in the cryogenic system, the impedance of the samples was measured as a function of time during the cryostat vacuum process, display in Fig. 4. It is important to remember that the absolute value of the impedance depends on the geometry that changes between measurements. In each measurement a new sample must be used, which has not yet undergone a thermal process. Therefore the absolute values are not the same in Fig. 4 as in Figs. 1 to 3. It is observed that in most cases the impedance modulus increases during the vacuum and also the capacitive behavior increases, supporting the idea of some carriers removal. However, this does not seem to be the only effect that changes the impedance, since the largest changes are observed between the first heating and the second cooling of the system.



Fig. 3. Temperature dependence during three consecutive cycles at 10 Hz of (a) impedance modulus and (b) phase for S2:9M and (c) impedance modulus and (d) phase for S1:10M.



Fig. 4. Time dependence of impedance modulus and phase at 10 Hz for all the samples during the vacuum process.

As was briefly mentioned before, evidence of the contribution of surface adsorbed water is observed in thermal history activation energy [19], anomalies in the imaginary part of the complex impedance [20–22] and loop hysteresis during temperature scan [23,24]. These samples show a history dependence behavior, peaks in the imaginary impedance and loop hysteresis, supporting the previous idea.

In the case of the S1:10M sample, there is one hysteresis loop in the region measured, that prevalence in the second and third cycle (Fig. 3). The electrical properties upon cooling down are smaller than their heating counterparts. This effect might be explained by the (re)adsorption of atmospheric water or an incomplete freezing of the superficial water. In our samples, it would probably be the second option since the system remains in vacuum throughout the measurement. It is assumed that water sorption leads to a conducting hydrolyzed surface layer on each grain of the titanate [14], forming macroscopic dipoles which interact strongly with each other. For the S2:9M case, the curve in cycles 2 and 3 tend to be very similar.

3.2. Structural characterization

X-ray diffraction (XRD) patterns for all samples before temperature cycling are shown in the left of Fig. 5, and after temperature cycle at the right. An attempt was made to discern between the effect of temperature and the effect of vacuum inside the cryostat. Therefore, the sample S2:9M was subjected to a vacuum treatment without a temperature cycling and a vacuum treatment plus temperature cycling.

The three diffractograms are observed in Fig. 6. The shape of all the diffractograms is very similar to those reported for this type of compound [25–28]. In particular, the structural model assigned to these samples was already discussed in a previous work [16]: refers to a mixture of sodium and hydrogen tri-titanates with a certain amount of structural water ($Na_{2-x}H_xTi_3O_7 \cdot nH_2O$).

In this work, we will focus on the changes produced by the effect of vacuum and temperature in the X-ray pattern. At first glance, there are no differences between the patterns. Rietveld refinement attempts were unsatisfactory because the fit could not be stabilized due to the width of the peaks, probably associated with strong confinement and high aspect ratio effects. The first peak, reflection (200), corresponds to half the distance between sheets in the coil, and its width is related to the crystalline domain size associated with the size of the tube wall. This will be the peak most influenced by the presence of structural water. Therefore, the (200) peak was studied with a Lorentzian function fitting, observing that in general there is a very small reduction in the interplanar distance, possibly indicating the beginning of structural water evaporation. This will be more supported when analyzing diffraction measurements with temperature in the next section. On the other hand, it is observed that for the first reflection, the crystalline domain size decreases, or rather becomes uniform among the samples after the temperature cycle, reducing from values in the 4-8 nm range to 5 nm. In addition there is no appreciable change in the first peak evaluating only vacuum. Furthermore, small changes can be detected in the 2θ region between 20° and $40^\circ,$ these cannot be quantified for a more



Fig. 5. X-ray scans for NaTNT pellets before undergoing a temperature cycling (left) and after a temperature cycling (right). The dotted lines indicate the peak indexation.



Fig. 6. X-ray scans for S2:9M before undergoing a temperature cycling (bottom), after a vacuum (middle) and after a temperature cycling (top). The dotted lines indicate the peak indexation. After temperature cycling it appears to be some carbonates present in the sample (narrow peak around 18°).

qualitative analysis. Concluding that between the measures presented there is no appreciable change after cycling.

To provide more evidence that the temperature cycle does not produce an appreciable change in the structure, Fig. 7 presents Raman measurements before and after the temperature cycling. The Raman pattern presents all the Raman Bands expected and explained for this compound [16]. In a principal component analysis (PCA), the first component includes up to 95% of the whole variance, the other components with values down to 1%. The difference between component #1 and #2 is presented in Fig. 7(a), in which very small differences can be observed. These differences could be majorly attributed to intensity changes probably produced by variations in the confocal plane, but showing the same Raman spectrum. Due to this analysis, we can argue that same structure, confirmed by Raman spectroscopy, can be observed before and after cycling.

Summarizing, the structure of the compound does not change, which would be in accordance with the loss of surface water and not structural water or a small structural water loss that is almost undetectable. Furthermore, this may simply indicate that the samples, when subjected to ambient humidity again, re hydrate and return to their initial behavior. To test this hypothesis, the impedance was measured for two consecutive cycles, recovering the behavior of Fig. 2, but with a slower rate of 0.7 K/min. After the second cycle, the sample was left at room temperature for a certain time exposed to ambient humidity. During that time, it is observed that the impedance of the sample drops, returning to the initial value. This can be seen in Fig. 8 for S1:10M, and it is summarized in Fig. 9 for all the samples. In the impedance module we observe an inverse effect to the vacuum process: the impedance of the sample decreases as it reabsorbs the water, generating new carriers. It is observed that the characteristic rehydration time is quite different between samples, for example the

sample S2:10M rehydrates much faster than the rest of the samples, however during the experimental vacuum process it behavior is similar to the others samples (Fig. 4).

We conclude that there is a component of water or surface moisture in the sample that modifies its electrical impedance when it is removed from the sample. However, an exposure of approximately one hour (or less) outside the vacuum or when returning to room temperature, returns to the initial state of humidity. The characteristic time can change between samples. In general, ambient humidity is controlled around 50%; the change in the water reabsorption rate can also be influenced by changes in relative humidity depending on the day of measurement. For these, structural changes will not be able to be detected.

3.3. Evolution with temperature: XRD and TGA

X-ray scan for different temperatures were performed for S1 samples, the samples were brought up to 180 °C at a rate of 10 K/min with 30 min stabilization on each temperature. The selected temperatures were 30 °C, 80 °C, 120 °C, and 180 °C as shown in Fig. 10 for 10M and 11M. The optics of the diffractometer used in this case does not allow the detection of contributions at large angles, so we will focus on the first range of the scan. We observe again the (200) reflection, which gives us information on the distance between the nanotube sheets and the nanotube wall size. In both samples it is observed that the distance between layers decreases (increasing the diffraction angle) with the increase in temperature, in accordance with some removal of structural water between the layers, further supporting the comments in Section 3.2. The crystalline coherence also experienced a slight increase. In general, it is reported that surface water evaporates or disappears up to 200 °C, and structural water above 500 °C. Finally, around



Fig. 7. (a) Principal component analysis, showing component #1 and #2 in 2D diagram, corresponding to 95.5% and 0.5% of the percentage of confidence before and after the temperature cycling for S1:11M. Average Raman spectra (b) before and (c) after a temperature cycling for the same sample.



Fig. 8. Temperature dependence of impedance modulus and phase at 10 Hz for S2:10M (top), during two consecutive cycles. Variation of impedance with time after the sample is left exposed to ambient humidity (bottom).



Fig. 9. Time dependence of impedance modulus and phase at 10 Hz for all the samples during the hydration process.

800 °C, all the water is lost (complete dehydration) and the system transforms to a hexa-titanate phase ($Na_2Ti_6O_{13}$) [8]. However, a small amount of structural water may begin to evaporate below 180 °C. In addition, the simplest structural water to remove is the water between the sheets, explaining the reduction in the inter-laminar distance. On the other hand, the removal of these excesses of water could increase the crystallinity, since more nanotubes would be similar to each other. Furthermore, the presence of sodium atoms in the structure changes the behavior after a post thermal treatment, for example, more sodium

content in TNT delays certain phase changes in temperature [25,29]. This explains why there are variations in the behaviors between the samples.

Fig. 11 shows DSC and TGA measurements for both sets. Below 200 °C two weight losses are observed by TGA corresponding to two endothermic peaks on DSC (around 90 °C and 130 °C), both connected to an important weight loss (about 14% for three of the samples, and 7% for S2:10M). Although sometimes these two peaks are mixed and seems to be a single contribution, in the case of S2:9M the two



Fig. 10. X-ray scans for pellets \$1:10M and \$1:11M for different temperatures (left), interplanar distance and coherent length corresponding to the [200] reflection (right).



Fig. 11. (a) DSC, (b) mass loss curves and (c) mass loss in the first stage vs H⁺ phase content for S1 and S2 sets.

contributions can be clearly distinguished since their relative intensity is different. The phenomenon is also observed for S1:11M. This is attributed to the evaporation of water and organic reaction residues. If we analyze the dependence between mass loss and H⁺ content, the mass loss is considerable minor for a lower H⁺ phase percentage, this suggests that the H⁺ (or Na⁺) content affects the amount of surface water that is available for evaporation. In general, for temperatures greater than 200 °C, a lower mass loss is still observed (in the order of 4%), associated with exothermic peaks. This may correspond to the formation of other phases and elimination of structural water, in accordance with the X-ray diffraction reports.

DSC, TGA and XRD measurements suggests that samples experience a first order phase transition (dehydration) around 90 $^{\circ}$ C and 130 $^{\circ}$ C, impacting this, at least partially, in the structural properties of the samples. In addition, there could be some changes in the surface structure that can be confused in DSC results, and might not be appreciable in TGA and XRD pattern.

3.4. Optical characterization

The absorption coefficient α was calculated from the direct transmittance as in previous works [16,18]. In Fig. 12 the α measurement before and after the temperature cycling are presented. There, it is shown an example of the band gaps estimations for S1:10M sample. As it was already explained in previous works for this types of samples it is necessary to consider two different type of band gap edges to explain the overall behavior [16,18]. Band gap energies, obtained from Tauc plots considering direct and indirect models, are listed in Table 2. Experimental data and the corresponding model are hold for S1:10M in Fig. 12(b) y (d).

Direct bandgap energy shows a blue shift in all the samples when they are exposed to thermal cycling. Despite the samples exhibit photoactivity under visible light before temperature cycling, all of them change their activity to UV–Vis wavelength after the cycle. The reduction of the energy difference between the direct and indirect gap after cycling is also appreciable. As it was shown in [30] for sodium titanates nanostructures, the presence of oxygen vacancies affect their optical absorption properties. In particular, they observe that in flower like-sodium titanates with a high concentration of superficial oxygen vacancies, they can tune the band gap absorption edge by changing the amount of oxygen defects. In fact, the oxygen vacancies promote the formation of a middle-band inside the forbidden band gap of the sodium titanates [30,31]. Diminishing the concentration of oxygen vacancies promotes a higher band gap energy. In [32,33], the authors studied the dehydration effect in optical properties finding less pronounced but similar results in some optical properties.

Assuming that the crystalline domain size establishes a second level confinement (compared to the particle size), it can be expected that the smaller the domain, the higher the gap energy [34]. Despite the fact that there are no appreciable structural changes, a reduction in the size of the crystalline domain is observed in the direction of the tube wall after the cycling. This size becomes very similar in all samples (around 5 nm), being able to explain to some extent an increase in the band gap values and a uniformity between samples.

Photoluminescence measurements (PL) at room temperature before and after the temperature cycling and the area evolution of each peak with the thermal process can be observed in Fig. 13. Considering that the PL spectra is composed by four emission process, the PL data is fitted as the sum of four Gaussian curves. From Fig. 13 it is clear that PL spectra show a red shift in the peaks position when the sample is thermally treated. This fact is in accordance with the observation made in [32,33]. It is also observed that the cycling changes the relative intensity between peaks suggesting a change in the predominant mechanisms that result in PL signal. Additionally, most of the spectra are narrower after the temperature treatment. These changes L. Amy et al.



Fig. 12. Absorption coefficient superimposed for all the samples (a) before, and (c) after the temperature cycling. Absorption coefficient with direct and indirect band gap fitting (b) before and (d) after cycling for S1:10M.



Fig. 13. Photoluminescence (PL) signal for all the samples (a) before temperature cycling and (c) after; and PL peak area as a function of H⁺ phase percentage before and after the cycling for different electronic contributions in (b) and (d).

Table 2				
Direct and Indirect	Band Gap energies	before and after	the temperature cycl	ing.

S1					S2				
Sample Before		ore After			Sample	Before		After	
	Direct	Indirect	Direct	Indirect		Direct	Indirect	Direct	Indirect
10 M	2.18 (5)	3.24 (6)	3.61 (8)	3.9 (5)	9 M	2.54 (5)	3.09 (6)	3.62 (7)	3.9 (3)
11 M	2.28 (4)	3.11 (8)	3.56 (8)	3.9 (2)	10 M	2.15 (1)	3.10 (10)	3.03 (8)	3.9 (3)

are also observed in the area under the peak of each considered process (Fig. 13). Comparing Fig. 12(b) and (d), the area under the corresponding 2.2 and 2.5 eV emission peaks remains relatively similar, with both contributions maximum around 35%–40% of the H⁺ phase. Contributions close to 2.8 eV and 3.0 eV decrease after the cycle, this has repercussions in a narrow spectra as mentioned.

According to [18,31] the 2.6–3.2 eV region is associated with oxygen vacancies defects, the 2.4 eV is related to the octahedron TiO_6 and the 2.1 eV corresponds to the OH defect signal. Taking this assignment into account, after a temperature vacuum cycling the oxygen vacancies defects are reduced (observed in a high band gap energy and in a reduction of the intensity in the energy region 2.7–3.2 eV of the PL emissions).

Changes in the amount of surface water could alter the sodium mobility at the superficial level, generating porosity and defect states on the surface, thus modifying the optical band gap and the PL signal [35]. Therefore, when the surface water is removed by a vacuum or evaporation process, it could reduce this type of defect states and make the PL signal uniform.

4. Conclusions

In this work, the effect of temperature on electrical, structural and optical properties was evaluated. This effect was studied by measuring the electrical impedance in several consecutive temperature cycles between 240 K and 325 K and analyzing the structural and optical behavior before and after the mentioned cycles.

The cycles in the temperature range studied do not seem to modify the structure. However, they present appreciable changes in their optical properties, standardizing the behavior of the samples regardless of the starting synthesis, at least in the range studied. All the samples present a blue shift in the absorbance and a red shift in the PL spectra, losing the photoactivity under visible light after a temperature cycling. Furthermore, the oxygen vacancies defects are reduced (observed in a high band gap energy and a reduction in PL emissions in the 2.7– 3.2 eV region). Modification in the surface water content produced by a vacuum or evaporation procedure could change the type of defect states on the surface, and within the effective gap and the PL signal. The reduced and similar crystal size values between the samples after cycling, may be related to the increase and standardization in energy band gap values.

During the first temperature cycle there are drastic changes in the charge carriers, increasing the impedance modulus and making the curve during ascending and descending temperature very different. We believe that the decrease in these charge carriers is associated with the evaporation of surface water and the freezing of structural water at temperatures below 0 °C, and can be related to the reduction of oxygen defects. In consecutive cycles the behavior stabilizes and the observed differences correspond to thermal hysteresis or due to freezing processes. However, we have observed that once the samples are exposed to the environment, the re-absorption of water occurs in very short times (less than a hour), returning to the original electrical behavior. For this reason, these effects are not observed in the structural properties, but their mark remains in the optical properties. Finally, we confirm that these samples lose a significant amount of surface water in the 90 °C and 130 °C region, as shown by TGA measurements and changes in structural properties like the decrease in the distance between sheets and the increase in nanotube wall size.

In summary, we have shown that nanostructured titanates present important changes in their optical and electrical response, particularly in humidity and temperature dependent conditions. This information could be highly relevant to its potential use in technological applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Chapter 7

Concluding Remarks

This thesis represents a challenging and comprehensive exploration of nanostructured sodium titanates for energy storage applications. Numerous experimental techniques were employed to investigate the material' morphological, structural, vibrational, and electronic properties, along with its response to temperature variations. Additionally, *First Principles* calculations in the framework of Density Functional Theory using VASP code were conducted to test potential structural phases representing the inner structure in the samples. Key findings from this work are summarized as follows together with prospects for future works.

The complexity of the materials studied needs the combination of several characterization techniques to gain a deep understanding of their structures. Nanostructured characteristics, particularly the lamellar structure in nanotubes, made a single technique inadequate for a comprehensive analysis. By employing multiple techniques, we could assemble the puzzle of information needed to draw conclusions about the material' behavior and structure. This interdisciplinary approach, while challenging, provides new perspectives and interpretations of the data.

Synthesis and morphology

Various hydrothermal synthesis conditions were tested. In a first stage, time and temperature of the reaction was varied while in a second stage the pH of reaction was modified for two selected time-temperature conditions. They were explored to obtain different sodium nanostructures, each with distinct physical properties.

Morphologies such as nanotubes, nanorods, and nanoparticles were found to be predominantly influenced by the synthesis time and temperature, while the reaction pH primarily affected the Na/H phase proportion. It's worth highlighting that these experiments were conducted under two specific conditions, exclusively involving the presence of nanotubes. Conditions of temperature in the range of $T = 105 \ ^{\circ}C$ to $145 \ ^{\circ}C$ and times between $t = 48 \ h$ and $96 \ h$ results in nanotubes, except for the most extreme condition ($T = 145 \ ^{\circ}C$ and $t = 96 \ h$) where a mixture of nanotubes and nanoparticles was found. Mixture of nanorods and nanotubes were obtained in conditions of low temperature but large synthesis time ($T = 105 \ ^{\circ}C$ and $t = 144 \ h$) or when pH is modify for intermediate conditions ($T = 125 \ ^{\circ}C$ and $t = 96 \ h$).

Perspectives

Concerning the synthesis process, the impact of the filling factor on the resulting product has no been examined yet. It would be intriguing to explore a range of filling factors while maintaining constant time, temperature, and pH parameters. As a preliminary guideline, the conditions set out in S1 and S2 ($T = (125, 105) \ ^{\circ}C$ and $t = 96 \ h$) with intermediary pH values (10M) could be taken into consideration. Furthermore, how pH influences different scenarios in which mixed structural phases manifest, as observed in the case of M2 remain ti be investigated.

Conversely, we believe that delving into broader pH ranges is unnecessary, given the considerable range of steps that can be employed and the consistent excess of sodium in the reaction. The existing trends were already discernible from the outcomes achieved within the explored parameter range.

Structural properties

XRPD techniques were crucial in understanding the characteristic distances and crystallographic unit cell that constitute the samples. Although nanostructures displayed different patterns from bulk crystalline materials, alternative analyses were used to interpret the experimental data correctly. In particular, the main peaks of the pattern were indexed. The low angle peak corresponding to the reflection (200) allowed us to study the wall size of the nanotube and correlate it with TEM measurements. Also, the interplanar distance of the mentioned peak is related to the distance between sheets, and allows estimating changes in the structural water content. On the other hand, the peak (020) corresponding to the axial direction of the nanotube always shows the same interplanar distance and a crystalline coherence of 10 - 13 nm, indicating polycystalline growth.

The presence of various phases was determined through different tests. Some samples exhibit phase mixtures involving $Na_xH_{(2-x)}Ti_3O_7 \cdot nH_2O$ structural phase, where it was possible to identify an H/Na proportion phase present in a 34% to 64% in the samples, meanwhile the sodium content, determined by EDS, was evaluated as 8% to 16%. The second test was induced by XRPD measurements varying temperature. When the samples are calcined above 800 °C the system shows the presence of sodium tri $Na_2Ti_3O_7$ and hexa $Na_2Ti_6O_{13}$ titanate phases. This led us to test the validity of these phases both with sodium and hydrogen, by computational calculations, finding an adequate correspondence with experimental measurements. This results demonstrated that the presence of all these phases is plausible and provided a possible interpretation linking synthesis conditions to XRPD patterns.

After temperature cycling, no structural changes are observed as confirmed by both XRPD and Raman measurements. Structural water was confirmed by temperature dependent XRPD, where the (200) reflection assigned to the distance between inter sheet increase in 2θ angle, thus reducing the interdistance when the temperature increase. Furthermore, hydration water was also confirmed experimentally by DSC and TGA measurements, revealing mass losses between 7% and 14% related to the dehydration of the structures. Phase changes at temperatures up to $600 \ ^{\circ}C$ were identified through DSC measurements and XRPD patterns taken at different temperatures from $30 \ ^{\circ}C$ to $800 \ ^{\circ}C$.

Perspectives

The theoretical study offers different structural paths that could be explored. For example, experimental XRD patterns can be fitted by structures resulting from simulation instead of simply comparing simulated patterns with measured ones. A major challenge is to model the nanostructures and to perform calculations directly on these atomic arrays arranged in a nanostructure rather than bulk. Later in the optical properties, calculations on the nanostructures can be studied. Finally, better simulations considering other optical properties calculations could be performed for all the set of structural phases.

Electrical properties

Room-temperature electrical properties were studied using EIS, fitted by two parallel RCPE in series, represent two different physical process. This reveal two main transport mechanism, one associated with carrier lifetime and bulk processes ($\sim 1 - 10\mu s$) and the other related to grain boundary or depletion zone effects ($\sim 1 - 100ms$). Samples with mixed structural phases showed the possibility of an additional contribution mechanism attributed to a bulk effect, especially for higher NaOH concentrations.

Studying electrical properties as a function of temperature showed promising results for the material's potential application in energy storage systems, it is observed that after several cycles at the operating temperature range of 240 to 325 K it reaches stability. Temperature cycling studies revealed initial variations that stabilized over time, and variations between temperature increases and decreases were attributed to evaporation and freezing processes of surface and interlaminar water. However, the samples are also very sensitive to humidity. Once the samples were exposed to ambient conditions again, their electrical behavior reverted to the initial state.

Perspectives

As mentioned, the samples show a high sensitivity to humidity. This characteristic, which may be good for some applications, could be problematic for energy storage applications. A possible continuation of the work is to explore some synthesis conditions that minimize the sensitivity of the samples to moisture. Additionally, the sample could be subjected to humidity-controlled environments and the effect this has on the recovery of its initial conditions could be studied.

Optical properties

The work also focused on revealing the optical properties of the material through absorption and photoluminescence measurements. Energy bandgap values were calculated considering both direct and indirect contributions in a mixed model, and the presence of additional processes was observed in the adsorption curves for samples with more pronunced phase mixing. A correlation between gap energies and sodium concentration suggested the possibility of tuning the gap with the amount of sodium in the sample. For the $T = 125 \ ^{\circ}C$ and $t = 96 \ h$ condition energy gap decreases when sodium concentration increases. Notably, *First Principle* calculations showed that the PBE functional was more suitable for gap calculations in these titanate structures, despite hybrid functionals typically offering more accurate results.

Temperature-induced blue shifts in absorption energies and standardized absorption curves indicated a permanent effect of temperature on optical properties, promoting the disappearance of defects in the lattice. Photoluminescence signals detected emission regions corresponding to oxygen vacancies, OH group defects, and $[TiO_6]$ octahedron distortions. In particular, the presence of OH group defects in the PL signal decreases as the synthesis pH increases. Conversely, the oxygen vacancies increase with increasing pH. Redshifts observed in the emission spectra of samples subjected to temperature cycling indicated a decrease in oxygen vacancies.

Perspectives

With respect to future work on optical properties, the effect of sample compaction remains to be evaluated. Preliminary measurements were conducted and some differences were found when comparing powder and pressed pellets. Different compaction pressures could be studied and their possible effect on energy gap and PL signal could be investigated.

Temperature-induced standardized absorption curves the permanent effect of temperature on optical properties, should be studied in depth. We find it interesting to understand the fundamentals that give rise to these changes in optical properties despite no changes in structural properties are found.

In addition, the PL signal at low temperatures was explored using a cryogenic system. Some difficulties in the experimental setup did not allow us to obtain good quality data. A possible future work could optimize this setup to explore the dependence of the PL signal on temperature. This will allow a more accurate exploration of the presence of defects in the sample.

Concerning the calculation of bandgap energies by means of *First Principle*, it may be interesting to explore new hybrid functionals that includes different contributions in the exchange and correlation terms in the xc-potencial. In addition, computational calculations were performed on the bulk material. In order to obtain results more in line with the synthesized structures, it is interesting to study nanometric structures. As a first approximation, the slab model can be used, since it is simpler to achieve and some preliminary studies are already available. Then, a more refined model that tries to describe the morphology of nanotubes can be included.

Final remarks

In conclusion, this thesis presents a comprehensive study of nanostructured sodium titanates for energy storage purposes, offering valuable insights into their morphological, structural, vibrational, electronic, and optical properties. The findings contribute to advancing the understanding of these complex materials and provide a basis for their potential applications in energy storage systems. The research demonstrates the importance of combining multiple techniques and interdisciplinary collaboration to gain a holistic understanding of challenging materials like nanostructured sodium titanates.

APPENDICES

Appendix A

Supplementary Material - The effect of morphology on the optical and electrical properties of sodium titanate nanostructures

A.1. More structural results

This section expands on the results obtained from the EXAFS analysis in Chapter 3. Figure A.1 shows the graphs of the real part of $|\chi(k)|$ for M1 and M2. Table A.1 presents the adjustment parameters and the relevant statistics parameters from the fitting procedure. The quality of the fit was evaluated by means of the R-factordefined as:

$$R - factor = \frac{\sum_{i} Re(\chi_{exp}(r_{i}) - \chi_{fit}(r_{i}))^{2} + Im(\chi_{exp}(r_{i}) - \chi_{fit}(r_{i}))^{2}}{\sum_{i} Re(\chi_{exp}(r_{i}))^{2} + Im(\chi_{exp}(r_{i}))^{2}}$$

Which depends on: $\chi_{exp}(r_i)$ the experimental value on r_i and $\chi_{fit}(r_i)$ the corresponded fitted function evaluated in the same point.

A.2. More morphological results

Figure A.2 shows all the SAXS curves obtained, superimposed to the adjustment by the Beaucage function. For this adjustment the method of least squares weighed

Table A.1: Fitted parameters from EXAFS analysis: Single Scattering Path atom, average number of atom neighbors (N) and Ti-O distances for Statistical parameters: S_0^2 , Energy Shift ΔE , R_{factor} , N_{indep} and N_{var} .

Atom involved in the single scattering path							Statis	tical para	meters					
		0	0	0	0	0	0	Ti	Ti	S_{0}^{2}	ΔE	R_{factor}	N_{indep}	N_{var} .
N		0.75	0.25	1.00	1.25	1.25	0.50	2.00	1.00					
d _{Ti-(O or Ti)}	M1	2.32(1)	1.81(1)	1.81(1)	1.89(1)	1.99(1)	2.01(1)	3.14(1)	2.96(1)	0.95	7.9 eV	0.098	14	7
(Å)	M2	2.00(1)	1.76(1)	1.90(1)	1.87(1)	1.82(1)	2.08(1)	3.06(1)	3.23(1)	0.95	8.6 eV	0.082	14	7



Figure A.1: EXAFS fitting real part of $|\chi(k)|$ for M1 (left) and M2 (right) samples.

according to the intensity was used. In all cases the fit was acceptable.



Figure A.2: Small angle X-Ray scattering curves (log(I) vs log(q)) for M1 to M5 with fitting curves as mentioned in Chapter 3.



Figure A.3: Room temperature photoluminescence spectra with an excitation diode of 300 nm, deconvoluted in four Lorentz's functions.

A.3. More optical results

Figure A.3 shows the deconvoluted photoluminescence measurements by the sum of four Lorentz's functions. The corresponding peak energy E_P and the FWHM for each peak is shown in Table A.2. The absorption coefficients as a function of energy, with the processing described Chapter 3, are presented in Figure A.4 for all the samples.

Table A.2: Energy peak position E_P and FWHM, for the four peaks presented in the PL specta.

	Peak 1		Peak 2			Peak 3		Peak 4
	E_P (eV)	FWHM (eV)						
Anatase	2.356 (17)	0.31 (3)	2.554 (5)	0.26 (3)	2.791(4)	0.20(2)	2.992 (3)	0.13 (1)
M1	2.222 (8)	0.34 (2)	2.479 (4)	0.34 (3)	2.773 (8)	0.24 (4)	2.933 (10)	0.19 (3)
M2	2.371 (15)	0.27 (3)	2.549 (5)	0.26(3)	2.791 (4)	0.26 (3)	2.972 (4)	0.20(1)
M3	2.358 (12)	0.24 (2)	2.529 (4)	0.25 (2)	2.795 (4)	0.31 (3)	3.002 (5)	0.35(1)
M4	2.280 (10)	0.35 (2)	2.515 (3)	0.32 (2)	2.810 (4)	0.30(2)	2.988 (4)	0.21(1)
M5	2.361 (17)	0.39 (3)	2.550 (5)	0.27 (3)	2.808 (4)	0.26 (2)	2.987(1)	0.13 (1)

A.4. More electrical characterizations

Figure A.5 shows, for the five samples studied, all the impedance curves: module, phase and imaginary part as a function of frequency, for DC applied voltages between 0 and 4 V.



Figure A.4: Absorption coefficient measurements with direct gap fitting (Tauc Plot $h\nu$ vs $(\alpha h\nu)^2$, where α represents the absorptance) and indirect gap fitting (Tauc Plot: $h\nu$ vs $(\alpha h\nu)^{1/2}$).



Figure A.5: Impedance modulus (left column), phase (middle column) and Impedance imaginary part (right column) versus frequency at Vdc = 0 - 4 V for the five samples presented in Table A.1 of the Chapter 3.

Appendix B

Supplementary Material - Structural, optical, and electrical properties of proton intercalation H^+/Na^+ phases in nanostructured titanates induced by pH during hydrothermal synthesis

B.1. More structural results

The diffraction spectra were adjusted by a sum of Lorenzian functions. Position and peak width results are shown in the Chapter 4. In Figs B.1 and B.2 the diffraction pattern resolved in the sum of Lorenzians can be observed.

Table B.1 summarizes the interplanar distances found by x-ray diffraction (XRPD), high resolution electron microscopy (HRTEM) and electron diffraction (ED). In Figure B.3 it is shown that the 1.88 Å plane corresponds to the growth direction. It is also shown the wall thickness mentioned in the main sections.



Figure B.1: Diffraction patterns resolved in the sum of Lorenzians functions can be observed for the S1 series.



Figure B.2: Diffraction patterns resolved in the sum of Lorenzians functions can be observed for the S2 series.

		S1: 105	5 °C, 96 hr, 150	S1: 105 °C, 96 hr, 150rev/min			
NaOH c	oncentration	9M	10M	11M	9M	10M	11 M
-	RX	1.883, 1.847	1.882, 1.846	1.881, 1.845	1.882, 1.843	1.881, 1.843	1.883, 1.851
$[0\ 2\ 0]$	HRTEM	1.8, 1.94	-	1.6	1.5,1.9	-	-
	ED	1.84	1.90	1.86	1.80	1.50, 1.90	1.82
	RX	3.173, 3.091	3.174, 3.097	3.149, 3.045	3.158, 3.039	3.159, 3.0339	3.167, 3.046
$[3\ 1\ 0]$	HRTEM	2.98	3.32	3.2, 3.02	3.30, 3.11	3.00	3.30, 3.20
	ED	-	3.10	-	-	3.00	-
-	RX	3.670, 3.579	3.669, 3.613	3.662, 3.557	3.664, 3.534	3.667, 3.546	3.659, 3.542
$[1\ 1\ 0]$	HRTEM	-	3.50, 3.70	-	3.80	3.50	-
	ED	3.8	3.7	3.6	3.76	-	3.55
	RX	2.610	2.603	2.588	2.589	2.588	2.59
$[3\ 0\ 1]$	HRTEM	-	2.47	2.70-2.86	2.70	2.54	2.70-2.70
	ED	-	-	-	-	-	-
	RX	2.330	2.325	2.330	2.331	2.330	2.340
$[5\ 0\ 1]$	HRTEM	2.33	2.47	-	2.20	-	-
	ED	2.20	-	-	-	2.18	-

Table B.1: Inter planar distance (A) obtained from XRPD, Electron diffraction (ED) and HRTEM.



Figure B.3: Isolated nanotube for S1:9M sample (left) and HRTEM image of the plane with 1.88 Å corresponding to the growth direction of the nanotube (right).

B.2. EDS results

EDS results are listed in Table B.2 and allow us to approximately obtained sodium content. Graphical representation of elemental content by EDS is shown in Figure B.4 for S2:11M sample as an example.

Table B.2: EDS analysis for each sample: k-factor and percentage mass % Wt of each element detected.

		S1: 10	5 °C, 96	hr, 150rev/min	S1: 10	5 °C, 96	hr, 150rev/min
NaO	H concentration	9M	10M	11M	9M	10M	11M
	k-factor			2.	.781		
С	%Wt	17.36	11.06	7.83	65.11	43.22	7.83
	%Wt sigma	0.28	0.29	0.22	0.19	0.31	0.22
	k-factor			2.	.028		
0	%Wt	27.34	14.06	3.79	13.04	17.18	3.79
	%Wt sigma	0.21	0.18	0.16	0.13	0.18	0.16
	k-factor			1.	.201		
Na	%Wt	7.63	9.85	5.89	3.32	8.41	5.89
	%Wt sigma	0.10	0.12	0.13	0.05	0.10	0.13
	k-factor			1.	.000		
Si	%Wt	0.34	0.18	0.44	-	0.28	0.44
	%Wt sigma	0.03	0.03	0.05	-	0.03	0.05
	k-factor			1.	.011		
Κ	%Wt	0.08	0.30	-	0.08	0.07	-
	%Wt sigma	0.02	0.03	-	0.01	0.02	-
	k-factor			0.	.988		
Ca	%Wt	0.23	-	-	0.75	0.18	0.18
	%Wt sigma	0.03	-	-	0.02	0.02	0.04
	k-factor			1.	.090		
Ti	%Wt	37.96	41.89	69.87	13.46	25.87	69.87
	%Wt sigma	0.21	0.22	0.30	0.09	0.17	0.30
	k-factor			1.	.230		
Cu	%Wt	8.13	20.60	11.00	3.92	3.87	11.00
	%Wt sigma	0.09	0.15	0.15	0.05	0.06	0.15
	k-factor			2.	.243		
Au	%Wt	0.93	0.91	1.00	0.25	0.59	1
	%Wt sigma	0.08	0.10	0.15	0.04	0.06	0.15



Figure B.4: EDS results for sample S2:11M.

B.3. More optical results

Figure B.5 shows all the absorption coefficient and their calculated indirect band-gap (red line-dot) and calculated direct band-gap (blue dot), meanwhile Figure B.6 shows that, for some cases, more than one indirect gap can be found.



Figure B.5: Absorption coefficient for both sets of samples (black line), calculated indirect band-gap (red line-dot) and calculated direct band-gap (blue dot).

Photoluminescence (PL) measurement with the superposition of a sum of Gaussian function is observed in Figure B.7. The peaks position in PL spectra as a



Figure B.6: Absorption coefficient for a selection of samples, present the possibility of more than one indirect band gap.

function of the samples is displayed in Figure B.8. The highlighted area for each energy peak position is calculated using the mean peak position (of all the samples) and an error of 4%. As it can be seen, the peak position is mostly unchanged in both sets.



Figure B.7: Room temperature photoluminescence spectra with an excitation diode of 300 nm, de-convoluted in four Gaussian functions.



Figure B.8: Peak position in PL spectra as a function of the samples. The highlighted area is calculated with the mean peak position and an error of 4%.

Appendix C

Supplementary Material - Structural phases of nanostructured sodium titanates obtained in different synthesis conditions: a theoretical study

C.1. XRPD pattern with temperature: Extra information

Before starting the Supplementary Material published together with the article in Chapter 5, some XRPD results with temperature are presented.

As mentioned in the introduction of Chapter 5, the phases used to perform the simulations are derived from successive heating of the samples and studying the variation of the XRPD patterns for each temperature. This test, together with the literature study, led to the selection of the phases to be modeled.

The results of performing XRPD patterns on three of the samples (S1:10M, S1:11M and S2:11M) at different temperatures varying over a range of $30 \degree C$ to $900 \degree C$ are shown in Figures C.1, C.2, C.3. The graphs show the dehydration process (shift of the low angle peak to higher angles) and the appearance of new phases from approximately $600 \degree C$ onwards. The Supplementary Material of the article is presented below.



Figure C.1: XRPD patterns with temperature for S1:10M sample. Small angle pattern is isolated and some displacement of the peak can be seen.



Figure C.2: XRPD patterns with temperature for S1:11M sample. Small angle pattern is isolated and some displacement of the peak can be seen.



Figure C.3: XRPD patterns with temperature for S2:11M sample. Small angle pattern is isolated and some displacement of the peak can be seen.

C.2. XRPD pattern

Figure C.4 shows simulated diffraction patterns for a rolled slab of the $Na_2Ti_2O_5$, $Na_2Ti_2O_5$. H_2O y $H_2Ti_2O_5$ phases, and a synthesized samples by hydrothermal method as a comparative example. For these simulation, a bound of (4, 50, 6) was used. The meaning of this vector is explained in the following paragraph.

Figures C.5 and C.6 show the simulated XRD Pattern for the six structural phases studied in this Chapter 5. For each subplot, the number of cells considered in each crystallographic direction was modified. That mean, lattice parameter a was repeated B1 times in the radial direction, lattice parameter b was repeated B2 times in the axial direction (tube length), and lattice parameter c was repeated in the tangential direction B3 times. Therefore, the vector shown in each graph refers to bound (B1, B2, B3). In Figure C.5 the patterns were simulated with B1 = 3, 5 and 6, B2 = 50, 60 and 70, and B3 = 6. Additionally, in Figure C.6 are presented the results for B1 = 3, 4, 5 and 6, B2 = 50 and 60, and B3 = 8.

Variations in the simulated nanotube geometry mainly affect the change in relative intensity between peaks but not the shape of the diffractogram. Also, the width of some peaks is modified by the bound chosen. For the comparison in the Chapter



Figure C.4: Simulated $\theta - 2\theta$ scans for $Na_2Ti_2O_5$, $Na_2Ti_2O_2H_2O$ and $H_2Ti_2O_5$ enrolling a slab, and an experimental $\theta - 2\theta$ scan for a synthesized samples by hydrothermal method as a comparative example.



Figure C.5: Simulated $\theta - 2\theta$ scans for the six simulated structures enrolling a slab, with ([3 5 6], [50 60 70], 6).



Figure C.6: Simulated $\theta - 2\theta$ scans for the six simulated structure with ([3 4 5 6], [50 60], 8).



Figure C.7: Experimental diffraction patterns for the sample synthesized at 125 $^{\circ}C$, 96 hr and 10 M, at air and vacuum.

5, we selected the geometry that causes the first peak to be narrower.

In Figure C.7 an experimental diffraction pattern for a NaTNT on air and vacuum is observed. This shows the presence of surface and structural water that is removed during the vacuum process.

C.3. More electronic results

Figure C.8 shows the density of states (DOS) calculated with the PBE-GGA functional, while in Figure C.9 we present DOS calculated with the HSE06 hybrid functional for the extreme cases x = 0 and x = 2. The latter consumes more computational time, and it yields worse results with respect to the band gaps estimations, therefore the case x = 1 was not calculated. Table C.1 compiles the band gap obtained from DOS measurements.

	Band Gap energies (eV)							
Phases	GGA-PBE	HSE06	Bulk [42]					
$H_2Ti_3O_7$	3.078	4.696	3.35					
$HNaTi_3O_7$	2.994	-						
$Na_2Ti_3O_7$	3.141	4.789	3.45					
$H_2 T i_6 O_{13}$	2.730	4.328	3.29					
$HNaTi_6O_{13}$	2.034	-						
$Na_2Ti_6O_{13}$	3.084	4.665	3.29					
$125^{\circ}C, 96h, 10M$	$E_D = 3.22(7)$	$E_I = 2.57$ (6)						
$105^{\circ}C,96h,10M$	$E_D = 3.11 (5)$	$E_I = 2.55$ (2)						

Table C.1: Estimation of the band gap values, compared to the bulk values reported in the literature and our previously reported gaps for nanostructures.



Figure C.8: Density of states calculated with the PBE-GGA functional.


Figure C.9: Density of states calculated with the HSE06 hybrid functional.

C.4. More vibrational results

Figure C.10 introduces the phononic state densities for the six phases studied.



Figure C.10: Phononic state densities calculated for (a) $H_2Ti_3O_7$, (b) $HNaTi_3O_7$, (c) $Na_2Ti_3O_7$, (d) $H_2Ti_6O_{13}$, (e) $HNaTi_6O_O13$ and (f) $Na_2Ti_6O_{13}$.

Appendix D

Credit authorship contribution statement

Declaración de autoría para las publicaciones en las que se basa una tesis doctoral por compilación de artículos:

La autoría de las ideas, desarrollos, programas de computación y resultados de la presente tesis doctoral pertenece exclusivamente al autor y el/los directores de la tesis, salvo cuando se hace mención expresa de la autoría.

La presente tesis doctoral está compuesta por **4** (cuatro) artículos que han sido publicados o aceptados para publicación en revistas arbitradas. El autor deja constancia de que sus contribuciones en estos artículos no forman parte de otra tesis. Las contribuciones del autor de la tesis a cada artículo y las posibles modificaciones o actualizaciones que la información en ellos incluida haya tenido para su inclusión en la tesis son las siguientes:

Artículo n: 1

Título: The effect of morphology on the optical and electrical properties of sodium titanate nanostructures.

Autores: Lucia Amy, Sofia Favre, Daniel L. Gau, Ricardo Faccio.

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Referencia bibliográfica: *Amy, L., Favre, S., Gau, D. L., & Faccio, R. (2021). The effect of morphology on the optical and electrical properties of sodium titanate nanostructures. Applied Surface Science, 555, 149610.*

DOI: https://doi.org/10.1016/j.apsusc.2021.149610

Estatus: Publicado

Contribuciones del autor de la tesis:

- Revisión de la literatura: Este trabajo se inicia con una revisión bibliográfica preliminar, principalmente apuntado a conocer el estado del arte de estos sistemas. Además, se estudia la Tesis de la Dra. Fernández-Werner que sondea en detalle diferentes condiciones de síntesis para los nanotubos de titanatos de sodio.
- Síntesis de las muestras: Se realizan las síntesis de las primeras muestras de nanotubos de titanatos de sodio explorando condiciones de síntesis diferentes a las exploradas por Fernández-Werner. En particular se exploran temperaturas altas y tiempos largos.
- Metodología, diseño y caracterización experimental: Se llevan adelante las medidas experimentales mostradas en este trabajo, salvo las medidas de EX-AFS/XANES que fueron tomadas en el LNLS en Brasil luego de establecer contacto con el investigador Santiago Figueroa responsable de la línea XAFS1. En particular se realizó el diseño e implementación del montaje para registrar absorción y fotoluminiscencia.
- Análisis formal y conceptualización: Una vez obtenidos los datos, se analizan y relacionan con el fin de comprender el comportamiento de las muestras.
- Escritura del artículo: Se participó en la redacción, así como en la corrección del texto presentado en el artículo.

Modificaciones o actualizaciones para inclusión en la tesis: Sin Modificaciones. Se adjunta el artículo publicado

Artículo n: 2

Título: Structural, optical, and electrical properties of proton intercalation H+/Na+ phases in nanostructured titanates induced by pH during hydrothermal synthesis.

Autores: Lucia Amy, Sofia Favre, Ricardo Faccio.

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Communications, 33, 104908.

DOI: https://doi.org/10.1016/j.mtcomm.2022.104908 Estatus: Publicado Contribuciones del autor de la tesis:

- Revisión de la literatura: Este trabajo contó con una extensa revisión bibliográfica apuntando a comprender las fases cristalinas de los nanotubos, así como las propiedades ópticas de ellos.
- Síntesis de las muestras: Se realizan las síntesis de muestras con varición en la concentración de la solución acuosa de hidróxido de sodio (pH).
- Metodología, diseño y caracterización experimental: Se llevan adelante las medidas experimentales mostradas en este trabajo. En particular se diseñó el sistema para medidas Z(T) donde se realizaron diferentes tipos de pruebas antes.
- Análisis formal y conceptualización: Una vez obtenidos los datos, se analizan y relacionan con el fin de comprender la influencia del pH de síntesis con las respuestas de las muestras.
- Escritura del artículo: Se participó en la redacción, así como en la corrección del texto presentado en el artículo.

Modificaciones o actualizaciones para inclusión en la tesis: Sin Modificaciones. Se adjunta el artículo publicado y un *Corrigendum* debido a un error en la notación en el manuscrito original.

Artículo n: 3

Título: *Structural phases of sodium titanate nanotubes obtained in diferent synthesis conditions: A theoretical study.*

Autores: Lucia Amy, Sofia Favre, Lucía Campo Schneider, Ricardo Faccio.

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Referencia bibliográfica: *Amy, L., Favre, S., Campo Schneider, L., & Faccio, R. (2023). Structural phases of sodium titanate nanotubes obtained in different synthesis conditions: A theoretical study. MRS Advances, 1-6.*

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Estatus: Publicado

Contribuciones del autor de la tesis:

- Revisión de la literatura: Este trabajo contó con una revisión bibliográfica buscando comprender las posibles fases cristalinas presentes en los titanatos de sodio nanoestructurados, así como valores de referencia para propiedades electrónicas y vibracionales en el material bulk.
- Síntesis de las muestras: Se realizan las síntesis de las muestras nanoestructuradas con las que se comparan los resultados teóricos.
- Caracterización experimental y cálculos numéricos: Se llevan adelante las medidas experimentales mostradas en este trabajo, con excepción de las mediadas de XRPD para muestras calcinadas, realizadas por la Msc.Ing. Lucía Campo. Se colabora en las simulaciones computacionales.
- Análisis formal y conceptualización: Una vez obtenidos los resultados del cálculo numérico, se colaboró con la interpretación de los mismos comparándolos con los resultados experimentales para nuestras muestras y también para muestras similares en bulk.
- Escritura del artículo: Se participó en la redacción, así como en la corrección del texto presentado en el artículo.

Modificaciones o actualizaciones para inclusión en la tesis: Sin Modificaciones. Se adjunta el artículo publicado

Artículo n: 4

Título: *Temperature cycling effect on structural, optical and electrical properties of nanostructured sodium titanates.*

Autores: Lucia Amy, Sofia Favre, Ricardo Faccio.

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Referencia bibliográfica: *Amy, L., Favre, S., & Faccio, R. (2023). Temperature cycling effect on structural, optical and electrical properties of nanostructured sodium titanates. Ceramics International, 49(19), 31691-31700.*

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Estatus: Publicado

Contribuciones del autor de la tesis:

 Revisión de la literatura: Este trabajo contó con una revisión bibliográfica sobre efectos de la temperatura sobre las propiedades eléctricas de los titanatos de sodio. En esta búsqueda aparecieron referencias muy significativas para el estudio estructural de las muestras.

- Síntesis de las muestras: Se realizan las síntesis de las muestras nanoestructuradas que son sometidas a ciclos de temperatura.
- Metodología, diseño y caracterización experimental: Se llevan adelante las medidas experimentales mostradas en este trabajo, con excepción de las mediadas de XRPD en función de la temperatura.
- Análisis formal y conceptualización: Una vez obtenidos los datos, se vinculan para comprener la variación de las diferentes propiedades de las muestras al ser sometidas a ciclos de temperatura y deshidratación.
- Escritura del artículo: Se participó en la redacción, así como en la corrección del texto presentado en el artículo.

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