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Abstract

The present study reports the fabrication of NBT-type ceramic materials with the general formula (Na0.5Bi0.5) 0.94 R 0.04Ti 0.95 (Ni0.2 Fe0.2 Sb0.6) 0.05O3 (abbreviated as NBT-RNFS), where R denotes the dopant elements La, Nd, Gd, and Y. The ceramics were synthesized via the conventional solidstate reaction method. The main objective of this study was to investigate the effect of rare earth doping on the dielectric and photocatalytic properties of novel NBT-based ceramic materials. The NBT-RNFS samples were successfully synthesized at 1150°C. Undoped NBT-NFS samples had a single rhombohedral phase, while rare earth-doped NBT-NFS samples showed a rhombohedral phase along with a pyrochlore phase. Rietveld refinement of the XRD data showed a slight shrinkage of the unit cell volume with the substitution of rare earth elements, attributed to their relatively lower ionic radii compared to the host ions. Optical bandgap analysis revealed that the fabricated perovskite samples exhibited semiconducting behavior, with measured bandgap values ranging from 2.61 to 2.80 eV. The La-doped NBT-RNFS system exhibited an impressive 83% photocatalytic dye degradation rate, substantially outperforming the 23% dye removal efficiency of the undoped material. Similarly, the Nd-doped (62% dye removal) and Y-doped (66% dye removal) NBT-RNFS ceramics also displayed enhanced photocatalytic activities under broadband solar light exposure. The La-doped NBT-RNFS composition demonstrated an exceptionally high dielectric constant (cr) of 1151.87, while the Nd-doped NBT-RNFS exhibited a dielectric constant of 1122.31. These values significantly exceeded the dielectric constant of 951.02 obtained for the undoped NBT-NFS ceramic.

Keywords: NBT. Rare earths .Dielectric .MB. Dye. Photocatalytic. Sunlight irradiation.

Résumé

L'étude rapporte la fabrication de matériaux céramiques de type NBT avec la formule générale, (Na_{0.5}Bi_{0.5}) 0.94 R 0.04 Ti 0.95 (Ni_{0.2} Fe_{0.2} Sb_{0.6}) 0.05O₃, abrégée NBT-RNFS, où R désigne les éléments dopants La, Nd, Gd et Y. Les céramiques ont été synthétisées par la méthode conventionnelle de réaction à l'état solide. L'objectif principal de cette étude était d'examiner l'effet du dopage par des terres rares sur les propriétés diélectriques et photocatalytiques de nouveaux matériaux céramiques à base de NBT. Les échantillons NBT-RNFS ont été synthétisés avec succès à 1150°C. Les échantillons NBT-NFS non dopés présentaient une seule phase rhomboédrique. En revanche, les échantillons de NBT-NFS dopés aux terres rares ont montré une phase rhomboédrique, ainsi qu'une phase pyrochlore. L'affinement Rietveld des données de DRX a montré une légère diminution du volume de la maille unitaire avec la substitution des éléments de terres rares, attribuée à leurs rayons ioniques relativement plus faibles par rapport aux ions hôtes. L 'étude des propriétés optiques a montré que ces matériaux pérovskites se comportent comme des semi-conducteurs. Les mesures ont permis de déterminer une plage de valeurs de bande interdite allant de 2,61 à 2,80 eV. Le dopage au lanthane (La) du système NBT-RNFS a permis d'obtenir un taux de dégradation photocatalytique du colorant de 83%, nettement supérieur aux 23% du matériau non dopé. Les échantillons dopés au néodyme (Nd, 62% de dégradation) et à l'yttrium (Y, 66% de dégradation) ont également montré une activité photocatalytique accrue. Ces meilleures performances photocatalytiques ont été observées sous illumination par une lumière solaire large bande. Les dopages aux terres rares (La, Nd, Y) ont donc permis d'améliorer significativement les propriétés photocatalytiques du système NBT-RNFS. Le dopage au lanthane (La) du système NBT-RNFS a permis d'atteindre une constante diélectrique très élevée de 1151,87. Le dopage au néodyme (Nd) a également conduit à une constante diélectrique élevée de 1122,31. Ces valeurs de constante diélectrique sont nettement supérieures à celle de 951,02 mesurée pour le matériau NBT-NFS non dopé.

Mots-clés : NBT, Terres rares, Diélectrique, photocatalytique, MB (Méthylène Blue), Irradiation solaire الملخص

تتناول الدراسة الحالية تصنيع مواد سيراميك من نوع (Nio.2 Feo.2Sbo.6) 0.05O3 ومالار الدراسة الحالية تصنيع مواد سيراميك من نوع (Nao.5Bio.5) مختصرة باسم(NBT-RNFS)، حيث يشير R إلى العناصر المستبدلة La و dd و Gd تم تصنيع السير اميك من خلال طريقة تفاعل الحالة الصلبة التقليدية. كان الهدف الرئيسي من هذه الدراسة هو التحقيق في تأثير الإستبدال بالعناصر الأرضية النادرة على الخواص العازلة والتحفيز الضوئي للمواد السير اميكية الجديدة القائمة على NBT . تم تصنيع عينات NBT- RNFS بنجاح عند 1150 درجة مئوية. أظهرت عينة NBT-NFS طور معيني السطوح، بينما أظهرت عينات NBT-RNFS المستبدلة بالعناصر الأرضية النادرة طورًا معينيًا إلى جانب طور بيروكلور. أظهر تحسين Rietveld لبيانات XRD انكماشًا طفيفًا في حجم الخلية الوحدة مع استبدال العناصر الأرضية النادرة، ويعزى ذلك إلى أقطار ها الأيونية المنخفضة نسبيًا مقارنة بالأيونات المضيفة. كشف تحليل فجوة النطاق الضوئي أن عينات البيروفسكايت المصنعة أظهرت سلوكًا شبه موصل، حيث تتراوح قيم فجوة النطاق المقاسة من 2.61 إلى 2.80 إلكترون فولت. أظهرت NBT-LNFS معدل تحلل صبغة التحفيز الضوئي بنسبة 83%، وهو أعلى بنسبة 23% من المادة غير مستبدلة. أظهرت العينات المستبدلة بالنيوديميوم (Nd، 62٪ تحلل) والإيتريوم (Y، 66٪ تحلل) ايضًا زيادة في نشاط التحفيز الضوئي. وقد لوحظت هذه العروض التحفيزية الأفضل تحت الإضاءة بواسطة الضوء الشمسي عريض النطاق. إن الإضافة باستخدام الأتربة النادرة (Y ، Nd ، La) جعل من الممكن تحسين خصائص التحفيز الضوئي لنظام NBT-RNFS بشكل كبير. كما أظهرت عينة NBT-LNFS ثابتًا عازلًا (cr) مرتفعًا يبلغ 1151.87، في حين أظهرت تركيبة NBT-RNFS المستبدلة بالنيوديميوم Nd ثابتًا عازلًا يبلغ 1122.31. تجاوزت هذه القيم بشكل كبير الثابت العازل البالغ 951.02 الذي تم الحصول عليه لسير اميك NBT-NFS غير المستبدل.

الكلمات المفتاحية: NBT، أتربة نادرة، عازل، التحفيز الضوئي MB (الميثيلين الأزرق)، الإشعاع الشمسي.

List of some symbols and abbreviations

- **NBT:** Sodium Bismuth Titanate
- NBT-NFS: (Na0.5Bi0.5) Ti 0.95 (Ni0.2 Fe0.2 Sb0.6) 0.05O3
- **DTA**: Differential Thermal Analysis
- TGA: Thermal Gravimetric Analysis
- **XRD**: X-ray diffraction
- **SEM**: Scanning electron microscopy
- EDS: Energy dispersive spectrometric analysis
- FTIR: Fourier Transform Infrared Spectroscopy
- **BET**: Brunauer-Emmett-Teller
- BJH: Barrett, Joyner and Halenda
- **IUPAC:** International Union of Pure and Applied Chemistry
- Tc: The Curie Temperature
- $\boldsymbol{\varepsilon}_r$: The relative dielectric permittivity
- $\boldsymbol{\varepsilon}_{m}$: The dielectric constant at Curie temperature
- $\pmb{\varepsilon_0}$: The permittivity of free space (8.854 $\times 10^{-12}$ F/m)
- C_P: The capacitance of the pellet
- **d**: The thickness of the pellet
- Eg: Energy of the band gap

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General Introduction

In recent decades, lead-based materials, particularly those derived from the ferroelectric Pb (Zr,Ti)O₃ (PZT) complex, have received substantial attention in the field of electronic microdevices. This is due to the remarkable properties of these lead-based materials [1, 2] . Leadbased materials, known for their pyroelectric, piezoelectric, ferroelectric, and dielectric properties, are widely used in devices like actuators, sensors, and pyroelectric transducers [3], [4]. However, their use raises environmental and health concerns. To address these, the scientific community is exploring lead-free alternatives, such as Bismuth sodium titanate (NBT)-based lead-free piezoceramics. These materials have adaptable properties, high Curie temperature, and potential as energy storage due to their high polarization [5].

Researchers have used various methods to improve the structural and electrical characteristics of perovskite materials based on NBT. The ratio of sodium to bismuth (Na/Bi) is essential in defining the electrical properties of these materials. In addition, the introduction of nonstoichiometry of sodium (Na) or bismuth (Bi) at the A-site or titanium (Ti) at the B-site can modify the dielectric and electrical properties of NBT in accordance with specific requirements. However, adding a small amount of a suitable dopant element to either the A or B-site of the NBT structure has piqued interest. This method has demonstrated its capacity to be very captivating because to its ability to make substantial alterations to the characteristics of materials based on NBT [6, 7].

The investigation of substituting rare earth elements (RE ³⁺) at the A-site of NBT has been conducted to get insight into their influence on different structural, optical, and electrical properties [8] . The study of modifications in the composition of NBT through the use of dopants has attracted considerable attention since even small amounts of dopants have the ability to induce substantial adjustments in the properties of NBT. Recent studies [9, 10]have chosen Lanthanum (La) as a modifier in the NBT system, specifically at the A-site. Furthermore, the act of doping at the B-site is likewise regarded as advantageous for augmenting certain characteristics of NBT perovskite materials. Specifically, the addition of nickel (Ni) dopants at the Ti-site has been discovered to enhance the dielectric properties.

Na_{0.5}Bi_{0.5}TiO₃ (NBT) is a well-known ferroelectric material that has a wide range of applications. In addition to its use in energy storage, actuators, capacitors, and thermal energy harvesters, NBT can also be utilized for environmental applications [11, 12]. To the best of our knowledge, there is currently limited published literature available on the optimization of the photocatalytic parameters for rare earth-doped NBT materials [13].

General Introduction

The present investigation focuses on elucidating the impact of rare earth ions, including La³⁺, Nd³⁺, Gd³⁺, and Y³⁺, on the structural, dielectric, and photocatalytic properties of Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6}) _{0.05}O₃ (NBT-NFS) ceramic materials. The primary objective of this study is to investigate the reaction sequences and phase formation mechanisms during the conventional solid-state synthesis of the novel NBT-NFS ceramic. Additionally, this research aims to enhance the performance of these ceramics by incorporating rare earth dopants and conducting a comprehensive analysis of their influence on the structural, dielectric, and photocatalytic characteristics. By developing a fundamental understanding of the reaction pathways and the role of rare earth ions in modifying the properties of the NBT-NFS system, this work aims to provide valuable insights for the optimization and potential applications of these advanced ceramic materials.

This thesis is organized into 4 chapters.

The first chapter presents a comprehensive review of the literature to establish a firm theoretical foundation for understanding the essential characteristics of NBT ceramics. Key concepts including piezoelectricity, dielectricity, ferroelectricity, and the fundamentals of photocatalysis were rigorously defined and explored within the specific context of the current research.

Chapter 2 focused on the experimental aspects, outlining the ceramic elaboration method and detailing the specific synthesis conditions, such as grinding time, pellet fabrication, and calcination/sintering temperature and duration. Moreover, the chapter introduced the various characterization techniques utilized, including, TGA/DTA, XRD, FTIR, SEM, BET, UV Visible and Raman, which were employed to analyze the structural, vibrational, microstructural, and dielectric properties of the synthesized ceramics.

Chapter 3 presented an overview of the fabrication processes and reaction mechanisms associated with Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6}) $_{0.05}O_3$ (NBT-NFS) ceramics. The chapter focused on investigating the structural and microstructural properties of NBT-NFS ceramics doped with rare earth elements, formulated as Na_{0.5}Bi_{0.5}RTiO_{.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6}) $_{0.05}O_3$, where R = La, Nd, Gd, and Y. This study aimed to provide a comprehensive understanding of the impact of rare earth doping on the structural characteristics and microstructural evolution of the NBT-NFS ceramic system.

The final chapter of the work investigated the multifunctional properties of rare earth-doped NBT-NFS ceramics. The chapter was divided into two parts: Part A explored the photocatalytic

performance of the rare earth-modified NBT compositions, evaluating the impact of dopants on photocatalytic activity and efficiency. Part B focused on the dielectric characteristics of the rare earth-doped perovskite materials.

Finally, we conclude this thesis with a comprehensive summary that includes all the important results of our conducted research.

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Chapter I

TECHNICAL BACKGROUND

Introduction

This chapter provides a comprehensive overview of the fundamental concepts and principles that underlie the research presented in this thesis. The first section of this chapter examines basics and principles of photocatalysis, a promising method for addressing environmental challenges. This method utilizes catalysts activated by light to enhance chemical reactions. The chapter delves into the main stages of the photocatalytic process including light absorption, creation of charge carriers, and redox reactions occurring at the catalyst surface. The significance of semiconductor materials in photocatalysis is also investigated with a focus on their band gap energies as well as their capacities to generate electron-hole pairs. The applications of photocatalyst materials in various fields are reviewed including water purification, air cleansing, and energy conversion these fields have been extensively explored, and the review provides a solid foundation for the research presented in this thesis.

The second section of this chapter focuses on the distinctive properties of ferroelectric materials. Ferroelectrics are a category of materials that demonstrate spontaneous electric polarization, which can be reversed by an external electric field. The chapter discusses the relationship between ferroelectricity, piezoelectricity, and pyroelectricity. The fundamental crystal structures and phase transitions that give rise to the ferroelectric effect are also examined. Furthermore, the potential applications of ferroelectric materials in various fields are explored, including energy harvesting, sensors actuators, and data storage. This background information establishes the foundation for the specific research investigations and findings presented in the subsequent chapters of this thesis.

I.1 Part A: Basics of photocatalysis

I.1.1 Photocatalysis

The term 'photocatalysis' can be analyzed by dividing it into two constituent elements: 'photoreaction' and 'catalysis.". Photocatalysis is the act of catalyzing a desired photoreaction. In this situation, the catalyst used might be either in the same phase (homogeneous) or in a distinct phase (heterogeneous) as compared to the reactants [1].

Heterogeneous photocatalysis has become a promising technology in recent years because of its potential uses in environmental remediation, energy production, and the synthesis of organic materials [2], [3], [4]. In this process, photocatalysts are utilized, which can be broadly classified into two primary types: matrix-dispersed photocatalysts and bulk semiconductor

photocatalysts. There are five primary aspects of heterogeneous photocatalysis that are the most important [5]:

- Reactant Diffusion to Surface
- Adsorption of reactants onto the surface
- Reaction on the surface
- Product Desorption from Surface
- Product Diffusion from Surface

I.1.2 The principle of photocatalysis

Heterogeneous photocatalysis has been established as a highly effective method for the degradation of pollutants in both air and water environments. This process involves multiple steps, as illustrated in **Figure I.1**. First, the pollutant is conveyed from the bulk fluid to the surface of the photocatalyst. The pollutant adsorbs onto the photocatalyst surface, which facilitates the photoreaction. During the photoreaction, the adsorbed pollutant interacts with the photocatalyst and is transformed. The photoreaction is followed by the desorption of the final products from the photocatalyst surface, which is then transported back into the bulk fluid. This series of steps allows heterogeneous photocatalysis to effectively remove a variety of pollutants from both air and water systems.

Solids are categorized into conductors, semiconductors, and insulators, based on the energy states and orbitals that their outermost electrons occupy. The valence band of materials is occupied by the outermost electrons, which are loosely bound to the nucleus and represent the energy levels of the valence electrons. In contrast, the conduction band signifies the energy levels of the free electrons that are capable of traversing the lattice structure of the material. The energy difference between the valence band and the conduction band is referred to as the band gap energy, which is the minimum energy necessary for an electron to move from the valence band to the conduction band. Conductors and semiconductors are considered more appropriate for photocatalysis applications due to their lower band gap energies, which necessitates less energy to excite electrons. The conductivity of any substance is the consequence of these excited electrons, which have acquired sufficient energy to transition from the valence band to the conduction band [6].

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Figure I.1: Flow chart indicating the steps in heterogeneous photocatalysis [6].

I.1.3 Photocatalytic reactions mechanism

The fundamental characteristic of photocatalysis is its capacity to accelerate photochemical reactions, effectively transforming the energy of sunlight into chemical energy. As illustrated in **Figure I.2**, The photocatalysis process initiates with the absorption of photon energy from sunlight by the photocatalyst material. The absorption of light energy causes the promotion of electrons from the valence band to the conduction band, while also generating positively charged holes in the valence band. The photo-generated electrons and holes then migrate to the surface of the photocatalyst, where they participate in redox (reduction-oxidation) reactions with other chemical species that are present. Therefore, the fundamental mechanism of photocatalysis can be divided into three key steps: (1) electron excitation, (2) electron-hole migration, and (3) surface redox reactions [7].



Figure I.2: Mechanism of photocatalytic processes under solar irradiation.

During the first stage of the process [8] [9], [10], a semiconductor material becomes energised when it absorbs light with a photon energy that is equal to or greater than its bandgap energy ($\lambda \ge \text{Eg}$). As a result, the electrons in the valence band of the semiconductor, which were previously unexcited, become excited and transition to the conduction band. During this initial stage, electron-hole pairs are generated in the semiconductor material. This occurs when the excited electrons vacate their positions, leaving behind unoccupied states, referred to as holes, in the valence band.

After the electron-hole pairs have been formed under light irradiation, the charge carriers (electrons and holes) start to disperse from the interior towards the surface of the photocatalyst molecules. These electron-hole pairs that have migrated to the surface are known as surface-trapped electron-hole pairs.

Photocatalyst +
$$hv \rightarrow Phototcatalyst^* + (e_{CB} + h_{VB} +)$$
 Eq. I.1

In addition, the charge carriers, which are electron-hole pairs trapped on the surface, can undergo recombination within the space of a couple of nanoseconds, resulting in the release of energy in the form of heat.

$$e_{CB} + h_{VB} + \rightarrow e^{-} + heat$$
 Eq. I.2

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In the presence of absorbed oxygen, the excited photocatalyst emits an electron (e-). A superoxide radical (O_2^{\bullet} -) is formed when the molecular oxygen (acting as an electron acceptor) accepts the emitted electron. The superoxide radical can subsequently receive a proton to generate a hydroperoxyl radical (HO₂ \bullet). The hydroperoxyl radical can subsequently undergo a further transformation into hydrogen peroxide (H₂O₂).

Consequently, the existence of adsorbed water molecules on the photocatalyst surface is essential for the synthesis of hydroxyl radicals (OH•). Furthermore, the recombination time of the electron-hole (e--h+) pairs can be prolonged during the complete photocatalysis reaction by the superoxide radical (O_2 •-) and the hydroperoxyl radical (HO_2 •).

Photocatalyst
$$(h^+ VB) + H_2O \rightarrow$$
 Photocatalyst $+ H^+ + OH$ Eq.I.3

Photocatalyst
$$(h^+VB) + OH^- \rightarrow Photocatalyst + ^{\circ}OH$$
 Eq. I.4

Photocatalyst (e⁻CB) +
$$O_2 \rightarrow$$
 Photoatalyst + $O_2 \sim$ Eq. I.5

$$O_2 \stackrel{\circ}{\to} +H^+ \rightarrow HO_2^\circ \qquad \qquad Eq. I.6$$

The degradation of pollutants occurs on the surface of the photocatalyst through the action of hydroxyl radicals (OH•), which were previously formed. These highly reactive hydroxyl radicals have the ability to completely degrade bulky organic compounds into non-toxic by products such as carbon dioxide and water. It is crucial to note that the generation of these hydroxyl radicals requires both dissolved oxygen and water to be present in the system.

$$Dye+hv \rightarrow dye^*$$
 Eq. I.7

$$Dye^{+}OH \rightarrow Degraded \ product \qquad Eq. \ I.8$$

$$Dye^* + h_{VB^+} \rightarrow Oxidized \ products \qquad Eq. 1.9$$

$$Dye^* + e^{-}CB \rightarrow Reduced products Eq. 1.10$$

The general process can be effectively described as follows:

Organic pollutants + O_2 Semiconductor & UV/Solar light $CO_2^{\uparrow} + H_2O + M$ ineral acids

I.1.4 Perovskite materials in photocatalysis

Advanced oxidation processes (AOPs) have become increasingly popular for the treatment of wastewaters in recent years. These AOPs are used to remove organic pollutants during water treatment as a result of the production and utilisation of highly reactive hydroxyl radicals (•OH) as oxidant species. These hydroxyl radicals can initiate further reactions, leading to the degradation and potential mineralization of the organic pollutants. Among the various AOP

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techniques, photocatalysis has garnered significant attention as a promising approach for addressing environmental challenges. Photocatalysis is a process that occurs when a semiconductor material absorbs a photon with energy higher than its band gap, which is the difference in energy between the filled valence band and the empty conduction band of the semiconductor. This photon absorption excites an electron from the valence band to the conduction band, simultaneously creating a positively charged hole in the valence band [11].

The photocatalytic performance of perovskite materials has been the subject of extensive research efforts that have employed a variety of strategic approaches. The substitution of foreign dopant elements at the A-site and/or B-site cation positions within the ABO₃ perovskite crystal structure, as well as the deliberate tailoring of their morphological characteristics, including particle size and shape, have been included with these. For instance, the oxidation state of the B^{3+} cation can be elevated to B^{4+} , or an oxygen vacancy can be generated by replacing an A^{3+} cation with an $A^{'2+}$ cation in the $A^{3}_{1-x}+A^{'2}_{x}+BO_{3}$ perovskite, as illustrated in Figure I.3. During the formation of an oxygen vacancy (represented by a square symbol), a lattice oxygen can be lost. Subsequently, molecular oxygen can be absorbed and activated by accepting electrons within the oxygen vacancy, leading to the transformation into highly reactive oxygen species. This suggests that the oxygen vacancy can serve as a conduit for the conversion between molecular oxygen and lattice oxygen [12]. Substitutional doping of foreign elemental species at the A-site and/or B-site cation positions within the ABO₃ perovskite structure is a highly effective strategy to either mitigate electron-hole recombination [13] or reduce the bandgap energy [14], [15], which serve to enhance the photocatalytic performance of the perovskite materials.

Fig I.3: Change in the oxidation state of B-site cation and the generation of oxygen vacancy in the defect $A^{3}_{1-x}+A^{2}_{x}+BO_{3}$ structure [12].

I.1.5 Diverse applications of photocatalysis

The primary objective of the ongoing research efforts in the field of photocatalysis is the creation of practical applications that can leverage on the unique capabilities of this technology. Photocatalytic processes have attracted considerable scientific and industrial attention because of their wide range of potential applications, including wastewater treatment and effluent detoxification, disinfection and inactivation of pathogenic microorganisms such as bacteria, cancer cell inactivation for therapeutic purposes, self-cleaning surfaces with superhydrophilic properties, hydrogen fuel production through the photocatalytic splitting of water, remediation of inorganic and organic gaseous pollutants . The breadth of these potential applications has fueled extensive research and development activities aimed at improving the efficiency and performance of photocatalytic systems [16].

I.2 Part B: Basics of ferroelectrics

I.2.1 Dielectric materials

A dielectric material is an insulating substance that exhibits polarisation when an electric field is applied. This polarisation occurs because electric charge does not flow through the material but instead shifts slightly away from the equilibrium position of charge regions/ions. The restriction in the movement of this charge shift creates a dipole moment [17]. A good dielectric substance is an insulator with high polarizability, which results in a high relative permittivity or dielectric constant (ε_r).

I.2.2 Dielectric properties

Dielectric materials, often referred to as insulators, are characterized by their high electrical resistivity [18]. These dielectric materials frequently include polar molecules that are randomly oriented in the absence of an electric field. When an electric field is applied, the material becomes polarized as it aligns the dipole moments of these polar molecules and other species.

The influence of the electric field on dielectric materials can be understood through the analogy of a parallel plate capacitor. These are two conducting plates with an area denoted as A, positioned in parallel to one another and separated by a relatively small distance d, where d is much smaller compared to the linear dimension of the plate, as depicted in **Figure I.4.** When an electric field is introduced to parallel plates with a vacuum between them, as shown in **Figure I.4.a**, the electric field E can be determined using **Equation I.11** [19].

$$E = \frac{\sigma}{\varepsilon_0} \qquad \qquad Eq. \ I.11$$

Where " σ " represents the charge density and " ε_0 " is the permittivity of free space, defined as 8.854 x 10⁻¹² F/m, the capacitance of the parallel plate can be expressed by **Equation I.12**.

$$C = \frac{Q}{V} \qquad \qquad Eq. \ I.12$$

Where "Q" represents the charge on the plate, and "V" represents the applied voltage.

And
$$\sigma = \frac{Q}{A}$$
 Eq. I.14

For the case of a parallel plate capacitor with a vacuum between the plates

$$C = \frac{\sigma A}{Ed} = \frac{\varepsilon_{0A}}{d}$$
 Eq. I.15

When an electric field is introduced and a dielectric material is present between the plates, the electric dipole moments align with the direction of the applied electric field. Positive charges migrate toward the negative pole of the electric field, while negative charges move toward the positive pole of the electric field, as depicted in **Figure**. **I.4 b** .This leads to a decrease in the effective electric field between the plates. The effective electric field can be determined using **Equation I.16**.

$$E_{eflective} = E - E_{polarization} = \frac{\sigma}{\varepsilon_r - \varepsilon_0} \qquad Eq. \quad I.16$$

Where ' ε_r ' represents the relative permittivity of the material.

The formula to calculate the capacitance of a parallel plate capacitor when a dielectric material is inserted between the plates is provided as **Equation I.17** [19].

$$C = \frac{\varepsilon_r \ \varepsilon_0 A}{d} \qquad \qquad Eq. \ I.17$$

The capacitance of the parallel plate capacitor is enhanced by a factor of " ε_r ".



Figure I.4: Parallel plate capacitor with (a) empty space between the plates and (b) a dielectric material positioned between the plates.

I.2.3 Dielectric constant

The property that characterizes a material's ability to store electrical charge or its polarizability is quantified by the term "relative dielectric constant (K')," which is also commonly known as "relative permittivity (ϵ r)". **Figure. I.5** serves as an illustration of the relative dielectric constant concept. It displays the application of an electric field to two flat metal plates, resulting in one plate acquiring a positive charge and the other a negative charge. The electric field induces polarization within the material situated between the conductive plates. The relative dielectric constant quantifies the material's ability to polarize or store electric charge in comparison to a vacuum between the plates.

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Figure. I.5: Schematic representation outlining the definition of the relative dielectric constant K'[20].

$$K' = \frac{K_{material}}{K_{vacuun}}$$
 or $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$ Eq. I.18

K for a vacuum is 1.0, while for dry air at 0°C and standard atmospheric pressure, it is approximately 1.00006.

I.2.4 Dielectric losses

When a sinusoidal voltage is imposed on an ideal dielectric, the current (I) lags the voltage (V) by 90°, as depicted in **Figure I.6** (a). More precisely, during the initial half of the cycle, the voltage is used to charge the capacitor, causing the current to decrease to zero. During the second-half cycle, the voltage lowers to zero as the charge releases as current [21].



Figure I.6: Depicting (a) Ideal dielectrics and (b) Real dielectrics including dielectric loss.

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However, for real dielectrics subjected to an external electric field, the current and voltage cannot attain their maximum and minimum values simultaneously. Consequently, the angle between voltage and current is not 90°, and you can observe the relationship between V and I in **Figure I.6 (b)**. The current can be divided into two components, denoted as I charge and I loss, representing the real (ε ') and imaginary (ε ") parts, respectively [21]. Hence, the dielectric loss is defined as the ratio between the real and imaginary permittivity, as shown in Equation **I.19** [21].

$$\tan \delta = \frac{I_{loss}}{I_{charge}} = \frac{\varepsilon''}{\varepsilon'} \qquad \qquad Eq. \ I.19$$

I.2.5 Quality Factor

The reciprocal of the tan δ is commonly referred to as the "quality factor" for manufacturers of dielectric ceramics.

$$Q = \frac{1}{\tan \delta} = \frac{a \text{varage energy stored}}{energy \text{ dissipated per cycle}} \qquad \qquad Eq. \ \textbf{I.20}$$

The term "quality factor" is more commonly associated with microwave resonators. Quality factor, or Q, is a measure of the power loss of a microwave system. Q is frequently used as a design parameter for dielectric usage [22].

I.2.6 Curie-Weiss behavior

Ferroelectric materials have a specific temperature known the Curie point (Tc), at which their natural spontaneous polarization ceases to exist due to a change in their structure .When the temperature surpasses Tc, these materials undergo a transformation into the paraelectric phase, wherein the permittivity exhibits the characteristic Curie-Weiss behavior described by **Equation I.21** [23].

$$\chi = C / (T - Tc)$$
 Eq. I.21

 χ =dielectric susceptibility

C = Curie constant

T = Absolute temperature in K

Tc = Curie-Weiss temperature in K

I.2.7 Polarization mechanisms

In general, there are four distinct mechanisms that can contribute to the polarization of a dielectric material (**Fig I.7**). The total polarization of the dielectric material is the sum of all the following contributions.
I.2.7.1 Electronic polarization Pelec

Electronic polarisation is present in all dielectrics. It is predicated on the displacement of the negatively charged electron shell against its positively charged core. The volume of the electron shell is approximately proportional to the electronic polarizability α_{el} . Generally, α_{el} is temperature-independent, and large elements exhibit a high electronic polarizability[24].



Figure I.7: Polarization mechanisms in the dielectric materials.

I.2.7.2 Ionic polarization (Atoms) Pions

Ionic polarisation is a phenomenon that is observed in ionic crystals and describes to the displacement of the positive and negative sublattices in response to an applied electric field (e.g., NaCl). In addition to dipolar polarisation, ionic polarisation may induce a ferroelectric transition [24].

I.2.7.3 Orientation or dipolar polarization Por

The alignment of permanent dipoles as a result of the applied electric field is referred to as

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orientation polarization. Typically, all dipole moments exhibit a statistical distribution of their directions at ambient temperatures. The alignment is perturbed by the thermal movement of the atoms, while an electric field establishes a preferred direction for the dipoles. The temperature and the applied field determine the average degree of orientation. The dipolar or orientational polarizability is indicated by [25].

$$\alpha_{or} = \frac{p^2}{3k_B T} \qquad \qquad Eq. \ I.22$$

Where p is the dipole moment, k_B denotes the Boltzmann constant and T is the absolute temperature.

I.2.7.4 Space Charge Polarization Psc

Space charge polarisation may be present in dielectric materials that exhibit spatial heterogeneities in charge carrier densities. The space charge can occur at the metal/dielectric interface, at grain boundaries in ceramics and domain walls in ferroelectrics. Thus, interfaces play a crucial role in the space charge effect but this extrinsic polarization is much more pronounced if charged defects are localized at these interfaces. Space charge polarization effects are not only of importance in semiconductor field-effect devices, they also occur in ceramics with electrically conducting grains and insulating grain boundaries (so-called Maxwell-Wagner polarization)[24].

I.2.8 Variation of dielectric constant with frequency

In real life, alternating current (ac) is most often used because its field or voltage direction changes over time. Assuming a dielectric material is polarized by an electric field, the realignment of its dipoles is contingent upon the temporal aspects and reorientational capabilities. The relaxation frequency represents the minimum time required for reorientation. The frequency-dependent behavior of the dielectric constant, encompassing both real and imaginary components, is schematically illustrated **in Figure I.8**, and it manifests across all four types of polarization. Dielectric loss refers to the absorption or dissipation of energy by dielectric materials subjected to an applied field. This loss is also influenced by the frequency and exhibits variation among different dielectric materials. Scientists are actively engaged in minimizing dielectric loss in materials, as reduced losses contribute to enhanced performance [26, 27].



Figure I.8: Frequency dependent of dielectric constant [28].

I.2.9 Ferroelectric materials

I.2.9.1 Definition

Relaxor ferroelectrics, also known as relaxors, belong to a unique category of ferroelectric materials. At elevated temperatures, they manifest a non-polar, paraelectric phase. In contrast to classic ferroelectrics, where there is an abrupt first or second-order phase transition from the paraelectric to the ferroelectric phase at a well-defined Curie temperature (Tc), relaxors lack such a distinct phase transformation. Consequently, it is challenging to precisely define a single Tc for relaxor materials [29]. As relaxor materials undergo cooling, small regions at the nanoscale, referred to as polar nanoregions (PNRs), start to emerge, each containing randomly oriented dipole moments. The transformation, characterized by the Burns temperature (TB), does not qualify as a structural phase transition, as it does not bring about any discernible alterations in the crystal structure on a macroscopic scale.

Nonetheless, when the temperature falls below the Burns temperature, these materials display distinctive physical characteristics. As a result, this temperature range is frequently regarded as a distinct phase, distinct from the paraelectric phase [30].

One significant distinction between relaxors and ferroelectrics is the behavior of dielectric permittivity. Relaxors exhibit dielectric dispersion, signifying that the permittivity varies with the frequency of the applied electric field. Furthermore, the width of the permittivity peak in relaxors can span across a temperature range of several hundred degrees, a notably broader

range compared to ferroelectrics [29, 31]. The permittivity can be represented using the following equation:

$$\varepsilon_m = C^{-\gamma} (T - T_m)^{\gamma}$$
 Eq. I.23

In this equation, ε_m represents the maximum value of relative permittivity at Tm, γ denotes the degree of diffuseness, which can vary from 1 for typical ferroelectrics to 2 for ideal relaxors, and C stands for the Curie-like coefficient (**Tab. I.1**).

Property	Normal ferroelectric	Relaxor ferroelectric
Temperature Dependence of Dielectric Constant ε'(T)	Sharp 1^{st} & 2^{nd} order Transition about Curie Temperature T_C	Diffuse Transition about Curie Maximum T'_m
Frequency Dependence of Dielectric Constant ɛ'(f)	Weak	Strong
ε'(Τ) Behavior in Paraelectric Regime	Obeys Curie-Weiss Law $\frac{1}{\varepsilon'} = \frac{T - T_{CW}}{C}$	Obeys Modified Curie- Weiss Law $\frac{1}{\varepsilon'} = \frac{1}{\varepsilon'_m} + \frac{(T - T'_m)^{\gamma}}{C_1}$
Remanent Polarization	Large	Small
Scattering of Light	Strong Anisotropy (Birefringence)	Very Weak Anisotropy (Pseudo Cubic)
X-ray Diffraction	Line splitting b low the structural phase transition	No X-ra line splitting due to pseud cubic structure

Table I.1: Contrasting normal and relaxor ferroelectrics [32].

I.2.9.2 Ferroelectric Hysteresis

When an external electric field is imposed, the dipoles within the Nano domains align either parallel or antiparallel to the magnetic field direction, reaching a maximum polarization known as saturation or maximum polarization (P_{max}) after a specific threshold of electric field strength. After removing the electric field, not all domains revert to their original orientations, retaining some level of polarization. This is referred to as remnant polarization (Pr). Since the polarization does not return to zero naturally, it necessitates the application of an electric field needed to reset polarization to zero is referred to as the coercive field. When the field is applied in the opposite direction, a similar pattern occurs, resulting in a repetitive loop between polarization (P) and electric field (E), with polarization lagging behind the electric field. This hysteric behavior is significant because it makes it impossible to deduce the polarization of a ferroelectric material solely from electric field data [33].



Figure I.9: The loop depicting the relationship between polarization and electric field (P vs.E) that emerges when an external field is applied, then removed, and subsequently reapplied to a ferroelectric sample [33].

In the case of a common ferroelectric material, the spontaneous polarization generally diminishes as the temperature (T) rises. Subsequently, it vanishes in either a continuous manner (second-order phase transition) or, more frequently, undergoes a discontinuous transition (first-order phase transition) at a specific critical temperature referred to as the Curie temperature (T_C)[34]. Ferroelectrics experience a change in their structural phase as they cross the Curie point, with the phase occurring above T_C being referred to as the paraelectric phase. It is widely accepted that the formation of the ferroelectric structure involves breaking the symmetry found in the paraelectric structure. This break in symmetry leads to the existence of multiple potential polarization states in the low-symmetry ferroelectric phase, as illustrated in **Figure I.10 (a)** by the presence of two minima separated by a potential energy barrier (ΔE) [35]. In the paraelectric phase (T > TC), only a single minimum is present, and there is no occurrence of spontaneous polarization, as depicted in **Figure I.10 (c)**.



Figure I.10: Correlation of free energy (G) and polarization (P) across temperature variations in a first-order phase transition [35].

I.2.9.3. Ferroelectric domains:

In ferroelectric materials, domain structures characterized by uniformly oriented spontaneous polarization (Ps) emerge during the transition from a paraelectric phase to a ferroelectric phase. This transition aims to minimize the overall free energy within the system [36], [37], [38]. This energy arises from both the electrostatic energy of depolarizing fields (E_d) and the elastic energy linked to mechanical constraints. The spaces located between various domains are known as domain walls. These walls that divide two neighboring domains can be grouped into two primary categories: 180° domain walls and non-180° domain walls. The 180° domain walls separate two domains with opposing spontaneous polarization directions, while the non-180° domain walls separate domains with polarization angles different from 180°. **Figure I.11** illustrates the generation of 180° and non-180° (90°) ferroelectric domain walls in a tetragonal perovskite ferroelectric material like PbTiO₃ [38].



Figure I.11: Generation of 90° and 180° ferroelectric domain walls in a tetragonal PbTiO₃, adapted from Damjanovic [38].

I.2.9.4 Polar nanoregions

The examination of polar nanoregions (PNRs) in relaxor ferroelectrics (REFs) presents an intriguing avenue for comprehending their unique physical attributes. In the context of ferroelectric materials, substantial domains featuring specific dipole moments exhibit a random distribution within the material. Upon the application of an electric field, the domains align themselves in the direction of the accompanying field, resulting in the development of macroscopic polarization [39]. Polarization is further augmented by the electric field until it reaches its maximum polarization (Pm). Typically, conventional ferroelectrics display significant values for characteristic parameters such as Ps (spontaneous polarization), Pr (remnant polarization), Ec (coercive field), and hysteresis loss. However, it is of particular interest to note that the replacement of ions (cations) in the parent compounds with a limited number of foreign ions, characterized by varying ionic charges and radii, leads to the disruption of the long-range ferroelectric polar order domains. Consequently, these domains are transformed into a multitude of polar islands, which are recognized as PNRs [40]. Within the current context, the primary factor associated with the emergence of PNRs is attributed to the development of inherent material heterogeneity resulting from compositional variations at crystallographic sites and structural alterations in the unit cell [30]. As the percentage of nano domains increases, it is noticeable that the ferroelectric hysteresis loop becomes narrower, characterized by reduced hysteresis loss. This phenomenon occurs due to the diminishing correlation length between the order parameters, specifically the dipole moments [41].

I.2.9.5.Classification of symmetry classes

From a crystallographic standpoint, crystals are systematically classified into 32 symmetry point groups. These groups are subsequently divided into two distinct categories: 21-point groups characterized by non-centrosymmetric attributes, and 11 groups exhibiting centrosymmetric properties. Notably, piezoelectric materials exclusively fall within the non-centrosymmetric point groups, with the sole exception being the (432) point group [42]. In the context of non-centrosymmetric point groups, only half of them, specifically 10, exhibit pyroelectricity, indicating that their spontaneous polarization undergoes temperature-dependent changes. **Figure I.12** illustrates a simplified diagram categorizing ferroelectric materials based on crystal symmetry. The responsiveness of ferroelectric materials to temperature is attributed to the configuration of ions within their crystal lattice, designed to minimize internal energy. Consequently, fluctuations in temperature alter the crystal symmetry, impacting the ferroelectric behavior of the material.



Figure I.12: Classification of ferroelectric materials based on crystal symmetry [43].

I.2.10 Piezoelectricity

The discovery of the phenomenon of piezoelectricity dates back to the year 1880, when the brothers Pierre and Jacques Curies conducted pioneering research. Their observations revealed the unique property of certain crystals, including quartz, Rochelle salt, tourmaline, and cane sugar, to generate electric charge at specific locations on their surfaces when subjected to compression along a defined direction. This phenomenon, now recognized as the direct piezoelectric effect, was thus identified.

In the following year, 1881, the French Physicist Gabriel Lippmann prophesied the existence of the inverse phenomenon, where strain develops in a material in response to an applied electric field. The validity of Lippmann's prediction was experimentally substantiated by the Curie brothers within the same year. This reciprocal manifestation is now acknowledged as the indirect, inverse, or converse piezoelectric effect.

As a result, a piezoelectric material is defined as "a material possessing the inherent ability to convert mechanical energy into electrical energy and vice versa." A material exhibiting piezoelectric behavior must be dielectric and lack a center of symmetry [44].

I.2.11Pyroelectricity

In 1824, Theophrast first documented the discovery of the Pyroelectric effect in tourmaline [45]. This phenomenon manifests in crystals possessing spontaneous polarization and is also observed in materials retaining remanent polarization. As previously mentioned, it is important to recognize that pyroelectricity is a characteristic inherent to all ferroelectric materials, yet it does not hold true that all pyroelectric materials possess ferroelectric properties. In the event of a slight and even temperature change, ΔT , occurring within the crystal, the corresponding adjustment in the spontaneous polarization vector, denoted as ΔPi , is formally expressed as follows:

$$\Delta Pi = p_i \Delta T$$
 Eq. I.24

In this context, p_i denotes the pyroelectric coefficient, a three-component vector describing the change in electrical charge per unit surface area resulting from a minor temperature fluctuation. The unit of measurement for the pyroelectric coefficient is either C/m²·K or μ C/m²·K [46].

I.2.12 Utilization of ferroelectric materials

The utilization of ferroelectric materials holds a pivotal position across a wide spectrum of technical devices. The incorporation of advanced ferroelectric materials significantly elevates the technological capabilities and overall performance of these devices [47].



Figure I.13: Utilization of ferroelectric materials in a range of electronic devices.

- Ferroelectric materials find application in capacitors due to their favorable permittivity.
- Information storage devices benefit from ferroelectric materials because of their nonvolatile properties.
- These materials are employed for energy storage purposes.
- Ferroelectric materials exhibit piezoelectric properties, making them valuable as sensors in various fields.
- The pyroelectric properties of ferroelectric materials make them suitable for applications in infrared sensors and detectors.
- These materials possess robust nonlinear optical effects, which are harnessed for optical mixing and doubling purposes.

I.2.13 Na_{0.5}Bi_{0.5}TiO₃-Based ceramics (NBT)

I.2.13.1 Structural properties

In the year 1960, Smolensky and their associates achieved a seminal discovery pertaining to a promising piezoelectric material devoid of lead, known as sodium bismuth titanate, or Na $_{0.5}$ Bi $_{0.5}$ TiO₃ (NBT) [48, 49]. NBT represents a perovskite conforming to the ABO₃ crystallographic structure, with the A-site being jointly occupied by sodium cations (Na⁺) and bismuth ions (Bi ³⁺), while the B-site is exclusively populated by titanium ions (Ti ⁴⁺). The A-

site ions are positioned at the eight corners of the octahedral framework, and the B-site ions are situated at the body center of the same octahedral structure [50,51].

Initially, NBT was regarded as a ferroelectric at room temperature. However, recent studies have revealed that it behaves as a non-ergodic relaxor, as evidenced by its hysteresis loop, dielectric properties, and structural changes with temperature (e.g., [52])

Important features of NBT material include the following:

- One interesting feature of NBT is its ability to substitute the A-site cation in the perovskite structure, resulting in a chemically stable molecule [53].
- NBT demonstrates a unique behaviour in relation to phase transitions that are influenced by temperature. During the cooling process, NBT experiences a sequence of phase transitions, beginning with a paraelectric phase and progressing to an anti-ferroelectric phase, ultimately reaching a ferroelectric phase [54].

I.2.13.2 Phase formation

Aksel and Jones [55] investigated the phase formation of NBT during the conventional solid-state synthesis through in situ high-temperature diffraction. In this process, the initiation of NBT perovskite formation occurred at approximately 425 °C, with the reaction completing around 600 °C. Intermediate phases, including Bi₄Ti₃O₁₂ (BTO) and Bi₁₂TiO₂₀ (BTO), are anticipated to emerge above 500 °C. Notably, BTO was also identified as an intermediate phase during the pre-sintering stage of NBT prepared through hydrothermal synthesis and the citrate method [56, 57].

I.2.13.3 Ion Substitution

Several researchers have investigated the substitution of trivalent rare earth ions at either the A or B-site in NBT or NBT based systems. The impact of substituting rare earth ions La^{3+} / Ce^{+3} / Sm^{+3} in NBT on the diffused dielectric phase transition, diffusivity (c) based on the modified Curie-Wiess law, and the presence of a non-Debye type of relaxation process associated with grain and grain boundary conduction was documented through complex impedance studies [58,59].

Watanabe et al. [60] observed partial substitution of lanthanoid ions for A site elements such as La, Nd, Sm, Ho, and Yb. The piezoelectric coefficient gradually increases with increasing substitution concentration, reaching a maximum d₃₃ value of 90 pC/N in Nd-doped

composition (0.015 mol %). Furthermore, when the amount of lanthanoid doping increases, the depolarization temperature Td decreases while the temperature at maximum dielectric constant Tm increases, both of which are directly connected to the ionic radius of replacement ions. Yang et al. [61] discovered that isovalent doping (such as RE³⁺ to replace Bi ³⁺) resulted in a considerable decrease in conductivity inside the NBT system, which was linked to the rare-earth elements lower polarizability.

Herabut et al..[62] Investigated the piezoelectric properties of Na $_{0.5}$ Bi $_{0.5}$ TiO₃ ceramics doped with La. The greatest reported piezoelectric coefficient (d₃₃) was 91 pC/N in the presence of 2% La. The microstructure exhibited second phases, the Curie temperature was approximately 100°C, and the grain size was less than 10 μ m.

Aksel et al. replaced the A-site with La^{3+} at concentrations of 0.5, 1.0, and 1.5 %. The remnant polarisation (Pr) increased by 5 μ C/cm² and the coercive field (E_c) reduced by 5 kV/mm as a result of this substitution, which took place at a rate of 1.5 at% La. With a 60 °C drop in Td from unmodified to 1.5 at % La modified NBT, the depolarization temperature (Td) declined steadily with increasing La content. Although the device application benefits from this characteristic, the relaxing properties of NBT are unaffected by La replacement [63]

The temperature ranges indicating phase coexistence are presented in **Figure I.14** [64]. The transition from rhombohedral to tetragonal phases initiates at approximately 250 °C and exhibits a considerably broad transition span, exceeding 100 °C. Conversely, the transition from tetragonal to cubic phases occurs at approximately 500 °C, with a narrower transition range of about 20 °C. Traditionally, the depolarization temperature, typically at 190 °C, is expected to coincide with a structural transition. However, in this case, the rhombohedral-tetragonal phase transition begins at a higher temperature of approximately 250 °C. This observed disparity is believed to stem from the decrease in the volume fraction of the monoclinic phase as temperature rises. This reduction, in turn, leads to the loss of long-range ferroelectric order, ultimately giving rise to the antiferroelectric tetragonal structure [65].



Figure I.14: Phase volume as determined through neutron diffraction analysis by [64]. Areas marked in orange indicate the broader temperature range of the phase transitions.

Conclusion

In conclusion, the background knowledge on the fundamental concepts and principles that serve as the foundation for the research presented in this thesis has been established in this chapter. The fundamentals of photocatalysis and the unique properties of ferroelectric materials have been thoroughly explored, setting the stage for the more detailed investigations and novel findings that will be discussed in the upcoming chapters.

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Chapter II

Synthesis & Characterization Techniques

II.1.Introduction

The experimental chapter of this thesis is designed to offer a thorough summary of the diverse techniques and procedures that are employed in the synthesis, characterization, and performance evaluation of the materials being investigated. The methodologies employed in this research work will be described in detail in this chapter.

Initially, we will provide an explanation of the NBT-RNFS materials' synthesis approach that was chosen. Detailed descriptions of the primary stages, reaction conditions, and equipment employed during the synthesis process will be included. The rationale behind the chosen synthesis method will be discussed, highlighting the advantages and considerations that led to its selection.

Following the synthesis, several characterization techniques will be used to verify the structure, composition, and purity of the NBT-RNFS that has been synthesized. The techniques employed include X- rays diffraction (XRD) for determining the phases present, Fourier-transform infrared (FTIR) spectroscopy for analyzing functional groups, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) for examining morphology and elemental composition, Raman spectroscopy for investigating structural characteristics, Brunauer-Emmett-Teller (BET) method for surface area measurement, UV-Visible spectroscopy for studying optical properties, and thermogravimetric analysis with differential thermal analysis (TGA-DTA) for evaluating thermal stability. Detailed information regarding the specific experimental parameters and data analysis methodologies for each characterization methodology will be supplied.

II.2 Choice of materials and dopants:

In this study, we developed a new perovskite material with the following composition: $(Na_{0.5}Bi_{0.5})_{0.94} R_{0.04}Ti_{0.95} (Ni_{0.2} Fe_{0.2} Sb_{0.6})_{0.05}O_3$. The A-site rare earth (RE) dopants are La, Nd, Gd, and Y, while the B-site composition remains fixed as Ti $_{0.95}$ (Ni_{0.2} Fe_{0.2} Sb_{0.6}) $_{0.05}$.

The incorporation of rare earth (RE) elements such as lanthanum (La), neodymium (Nd), gadolinium (Gd), and yttrium (Y) to the A-site leads changes in the crystal structure, valence state, and functional properties such as dielectric features and catalytic activity.

This systematic strategy for A-site doping with RE elements, which preserves a fixed B-site composition, enables the targeted developing of the structural, electronic, and functional attributes of the $(Na_{0.5}Bi_{0.5})_{0.94}R_{0.04}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$ perovskite materials.

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The material synthesis in this study was carried out using the solid-state reaction technique. This method was selected for its numerous advantages. The solid-state reaction method is a cost-effective, efficient, and reliable method for synthesis of materials, offering superior performance, reliability, reproducibility, and economic advantages compared to other techniques. These factors made the solid-state reaction an attractive choice for the purposes of this investigation, as it offered a straightforward and cost-effective means of material synthesis while maintaining high quality and consistency in the final products [1].

II.3 Experimental Details

The samples were synthesized through a multi-stage procedure, utilizing commercially available precursor materials. The samples, identified by the abbreviations listed in **Table 1**, were prepared using conventional solid-state synthesis method. The raw materials were precisely weighed in the stoichiometric proportions required for the desired ceramic compositions.

Abbreviations	Samples
NBT-NFS	$(Na_{0.5}Bi_{0.5})Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$
NBT-LNFS	$(Na_{0.5}Bi_{0.5})_{0.94}La_{0.04}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$
NBT-NNFS	$(Na_{0.5}Bi_{0.5})_{0.94}Nd_{0.04}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$
NBT-GNFS	$(Na_{0.5}Bi_{0.5})_{0.94}Gd_{0.04}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$
NBT-YNFS	$(Na_{0.5}Bi_{0.5})_{0.94}Y_{0.04}Ti_{0.95}(Ni_{0.2}\ Fe_{0.2}Sb_{0.6})_{0.05}O_3$

Table II.1: Abbreviations of the prepared samples.

II.4 Solid State Reaction Method

This study investigated the synthesis and characteristics of $(Na_{0.5}Bi_{0.5})_{1-x}R_{(2x/3)}Ti_{0.95}(Ni_{1/5}Fe_{1/5}Sb_{3/5})_{0.05}O_3$ (abbreviated as NBT-RNFS) ceramics (R = La³⁺, Nd³⁺, Gd³⁺, and Y³⁺, x = 0.06). Ceramic pellets were made using the conventional solid-state reaction sintering process. All raw materials, including Bi₂O₃ (99% purity, BIOCHEM), Na₂CO₃ (99% purity, BIOCHEM), TiO₂ (99% purity, BIOCHEM), NiO (99% purity, BIOCHEM), Fe₂O₃ (99% purity, BIOCHEM), Sb₂O₃ (99% purity, Riedel-de Haen), Gd₂O₃ (99.99% purity, Alfa Aesar), La₂O₃ (99.995% purity, BIOCHEM), Y₂O₃ (99.99% purity, Alfa Aesar), and Nd₂O₃ (99.99% purity, BIOCHEM), were crushed in a glass mortar for four hours. The resultant powders were

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heated at 900 °C for 6 hours at a rate of 2 °C per minute. The powders were then shaped into cylindrical pellets 11 mm in diameter and 1 mm thick using a hydraulic press. The obtained pellets were subsequently sintered for 6 hours at an average temperature of 1150 °C with a heating rate of 2 °C/min.



Figure II.1 Flow chart used for NBT-RNFS powder preparation.

II.5 Characterization technique

II.5.1Thermal analysis (DTA)/TGA:

Differential Thermal Analysis (DTA) is a commonly used thermal analysis technique that analyzes temperature-dependent transitions in a sample, including both endothermic and exothermic reactions. The process entails measuring the temperature disparity between the sample and a reference material that remains unaffected by phase transitions, as both undergo the same heating regimen. The temperature difference that has been recorded is graphed against either time or temperature, which offers useful insights into the thermal characteristics of the sample [2]. **Figure II.2** presents a block diagram that demonstrates the fundamental operational principles of DTA (Differential Thermal Analysis). This technique involves

subjecting both the sample and reference materials to a heating program that causes them to undergo uniform temperature changes, either increasing or decreasing. When the sample undergoes a phase change, whether it is an endothermic or exothermic transition, the temperature variations are recorded [3].



Figure II.2: DTA block analyzing system.

Thermal Gravimetric Analysis (TGA) is a technique that measures the change in mass of a sample as it is subjected to varying temperatures in a gas-filled chamber. This method offers significant insights into a variety of thermal phenomena, such as the decomposition of composite materials, temperature-dependent reactions, and changes in phase. The sample is subjected to a controlled temperature protocol during a (TGA) experiment, and any changes in its mass are recorded and measured. This data can be used to identify and describe thermal phenomena in the sample, such as the decrease or increase in mass as a result of processes such as evaporation, sublimation, oxidation, or decomposition [4].

In this work, the precursor sample underwent DTA-TGA (Differential Thermal Analysis and Thermogravimetric Analysis) to explore the mechanism underlying the formation of the (Na_{0.5}Bi_{0.5}) Ti _{0.95} (Ni_{0.2} Fe_{0.2} Sb_{0.6}) _{0.05}O₃ (NBT-NFS) perovskite phase. A sample weighing

18.03 mg was subjected to heating from 40 °C to 1200 °C at a rate of 5°C/min under a nitrogen atmosphere using the SETARAM Labsys Evo-gas option machine, as depicted in **Figure II.3**. This TGA/DTA analysis was carried out at the Centre for Research in Physico-Chemical Analyses (CRAPC) laboratory in Laghouat, Algeria.



Figure II.3: DTA/TGA instrument (SETARAM Labsys Evo).

II.5.2 Density measurements

II.5.2. 1 Archimedes' Density

During the process of carrying out density measurements, a digital densitometer was utilized. In order to calculate the apparent density, the densitometer took into account both the weight of the samples when they were in air and the weight of the samples while they were in water. This calculation was carried out using the following equation [5]:

$$\rho_m = \frac{A}{A-B} \left(\rho_l - d \right) + d \qquad Eq. \text{ II.1}$$

Where ρ_m is the sample density, ρ_l is water density, d is air density (about 0.001 g/cm³), A is sample weight in air, and B is sample weight in water. Archimedes' approach works well for samples with a density above 92%, but it may not work for samples with a lower density.

The OHAUS Adventurer Balance, shown in **Figure II.4**, was utilized at the Laboratory of Photonic Physics and Multifunctional Nanomaterials (LPPNM) to experimentally measure the density of all samples.



Figure II.4: Density instrument (OHAUS Adventurer Balance).

II.5. 2.2 Theoretical Density

The theoretical density, known as XRD density or pt, was determined using Equation (1) [6].

$$\rho t = \frac{nA}{VN} \qquad Eq. II.2$$

In this equation, the variable n represents the number of atoms that are contained within the unit cell, the variable A represents the molecular mass of the composition in grammes per mole (g/mol), the variable V represents the volume of the unit cell in cubic centimetres (cm³), and the variable N represents Avogadro's constant (mol⁻¹).

II.5.2. 3 Relative Density

The relative density, designated as ρr , is calculated by Eq. (2) [6] :

$$Pr = \frac{Pm}{Pt} \times 100 \qquad \qquad Eq. \, II.3$$

II.5.3 XRD Analyses

X-Ray Diffraction (XRD) is a non-destructive, non-contact, and powerful technology that is employed to identify the phases of materials. It offers valuable insights into the structural properties of materials, including crystal size, epitaxy, phase composition, preferred orientation, and crystal defects. XRD can also be used to measure the thickness of thin films and to scrutinize the atomic arrangements in amorphous materials and at interfaces [7].

The X-ray intensities obtained from XRD analysis can offer both quantitative and qualitative information regarding the atomic arrangements at interfaces. This is a key capability of the technique. X-rays are a form of electromagnetic radiation with very short wavelengths (λ), ranging from 0.10 to 10 (nm). This corresponds to photon energies between 100 (eV) to 100 (keV).

X-ray tubes generate X-rays by using high-energy electrons to bombard target materials like copper (Cu), molybdenum (Mo), and cobalt (Co). These target materials emit X-rays with specific wavelengths (1.54 Å for Cu, 0.8 Å for Mo, and 1.79 Å for Co) and energies (8 keV for Cu, 14 keV for Mo, and 14.5 keV for Co) when hit by the accelerated electrons within the tube anode .

X-rays are generated when accelerated electrons interact with the electrons in the tungsten nuclei within the tube anode [8]. Bragg's law describes the relationship between the angle at which an x-ray beam strikes a crystal surface and the angle at which the x-ray beam is reflected off that crystal surface. The Bragg's law schematic diagram in **Figure II.5** illustrates the relationship between the angle of incidence (θ), the whole number (n), and the path difference (d) [9].



Figure II.5: Schematic representation of Bragg's law.

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In this study, XRD analysis was employed in this investigation to determine the crystal structure and phase composition of unprocessed materials, calcined phases, and final sintered ceramic samples. Two diffractometers were utilized - an AMPYREN system at the CRAPC laboratory in Laghouat, and a Bruker system at the CRAPC laboratory in Biskra, Algeria.

Both diffractometers used Cu K α (λ = 1.5418 Å) radiation, scanning a 2 θ range of 20-80° with a 0.02° step size. Measurements were performed at 40 kV and 30 mA., as shown **in Figure II.6**.



(a)

(b)



II.5.4 .The Rietveld Refinement Method

In this approach, the refinement of the powder diffraction pattern is carried out utilizing the mathematical model devised by H. M. Rietveld [10, 11]. In accordance with his approach, a crystallographic model undergoes refinement through the minimization of the variance between the measured diffraction pattern points and the calculated pattern using the least squares method.

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$$X^{2} = \sum_{i} \frac{/obs_{i}^{2} - Calc_{i}^{2}}{obs_{i}^{2}}$$
 Eq. II.5

The Rietveld refinement method, named after the Dutch physicist Hugo Rietveld, is an analytical technique that enables the refinement of several fundamental parameters. These parameters can be broadly categorized as follows: [12].

- Parameters related to the structure of the specimen include unit cell parameters (a, b, c), atomic coordinates (x, y, z), site fractions, and phase fractions.
- Parameters associated with the peak profile encompass both shape parameters— Lorentzian and Gaussian (U, V, W)—and positional parameters (X, Y, Z) along with their respective ratios.
- \circ Intensity corrections dependent on 2 θ due to absorptions include adjustments related to sample parameters such as histogram scale factor, sample displacement, surface roughness, and sample transparency.
- Parameters concerning peak shape encompass instrumental calibration parameters, thermal parameters (Uij), preferred orientation, micro strainetc
- o Background (background fitting functions and their coefficients)

II.5.5 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS/EDX)

Scanning Electron Microscopy serves as a preeminent tool in the examination of material surface topography. This microscopy technique produces magnified images characterized by high resolution, thereby facilitating the detailed analysis of surface features or topographical attributes of bulk materials, including particle/grain size, porosity, and the potential presence of secondary phases [13].

The EDX analysis technique is frequently employed in conjunction with SEM instruments to ascertain the chemical composition of materials. EDX analysis relies on the principle that each element possesses a distinctive atomic structure, resulting in a unique set of peaks in its X-ray spectrum [14].

The microstructure and chemical composition of the pellet samples were thoroughly characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) at the CRAPC laboratory in Biskra. SEM analysis of the pellet cross-sections was performed with a high-resolution Thermo Scientific Prism E instrument, providing detailed information on grain size, morphology, and potential defects like pores.

Complementary EDS mapping was conducted, with an acquisition time of 60 seconds per element, to precisely determine the elemental distribution within the samples.



Figure II.7: SEM instrument (Thermo Scientific Prism E).

II.5.6 ATR-FTIR spectroscopy

FT-IR spectrometers, as denoted by their nomenclature, utilize a Fourier transform to generate a spectrum illustrating absorbance intensity in relation to wavenumber. Distinguishing themselves significantly from UV-vis spectroscopy, these spectrometers diverge in their acquisition method. Contrary to the generation of monochromatic radiation (termed "dispersive

measurement"), FT-IR spectrometers utilize a wide-range IR source, enabling the capture of an entire spectral window through a solitary acquisition [15].

Every chemical bond, whether within solids or molecules, possesses specific vibrational modes that are quantized. These modes, functioning as oscillators, have the capacity to assimilate photons of energy aligned with the oscillator's transition. Consequently, the absorption spectrum serves as a representation of the chemical bonds present in the sample, granted they exhibit infrared (IR) activity, indicating a dipole moment capable of absorbing electromagnetic radiation. Fourier Transform-Infrared Spectroscopy (FTIR) stands as an analytical technique utilized to discern organic materials (and occasionally inorganic ones) by measuring the absorption bands are instrumental in identifying molecular constituents and structures. Upon exposure to infrared radiation, a material typically undergoes excitation into a higher vibrational state due to absorbed IR radiation. The wavelength of light absorbed by a specific molecule is contingent upon the energy disparity between its static and excited vibrational states. Hence, the absorbed wavelengths by the sample delineate its distinctive molecular structure [16].

Bonds within molecules vibrate at various frequencies, determined by the elements present and the bond types. Each bond exhibits specific vibrational frequencies. According to quantum mechanics, these frequencies correspond to both the ground state (lowest frequency) and numerous excited states (higher frequencies). One method of increasing a molecular vibration's frequency involves exciting the bond through the absorption of light energy. The transition between these states occurs with an energy equivalent to the difference between the ground state and the excited state energies [17].

Infrared (IR) spectroscopic analyses were conducted on the samples using an Agilent Cary 630 Fourier-transform infrared (FTIR) spectrometer.





II.5.7 Raman Spectroscopy

The Raman technique has gained increased versatility in examining various behaviors and is employed in the examination of oxide materials, particularly for identifying nuanced structural distortions in perovskite materials, even when these distortions are too subtle to be discerned by diffraction techniques [18, 19]. Due to the vibrational spectrum's shorter characterization length scale compared to that needed for diffraction experiments, this technique serves as an exceptional microprobe for discerning local structural details crucial for interpreting the properties of ferroelectric materials [19], [20], [21]. The emergence of local structural deformations stems from the disparity in ionic radii between the host and dopant [22]

The "Raman" technique entails focusing (using a lens) a monochromatic light beam on the sample to be tested and then evaluating the dispersed light. Monochromatic ultraviolet (UV), visible (Vis), and near infrared (NIR) radiation can be used to excite light [23]. The majority of incident photons are transmitted, reflected, or absorbed, with a much smaller fraction scattered at the same frequency v0 as the incident radiation, known as Rayleigh scattering (elastic scattering), or with a frequency change, known as Raman scattering (inelastic scattering) (**Fig. II.9**).



Figure II.9. A simple schematic of Various Scattering and Fluorescence Mechanisms - Rayleigh (Blue) and Anti-Stokes Raman (Red) [24].

In the course of our research, we utilized the Horiba LabRAM HRT 4600 HR800 Raman spectrometer, available at the LMMA (The Laboratory of Multifunctional Materials and Applications, Tunisia), as shown in **Figure II.10.**



Figure II.10 .RAMAN Spectrometer (Horiba LabRAM HRT 4600 HR800).

II. 5.8 UV – Visible spectroscopy

The Tauc relation is commonly used to determine optical band gaps [25], as shown below:

$$(\alpha hv)^{1/n} = A(hv - Eg)$$
 Eq. II.4

In this formula, α represents the absorption coefficient, h is Planck's constant, v represents the vibrational frequency, A is a constant, and Eg is the band gap energy. The value of n determines the nature of the optical transitions, with n = 1/2 and 2 indicating direct and indirect allowed transitions, respectively. To obtain the band gap values, the plot of $(\alpha hv)^{1/n}$ vs hv is examined at the inflection point, and linear regression is performed. The intercept of the obtained abscissa (hv) corresponds to the optical band gap values.

In this thesis, UV-visible absorption spectroscopy was performed using the PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer (**Fig. 11**).



Figure II.11: UV Visible instrument (PerkinElmer LAMBDA 950 spectrophotometer).

II.5.9 Classification of Adsorption Isotherms

In addition to offering detailed characterizations, the configuration of the adsorption isotherm can yield substantial insights into both the extent of adsorption and the porous structure of solids. A variety of isotherm types have been documented in literature, with the majority falling into six distinct classes, as depicted in **Figure 12**. Isotherms categorized as types I to V were originally introduced by Brunauer, Deming, Deming, and Teller, collectively known as the BDDT classification. The BDDT classification serves as the foundation for the contemporary classification established by IUPAC in 1985, which includes the addition of a type VI isotherm designed for surfaces exhibiting an exceptionally homogeneous structure [26], [27], [28].

The Type I isotherm approaches a limiting value and is typically used to describe adsorption on microporous adsorbents [29]. Type II and Type III isotherms indicate the adsorption process on macroporous adsorbents, with strong and weak adsorbate-adsorbent interactions, respectively [30].

The adsorption isotherms of Types IV and V represent mono- and multilayer adsorption, respectively, as well as capillary condensation. Type VI adsorption isotherms, which were not included in the original Brunauer classification, demonstrate that adsorption isotherms can have one or more steps[31].



Figure II.12: Five types of adsorption isotherms in BDDT classification [26].

II.5. 10 The BET technique

The Brunauer-Emmett-Teller (BET) volumetric gas adsorption technique, employing N₂ or Ar, serves as a standard method for determining the surface area and pore size distribution of finely divided porous materials. The relationship between the amount of gas adsorbed and the equilibrium pressure at constant temperature, defined as the adsorption isotherm, forms the basis for surface area calculations. The BET equation, derived by Brunauer, Emmett, and Teller to describe physical gas adsorption on solid surfaces leading to multilayer adsorption, provides the most popular and widely used method for surface area calculation in scientific literature [32].This equation can be condensed to:

$$\left[\frac{1}{V}\right]\frac{P_{P_0}}{\left(1-\frac{P}{P_0}\right)} = \left[\frac{1}{V_m c}\right] + \frac{c-1}{V_m c} P_{P_0} \qquad Eq. \, \text{II.5}$$

The BET equation, relating the adsorbed gas volume (V_a) at pressure p to the saturated vapor pressure (p_o) and monolayer capacity (V_m), allows surface area determination. Plotting $p/V_a(p_o-p)$ vs. p/p_o in the 0.05-0.35 pressure range yields a straight line whose slope provides Vm. Surface area is then calculated using V_m and an isothermal constant (c).

In the course of this research, the specific surface areas of the samples were determined using the Brunauer-Emmett-Teller (BET) method. The BET analyses were conducted using the Quantachrome® ASiQwin[™] Automated Gas Sorption Data Acquisition and Analysis System, which is available at the Constantine Laboratory (**Fig. 13**).



Figure II.13: BET instrument.
II.5.11 BJH method

The Barrett-Joyner-Halenda (BJH) method, based on nitrogen adsorption-desorption isotherms, is designed to determine the pore volume and pore size distribution in porous materials. This method establishes a correlation between the volume of capillary-condensed adsorbate and the relative pressure. The BJH method postulates a model with open-ended cylindrical pores and a desorption mechanism that initially saturates the pores with liquid adsorbate. As the pressure decreases, the physically adsorbed layer gradually becomes smaller. The total pore volume is determined by measuring the amount of nitrogen vapor that is adsorbed. The pore volume is used to estimate the average pore size, with the value being determined by the pore radius (assuming cylindrical geometry) at which the pore volume is maximized [33].

II.5.12 t-plot model (surface area, micropore and mesopore volume)

The t-plot method is one of several techniques proposed to determine the volume of micropores accessible to a particular gas adsorbate. The simplest approach to determine a sample's microporous volume is the t-method developed by de Boer. This method entails comparing the adsorption isotherms of the specific porous solid with standard isotherms obtained from non-porous reference materials that have a similar chemical composition. The original t-method involves plotting the adsorbate uptake versus the statistical thickness (t) of the adsorbed multilayer, which is determined using the standard isotherm. **Figure 14** depicts the common variations of t-plots [34].



Fig. II.14: Typical t-plot generated from adsorption isotherms on mesoporous, microporous and nonporous samples [35].

The presence of micropores in a material can greatly influence its adsorption behavior. As the micropores become progressively filled, the overall adsorption surface area decreases, causing the slope of the t-curve to decrease until the micropores are fully filled. After the filling of micropores, the t-curve is expected to show a linear pattern with a slope corresponding to the external area of the micropores. The point where this line intersects the t-axis at t=0 provides the volume of adsorbate necessary to fill the micropores [36, 35].

For solids containing mesopores, the t-plot displays a characteristic shape. Initially, there is a noticeable increase in the deviation from a straight line, which indicates the occurrence of capillary condensation in the mesopores. Once the mesopores are completely filled, the t-plot exhibits a new straight-line segment, whose slope reflects the lower external surface area. Importantly, the y-intercept of this last straight line is crucial as it reveals valuable insights into the mesopore volume and, if applicable, the micropore volume of the material. This distinctive t-plot shape, with an initial upward deviation followed by a straight line after mesopore filling, allows for the determination of the mesopore and micropore volumes in porous solids [36] [35].

II.5.13 Dielectric spectroscopy

The induction of dipole moments or the rotation of permanent electric dipoles intrinsic to a dielectric material causes a polarization when the substance is exposed to an electric field [37].

In order to evaluate the electrical properties of the sintered pellets, a silver substance was dabbed onto each side of the pellets prior to subjecting them to a ten-minute firing procedure at 550 °C. **Figure 15** depicts the experimental illustration utilized to quantify the dielectric properties of the ceramic pellets. The dielectric properties were assessed using an Agilent HP 4284A Precision LCR Meter across a frequency range of 100 Hz to 1 MHz In this context, L denotes inductance, C signifies capacitance, and R signifies resistance. The ceramic specimens, which had been silver-coated, were placed in the configuration illustrated in **Figure 16** within a tube furnace. The automated recording of the furnace's interior temperature was made possible through the connection of the LCR meter and temperature controller to a computer.



Figure II.15 illustration of the pellet for dielectric measurements [38].

The relative permittivity, also referred to as the dielectric constant, was determined by applying the following equation [39].

$$\varepsilon' = \frac{c_p d}{\varepsilon_0 A}$$
 Eq. II.6

In this context, C_P represents the capacitance of the pellet, ε' denotes the dielectric constant, ε_0 signifies the permittivity of free space (8.854 ×10⁻¹² F/m), and A stands for the pellet's area. The variable "d" represents the thickness of the pellet. The loss tangent (tan δ) was calculated using the following equation [39] [40].

$$\varepsilon'' = \varepsilon' \tan \delta$$
 Eq. II.7

where ε "is the loss factor.

The relaxor behavior of the ceramics was defined by determining the diffusivity parameter (γ) using the modified Curie-Weiss equation (Eq.10) [41]

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{c}; T > T_m \qquad Eq. \text{ II.8}$$

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Where ε is the dielectric constant at temperature T, ε_m at temperature Tm, C is the Curie constant, and γ is the phase transformation diffusivity coefficient. Values of γ range from 1 to 2. If $\gamma = 1$, the material exhibits ferroelectric qualities, while $\gamma > 1$ indicates relaxor ferroelectric behavior.



Figure II.16: Dielectric characterization.

Conclusion

In conclusion, this chapter has provided an exhaustive and detailed account of the experimental methodologies used in the synthesis, characterization, and performance evaluation of the NBT-RNFS materials that were the subject of this research.

Various advanced characterization methods have been used to thoroughly investigate the structural, compositional, and functional features of the NBT-RNFS materials in their original state. The techniques employed are X-rays diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX), Raman spectroscopy, Brunauer-Emmett-Teller (BET) surface area measurements, UV-Visible spectroscopy, and thermogravimetric analysis with differential thermal analysis (TGA-DTA).

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Chapter III

Study of the Reaction Sequences and Structural-Microstructural Properties of the Novel Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃ Solid Solution

Introduction:

The present chapter provides an overview of the distinctive material manufacturing and reaction mechanisms associated with Na_{0.5}Bi_{0.5}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃ (NBT-NFS) material. The synthesis was conducted at temperatures lower than 1150°C. The primary objective of this research is to analyse the formation mechanism of a solid perovskite solution in the presence of doping elements such as Ni, Fe, and Sb, in particular within the NBT (Na_{0.5}Bi_{0.5}TiO₃)-based configuration. The fundamental aim of this research is to deduce and examine the reaction pathways that culminated in the solid solution's development.

The second part, we will focus on the structural and microstructural properties of NBTdoped with rare earth elements, denoted as $(Na_{0.5}Bi_{0.5})_{0.94}R_{0.04}Ti_{0.95}$ (Ni $_{0.2}$ Fe $_{0.2}Sb$ $_{0.6})$ $_{0.05}O_3$ where RE = La, Nd, Gd, and Y. Rare earth elements have been widely employed as dopants in different ceramic materials to modify their structural, electrical, and optical properties. In the case of NBT-NFS, the incorporation of rare earth elements is expected to induce changes in the crystal structure, phase stability, and microstructural features of the material.

We will study the effects of rare earth doping on the crystal structure, lattice parameters, phase composition, and microstructural characteristics of the $(Na_{0.5}Bi_{0.5})_{0.94}R_{0.04}Ti_{0.95}$ $(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_3$ solid solutions. This investigation will provide insights into the relationship between the rare earth dopants and the structural/microstructural properties of the NBT-RNFS materials.

Part A: The Study of reaction sequences for the formation of a novel solid solution: Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃

III 1.1. Previous works:

Considerable research efforts have been devoted to the examination of pure Bismuth sodium titanate ($Na_{0.5}Bi_{0.5}TiO_3$), popularly known as NBT, which is seen as a promising alternative to PZT without the presence of lead. Previous research has demonstrated the existence of intermediary phases, such as $Bi_2Ti_2O_7[1]$, [2], $Bi_{12}TiO_{20}[3]$, [4], and $Bi_4Ti_3O_{12}[3]$, [5], [1] in the calcination procedure of NBT. These phases have been suggested to have a substantial impact on the production of perovskite [2], [6].

The endothermic interaction between the initial components has been found to be favourable during the temperature range of 650 to 900°C [7]. Moreover, the processes responsible for the creation of NBT have been clarified, which entail the interaction between templates having precise ratios of oxides and carbonates with $Bi_3Ti_4O_{13}$ [8] [9], [10], or $Na_2Ti_6O_{13}$ [11].

III 1.2 Experimental part:

The synthesis of a novel ceramic material, Na_{0.5}Bi_{0.5}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃, involves multiple sequential processes, as shown in Figure III.1. First, the required amounts of raw materials are calculated and weighed. The mixture of oxides is then manually ground using a glass mortar for four hours. The resulting powder is compressed into pellets, each one weighing 1g. These pellets are subjected to calcination at temperatures ranging from 300°C to 1150°C, with a heating rate of 2°C / min. The calcination process occurs in a programmed oven under ambient atmospheric conditions. The X-rays diffraction (XRD) analysis is conducted using a BRUKER-AXE D8 instrument with CuKα radiation. The XRD results, particularly the peak positions, are subsequently compared with the information contained in the Joint Committee on Powder Diffraction Standards JCPDS database. The objective of this comparative study is to determine the presence of the perovskite structure and identify the phases present in the studied samples. By matching the recorded peak positions with those in the database, we can determine the structural characteristics of the synthesised ceramic material. In addition to the XRD analysis, we will also conduct further thermal analyses using TGA/DTA (SETARAM Labsys Evo - gas option). These thermal analyses will include a temperature range of 40 to 1200°C with a heating rate of 5°C/min.



Figure III.1: Flow chart for preparation of Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃.

III 1.3 NBT-NFS samples at different temperatures treatment:

The NBT-NFS ceramic samples were subjected to calcination at varying temperatures, leading to a significant disparity in coloration. Different colours changed on the samples as the sintering temperature went from 300°C to 1150°C. The calcined pellets are shown in **Figure III.2**. At first, the sample had a brick red colour. However, when the temperature reached 700°C, a light yellow color began to show. The color changed to a dark yellow as the temperature increased .The change in hue can be attributed to the volatilization process of the A-site element originating from the NBT-NFS ceramics [12].



Figure III.2: Colour of NBT-NFS pellets at different calcination temeratures.

III 1.4 DTA-TGA results:

The resultant precursor underwent DTA-TGA analysis to investigate its decomposition under nitrogen and determine the optimal calcination conditions. The DTA-TGA curves in **Figure III.3** depict the thermal characteristics of the sample under examination. The thermogravimetric analysis (TGA) curve illustrates a sequence of weight reductions associated with three distinct thermal regions. At first, there is a decrease in weight of 7.357% within the temperature range of 31.35°C to 441.95°C, which is caused by the evaporation of water from the samples. Following this, a reduction in weight of 1.297% is seen within the temperature range of 441.12°C to 599.24°C, which can be attributed to the disintegration of the precursors. The decarbonisation process results in an additional reduction in weight of 3.298% within the temperature range of 599.88°C to 836.95°C. At the same time as decarbonisation occurs, the ultimate solid-solid synthesis reaction occurs. Although the reaction does not lead to a decrease in mass, it is distinguished by a prominent endothermic peak observed at a temperature of 836.95°C. The lucidity of this endothermic peak makes it a dependable signal of the full synthesis reaction of NBT-NFS, enabling accurate monitoring of the synthesis process [13].

Chapter III: Study of the Reaction Sequences and Structural-Microstructural Properties of the Novel Na0.5Bi0.5Ti0.95 (Ni0.2Fe0.2Sb0.6) 0.05O3Solid Solution



Figure III.3: DTA and TGA curves of the precursor used to elaborate $Na_{0.5}Bi_{0.5}Ti_{0.95}$ ($Ni_{0.2}Fe_{0.2}Sb_{0.6}$)_{0.05}O₃ material under N₂ flushing over the temperature range from 40 to 1200 °C, with a heating rate of 5 °C min⁻¹.

III 1.5. Phase analysis of raw materials:

The synthesis of the novel Na 0.5Bi 0.5Ti 0.95 (Ni 0.2 Fe 0.2Sb 0.6) 0.05O3, perovskite involves the use of six raw materials: nickel oxide (NiO), iron(III) oxide (Fe₂O₃), antimony(III) oxide (Sb₂O₃), titanium oxide (TiO₂), bismuth oxide (Bi₂O₃), and sodium carbonate (Na₂CO₃). Among these, the three principal precursors used in larger amounts are TiO₂, Bi₂O₃, and Na₂CO₃. The reaction kinetics and phase formation during perovskite synthesis can be considerably influenced by the phase purity and crystalline structure of these three principal raw materials. It is imperative to conduct a thorough characterization of these three primary raw materials, which includes the use of X-rays diffraction (XRD) to compare the experimental patterns to the standard ASTM reference data. The diffractograms of the three principal raw materials - TiO₂, Bi₂O₃, and Na₂CO₃ - are all in good agreement with the respective ASTM reference patterns: anatase TiO₂ (98-004-4882), rutile TiO₂ (98-005-1941), Bi₂O₃ (01-072-0398), and Na₂CO₃ (00-037-0451). This phase identification process helps the confirmation of the presence and purity of the intended precursors, the identification of any potential impurities or secondary phases, and the elucidation of the crystal structures of the raw materials. The phase purity and crystalline structure of these three principal raw materials can significantly impact the reaction kinetics and phase formation during perovskite synthesis. Optimizing the use of these three principal raw materials is a crucial initial step towards the successful synthesis of the Na 0.5Bi 0.5Ti 0.95 (Ni 0.2 Fe 0.2Sb 0.6) 0.05O3 perovskite.





Figure III.4: XRD patterns of raw materials: Na₂CO₃, Bi₂O₃, and TiO₂.

III 1.6 XRD outcomes:

X-rays diffraction (XRD) examination was performed to determine the phase of the samples under investigation. These samples underwent calcination at temperatures ranging from 500°C to 1150°C in order to investigate the process by which the NBT-NFS ceramic phase was formed. The obtained XRD patterns were directly compared with those in the JCPDS database using the X'Pert High Score programme package, as shown in **Figure III .5.** The diffraction profiles obtained from the sample subjected to calcination in the temperature range of 300°C to 500°C displayed clear patterns suggesting the existence of sodium carbonate (Na₂CO₃), bismuth oxide (Bi₂O₃) (01-072-0398), and different forms of titanium oxide (TiO₂) such as anatase (98-004-4882) and rutile (98-005-1941).



Figure III.5: XRD patterns of the precursor material at room temperature and following calcination in the 300–500°C range.

After conducting an analysis of the X-rays diffraction (XRD) pattern of the sample subjected to calcination at a temperature of 600° C, it was observed that the sillenite phase Bi₁₂TiO₂₀ (00-

034-0097) formed in conjunction with the residue of the chemicals found at 500°C. These findings align with the results reported by J. Zhou et al. [14].



Figure III.6: XRD pattern of the precursor material calcined at 600°C.

The X-rays diffraction (XRD) pattern of the sample subjected to calcination at a temperature of 700°C revealed the presence of a powder composition consisting of different phases. These phases include $Na_{0.5}Bi_{0.5}TiO_3$ (00-046-0001), bismuth titanate pyrochlore $Bi_2Ti_2O_7$ (98-009-9436), sillenite $Bi_{12}TiO_{20}$ (00-034-0097), and bismuth oxide Bi_2O_3 (01-072-0398). These findings are consistent with previous research conducted on NBT ceramics [15]. The equation that describes the creation of bismuth titanate pyrochlore $Bi_2Ti_2O_7$ (98-009-9436) is as follows:

$$Bi_2O_3 + 2TiO_2 \rightarrow Bi_2Ti_2O_7$$



Figure III.7: XRD pattern of the precursor material calcined at 700°C.

The examination of X-rays diffraction (XRD) patterns obtained from samples subjected to calcination at temperatures of 800°C and 900°C revealed the absence of $Bi_{12}TiO_{20}$, resulting in the formation of a ternary system including $Na_{0.5}Bi_{0.5}TiO_3$, $Bi_2Ti_2O_7$, and Bi_2O_3 phases.



Figure III.8: XRD pattern of the precursor material calcined at 800°C.



Figure III.9: XRD pattern of the precursor material calcined at 900°C.

Upon investigating the X-rays diffraction (XRD) pattern of the sample subjected to calcination at a temperature of 950°C, it was seen that Bi₂O₃ was not present in the earlier ternary system. The X-rays diffraction (XRD) pattern of the sample subjected to calcination at a temperature of 1150°C exhibited distinct peaks that closely corresponded to those of Na_{0.5}Bi_{0.5}TiO₃. This observation suggests that the Ni, Fe, and Sb elements have undergone complete diffusion inside the NBT matrix, resulting in the successful formation of the NBT-NFS ceramic phase.



Figure III.10: XRD pattern of the precursor material calcined at 950°C.



Figure III.11: XRD pattern of the precursor material Sintered at 1150°C.

The combination of DTA-TGA and XRD data enabled us to monitor the intermediate reactions that result in the production of NBT-NFS, thereby identifying these distinct phases:

- **4** A water evaporation-induced endothermic peak is observed at around 81.42°C.
- An endothermic peak is observed at around 582°C, indicating the formation of Bi₁₂TiO₂₀.
- ♣ An endothermic peak is observed at around 721°C, which is attributed to the creation of monoclinic NBT. This peak coincides with the structural modification of Bi₂O₃ caused by decarbonization.
- An endothermic peak is observed at approximately 836°C, indicating the generation of hexagonal NBT.
- The formation of hexagonal NBT begins at a temperature of 900°C and reaches 1150°C to achieve a single-phase structure.

Part B: Structural and microstructural properties of the novel (Na $_{0.5}$ Bi $_{0.5}$) 0.94 R0.04Ti 0.95 (Ni 0.2 Fe 0.2Sb 0.6)0.05O3 (R = La, Nd, Gd, Y) solid solution.

III 2.1 Phase identification

The X-rays diffraction (XRD) patterns shown in **Figure III.12** (**a-d**) provide valuable insights into the structural characteristics of the NBT-RENFS system, specifically when doped with rare-earth elements such as La, Nd, Gd, and Y. The displayed diffractograms of all samples clearly indicate the formation of a stable ABO₃ perovskite structure with high crystallinity.

The undoped composition NBT-NFS was found to be of a pure rhombohedral perovskite structure (ABO₃) with (R3c) symmetry, as shown **in Figure III.12 (a).**



However, the doped NBT-RENFS compositions were found to exhibit a more complex crystal structure with two distinct phases (**Fig. III.12. (b-d**)). The majority phase was a rhombohedral crystal structure, identified by the indexing of the XRD reflections matching ICSD card 98-028-0983 and the space group of R3c.The dominance of the rhombohedral phase suggests that it constitutes the major component of the solid solution. In addition to the main rhombohedral phase, a minor secondary phase was detected, which exhibited cubic symmetry. The indexation of the XRD reflections of the main Rhombohedral phase is consistent with ICSD card number 98-028-0983 with R3c as the space group. Whereas the indexation of the reflection peaks of the secondary phase (Bi₂Ti₂O₇) was found to be in accordance with ICSD card number

98-009-9436 with a cubic phase and Fd-3m as the space group.

For further structural characterization and accurate parameters determination, Rietveld refinement of the XRD data was employed using the FullProf software [16]. As shown in **Fig. III.12 (a-e)** the Rietveld refined outputs of the recorded data were well matched with the observed pattern. The peak shape was better described using a pseudo–Voigt function while the background level adjustment was conducted using a six-coefficient polynomial function.





Figure III.12: (a-d) X-ray diffraction pattern for NBT-RNFS with an R3C fit.

The expanded XRD diffractograms of all samples were compared in **Figure III.12-f**, focusing on the 2theta range of 32°-33°. Notably, the NBT-RNFS samples exhibited a distinct shift in the peak's position towards higher 2theta angles. This shift signifies a reduction in the interplanar spacing, which, in turn, corresponds to shrinkage in the unit cell volume.



Figure III.12: e) Diffractograms of All Samples in the 2θ Range 32°-33°.

III 2.2.Evolution of lattice parameters:

The refined lattice parameters and unit cell volume illustrated in **Table III** .1 clearly show a slight shrinkage of the unit cell with the RE substitution due to their relatively lower ionic radius. To further elucidate, we might refer to our previous work [17], we established that the undoped NBT-NFS composition possesses a pure rhombohedral perovskite structure (ABO₃) with (R3c) symmetry. In this structure, the A site (6a) is occupied by Na⁺ (r_{Na}^+ =1.39 Å) and Bi³⁺ (r_{Bi3}^+ =1.38 Å) ions, with their general positions denoted as (0, 0, z). On the other hand, the B site (6a) is occupied by Ti ⁴⁺, Fe³⁺ Ni ²⁺, and Sb³⁺ cations, positioned at (0, 0, z). The oxygen atoms are located at the (18b) site, with general positions denoted as (x, y, z). By substituting the Bi ³⁺ and Na⁺ ions at the A site with rare earth ions such as La ³⁺, Nd ³⁺, Gd ³⁺, and Y ³⁺, which possess smaller ionic radii (r_{La3+} = 1.16 Å, r_{Nd3+} = 1.109 Å, r_{Gd3+} = 1.053 Å, r_{Y3+} = 1.019 Å), the resulting effect is a shrinkage in the unit cell volume [18].

Sample	NBT-NFS	NBT-LNFS	NBT-NNFS	NBT-GNFS	NBT-YNFS
Space group	R 3 c	R 3 c	R 3 c	R 3 c	R 3 c
Cell parameters	a=b= 5.5349 c= 13.5949 alpha=beta=90° gamma=120°	a=b= 5.4884 (Å) c= 13.4661 (Å) alpha=beta=90° gamma=120°	a=b= 5.4834(Å) c= 13.4565 (Å) alpha=beta=90° gamma =120°	a=b= 5.4777 (Å) c= 13.4502 (Å) alpha=beta=90° gamma=120°	a=b=5.4769 (Å) c= 13.4532 (Å) alpha=beta=90° gamma=120°
V (Å ³)	360.6890	351.2842	350.4032	349.5023	349.4829
NBT %	100	94.83	93.66	94.74	92.78
Bi ₂ Ti ₂ O ₇ %	0.00	5.17	6.34	5.26	7.22
Rp Rwp Rexp χ ² D	3.35 4.28 4.11 1.09 46.37	2.92 4.41 4.13 1.14 49.34	3.06 4.59 4.47 1.06 49.69	2.98 4.34 3.87 1.26 49.91	3.48 5.39 4.47 1.45 51.35

Table III.1: Lattice parameters of NBT-RNFS.

III 2.3. Influence of the rare earth element on interatomic distances in NBT-RNFS samples

To analyse the effect of the rare earth substitution on the interatomic distances, **Figure III.13** (**a-b**) displays the average Ti-O and Bi/Na/RE-O bond lengths of all NBT-RENFS samples. The results indicate that the average Bi/Na/RE-O bond lengths were consistently around 2.76 Å. Interestingly, as the ionic radius of the rare earth element (RE) decreased, starting from La^{3+} with a radius of 1.16 Å and progressing to Y^{3+} with a radius of 1.019 Å, a gradual reduction in the Bi/Na/RE-O bond length was observed. This trend was also observed for the Ti-O bond length in all the samples.

The crystal structure and atomic positions of NBT-RENFS samples, represented using Vesta software, is depicted in **Figure III.14 (a-d)**. This schematic illustration offers a visual representation of how atoms are arranged within the crystal lattice.



Figure III.13: Bond length of (a) titanium, (b) bismuth/Sodium/rare-earth with oxygen atom for all studied compositions.

NBT-NFS

NBT-NFS			
atoms	(x ; y ; z)		
Na/Bi	0.00000 ;0.00000; 0.24580		
Ti/Ni/Fe/Sb	0.00000; 0.00000; 0.00690		
0	0.15121; 0.35133; 0.05827		

NBT-LNFS			
atoms (x ; y ; z)			
Na/Bi/La	0.00000 ;0.00000; 0.24179		
Ti/Ni/Fe/Sb	0.00000; 0.00000; -0.0057		
0	0.19418; 0.35442; 0.05065		

NBT-NNFS			
atoms	(x ; y ; z)		
Na/Bi/Nd	0.00000 ;0.00000; 0.27774		
Ti/Ni/Fe/Sb	0.00000; 0.00000; 0.03206		
0	0.22423; 0.38252; 0.10111		

NBT-GNFS			
atoms	(x ; y ; z)		
Na/Bi/Gd	0.0000;0.00000; 0.26786		
Ti/Ni/Fe/Sb	0.00000;0.00000; 0.02005		
0	1.4809;0.34682; 0.07468		

NBT-YNFS			
atoms	(x ; y ; z)		
Na/Bi/Y	.00000 ;0.00000; 0.28290		
Ti/Ni/Fe/Sb	0.00000; 0.00000; 0.03382		
0	0.20279; 0.34431; 0.08762		





III 2.4. Charge density

The Rietveld refinement technique was used to produce an electron density map of the crystal lattice. This electron density map was then analyzed using the GFourier program to characterize and visualize the electron density distribution within the crystal unit cells.

Examination of the electron charge density allowed the identification of the atomic positions corresponding to the constituent elements in the crystal unit cells [19]. This provided valuable insights into the nature of the chemical bonds holding the ions of the NBT-RNFS powders together.

The dielectric constant is a fundamental property that is influenced by the microscopic behavior of the material, particularly the distribution and behavior of the electrons within the material. The spatial distribution of electron density refers to the way the electrons are distributed throughout the material. This distribution is not uniform and can vary depending on the atomic structure, chemical composition, and other factors. The spatial variation of electron density can have a significant impact on the overall dielectric properties of the material [19].

The 3D Fourier maps presented in **Figure III.15** provide detailed visualizations of the atomic arrangements within the unit cell structures of various NBT-RNFS ceramic compositions.

The undoped NBT-NFS displays a charge density of 16.90 e/Å³. When Nd, Gd, and Y dopants are introduced, the charge density increases to 17.00 e/Å³, 26.00 e/Å³, and 17.30 e/Å³, respectively. This suggests that the incorporation of various elements can significantly impact the charge density of the NBT-NFS material, with Gd doping resulting in the greatest enhancement. In contrast, the undoped NBT-LNFS exhibits a slightly lower charge density of 16.60 e/Å³ compared to the undoped NBT-NFS.







Figure III.15: Electron density map in the unit cell of NBT-RNFS samples.

III 2.5. The Goldschmidt Factor

The wide range of applications of perovskite structures is influenced by the flexibility offered by the selection of atoms at the A and B sites. An important factor in determining the properties of these materials is the relationship between the lengths of the A-O and B-O sub-lattices. This relationship is commonly characterized by Goldschmidt's tolerance factor (t) [20].

In the ideal structure, where the atoms are in contact with each other, the distance between B and O atoms (B-O) is equal to a/2, where "a" represents the cubic cell parameter. On the other

hand, the distance between A and O atoms (A-O) is $a/\sqrt{2}$, resulting in the following relationship between the ion radii: $r_A + r_O = (r_B + r_O)/\sqrt{2}$. In ABO₃ compounds, the ideal equality between the distances A-O and B-O is not strictly followed. The deviation from the ideal situation of compact stacking of atoms is quantified by the Goldschmidt tolerance factor (**1.2**). This factor provides insights into the stability of the perovskite structure and how it varies with the radii of the A, B, and O ions [21].

$$t = \frac{(R_a + R_o)}{\sqrt{2} * (R_B + R_o)}$$
(1.2)

The average ionic radii of the A-site, B-site, and oxygen atoms in the perovskite structure can be determined using the following values: $Bi^{3+}(1.38 \text{ Å})$, $Na^+(1.39 \text{ Å})$ [22] $La^{3+}(1.16 \text{ Å})$, $Nd^{3+}(1.109 \text{ Å})$, $Gd^{3+}(1.053 \text{ Å})$, $Y^{3+}(1.019 \text{ Å})$ [23], $Ti^{4+}(0.61 \text{ Å})$ [24], $Fe^{3+}(0.645 \text{ Å})$ [25], $Sb^{3+}(0.76 \text{ Å})$ [26] Ni²⁺ (0.69 Å) and O²⁻(1.35 Å)

The rhombohedral structure is stabilized when the tolerance factor (t) is in the range of 0.96 < t < 1. Specifically [27].

Cubic perovskite structure: $t \approx 1$

Rhombohedral structure: 0.96 < t< 1

Orthorhombic structure: t < 0.96

The tolerance factor values of 0.9721 to 0.987 indicate that the perovskite materials possess a stable, well-ordered crystal structure.

Sample	NBT-NFS	NBT-LNFS	NBT-NNFS	NBT-GNFS	NBT-YNFS
t	0.987	0.974	0.973	0.972	0.9721

 Table III.2: The tolerance factor of NBT-RNFS.

III 2.6 Density (g/cm³)

The relative density values for different NBT-RNFS samples indicate the compactness or packing efficiency of the material. A higher relative density corresponds to a denser and more tightly packed structure. In this case, the NBT-NFS sample has the highest relative density of 99%. This suggests that it has the highest level of compactness and closely matches the theoretical density of the material. A higher relative density implies a lower amount of void spaces or porosity within the structure. The other NBT-LNFS, NBT-NNFS, NBT-GNFS, and NBT-YNFS samples have slightly lower relative density values of 96.82 %, 96.61 %, 96.38%, and 96.34 %, respectively. These values indicate that these samples have a slightly lower packing efficiency compared to the NBT-NFS sample.

· ·	Density				
Composition	Theoretical (g /cm ³)	Experimental (g /cm ³)	Relative (%)		
NBT-NFS	5.860	5.8520	99.87		
NBT-LNFS	6.037	5.8450	96.82		
NBT-NNFS	6.058	5.8527	96.61		
NBT-GNFS	6.089	5.8688	96.38		
NBT-YNFS	6.011	5.7912	96.34		

Table III.3: Theoretical, experimental and relative densities of the sintered NBT-RNFS ceramics.

III 2.7. Microstructural analysis

Figure III.16 Shows the SEM image of the sintered ceramics NBT-RNFS, with R denoting La³⁺, Nd³⁺, Gd³⁺, and Y³⁺. SEM is particularly useful for imaging as-sintered ceramic surfaces in their original form. The average grain size of each sample was calculated by analysing micrographs using ImageJ software.

The grain size distribution histograms for all compositions are displayed in **Figure III.16**, exhibiting various shapes across the samples. The mean grain sizes for the NBT-NFS, NBT-LNFS, NBT-GNFS, and NBT-YNFS compositions were around 4.34 μ m, 4.35 μ m, 4.62 μ m, 4.86 μ m, and 4.92 μ m, respectively. The SEM image of the NBT-NFS sample reveals a dense microstructure without the presence of any pyrochlore phase. The diffusion behaviour of the rare earth ions within the NBT-NFS host matrix affects the grain size of the samples. The diffusion process is affected by factors such as the ionic radii and atomic mass of the dopant ions, which are important in determining the degree of grain development in the samples [28] . The NBT-LNFS composition, which includes a dopant with the smallest ionic radius, has a greater grain size. A direct correlation is observed between the average grain size and crystallite size. The NBT-LNFS composition exhibits a smaller average grain size, indicating a smaller crystal size, as indicated in **Table III 1**.

In addition, the presence of a secondary phase was detected, which aligns with the findings of the X-ray diffraction (XRD) analysis. The relative densities of NBT-NFS, NBT-LNFS, NBT-NNFS, NBT-GNFS, and NBT-YNFS ceramics are 99.87%, 96.82 %, 96.61%, 96.38%, 96.34%. A clear correlation exists between relative density and average grain size. As the average grain size decreases, the relative density generally increases. This is because smaller

grain sizes facilitate tighter packing and more compaction, resulting in higher relative densities.





Figure III.16: SEM images of the NBT-RNFS ceramics.

III 2.8 Energy dispersive spectrometric analysis EDS

Energy Dispersive X-ray Spectroscopy (EDS) was employed to perform qualitative and quantitative analyses of the components within the formed crystals. As depicted in **Figure 5**, EDX was used to scrutinize the elemental compositions of the synthesized samples of NBT-RNFS. The analysis confirmed the presence of all the required elements (Na, Ti, Fe, Ni, Sb, Bi, Gd, La, Y, Nd, and O) in the grown crystals, without any additional impurities beyond the constituent elements of the crystals.

Figure III.17 presents the atomic percentage composition of sodium (Na), bismuth (Bi), titanium (Ti), oxygen (O), iron (Fe), nickel (Ni), antimony (Sb), gadolinium (Gd), neodymium (Nd), yttrium (Y), and lanthanum (La). Furthermore, the atomic percentage composition presented in Figure **III.17** demonstrates that the experimentally determined proportions closely match the calculated values.









Figure III.17: EDAX Spectra of NBT-RNFS.

III 2.9. Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectroscopy is a valuable technique utilized for studying the structural and vibrational properties of ceramic materials [29]. In this investigation, the FTIR spectra of NBT-RNFS samples were measured at room temperature, covering a wave number range of 400-4000 cm⁻¹ and depicted in Figure III.18. The obtained spectra revealed that there were no notable changes in transmittance over the wider spectral range of 4000-1000 cm⁻¹. Within the perovskite structure, the Ti-O octahedral group displays a distinct and asymmetric band in the FTIR spectra, which spans the wave number range of 400 to 1000 cm⁻¹[30]. Similar bands near to 663 cm⁻¹ are observed consistently in the FTIR spectra of NBT-RNFS samples. This particular band is characteristic of perovskite materials. The band at ~430 cm⁻¹ band indicates the presence

of metal-oxygen vibrations. The absorption peak observed at approximately 802 cm⁻¹ can be assigned to the vibrational modes of the Ti-O-Ti bonds within the TiO_6 octahedral structures. The shifting of vibrational bands in the FTIR spectra can be attributed to changes in the lattice parameters of the crystal structure.



Figure III.18: FTIR spectra of NBT-RNFS.

III 2.10. Raman spectroscopy analysis:

Raman spectroscopy (RS) serves as a powerful tool for investigating structural characteristics at short-length scales, providing valuable complementary information to the long-length scale results obtained from X-ray diffraction (XRD) analysis [31]. According to literature, the NBT-based system typically exhibits 13 Raman active optical modes. In the case of Rhombohedral (R) symmetry, the irreducible representation is given as Γ Raman, R3C = 4A1 + 9E .Where, , A1 represents the Raman modes parallel to the c-axis of the unit cell, while E represents the Raman modes perpendicular to the c-axis [32].
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Figure III.19 shows the Raman spectra of NBT-RNFS (R = La, Nd, Gd, Y) ceramic samples in the broad frequency range between 30 and 1300 cm⁻¹. The Raman spectrum reveals a unique mode around 78 cm⁻¹ in the low-frequency region below 100 cm⁻¹. Many previous studies on NBT Raman spectra were unable to investigate this specific low-frequency region, despite its significant importance. When examining the influence of rare earth (RE) doping on the A-site of the (Na_{0.5}Bi_{0.5})Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O₃ system, it is crucial to understand how the addition of RE elements changes the low-frequency vibrations of the A-site cations. Interestingly, certain researchers have displayed a particular interest in investigating this range of frequencies [33], [34]. The Raman spectrum of NBT-RNFS can be broadly categorized into two distinct regions, denoted as A and B. The low-frequency region A, which ranges from 30 to 300 cm-1, displays Raman modes v1, v2, and v3. Among these modes, the first mode v1, observed at around 78 cm-1, is associated with the vibrations that involve the Bi-O and RE-O (rare earth-oxygen) bonds within the material [23]. The vibrations offer valuable information about the precise bonding and interactions between bismuth, rare earth elements, and oxygen in the NBT-RNFS material. The second mode, v2, appears at approximately 137 cm-1 and is associated with the vibrations of the Na-O bonds [35]. The most notable characteristic detected in the Raman spectra of the NBT-RNFS system is the third mode, denoted as v3, which has an estimated frequency of 287 cm-1. This mode primarily involves the vibrations of the B-site cations, specifically the Ti/Ni/Fe/Sb-O vibrations within the material. In the high-frequency region (B) of the Raman spectrum, the modes v4, v5, v6, and v7 have been observed at frequencies around 553 cm⁻¹, 620 cm⁻¹, 824 cm⁻¹, and 854 cm⁻¹, respectively. These high-frequency modes have been identified as BO₆ tilting modes in previous studies [36, 37]. A shift towards higher wave numbers as the bond length (Ti-O) increases. The expansion of the bond length between the titanium (Ti) and oxygen (O) atoms leads to alterations in the bond strength and stiffness, leading to an increase in wave numbers. Increased bond lengths generally suggest lower strength and greater flexibility in the bonds, resulting in elevated vibrational frequencies and, consequently, higher wavenumbers in the spectra.





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Figure III.19: Raman spectra of NBT-RNFS from 30 to 1300 cm⁻¹.

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Conclusion

The present study describes reaction mechanisms associated with $Na_{0.5}Bi_{0.5}Ti_{0.95}$ ($Ni_{0.2}Fe_{0.2}Sb_{0.6}$)_{0.05}O₃ (NBT-NFS) material and the influence of rare earths dopant on the structural and microstructure properties of NBT-RNFS (R=La, Nd, Gd, Y) perovskite. Different Samples were synthesized by the solid-state method.

- TGA-DTA and XRD analyses demonstrated that the NBT-NFS solution was effectively synthesised at 1150°C and crystallised in a rhombohedral phase structure with the R3c space group.
- The sillenite phase Bi₁₂TiO₂₀ and the bismuth titanate pyrochlore Bi₂Ti₂O₇ were identified in the XRD analysis of the sample calcined at 600°C and 700°C, respectively.
- The undoped NBT-NFS samples displayed a single rhombohedral phase, while the rare earth-doped NBT-NFS samples exhibited a rhombohedral phase with a pyrochlore phase, as confirmed by the XRD analysis.
- Rietveld refinement of the XRD data showed a slight shrinkage of the unit cell volume with the substitution of rare earth elements, due to their relatively lower ionic radii.
- Raman spectroscopy, in agreement with the XRD data, definitively confirmed the existence of bond vibrations related to Bi-O, Na-O, RE-O, and TiO6 in the sintered ceramic sample.
- FTIR study showed an intense band at 421 cm -1, indicating metal-oxide vibrations in the NBT-RNFS spectrum.
- The SEM micrographs revealed that the particle size of the samples increased as the ionic radius of the dopant decreased.
- SEM micrographs indicated the presence of secondary phases, supporting the XRD results.
- EDS analysis confirmed the presence of all the constituent atoms in the different compositions, in accordance with the stoichiometry.

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Chapter IV

Photocatalytic and Dielectric Performance of Novel Rare-Earth Doped NBT-RNFS Ceramic Materials

INTRODUCTION

Perovskite materials exhibit a distinctive crystal structure characterized by the general chemical formula ABO₃. These materials have emerged as promising candidates for photocatalytic applications due to their unique properties, including excellent light absorption capabilities, favorable charge carrier mobilities, and inherent catalytic activities [1].

Among the perovskite family, bismuth sodium titanate (NBT)-based compositions have garnered significant research attention in recent years. This heightened interest is driven by the unique attributes and promising potential of NBT-based photocatalysts for various photocatalytic processes. Researchers are actively exploring strategies to enhance the photocatalytic activity of NBT-based perovskite photocatalysts [2,3]. This includes the incorporation of various dopant elements, which aims to modify the electronic band structure, surface properties, and charge carrier dynamics of NBT. Such doping approaches hold the potential to improve the overall efficiency of NBT in photocatalytic reactions [4].

Furthermore, previous studies have highlighted the importance of the Na/Bi ratio and nonstoichiometry at the A-site (Na, Bi) and B-site (Ti) in determining the dielectric and electrical properties of NBT-based perovskites. Compositional variation by introducing a small amount of suitable dopant elements at the A or B-site of the NBT structure has attracted more interest, as this can significantly modify the properties of NBT [5].

This chapter will present a comprehensive investigation into the photocatalytic and dielectric properties of novel $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based materials, with a particular focus on the influence of rare earth dopants. NBT is an important lead-free perovskite material that has garnered significant attention in recent years due to its promising ferroelectric, piezoelectric, and dielectric characteristics. The incorporation of rare earth elements, such as lanthanum, neodymium, or samarium, has been shown to significantly alter the structural, electronic, and functional properties of NBT, leading to an enhanced performance in a variety of applications.

This chapter is divided into two main parts: Part A will explore the photocatalytic properties of rare earth-doped NBT materials, while Part B will focus on the dielectric characteristics of these doped perovskite compositions. Photocatalysis is an emerging field with numerous environmental and energy-related applications, and the unique electronic structure of rare earthdoped NBT makes it a compelling candidate for photocatalytic processes. Similarly, the

dielectric properties of these materials are crucial for their use in capacitors, sensors, and energy storage devices.

Part A: Characterization and Evaluation of Photocatalytic Performance of Novel Ceramic NBT-RNFS

IV.1.1 Optical analysis

The direct band gaps of the various rare earth ion-doped NBT-RNFS materials can be readily determined by analyzing the Tauc plots, as shown in **Figure IV.1**. The Tauc plot is a graph of $(\alpha hv)^2$ versus photon energy (hv), where α is the absorption coefficient of the material. By extrapolating the linear region of the $(\alpha hv)^2$ versus hv plot to the x-axis intercept.

The measured bandgap values for the samples under probe ranging from 2.61 to 2.80 eV, which confirms their semiconducting nature. The observed values of Eg are 2.73, 2.61, 2.69, 2.80 and 2.68 eV for NBT-NFS, NBT-LNFS, NBT-NNFS, NBT-GNFS and NBT-YNFS, respectively.

The undoped NBT-NFS sample exhibits a bandgap of 2.73 eV. When lanthanum (La) is doped, the bandgap decreases to 2.61 eV. Similarly, when yttrium (Y) is doped in NBT-YNFS, the bandgap is reduced to 2.68 eV, while neodymium (Nd) incorporation in NBT-NNFS reduces it to 2.69 eV. The lower bandgap values of the NBT-LNFS, NBT-YNFS, and NBT-NNFS samples suggest their enhanced potential for improved photocatalytic performance compared to the undoped NBT-NFS material. The narrower bandgap allows for more efficient light absorption and charge carrier generation, which can lead to improved photocatalytic activity.





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Figure IV.1: Tauc plots for NBT-RNFS systems. Lowest direct band gap is observed for NBT-LNFS.

IV.1.2 BET analysis

The adsorption-desorption isotherms of N₂ for the NBT-RFNS samples, as shown in Figure IV.2, exhibit a composite type (II+IV) behavior. This is characterized by the absence of a saturation layer, which is typically observed in type IV isotherms at a relative pressure range of approximately 0.9 < P/PO < 1. This observation establishes the presence of both mesopores and macropores in the NBT-RFNS samples.

Furthermore, the hysteresis loop displayed in the isotherm exhibits two non-parallel adsorption and desorption branches, which corresponds to the IUPAC classification type H3, indicating the presence of non-rigid aggregates of sheet-like particles or assemblies of slitshaped pores. The hysteresis loop provides valuable information about the pore configuration.



Figure. IV.2: The N₂ adsorption-desorption isotherms of NBT-RNFS samples.

IV.1.3 BJH Method (Pore size distribution)

The analysis of pore size and pore size distribution in samples containing meso and/or macro pores can be conducted using the BJH method. **Figure IV.3** presents the pore size distribution of NBT-RNFS, which was determined using the Barrett-Joyner-Halenda (BJH) method. The analysis of the samples reveals the presence of both mesopores and macropores. According to the guidelines established by the International Union of Pure and Applied Chemistry (IUPAC), pores are typically classified into three primary groups based on their size: micropores (less than 2 nm), mesopores (2-50 nm), and macropores (greater than 50 nm) [6].

The pore size distribution curves of the NBT-RNFS sample exhibit a wide range of pore radii, spanning from 3.9 nm to greater than 90 nm. This indicates the presence of both mesopores and macropores within the sample. The coexistence of these two types of pores is reflected in the mixed nature of the adsorption isotherm, which displays characteristics of both Type II and Type IV isotherms.



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Figure IV.3: Pore size distribution

Table IV.1: Pore	Volume and	Pore Radius	of All	the samples.
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Sample	Pore Volume (cc/g)	Pore Radius Dv(r) (Å)
NBT-NFS	7.112	153.886 Å
NBT-LNFS	1.945	47.880
NBT-NNFS	0.048	47.850
NBT-GNFS	0.108	48.132
NBT-YNFS	2.491	151.466

IV.1.4 T-plot

The T-plot analysis, while grounded in the fundamental principles of the BET (Brunauer, Emmett, and Teller) theory, provides a more intricate and detailed characterization of adsorbent materials. The T-plot analysis is a powerful tool that provides insights into the characteristics of both non-porous and porous solid materials. For non-porous solids, the T-plot typically forms a linear representation that originates at the graph's origin and exhibits a slope equivalent to the specific surface area of the material [7]. However, the T-plot behavior observed in Figure IV.4 differs from the expected pattern for non-porous solids. Upon examining the graph, it becomes evident that when the thickness of the multimolecular adsorbate layer is less than 8.5 Å, the resulting transformed curve forms a continuous straight line starting from the graph's origin. This linear region suggests that the adsorption is occurring in a monolayer-multilayer fashion, as described by the BET theory, and indicates a uniform and well-defined microporous structure in the adsorbent material [7]. Interestingly, once the multimolecular layer thickness exceeds 8.5 Å, a noticeable change in the slope of the T-plot curve is observed, indicating a distinct "slope rupture." This alteration in the slope is likely attributable to the filling of two distinct types of pores within the adsorbent material. A deviation towards the right on the graph can arise from two potential factors. Firstly, it may be a consequence of the existence of small micropores, manifesting as a descending slope observed at low pressures. Alternatively, it could indicate capillary condensation occurring in the mesopores, leading to an ascending slope at high relative pressures, as shown in Figure IV.4.



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Figure IV.4: t-plot of NBT-RNFS samples.

IV.1.5 Photocatalytic activity

Photocatalytic degradation experiments were conducted for all compounds using natural sunlight as the irradiation source, with methylene blue (MB) serving as the model organic pollutant. The experiments were carried out in a 100 mL aqueous solution containing a 100 mg suspension of the photocatalyst. Prior to sunlight exposure, the mixture was stirred in the dark for 30 minutes to establish the adsorption-desorption equilibrium between the MB dye and the catalyst surface .Following this pre-treatment step, the solution was exposed to natural sunlight, and at regular 30-minute intervals, 4 mL aliquots of the irradiated dye solution were withdrawn using a syringe. These periodic samples were then analyzed to monitor the evolving concentration of the MB dye over the course of the photocatalytic degradation process. The withdrawn solutions were then analyzed using a UV-Visible spectrophotometer at room temperature. The percentage of dye removal was calculated using the following equation [8], [9]:

Degradation (%) =
$$\left(\frac{C_{i-}-C_t}{C_i}\right) \times 100\%$$

In this equation, C_i represents the initial dye concentration before the start of the photocatalytic irradiation, while C_t represents the dye concentration after t minutes of irradiation.



Figure IV.5: Schematic representation of the photocatalytic experiment steps. The time-dependent degradation spectra of the methylene blue (MB) solution are presented in **Figure IV.6 a-e**. The MB solution was subjected to sunlight exposure in the presence of both

undoped and doped (NBT-RNFS) photocatalysts. The spectral evolution over time has revealed a decrease in the characteristic absorption band of the targeted dye, which is located at 664nm. Additionally, there has been a significant colour transformation from blue to transparent indicating that the methylene blue (MB) dye was photodegraded under the effect of different studied photocatalysts.





Figure IV.6: Photocatalytic degradation curves a) NBT-NFS b) NBT-LNFS, C) NBT-NFS,d)NBT-GNFS,e)NBT-YNFS .

The maximum colorant-removal efficiency is 83% in 210 minutes for the NBT-LNFS sample, whereas the colorant-removal efficiencies for NBT-YNFS+MB, NBT-NNFS+MB, NBT-NFS+MB and NBT-GNFS are 66%, 62%, 60%, and 56%, respectively.

The superior photocatalytic activity of the NBT-LNFS sample can be explained by its smaller bandgap, which facilitates more efficient light absorption and charge separation, ultimately leading to enhanced photocatalytic efficiency. This strong inverse correlation can be attributed to the fact that materials with smaller bandgaps can more effectively absorb solar energy and facilitate the separation of photogenerated electron-hole pairs, which are crucial factors in enhancing the photocatalytic activity. The samples NBT-LNFS, NBT-YNFS, and NBT-NNFS were more efficient in the removal of methylene blue (MB) compared to the undoped NBT-NFS sample. This suggests that the strategy of doping the NBT-NFS material with rare-earth cations, such as La, Y, and Nd, was successful in enhancing the photocatalytic

performance of NBT-NFS. The NBT-LNFS material was the most efficient one in terms of colorant-removal efficiency. As shown in **Figure IV.7**.



Figure IV.7 Colorants removal efficiencies corresponding to the studied formulations.

IV.1.6 Photocatalytic mechanism

The simplified schematic diagram in **Figure IV.8** illustrates the photocatalytic degradation of methylene blue (MB) dye using NBT-RNFS samples. This photocatalytic process involves four key stages. (1) Light absorption by NBT-RNFS samples ($hv \ge Eg$), (2) electron-hole pair generation, (3) the NBT-RNFS samples capture the excited electrons generated by the light absorption, and (4) oxidation-reduction (redox) interactions take place.

As mentioned above, The NBT-LNFS sample exhibits the highest photocatalytic degradation efficiency among the samples. This is attributed to the material's smaller bandgap energy (Eg) compared to the other compositions. The small band gap of the material facilitates

the generation of electron-hole (e/h) pairs, but their increased recombination rate is also a result of this small band gap value. The e/h pairs that are prevented from recombining can participate in redox reactions to generate reactive species. Specifically, reactive oxidative species like the hydroxyl radical (OH•) and superoxide radical ($O^{\bullet}_{2}^{-}$) are formed. These reactive oxygen species, generated in the presence of the photocatalyst (NBT-RNFS) and light energy (hv \geq Eg), can then degrade pollutants like methylene blue (MB) into safe final products, namely carbon dioxide (CO₂↑) and water (H₂O). The equations provided summarize and clarify the preceding steps [10].

```
NBT-RNFS (R=La, Nd, Gd, Y) + hv (Photon) \rightarrowNBT-RNFS [e + h]
e (trapped) + O_2 \rightarrow O_2^{\bullet-}
h + OH-\rightarrowOH•
```

 $(O^{\bullet}_{2}, OH^{\bullet}) + MB dye \rightarrow safe components (CO_{2}(\uparrow) + H_{2}O)$



Figure IV.8: Schematic diagram of photocatalytic degradation of methylene blue using the NBT-RNFS photocatalyst.

IV.1.7 Kinetic studies

If the photocatalytic degradation of MB using photocatalysts follows a pseudo-first-order kinetic model [11], then the observed degradation rate coefficient (k) of the photocatalytic degradation can be expressed as follows:

$$\frac{\mathbf{d}(\mathbf{C}(\mathbf{t})}{\mathbf{d}\mathbf{t}} = -\mathbf{k}_{1}\mathbf{C}(\mathbf{t}) \tag{1}$$

Where K is the degradation rate constant, with the dimension of inverse of time; s^{-1} . The initial condition is [12], [13]

$$C(t)_{(t=0)} = \mathbf{C0} \tag{2}$$

 C_0 is the initial concentration at t=0, which is the time when irradiation begins. The solution of differential equation (1) with the above initial condition can be rewritten as :

$$C(t) = C_0 e^{-k_1 t}$$
 $Ln(C_0/C) = k_1 t$ (3)



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Figure IV.9: a) Kinetics studies of MB degradation with all the samples b) Photocatalytic degradation of MB by NBT-RNFS samples.

The photocatalytic degradation of methylene blue (MB) dye was investigated using five different photocatalyst materials. The degradation kinetics were analyzed using a pseudo-first-order kinetic model, which allowed for the determination of the observed rate constants (k) and correlation coefficients (\mathbb{R}^2) for each photocatalyst.

The rate constants were as follows: NBT-LNFS, 0.0075; NBT-YNFS, 0.00401; NBT-NNFS, 0.00359; NBT-NFS, 0.00356; and NBT-GNFS, 0.00312. These values indicate that NBT-LNFS exhibited the highest photocatalytic activity, leading to the fastest degradation rate of the MB dye. The other photocatalysts demonstrated progressively lower degradation rates in the order presented.

The correlation coefficients (\mathbb{R}^2) for the pseudo-first-order kinetic model ranged from 0.94593 to 0.98866, suggesting an excellent fit of the experimental data to the proposed kinetic model. This confirms the applicability of the pseudo-first-order kinetic approach in describing the photocatalytic degradation of methylene blue dye using the investigated photocatalyst materials.



Figure IV.10 Histogram of reaction rate constant k for MB degradation by NBT-RNFS under sunlight.

IV.2 Part B: Effect of rare-earth elements doping (R = Gd, La, Y, and Nd) on the dielectric properties of NBT-NFS ceramics.

IV.2.1 Dielectric constant

Figure IV.11 (a-e) show the temperature dependence of the relative dielectric permittivity (ε_r) for NBT-LNFS, NBT-NNFS, NBT-GNFS, and NBT-YNFS ceramics at various frequencies. The dielectric properties of NBT-NFS ceramics doped with rare earths change slightly with temperature because of small changes in the crystal structure. The dielectric properties of NBT-NFS ceramics doped with rare earth elements exhibit subtle variations that depend on temperature and frequency. These changes can be attributed to subtle modifications in the crystal structure [69].

Two anomalies are observed in the temperature-dependent dielectric spectra of all samples. NBT-RNFS ceramics show two distinct dielectric anomalies at around 500 K (depolarization temperature " T_d ") and 600 K (maximum temperature " T_m ") [70, 71]. The depolarization temperature marks the shift from the ferroelectric (rhombohedral) phase to the antiferroelectric

(tetragonal) phase, leading to depolarization and a decrease in piezoelectric activity. The transition from the antiferroelectric to the paraelectric phase happens at a temperature known as Tm or Tc [72].





Figure IV.11: Temperature dependence of dielectric permittivity (ϵ_r) at various frequencies of the NBT-RNFS.

IV.2.2 Dielectric loss (tanδ)

The analysis of the dielectric loss $(\tan \delta)$ curve indicates that the losses remain minimal until around 500 K, after which they significantly increase with temperature. From room temperature to 500 K, the loss tangent (tan) shows little variation and remains in a stable state. However, when the temperature rises at lower frequencies, it only shows a slight increase.

The results of this study indicate the material initially demonstrates low losses within a specific temperature range. When the temperature exceeds 500 K, however, the losses become greater. Moreover, the slight increase in the loss tangent at lower frequencies as the temperature increases may be attributed to temperature-dependent influences on the material's electrical conductivity or relaxation mechanisms.

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Figure IV.12: Temperature dependence of dielectric loss (tanδ) at different frequencies of the NBT-RNFS.

IV.2.3. Exploring the impact of rare earth elements on the dielectric properties of NBT-NFS ceramics:

The incorporation of rare earth (RE) elements into the NBT-NFS matrix has led to notable changes in the dielectric behavior of the material. Undoped NBT-NFS has a relatively high dielectric constant of around 951.02. However, When the NBT-NFS samples are doped with smaller cations such as Y³⁺ and Gd ^{3+,} the dielectric permittivity values are reduced to approximately 526.98 and 768.17, respectively. In contrast, the introduction of the larger La³⁺ cation, with an ionic radius closer to that of Bi³⁺, results in a significant enhancement of the dielectric properties. The La³⁺ doped NBT-RNFS ceramic exhibits an exceptional dielectric constant of 1151.87, surpassing even the high value of the undoped material. Iinterestingly, the Nd³⁺ dopant, with an intermediate ionic radius, also displays an enhanced dielectric permittivity of 1122.31 compared to the undoped ceramic.

In a parallel study, O. Turki et al. found that NBT doped with the bigger La^{3+} ions have better dielectric permittivity than those doped with the smaller Gd^{3+} ions [14]. Moreover, there is a shift in the transition temperature (T_m) that appears to be related to the equality of the chemical

valence, as proposed by the work of K Chandra et al., suggesting that changes in the relative proportions or arrangements of the chemical species with different valence states may be responsible for the observed shift in T_m [15], [16]. The undoped NBT-NFS ceramic has been reported to exhibit a transition temperature (Tm) of 636 K. However, when La³⁺ is incorporated as a dopant into the A-site of the NBT perovskite structure, the transition temperature increases to 639K in the NBT-LNFS composition. This shift to a higher T_m can be attributed to the better structural compatibility of the larger La $^{3+}$ ion (ionic radius = 1.16 Å) compared to the Bi $^{3+}$ (ionic radius = 1.38 Å) [17] ion in the host NBT-NFS matrix. For the other rare earth (RE) doped compositions, the transition temperature (T_m) is observed to decrease. Specifically, the Tm decreases to 632 K for NBT-NNFS, 600 K for NBT-GNFS and 530 K for NBT-YNFS. This shift to lower T_m values can be attributed to the smaller ionic radii of the Nd³⁺ (1.109 Å), Gd³⁺ (1.053 Å), and Y³⁺ (1.019 Å) dopants compared to the host Bi³⁺ ion (1.38 Å) in the NBT-NFS matrix. If the dopant element at the A-site is a rare earth (RE) ion, it might distort the crystal structure due to the electronic configuration of the outermost electrons in the orbital. The outermost electrons in the RE ions' orbitals strive to change, which can lead to a shift in the Curie temperature (T_c) of the material [18],



Figure IV.13: Influence of rare earth elements on the dielectric constant (ϵ_m) in NBT-NFS. Ceramic.

Table IV.2: Comparison of Tm	(K), ɛr (at Tm),	Tand (at Tm)	and Td for I	NBT-RNFS
	ceramics at 100) Hz.		

Sample	Em	Tgδ	Tm	Td
NBT-NFS	951.02	0. 0496	636	490
NBT-LNFS	1151.87	0. 0363	639	480
NBT-NNFS	1122.31	0. 0235	632	483
NBT-GNFS	768. 17	0. 0366	600	484
NBT-YNFS	526.98	0. 0210	530	486

IV.2.4 The effect of frequency

The variation of relative permittivity (constant) of NBT-RNFS with frequency at specified temperatures (300-800K) is illustrated in **Figure IV.13**. The dielectric dispersion curves exhibit significant dependence on both frequency and temperature. As the frequency increases, the relative dielectric constant of the NBT-RNFS material decreases linearly. This behavior can be attributed to the fact that only a limited number of dipoles are able to respond to the applied electric field at higher frequencies [19].





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Figure IV.14: Frequency dependence of dielectric constant for all the samples.

IV.2.5. The diffusivity parameter (γ)

The variation of the dielectric constant with temperature after the phase transition (Tc) was analyzed by the modified Curie-Wiess law.

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{c}; T > T_m$$

In this equation, ε represents the dielectric constant at temperature T, ε_m represents the dielectric constant at temperature T_m, C is the Curie constant, and γ is the phase transformation diffusivity coefficient. The value of γ varies from 1 to 2. If $\gamma = 1$, the material has ferroelectric properties, while a value greater than 1 indicates relaxor ferroelectric behaviour [20]. **Figure IV.15** (a, b, c, d, e) illustrates the diffusivity curves for NBT-NFS, NBT-LNFS, NBT-NFS, NBT-NFS, NBT-S, NBT-NFS, NBT-NFS, NBT-NFS, NBT-S, NBT-S,

insights into the relaxation behaviors of the NBT-NFS-based ceramics. For the undoped NBT-NFS sample, the γ value was estimated to be around 1.67.

However, the doped samples exhibited varied γ values depending on the rare earth element dopant. The NBT-LNFS sample, containing a rare earth element with a large ionic radius, had a higher γ value of 1.79. This suggests that the introduction of rare earth dopants with large ionic radii can enhance the relaxation behaviors in these materials. In contrast, the NBT-NNFS, NBT-GNFS, and NBT-YNFS samples, which contained rare earth dopants with smaller ionic radii, had lower γ values of 1.51, 1.50, and 1.29, respectively. This indicates that the smaller ionic radius rare earth dopants tend to suppress or reduce the relaxation characteristics compared to the undoped NBT-NFS.





Figure IV.15: Diffusivity curve for (a) NBT-NFS, (b) NBT-LNFS, (c) NBT-NNFS, (d) NBT-GNFS, (e) NBT-YNFS.

IV.2.6 Curie-Weiss Behavior

The temperature T_{cw} denotes the point at which the dielectric constant ε_r begins to deviate from the Curie-Weiss law behavior. The reciprocal of ε_r starts to diverge from the linear Curie-Weiss relationship at the temperature T_{cw} , which is notably higher than the temperature $T_m[21]$

The parameter ΔT_m , which is commonly used to indicate the degree of deviation from the Curie-Weiss law, is defined as follows [22], [23]:

$\Delta T_m = T_{CW} - Tm$

Where T_{CW} denotes the temperature at which the dielectric permittivity starts to depart from the Curie-Weiss law and T_m represents the temperature at which the dielectric constant attains its maximum value.

Figure IV.16 depicts the inverse of the dielectric constant as a function of temperature, measured at a frequency of 1 kHz, for the NBT-RNFS ceramic samples. The wide range of Δ Tm values reported for the NBT-RNFS ceramic materials, spanning from 55 K down to 14 K, is a clear indication of their highly diffuse phase transition behavior. A larger Δ Tm corresponds to a more smeared-out and broadened dielectric response, rather than a sharp, well-defined peak. The varying Δ Tm values across the different compositions, such as NBT-NFS (55 K), NBT-LNFS (31 K), NBT-NNFS (30 K), NBT-GNFS (25 K), and NBT-YNFS (14 K),

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Figure IV.16 Temperature dependence of $1/\varepsilon_r$ of NBT-RNFS ceramics at 1 kHz.

IV.2.7 Conductivity studies

Figure IV.17 shows the temperature-dependent electrical conductivity at 100 Hz of NBT-RNFS ceramics. It can be observed that in the temperature range below the transition temperature (T < Tc), the electrical conductivity remains relatively constant. However, in the higher temperature region (T > Tc), the conductivity exhibits an exponential increase with rising temperatures. This exponential variation is characteristic of thermally activated charge transport processes, where the increased thermal energy enables more efficient charge carrier transport, leading to the observed exponential rise in electrical conductivity [24].



Figure IV.17. The electrical conductivity as a function of temperature of NBT-RNFS ceramics at 100 Hz.
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Conclusion

This chapter has provided a comprehensive overview of the recent advancements in the development and characterization of rare-earth doped NBT-RNFS ceramic materials. The strategic incorporation of various rare-earth elements, including La, Nd, Gd, and Y, into the NBT-RNFS matrix has been shown to significantly enhance the photocatalytic and dielectric properties of the resulting ceramic compositions.

From a photocatalytic perspective, the RE-doped NBT-RNFS compositions exhibited markedly improved performances under simulated solar irradiation conditions compared to the undoped parent NBT-RNFS ceramic. Notably, the La-doped NBT-RNFS system achieved an impressive 83% photocatalytic dye degradation rate, substantially outperforming the 23% dye removal efficiency of the undoped material. Similarly, the Nd-doped (62% dye removal) and Y-doped (66% dye removal) NBT-RNFS ceramics also displayed enhanced photocatalytic activities under broadband solar light exposure.

The dielectric characteristics of the rare-earth doped ceramic materials were also found to be greatly enhanced. Specifically, the La-doped ($\varepsilon r = 1151.87$) and Nd-doped ($\varepsilon r = 1122.31$) NBT-RNFS compositions demonstrated exceptionally high dielectric constants, significantly exceeding the value of 951.02 obtained for the undoped NBT-NFS.

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General Conclusion And Future work

General Conclusion

In conclusion, this work has successfully synthesized and characterized novel NBT-RNFS ceramics, where R represents La, Nd, Gd, and Y. The solid-state reaction method was employed to prepare these materials, which exhibited promising dielectric and photocatalytic properties. The main findings and goals achieved include:

The TGA-DTA and XRD analyses demonstrated that the Na_{0.5}Bi_{0.5}Ti_{0.95} (Ni_{0.2}Fe_{0.2}Sb_{0.6}) 0.05O₃ solution was effectively synthesized at 1150°C and crystallized in a rhombohedral phase structure with the R3c space group. The XRD analysis of the sample calcined at 600°C identified the sillenite phase Bi₁₂TiO₂₀, while the sample calcined at 700°C exhibited the bismuth titanate pyrochlore Bi₂Ti₂O₇ phase. The undoped NBT-NFS samples displayed a single rhombohedral phase, while the rare earth-doped NBT-NFS samples exhibited a rhombohedral phase along with a pyrochlore phase, as confirmed by the XRD analysis.

Rietveld refinement of the XRD data showed a slight shrinkage of the unit cell volume with the substitution of rare earth elements, attributed to their relatively lower ionic radii compared to the host ions. Overall, the key objectives achieved were the successful synthesis of the NBT-NFS material, the identification of the rhombohedral crystal structure and the impact of rare earth doping, as well as the detection of secondary phases formed at different calcination temperatures, all through the comprehensive XRD and thermal analyses.

The SEM micrographs revealed that the particle size of the samples increased as the ionic radius of the dopant decreased. Specifically, the NBT-LNFS composition, which includes a dopant with the largest ionic radius, exhibited a reduced grain size. Conversely, the NBT-YNFS composition, which includes a dopant with the smallest ionic radius, had a greater grain size. A direct correlation was observed between the average grain size and crystallite size, where the NBT-LNFS composition with the smaller average grain size also indicated a smaller crystal size. These results suggest that the substitution of rare earth dopants with varying ionic radii had a direct impact on the microstructural development, with smaller ionic radii leading to larger grain and crystallite sizes. The EDS analysis confirmed the presence of all the constituent atoms in the different compositions, in accordance with the expected stoichiometry.

The tolerance factor values calculated for the perovskite materials ranged from 0.9721 to 0.987. This tolerance factor range of 0.96 < t < 1 is characteristic of a stable, well-ordered rhombohedral perovskite crystal structure.

The Raman spectroscopy data was in agreement with the XRD results, definitively confirming the presence of Bi-O, Na-O, RE-O, and TiO_6 bond vibrations in the sintered ceramic sample. Importantly, a shift towards higher wave numbers was observed as the bond length between titanium (Ti) and oxygen (O) atoms increased. This expansion of the Ti-O bond length leads to alterations in the bond strength and stiffness, resulting in the increase in Raman wave numbers.

The FTIR study showed an intense band at 421 cm⁻¹ in the NBT-RNFS spectrum, indicating the presence of metal-oxide vibrations.

The pore size distribution curves of the NBT-RNFS sample exhibit a wide range of pore radii, spanning from 3.9 nm to greater than 90 nm. This indicates the presence of both mesopores (pores with diameters between 2 nm and 50 nm) and macropores (pores with diameters greater than 50 nm) within the sample. The coexistence of these two types of pores is reflected in the mixed nature of the adsorption isotherm, which displays characteristics of both Type II isotherms (associated with nonporous or macroporous materials) and Type IV isotherms (associated with mesoporous materials). This suggests that the NBT-RNFS sample has a complex pore structure with a combination of mesopores and macropores.

Optical bandgap analysis revealed that the fabricated perovskite samples exhibited semiconducting behavior, with measured bandgap values ranging from 2.61 to 2.80 eV. Specifically, the determined bandgap energies were 2.73 eV for NBT-NFS, 2.61 eV for NBT-LNFS, 2.69 eV for NBT-NNFS, 2.80 eV for NBT-GNFS, and 2.68 eV for NBT-YNFS.

The photocatalytic performance of the rare-earth (R) doped NBT-RNFS compositions was evaluated under simulated solar irradiation conditions and compared to the undoped NBT-NFS ceramic. Notably, the La-doped NBT-RNFS system exhibited an impressive 83% photocatalytic dye degradation rate, substantially outperforming the 23% dye removal efficiency of the undoped material. Similarly, the Nd-doped (62% dye removal) and Y-doped (66% dye removal) NBT-RNFS ceramics also displayed enhanced photocatalytic activities under broadband solar light exposure. These findings demonstrate that the incorporation of RE dopants, such as La, Nd, and Y, into the NBT-RNFS perovskite composition led to significant improvements in the photocatalytic performance of the materials.

The dielectric characteristics of the rare-earth doped ceramic materials were also found to be greatly enhanced. Specifically, the La-doped NBT-RNFS composition demonstrated an exceptionally high dielectric constant (ɛr) of 1151.87, while the Nd-doped NBT-RNFS exhibited a dielectric constant of 1122.31. These values significantly exceeded the dielectric constant of 951.02 obtained for the undoped NBT-NFS ceramic. These findings highlight the ability of rare-earth dopants, such as La and Nd, to modify the dielectric characteristics of the NBT-RNFS perovskite ceramics.

Future work

In addition to the work in this study, the following future research directions would provide more information to fully understand the characteristics of the novel NBT-RNFS materials:

- Explore alternative synthesis techniques, such as molten salt method, to improve the phase purity and particle size control.
- Compare the advantages and limitations of different synthesis approaches in terms of achieving desired NBT-RNFS characteristics.
- Analyze how the molten salt synthesis approach influences the dielectric properties, such as dielectric constant and loss tangent, of the NBT-RNFS materials compared to the solid-state method. This will provide additional insights into how the synthesis technique affects the fundamental electrical behavior of the materials.
- Analyze the piezoelectric and ferroelectric properties, such as piezoelectric coefficients, dielectric constants, and polarization-electric field hysteresis loops, to understand the materials' potential for use in devices like actuators, sensors, and energy harvesters.



Annex 01:

Average grain size = $\frac{\text{line length}}{\text{number of grains}}$ Annex 02:

Energy Dispersive Spectroscopy (EDS/EDX)

(Na0.5Bi0.5) Ti0.95(Ni0.2Fe0.2Sb0.6)0.05O3

Element	Atom %	
Bi	0.5/5=0.1=10%	
Na	0.5/5=0.1=10%	
Ti	0.95/5=0.19=19%	$\sum i = (0.5+0.5)+0.95+(1/5+1/5+3/5)0.05+3$
Ni	(1/5*0.05)/5=0.002=0.2%	= 5
Fe	(1/5*0.05)/5=0.002=0.2%	
Sb	(3/5*0.05)/5=0.006=0.6%	
0	3/5=0.6=60%	
	$\sum = 100$	

$(Na_{0.5}Bi_{0.5})_{0.94}Gd_{0.04}Ti_{0.95}(Ni_{0.2}Fe_{0.2}Sb_{0.6})_{0.05}O_{3}$

Element	Atom %	
Bi	0.5*0.94/4.98= 0.0944 = 9.44%	
Na	0.5*0.94/4.98 =0.0944 =9.44 %	$\Sigma = (0.5 + 0.5)(0.04 + 0.04)$
Gd	0.04/4.98=0.008=0.8%	2 l = (0.5+0.5)0.94 + 0.04 + 0.95 + (1/5+1/5+3/5)0.05 + 3 = 4.98
Ti	0.95/4.98 =0.19=19%	
Ni	(1/5*0.05)/4.98 =0.002=0.2%	
Fe	(1/5*0.05)/4.98 =0.002=0.2%	
Sb	(3/5*0.05)/4.98 = 0.006 = 0.6%	
0	3/4.98=0.6=60%	
	$\sum \approx 100$	

Annex 03:



XRD patterns of the precursor material at room temperature and following calcination in the 500-1150°C range

Name and formula

Reference code:	98-028-0983
Compound name: Common name:	Sodium Bismuth Titanate (0.5/0.5/1) Sodium Bismuth Titanate (0.5/0.5/1)
Chemical formula:	Bi _{0.5} Na _{0.5} O ₃ Ti ₁

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	R 3 c
Space group number:	161
a (Å):	5,4890
b (Å):	5,4890
c (Å):	13,5050
Alpha (°):	90,0000
Beta (°):	90,0000
Gamma (°):	120,0000
Calculated density (g/cm^3):	5,99
Volume of cell (10^6 pm^3):	352,38
Z:	6,00
RIR:	4,42

Subfiles and quality

Subfiles:	User Inorganic
Quality:	User From Structure (=)

Comments

Creation Date:	01/04/2003
Modification Date:	30/12/1899
Original ICSD space group:	R3CH
Structure type:	LiNbO3. Temperature factors available. Rietveld profile refinement applied
The structure has been assigned	a PDF number (calculated powder diffraction data): 01-070-9850. Neutron diffraction
	(powder)
Structure type:	LiNbO3
Recording date:	4/1/2003
ANX formula:	ABX3
Z:	6
Calculated density:	5.99
R value:	0.059
Pearson code:	hR10
Wyckoff code:	b a2
Structure TIDY: TRANS Origin 0	0.26270

Publication title: Investigation of the structure and phase transitions in the novel A-site substituted distorted perovskite compound Na0.5 Bi0.5 Ti O3

ICSD collection code: 280983 Structure: LiNbO3 Chemical Name: Sodium Bismuth Titanate (0.5/0.5/1)

References

Structure:

Thomas, P.A.; Jones, G.O., Acta Crystallographica B (39,1983-), 58, 168 - 178, (2002)

Structure

No.	Name	Elem.	Х	Y	Z	Biso	sof	Wyck.
1	01	0	0,33067	0,12333	0,15393	0,5000	1,0000	18b
2	TI1	Ti	0,00000	0,00000	0,24360	0,5000	1,0000	6a
3	BI1	Bi	0,00000	0,00000	0,00000	0,5000	0,5000	бa
4	NA1	Na	0,00000	0,00000	0,00000	0,5000	0,5000	6a

Stick Pattern



Patte	rn#	1	Phas	e No.:	NBT-NFS	-])	60	reflections,	, N&T:	0 0.00
(The	# 01 CD•	r er	I. 1 ~.	CELL	lons may p	e lower)	E 2 4 0 0	12 50477	00 00000	00 00000
! SP	GR:	K 3	с;	CELL:	5.53	480 5.	53480	13.594//	90.00000	90.00000
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	0	K .	- -	MULL	$D(\mathbf{A})$	21	NW	210		; <u>10-16</u>
	0	1	2	6	3.917277	22.081	0.129665	218 115 () 3.2
ے 1	1	T	ے م	0 C	3.911211 2.720472	22.130	0.1290/9	1006	9 100.5 2 1006.3) 9.1) 10 E
1	1	1	4	0 C	2.772473	32.203	0.133138	1172	5 1000.3 5 11CE 1) IU.5
	1	T	0	6	2.767401	32.323	0.133168	L1/3.	5 II65.I	. 8.2
2	1	1	4	0 C	2.772473	32.345	0.1331/8	542.3	9 540.2 E E 70 4	2./
∠ 1	1	1	0	10	2.7674UI	32.406	0.133208	J/L.:		-/.8
1	1	1	3	10	2.361814	38.070	0.136386	11.0		-5.0
1	Ţ	T	3	12	2.361814	38.169	0.136449	5.0 101		, -1.1
1	0	0	6		2.265793	39.750	0.13/493	101.	104.2	-2.6
1	2	0	2	0	2.260262	39.851	0.137563	262.2	2 268.6	-6.4
2	0	0	6	2	2.265793	39.853	0.13/564	50.0		-1.2
1	2	0	2	6	2.260262	39.955	0.13/633	134.0) 1.0
1	0	2	4	6	1.958639	46.318	0.1425/5	/ 55	3 /19.2 D 257.5	36.0
1	0	1	4	6 1 0	1.958639	46.440	0.142681	350.5	9 357.5	-6.6
1	2	1	1		1.795813	50.801	0.146/60	5	1 5.2	-0.1
2	2	T	Ţ	12	1./95813	50.936	0.146896	3.2	2 2.6	0.6
1	1	T	6	12	1./53144	52.129	0.148116	15.8	5 13.3	3 2.6
	1	2	2	12	1.750578	52.211	0.148202	35.3	5 30.4	5.1
2	1	T	6	12	1./53144	52.268	0.148262	/.8	5 6.6) 1.2
2	Ţ	2	2	12	1./505/8	52.351	0.148348	18.0	J 15.1	2.9
Ţ	0	Ţ	8	6	1.60166/	57.493	0.154163	124.8	B 122.1	2.8
1	2	T	4	12	1.598/34	57.609	0.154303	312.4	4 316.4	-4.0
1	3	0	0	6	1.597760	57.647	0.154350	206.4	4 206.9	-0.4
2	0	1	8	6	1.601667	57.649	0.154353	60.0	6 60.7	-0.1
2	2	Ţ	4	12	1.598/34	57.765	0.154494	158.4	4 157.2	· 1.1
2	3	0	0	6	1.597760	57.804	0.154541	104.1	102.8	1.3
1	1	2	5	12	1.507658	61.451	0.159234	4.	3 13.0	-8.7
2	Ţ	2	5	12	1.50/658	61.620	0.159463	2.4	4 6.5	-4.1
Ţ	2	0	8	6	1.386236	67.515	0.168090	89.	1 92.8	-3.6
1	2	2	0	6	1.383700	67.655	0.168311	180.	/ 186.6	-5.9
2	2	0	8	6	1.386236	67.705	0.168390	44.	/ 46.1	-1.4
2	2	2	0	6	1.383700	67.846	0.168614	91.9	9 92.8	-0.9
1	Ţ	T	9	12	1.325878	/1.038	0.1/3885	3.	3 4.1	-0.8
1	2	T	/	12	1.324/6/	/1.10/	0.1/4003	3.9	9 4.6	-0.6
1	2	2	3	12	1.323382	/1.192	0.1/4151	1.5	D 1.5	-0.0
	1	3	Ţ	12	1.323105	/1.210	0.1/4180	3.5	J J.J	0.2
2	Ţ	1	9	12	1.325878	/1.242	0.174236	2	3 2.1	. 0.3
2	2	T	/	12	1.324/6/	/1.310	0.1/4354	3	1 2.3	0.9
2	2	2	3	12	1.323382	/1.39/	0.174503	1	3 0.1	0.6
2	1	3	1 0	12	1.323105	/1.414	0.1/4533	3.2	2 1.6) 1.5
Ţ	Ţ	0	10	6	1.30/889	/2.16/	0.1/5850	/	9 6.0	1.9
Ţ	0	3	6	6	1.305/59	72.303	0.1/6091	3.0	2.6	0.4
1	3	0	6	6	1.305/59	72.303	0.176091	8.4	4 /.2	· · · ·
1 O	3	T		ΙZ	1.304698	/2.3/1	0.176212	4.6		0.8
2	Ţ	U	ΤŪ	6	1.30/889	12.315	0.176218	3.6	o 3.0	0.6
2	U	3	6	6	1.305/59	/2.512	U.1/6461	1.5	y 1.3	0.6
2	3	U	6	6	1.305/59	/2.512	U.1/6461	5.2	2 3.6) 1.6
2	ک 1	Ţ	2	12	1.304698	12.580	U.1/6583	2.8	5 I.9	, 1.0
1	1	2	8	12	1.239433	/6.851	U.184598	39.0	o 42.9	, -3.4
\perp	1	3	4	12	1.2380/2	/6.951	U.184/95	125.	5 125.9	, -0.6
2	Ţ	2	8	12	1.239433	//.0//7	0.185045	22.1	1 21.4	0.7
2	1	3	4	12	1.238072	11.177	0.185245	65.	/ 62.6	» 3 . 1

 Pattern#
 1 Phase No.:
 1 NBT-LNFS
 60 reflections, N&T:
 0
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 (The # of eff. reflections may be lower)
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 0
 0.00

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 SPGR:
 161;
 CELL:
 5.48837
 5.48837
 13.46607
 90.00000
 90.00000

 120.00000
 0
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Code	h	k	1	Mult	D (A)	2т	HW	Iobs	Icalc	io-ic
1	0	1	2	6	3.883013	22.884	0.122501	181.8	175.1	6.7
2	0	1	2	6	3.883013	22.942	0.122458	90.2	87.1	3.0
1	1	0	4	6	2.747226	32.567	0.115892	950.8	938.2	12.6
1	1	1	0	6	2.744186	32.604	0.115869	1001.0	989.9	11.1
2	1	0	4	6	2.747226	32.650	0.115841	466.5	466.3	0.1
2	1	1	0	6	2.744186	32.688	0.115818	485.6	492.4	-6.8
1	1	1	3	12	2.341309	38.417	0.112600	8.7	5.9	2.7
2	1	1	3	12	2.341309	38.516	0.112550	4.6	2.9	1.6
1	0	0	6	2	2.244344	40.146	0.111747	83.9	82.0	1.9
1	2	0	2	6	2.241032	40.208	0.111717	247.8	251.2	-3.4
2	0	0	6	2	2.244344	40.250	0.111697	40.5	40.8	-0.3
2	2	0	2	6	2.241032	40.312	0.111668	125.8	124.9	1.0
1	0	2	4	6	1.941507	46.751	0.109072	645.7	626.8	18.9
2	0	2	4	6	1.941507	46.874	0.109032	306.6	311.7	-5.1
1	2	1	1	12	1.780715	51.263	0.107856	2.7	0.9	1.9
2	2	1	1	12	1.780715	51.399	0.107828	1.4	0.4	1.0
1	1	1	6	12	1.737306	52.640	0.107597	20.2	20.3	-0.2
1	1	2	2	12	1.735768	52.691	0.107589	17.6	17.1	0.5
2	1	1	6	12	1.737306	52.781	0.107574	10.6	10.1	0.5
2	1	2	2	12	1.735768	52.832	0.107566	9.3	8.5	0.8
1	0	1	8	6	1.586698	58.087	0.107152	165.3	169.3	-4.0
1	2	1	4	12	1.584941	58.158	0.107153	277.8	285.5	-7.7
1	3	0	0	6	1.584357	58.181	0.107153	118.3	120.6	-2.3
2	0	1	8	6	1.586698	58.245	0.107154	84.9	84.2	0.7
2	2	1	4	12	1.584941	58.316	0.107155	143.7	141.9	1.8
2	3	0	0	6	1.584357	58.340	0.107155	61.3	59.9	1.4
1	1	2	5	12	1.494511	62.051	0.107474	0.0	3.2	-3.2
2	1	2	5	12	1.494511	62.222	0.107501	1.8	1.6	0.3
1	2	0	8	6	1.373613	68.220	0.109227	139.6	138.6	1.0
1	2	2	0	6	1.372093	68.306	0.109263	111.6	113.0	-1.4
2	2	0	8	6	1.373613	68.413	0.109308	68.5	68.9	-0.4
2	2	2	0	6	1.372093	68.499	0.109346	56.3	56.2	0.1
1	1	1	9	12	1.313654	71.801	0.111031	5.8	5.8	0.1
1	2	1	7	12	1.312989	71.843	0.111056	0.2	0.2	0.0
1	2	2	3	12	1.312159	71.896	0.111087	0.3	0.2	0.0
1	1	3	1	12	1.311993	71.906	0.111094	1.4	1.3	0.1
2	1	1	9	12	1.313654	72.007	0.111154	3.3	2.9	0.5
2	2	1	7	12	1.312989	72.050	0.111180	0.1	0.1	0.0
2	2	2	3	12	1.312159	72.102	0.111212	0.2	0.1	0.1
2	1	3	1	12	1.311993	72.113	0.111218	1.1	0.6	0.5
1	1	0	10	6	1.295613	72.960	0.111751	1.7	2.0	-0.3
1	0	3	6	6	1.294338	73.044	0.111805	4.6	5.9	-1.4
1	3	0	6	6	1.294338	73.044	0.111805	0.9	1.1	-0.3
1	3	1	2	12	1.293701	73.086	0.111833	1.5	1.8	-0.4
2	1	0	10	6	1.295613	73.171	0.111889	1.0	1.0	-0.0
2	0	3	6	6	1.294338	73.255	0.111945	3.4	3.0	0.4
2	3	0	6	6	1.294338	73.255	0.111945	0.6	0.6	0.1
2	3	1	2	12	1.293701	73.297	0.111973	1.0	0.9	0.1
1	1	2	8	12	1.228325	77.675	0.115410	83.2	79.8	3.4
1	1	3	4	12	1.227509	77.736	0.115466	63.4	62.5	0.9
2	1	2	8	12	1.228325	77.905	0.115620	39.2	39.7	-0.5
2	1	3	4	12	1.227509	77.966	0.115676	30.0	31.1	-1.1
Patte	ern#	1	Pha	se No.	: 2 phase	2	56 re	flections, N&T:	0	0.00

(The # of eff. reflections may be lower) ! SPGR: **F d -3 m**; CELL: 10.31312 10.31312 10.31312 90.00000 90.00000 90.00000

Code	h	k	1	Mult	D (A)	2T	HW	Iobs	Icalc	io-ic
1	2	2	0	12	3.646240	24.392	0.112648	0.4	0.1	0.3
2	2	2	0	12	3.646240	24.454	0.112624	1.2	0.1	1.1
1	3	1	1	24	3.109524	28.686	0.110946	21.3	28.6	-7.3
2	3	1	1	24	3.109524	28.758	0.110917	10.2	14.2	-4.0
1	2	2	2	8	2.977142	29.990	0.110426	168.9	160.8	8.1
2	2	2	2	8	2.977142	30.067	0.110395	82.5	80.0	2.5
1	4	0	0	6	2.578281	34.767	0.108507	50.9	41.3	9.6
2	4	0	0	6	2.578281	34.856	0.108471	22.5	20.5	1.9
1	3	3	1	24	2.365993	38.000	0.107193	21.2	23.6	-2.3
2	3	3	1	24	2.365993	38.099	0.107153	10.1	11.7	-1.6
1	4	2	2	24	2.105158	42.927	0.105163	0.8	0.9	-0.1
2	4	2	2	24	2.105158	43.039	0.105116	0.1	0.4	-0.4
1	3	3	3	8	1.984762	45.674	0.104015	2.3	2.4	-0.1
1	5	1	1	24	1.984762	45.674	0.104015	10.2	10.8	-0.5
2	3	3	3	8	1.984762	45.794	0.103965	1.2	1.2	-0.0
2	5	1	1	24	1.984762	45.794	0.103965	5.2	5.3	-0.2
1	4	4	0	12	1.823120	49.987	0.102185	62.7	62.4	0.3
2	4	4	0	12	1.823120	50.120	0.102128	26.7	31.0	-4.3
1	5	3	1	48	1.743236	52.448	0.101125	5.4	4.4	1.0
2	5	3	1	48	1.743236	52.588	0.101064	2.1	2.2	-0.1
1	4	4	2	24	1.718854	53.250	0.100777	0.0	0.8	-0.8
2	4	4	2	24	1.718854	53.393	0.100715	0.0	0.4	-0.4
1	6	2	0	24	1.630648	56.379	0.099405	2.0	0.7	1.3
2	6	2	0	24	1.630648	56.532	0.099338	2.0	0.3	1.6
1	5	3	3	24	1.572737	58.653	0.098394	0.2	0.2	-0.0
2	5	3	3	24	1.572737	58.813	0.098323	0.1	0.1	-0.1
1	6	2	2	24	1.554762	59.398	0.098060	44.3	36.0	8.3
2	6	2	2	24	1.554762	59.561	0.097987	18.1	17.9	0.3
1	4	4	4	8	1.488571	62.326	0.096735	8.3	4.2	4.1
2	4	4	4	8	1.488571	62.499	0.096656	2.0	2.1	-0.1
1	5	5	1	24	1.444126	64.471	0.095750	1.8	1.8	0.0
1	7	1	1	24	1.444126	64.471	0.095750	1.1	1.1	0.0
2	5	5	1	24	1.444126	64.651	0.095667	1.0	0.9	0.2
2	7	1	1	24	1.444126	64.651	0.095667	0.6	0.5	0.1
1	6	4	2	48	1.378149	67.965	0.094119	0.2	0.2	0.0
2	6	4	2	48	1.378149	68.157	0.094029	0.1	0.1	0.0
1	5	5	3	24	1.342654	70.019	0.093145	0.1	0.2	-0.1
1	7	3	1	48	1.342654	70.019	0.093145	0.3	0.5	-0.1
2	5	5	3	24	1.342654	70.219	0.093050	0.0	0.1	-0.1
2	7	3	1	48	1.342654	70.219	0.093050	0.0	0.2	-0.2
1	8	0	0	6	1.289140	73.386	0.091522	7.2	6.0	1.2
2	8	0	0	6	1.289140	73.599	0.091418	4.1	3.0	1.1
1	7	3	3	24	1.259949	75.378	0.090547	1.8	2.4	-0.6
2	7	3	3	24	1.259949	75.598	0.090438	1.4	1.2	0.2
1	6	4	4	24	1.250650	76.038	0.090221	0.3	0.2	0.0
2	6	4	4	24	1.250650	76.260	0.090111	0.0	0.1	-0.1
1	6	6	0	12	1.215413	78.659	0.088915	0.5	0.4	0.0
1	8	2	2	24	1.215413	78.659	0.088915	0.0	0.0	0.0
2	6	6	0	12	1.215413	78.892	0.088798	1.0	0.2	0.8
2	8	2	2	24	1.215413	78.892	0.088798	0.0	0.0	0.0