EFFECT OF HOLMIUM DOPING ON STRUCTURAL AND LUMINESCENCE PROPERTIES OF $BaBi_2Nb_2O_9$ FERROELECTRIC CERAMICS

A DISSERTATION THESIS

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Submitted by:
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CANDIDATE'S DECLARATION

I, LAKSHYA SAINI, Roll No. 23/MSCPHY/67 student of M.Sc. Physics hereby declares that the project Dissertation titled "Effect Of Holmium Doping On Structural And Luminescence Properties Of $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.00 – 0.08) Ferroelectric Ceramics" which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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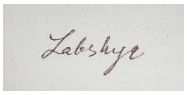

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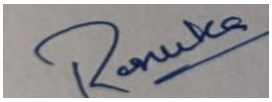
CERTIFICATE

I hereby certify that the Project Dissertation titled "Effect Of Holmium Doping On Structural And Luminescence Properties Of $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.00 – 0.08) Ferroelectric Ceramics" which is submitted by Lakshya Saini Roll No. 23/MSCPHY/67, Department of Applied Physics, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Science, is a record of the project work carried out by the students under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.



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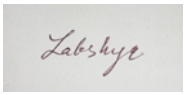

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ABSTRACT

This study presents a comparative investigation of $BaBi_{2-y}Nb_2Ho_yO_9$ ceramics doped with varying concentrations of holmium (y = 0.00 to 0.08). The materials were developed via solid-state synthesis route. This study investigates the structural, optical, electrical, and luminescent properties of pure and Ho^{3+}-doped $BaBi_2Nb_2O_9$ ceramics. X-ray diffraction (XRD), photoluminescence (PL), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible (UV-Vis) spectroscopy, and ferroelectric (PE loop) measurements were used for comprehensive characterization.

The XRD pattern indicated the presence of a single-phase orthorhombic structure and no other secondary phase was found. SEM micrographs revealed a plate-like, randomly oriented microstructure with non-uniform grain distribution. PL spectra under 455 nm excitation exhibited enhanced emission intensity in Ho-doped samples, confirming the effective luminescence contribution of Ho^{3+} ions. FTIR spectra showed distinct vibrational bands near 422, 614, and 828 cm^{-1} corresponding to metal-oxygen bond stretching and bending modes, indicating the presence of NbO_6 octahedra and Bi–O linkages. Shifts in these peaks with increasing Ho content suggest successful incorporation of Ho^{3+} into the lattice and induced structural distortions.

UV-Vis reflectance spectra revealed a reduction in reflectance with Ho doping and a redshift in the absorption edge, implying a slight decrease in optical band gap energy, possibly due to the introduction of intermediate energy states by Ho^{3+} ions. The PE loop measurements displayed unsaturated and slim hysteresis loops for all samples, with maximum polarization observed at y = 0.04, indicating improved ferroelectric response at this doping level. The

degradation of ferroelectric behavior at higher doping concentrations (y = 0.06 and 0.08) can be attributed to increased defect density and structural disorder.

These findings demonstrate that Ho^{3+} doping induces significant modifications in structural, optical, and electrical behaviour, making these ceramics promising candidates for multifunctional applications in optoelectronics and memory devices.

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 INTRODUCTION

Ferroelectric materials have become central to advancements in materials science because of their distinct combination of electrical, optical, and thermal functionalities. One of their hallmark features is spontaneous polarization, which can be reversed when subjected to an external electric field. This switchable polarization makes them highly suitable for integration into capacitors, memory storage devices, piezoelectric transducers, and sensor technologies (Façanha et al., 2017). Among the various classes of ferroelectric materials, Aurivillius-type layered perovskites stand out for their excellent thermal stability, fatigue resistance, and environmentally friendly, lead-free nature.

$BaBi_2Nb_2O_9$ (BBN) is a member of the Aurivillius family and is known for its high dielectric constant, good thermal stability, and layered perovskite structure. Due to these features, BBN holds great potential for use in high-temperature capacitors, piezoelectric actuators, and optoelectronic devices. However, the intrinsic properties of BBN, such as moderate ferroelectric polarization and limited luminescence efficiency, restrict its broader utility. To address these limitations, doping with rare-earth elements has emerged as an effective strategy to tailor the structural, electrical, and luminescent properties of ferroelectric ceramics.

1.2 OBJECTIVES OF THE STUDY

The motive of the research is to explore how doping $BaBi_2Nb_2O_9$ ferroelectric ceramics with holmium (Ho^{3+}) ions affects their structural, optical, and luminescent properties. (Afqir et al., 2018). To achieve this, the following specific objectives were outlined:

Synthesis: To synthesize pure and holmium-doped $BaBi_{2-y}Nb_2Ho_yO_9$ ceramics using a reliable method.

Structural Analysis: To analyze the structural changes induced by holmium doping using techniques such as XRD and FTIR spectroscopy.

Morphological Studies: To study the microstructural evolution of the ceramics using SEM.

Luminescence Characterization: To evaluate the photoluminescence properties of holmium-doped $BaBi_{2-y}Nb_2Ho_yO_9$ and identify key emission mechanisms.

Optical Characterization (UV-Vis Spectroscopy):

To investigate the optical absorption behaviour and estimate the band gap of pure and Ho-doped $BaBi_{2-y}Nb_2Ho_yO_9$ ceramics using UV-Vis spectroscopy, assessing the influence of holmium on electronic structure.

Ferroelectric Properties (P-E Loop):

To measure and interpret the ferroelectric hysteresis behavior (P–E loops) of the ceramics, focusing on changes in remnant polarization, coercive field, and saturation polarization with varying dopant levels.

Comparison with Literature: To compare the findings with existing studies on rare-earth-doped BLSFs and establish the uniqueness of holmium's effects on BBN.

1.3 LITERATURE REVIEW

1.3.1 Ferroelectric Ceramics: Properties and Applications

Ferroelectric ceramics exhibit unique behaviours such as spontaneous polarization, high dielectric constant, and piezoelectricity, making them invaluable in applications like capacitors, actuators, sensors, and memory devices. Among the numerous ferroelectric families, Aurivillius-type layered perovskites have gained considerable recognition for their excellent fatigue resistance, high thermal stability, and lead-free composition, making them environmentally friendly alternatives for sustainable technologies(Karthik & Varma, 2006).

The Aurivillius family of compounds is depicted by the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, where A is a mono-, di-, or trivalent ion, and B is a transition metal ion. These materials consist of alternating (Bi_2O_2) fluorite-like layers and $(A_{n-1}B_nO_{3n+1})$ perovskite layers. $BaBi_2Nb_2O_9$ (BBN), a member of this family, is a two-layer Aurivillius structure (n=2), known for its excellent thermal stability and promising dielectric and ferroelectric properties.

1.3.2 Bismuth Layered Structure Ferroelectrics (BLSFs)

BLSFs, a subset of Aurivillius phases, are characterized by their layered architecture and are extensively studied for practical uses in non-volatile ferroelectric random-access memory (FeRAM), piezoelectric actuators, and energy harvesting devices(Patri et al., 2018). The layered structure of BLSFs offers high resistance to polarization fatigue, making them superior in applications requiring long-term reliability.

Key characteristics of BLSFs include:

Layered Perovskite Units: Alternating ferroelectric perovskite layers and (Bi_2O_2) type insulating layers, which contribute to anisotropic electrical and thermal properties.

Flexibility in Doping: The structure accommodates a wide variety of dopants, enabling tunability of ferroelectric, dielectric, and luminescent properties. Lead-Free Composition: Unlike traditional ferroelectrics, BLSFs offer an environmentally friendly alternative, aligning with global sustainability goals. The properties of BBN, a BLSF material, can be altered by modifying with rare-earth elements like holmium, which modifies its structural and luminescence behavior for potential use in optoelectronic devices.

1.3.3 Rare-Earth Doping in BLSFs

Rare-earth doping in BLSFs, including $BaBi_2Nb_2O_9$, has been a focus of research due to its ability to tailor both structural and functional properties. Rare-earth ions such as Ho^{3+} are known for their localized 4f orbitals, which interact weakly with the surrounding crystal field, resulting in sharp optical transitions and minimal thermal quenching. This makes them ideal for improving photoluminescent properties.

Studies on rare-earth-doped BLSFs reveal:

Enhanced polarization due to reduced oxygen vacancy concentration, Modified crystal structures, with slight distortions or symmetry changes, influencing dielectric and ferroelectric properties, Improved luminescence due to efficient energy transfer mechanisms.

1.3.4 Structural Modifications in $BaBi_2Nb_2O_9$ Due to Doping

$BaBi_2Nb_2O_9$ has a structure exhibiting orthorhombic symmetry with the space group Fmmm. Doping with rare-earth elements like holmium introduces localized distortions and alters lattice parameters, which can have a substantial effect on the material's mechanical strength and functional efficiency (Shaily & Bokolia, 2021). Holmium ions, typically substituting for A-site barium or bismuth, introduce additional defect states and modify the local bonding environment.

X-ray Diffraction (XRD) Studies:

Rare-earth doping often leads to peak broadening in XRD patterns, indicative of reduced crystallite size. Lattice parameters may expand or contract depending on ionic radii differences between the host and dopant ions.

Holmium doping may also suppress secondary phase formation, stabilizing the perovskite structure.

1.3.5 Microstructural and Morphological Effects

The microstructural evolution in BLSFs, particularly $BaBi_2Nb_2O_9$, is highly sensitive to dopant concentration. SEM studies of rare-earth-doped BLSFs typically reveal:

Reduction in grain size, which enhances mechanical stability and dielectric properties. Improved grain boundary connectivity, leading to better charge transport and reduced leakage current. Secondary phase formations at high dopant concentrations, which may impact luminescence and ferroelectric properties.

Holmium doping is anticipated to refine the grain morphology of $BaBi_2Nb_2O_9$, facilitating a uniform and dense microstructure beneficial for electrical and optical applications.

1.3.6 FTIR Analysis for Functional Group Characterization

Fourier Transform Infrared (FTIR) spectroscopy provides critical insights into the vibrational modes of the ceramic structure. In $BaBi_2Nb_2O_9$, characteristic peaks are observed for:

Nb–O bond stretching, corresponding to the octahedral vibrations in the perovskite layers. Bi–O bonds in the (Bi2O2) layers. Holmium doping typically shifts these vibrational peaks due to modifications in local bonding and lattice dynamics. The presence of Ho–O stretching

vibrations may introduce additional peaks or modify existing ones, highlighting the incorporation of holmium into the lattice.

1.4 Significance of the Study

The study of holmium-doped $BaBi_2Nb_2O_9$ (BBN) ferroelectric ceramics is significant for several reasons, addressing both fundamental scientific questions and practical applications. This research contributes to the growing field of rare-earth-doped materials and highlights their potential for multifunctional applications.

Advancing Fundamental Understanding of Doped BLSFs

Bismuth Layered Structured Ferroelectrics (BLSFs), such as $BaBi_2Nb_2O_9$, possess a unique layered architecture that allows for extensive modification through doping. This study focuses on holmium doping, which introduces localized structural changes that can significantly affect the material's physical and chemical properties. By exploring the impact of holmium on the crystal lattice, defect chemistry, and microstructure, this research provides valuable insights into the mechanisms underlying doping-induced enhancements in BLSFs. These insights are crucial for developing materials with tailored properties.

Enhancing Ferroelectric and Optical Properties

The structural modifications induced by holmium doping can stabilize the ferroelectric phase and reduce the concentration of oxygen vacancies in $BaBi_2Nb_2O_9$. These improvements have direct implications for enhancing the material's ferroelectric and optical properties, such as Increased polarization and reduced coercive field, Improved thermal and electrical stability, Better resistance to fatigue during prolonged electrical cycling. Such enhancements make holmium-doped BBN a strong candidate for energy storage devices, high-temperature capacitors, and piezoelectric actuators.

Luminescence for Optoelectronic Applications

One of the most significant aspects of holmium doping is its potential to introduce and enhance luminescence in $BaBi_2Nb_2O_9$. The sharp f–f electronic transitions of holmium ions produce characteristic emissions in the visible and near-infrared regions, making them highly desirable for: Light-emitting devices (LEDs), Laser materials, Phosphors for display technologies.

The study's focus on understanding and optimizing these luminescent properties opens new avenues for using BBN in optoelectronic and photonic devices.

Contribution to Sustainable Material Development

The global shift toward environmentally friendly materials has increased interest in lead-free alternatives to traditional ferroelectrics. $BaBi_2Nb_2O_9$, being a lead-free material, aligns with sustainability goals. By enhancing its performance through holmium doping, this study contributes to the development of high-performance, eco-friendly materials for advanced technologies.

Broadening the Applications of Rare-Earth-Doped Ferroelectrics

Rare-earth-doped ferroelectrics have traditionally been explored for specific applications such as capacitors or piezoelectric devices. By combining structural, dielectric, and luminescence enhancements, this study positions holmium-doped BBN as a multifunctional material suitable for: Integrated electronic devices, Energy harvesting systems, Advanced photonic and optoelectronic technologies.

This multidimensional improvement broadens the applicability of rare-earth-doped ferroelectrics and underscores the versatility of holmium as a dopant.

CHAPTER-2

EXPERIMENTAL METHODOLOGY

This chapter details the experimental procedures followed to synthesize, characterize, and analyze the holmium-doped $BaBi_2Nb_2O_9$ (BBN) ceramics. The methodology covers the synthesis route, doping strategy, and the characterization techniques employed to study the structural, morphological, and luminescent properties of the samples.

2.1 Synthesis of Holmium-Doped $BaBi_2Nb_2O_9$

The synthesis of holmium-doped $BaBi_2Nb_2O_9$ ceramics was carried out using the **solid-state reaction method**, a widely used technique for preparing ceramic materials of high-purity.

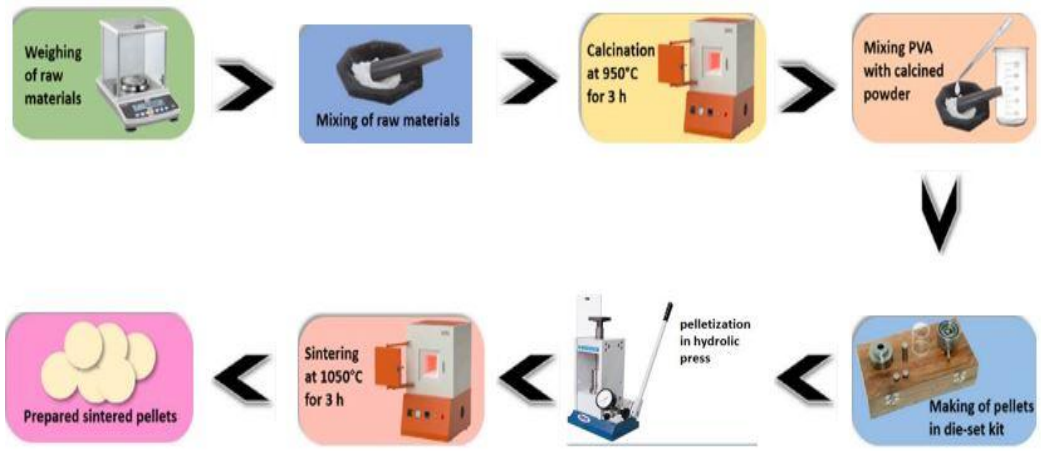

Fig 1: experimental methodology

2.1.1 Initial precursor

The following high-purity (≥99.9%) precursors were used:

Barium carbonate ($BaCO_3$) – Source of barium.

Bismuth oxide (Bi_2O_3) – Source of bismuth.

Niobium pentoxide (Nb_2O_5) – Source of niobium.

Holmium oxide (Ho_2O_3**)** – Source of holmium dopant.

2.1.2 Composition

Holmium was introduced into the BBN structure with the general formula $BaBi_{2-y}Ho_yNb_2O_9$ where x represents the doping concentration. Doping concentrations of y=0.00, y=0.02, y=0.04, y=0.06, y=0.08 were utilized to examine how holmium content affects the properties of the material.

2.1.3 Synthesis Procedure

Weighing and Mixing: An electronic balance was used to accurately weigh the stoichiometric proportions of the starting materials. The precursors were thoroughly mixed in an agate mortar with ethanol as a dispersant for uniform mixing(Banwal & Bokolia, 2022).

Calcination: The mixed powders underwent heat treatment process called calcination in an alumina crucible at 950°C for 3 hours in a muffle furnace. The calcination process decomposed carbonates and oxides, causing the onset of the preferred phase formation.

Pelletization: The calcined powders were compacted into cylindrical discs incorporating a uniaxial hydraulic press operated at a pressure of 5 MPa. To enhance the binding and mechanical integrity of the green bodies, a small quantity of polyvinyl alcohol (PVA) was incorporated as a temporary binder.

Sintering: The green pellets were undergone to a sintering process at 1050°C for a time period of 3 hours to promote densification and crystallization. After sintering, the specimens were allowed to cool gradually to ambient temperature in the furnace.

CHAPTER-3

Characterization Techniques

To comprehensively analyze the structural, microstructural, and functional properties of holmium-doped $BaBi_2Nb_2O_9$ ceramics, various characterization methods were utilized:

3.1 XRD

- **Instrument**: A Cu-Kα source X-ray diffractometer (λ = 1.5406 Å) was employed.
- **Purpose**:
    - Identify the crystal structure and phase purity of the samples.
    - Analyze lattice parameters, crystallite size, and strain.
- **Procedure**:
    - XRD scans were conducted across a 2θ range from 20° to 80°, with a step size of 0.02°.

3.2 SEM

- **Instrument**: SEM unit equipped with Energy Dispersive X-ray Spectroscopy (EDX) capability.
- **Purpose**:
    - Study the microstructural features, including grain size and morphology.
    - Confirm elemental composition and homogeneity using EDX.
- **Procedure**:
    - The sintered samples were polished and coated with a thin layer of gold to prevent charging during imaging.

3.3 FTIR Spectroscopy

- **Instrument**: FTIR spectrometer in the range of **400–4000 cm^{-1}**.

- **Purpose**: Identify the vibrational modes corresponding to functional groups in the ceramic structure and detect the existence of Nb–O, Bi–O, and Ho–O bonds.
- **Procedure**:
    - The powdered samples were mixed with KBr in a 1:10 ratio and pressed into pellets for measurement.

3.4 Photoluminescence (PL) Spectroscopy

- **Instrument**: PL spectrometer.
- **Purpose**: To analyze the luminescence properties of the samples and identify emission peaks associated with holmium doping(Banwal & Bokolia, 2021a).
- **Procedure**:
    - Emission spectra were noted primarily in the visible and near-infrared range.
    - The intensity of emissions was compared across different doping concentrations.

3.5 UV-Visible (UV-Vis) Spectroscopy

- **Instrument:** UV-Vis spectrophotometer operated in the wavelength range of 200–800 nm.
- **Purpose:**
    - To investigate the optical absorption behavior of pure and Ho-doped BBN ceramics.
    - To estimate the optical band gap and observe the impact of holmium modification on electronic transitions.
- **Procedure:**
    - Finely ground ceramic powders were dispersed uniformly for reflectance measurements.

- Absorbance data was converted to Tauc plots to determine the band gap energy.

3.6 P-E Loop Measurement

- **Instrument:** Ferroelectric loop tracer (e.g., RT66A or similar) with a high-voltage amplifier.
- **Purpose:**
  - To study the ferroelectric properties of the ceramics, including remnant polarization (Pr), coercive field (Ec), and saturation polarization (Ps).
  - To evaluate the effect of holmium doping on ferroelectric behavior and domain switching.
- **Procedure:**
  - Disc-shaped sintered samples were coated with silver paste as electrodes and dried.
  - At room temperature, P-E hysteresis loops were captured under the influence of an electric field.

3.7 Data Analysis

- **3.7.1 XRD Analysis**:

This technique was employed to examine the phase purity, crystallographic structure, and any structural changes induced by holmium (Ho^{3+}) doping in $BaBi_2Nb_2O_9$ (BBN) ceramics. The measurements were performed using Cu-Kα radiation (λ = 1.5406 Å) in a 2θ range of 10° to 80°, with a step interval of 0.02°. (Rerak et al., 2022). The XRD pattern of pure $BaBi_2Nb_2O_9$ closely matches the standard JCPDS card no. 00-012-0403, confirming its single-phase layered perovskite structure with an orthorhombic symmetry having an Fmmm phase group.

With the incremental substitution of Bi^{3+} by Ho^{3+} ions ($BaBi_{2-y}Nb_2Ho_yO_9$; y = 0.02–0.08), no secondary phases or impurity peaks were detected, demonstrating the successful incorporation of holmium into the BBN lattice without altering its phase integrity. A slight shift in peak positions toward higher 2θ values can be noted with increasing Ho content, suggesting lattice contraction because of the smaller ionic radius of Ho^{3+} (1.015 Å) compared to Bi^{3+} (1.17 Å). This substitution causes local lattice distortion and strain, which is consistent with Vegard's law.

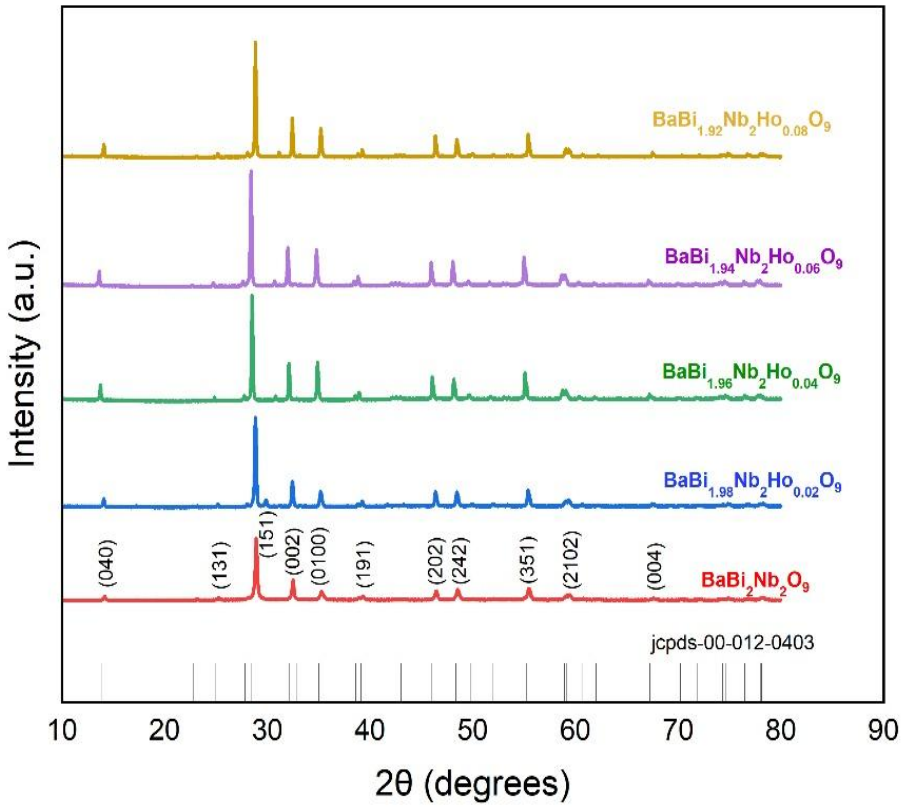

Fig 2: XRD spectra of pure and Ho^{3+} doped $BaBi_{2-y}Nb_2Ho_yO_9$; (y = 0.02–0.08)

3.8.2 SEM Analysis:

The microstructural properties of pure $BaBi_2Nb_2O_9$ (BBN) and holmium-doped $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.02–0.08) ceramics were analyzed using SEM. The SEM images

provided a detailed understanding of the surface morphology, grain size, and grain distribution in both samples. The analysis emphasizes how holmium incorporation influences the microstructural characteristics of the material.

The average particle size of pure and Ho-doped $BaBi_2Nb_2O_9$ (BBN) ceramics were investigated(Banwal & Bokolia, 2021b). SEM micrographs revealed that the synthesized powders exhibit relatively dense morphology with slight grain agglomeration, which is common in ceramics prepared via solid-state reaction methods.

The particle sizes were estimated from SEM images using image analysis software, and the variation in average particle size with different holmium doping concentrations is summarized below:

Table 3.2: Deviation of mean Particle Size with Holmium Doping Concentration.

Ho Concentration (y)	**Average Particle Size (µm)**
0.00	1.1133
0.02	1.4674
0.04	1.8429
0.06	1.8669
0.08	1.2822

From the data, it is observed that the average particle size increases with holmium doping up to x = 0.06. This increase in grain growth may be attributed to the role of Ho^{3+} ions in enhancing mass transport and densification during sintering. However, at the highest doping level (x = 0.08), a reduction in particle size is observed, which may be due to the excess dopant inhibiting

grain boundary mobility or causing defect-induced pinning effects that restrict further grain growth.

Overall, the SEM analysis confirms the influence of holmium doping on the microstructural evolution of BBN ceramics, which could significantly impact their electrical and optical properties.

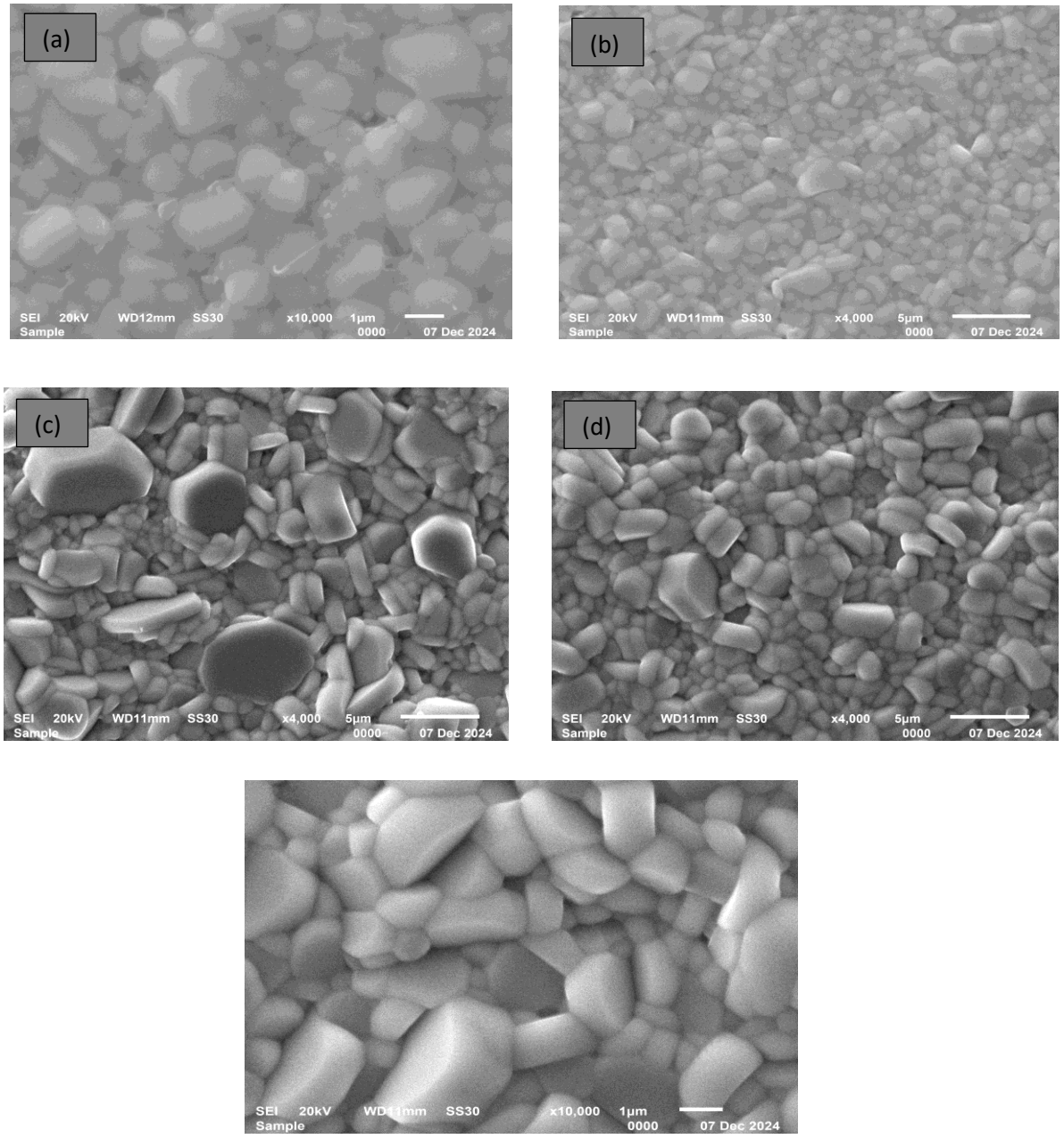

Fig3: (a) Sem image of $BaBi_2Nb_2O_9$ (b)Sem image of $BaBi_{1.98}Nb_2Ho_{0.02}O_9$. (c) Sem image of $BaBi_{1.96}Nb_2Ho_{0.04}O_9$. (d) Sem image of $BaBi_{1.94}Nb_2Ho_{0.06}O_9$. (e) Sem image of $BaBi_{1.92}Nb_2Ho_{0.08}O_9$

3.8.3 FTIR Analysis:

FTIR spectroscopy was used to analyze the vibrational modes and bonding characteristics in pure and holmium-doped $BaBi_2Nb_2O_9$ ceramics. Spectral data were collected across a wavenumber range of 400 to 3500 cm^{-1} for samples with different Ho^{3+} concentrations (y = 0.00 to 0.08), with the obtained spectra illustrated in Figure 4.

The FTIR spectra exhibit distinct absorption bands corresponding to characteristic metal–oxygen vibrations in the perovskite structure. A prominent and broad absorption band is observed in the region between **400 cm^{-1} and 1000 cm^{-1}**, which is typically associated with metal–oxygen stretching and bending vibrations in the NbO_6 octahedra. The peak observed at **~422 cm^{-1}** is attributed to the bending vibration of Nb–O bonds. A strong absorption band centered at **~614 cm^{-1}** corresponds to the symmetric stretching mode of Nb–O–Nb linkages within the NbO_6 octahedra. The sharp peak at **~828 cm^{-1}** is ascribed to the antisymmetric stretching vibration of Nb–O bonds in the distorted octahedral environment.

These peaks validated the formation of the layered perovskite structure and the presence of Nb–O bonding environments, essential for ferroelectric and dielectric properties.

As the Ho^{3+} doping concentration increases, The intensity of the characteristic bands changes, and slight shifts in peak positions are observed, indicating that Ho^{3+} ions are successfully incorporated into the lattice, replacing Bi^{3+} ions. The changes in band sharpness and intensity with doping suggest modifications in the local structural environment and possible lattice distortions due to ionic radius mismatch between Ho^{3+} and Bi^{3+}.

In the high wavenumber region (2500–3500 cm^{-1}), broad bands are noticed due to the O–H stretching vibrations, indicating the presence of adsorbed moisture or hydroxyl groups, which is typical in oxide ceramics exposed to atmospheric conditions. Overall, the FTIR analysis confirms the structural integrity of the $BaBi_2Nb_2O_9$ framework upon Ho doping and provides evidence of successful substitution and interaction of dopant ions with the host lattice.

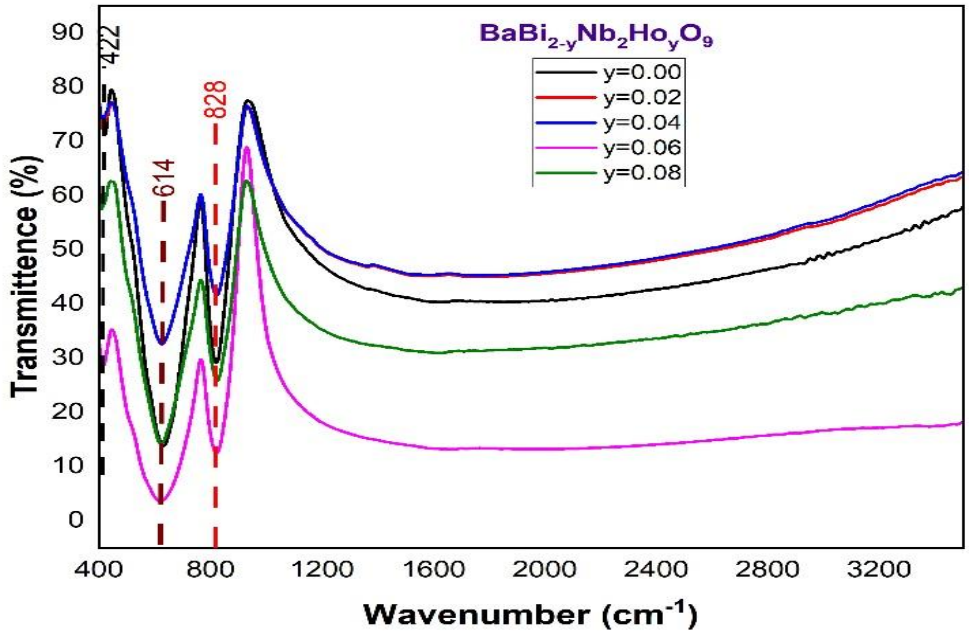

Fig 4: FTIR spectra of pure and Ho^{3+} doped $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.02–0.08)

3.8.4 PL Analysis:

To examine the optical emission characteristics of Ho^{3+}-doped $BaBi_2Nb_2O_9$ ceramics, photoluminescence (PL) spectroscopy was employed using ultraviolet-blue excitation. Spectra were captured at room temperature with a 454 nm excitation source, as presented in Figure 3.5. The emission spectra corresponding to Ho^{3+} concentrations (y = 0.02, 0.04, 0.06, and 0.08) exhibited several peaks, predominantly in the green and red regions, indicative of typical downconversion emission behavior. (Bokolia et al., 2015).

The dominant emission peak observed at approximately **546 nm** corresponds to the $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ transition of Ho^{3+} ions, responsible for green luminescence. A weaker red emission is observed around **660 nm**, which is attributed to the $^5F_5 \rightarrow {}^5I_8$ transition. These transitions are parity-forbidden electric dipole transitions that become allowed due to the asymmetric crystal field surrounding the Ho^{3+} ions in the $BaBi_2Nb_2O_9$ host lattice.

With increasing doping concentration from **0.02 to 0.08**, the emission intensity initially increases and then decreases beyond a certain threshold (observed most strongly at y = 0.02). This trend is attributed to concentration quenching, where non-radiative energy transfer among closely spaced Ho^{3+} ions leads to a decrease in emission efficiency at higher doping levels.

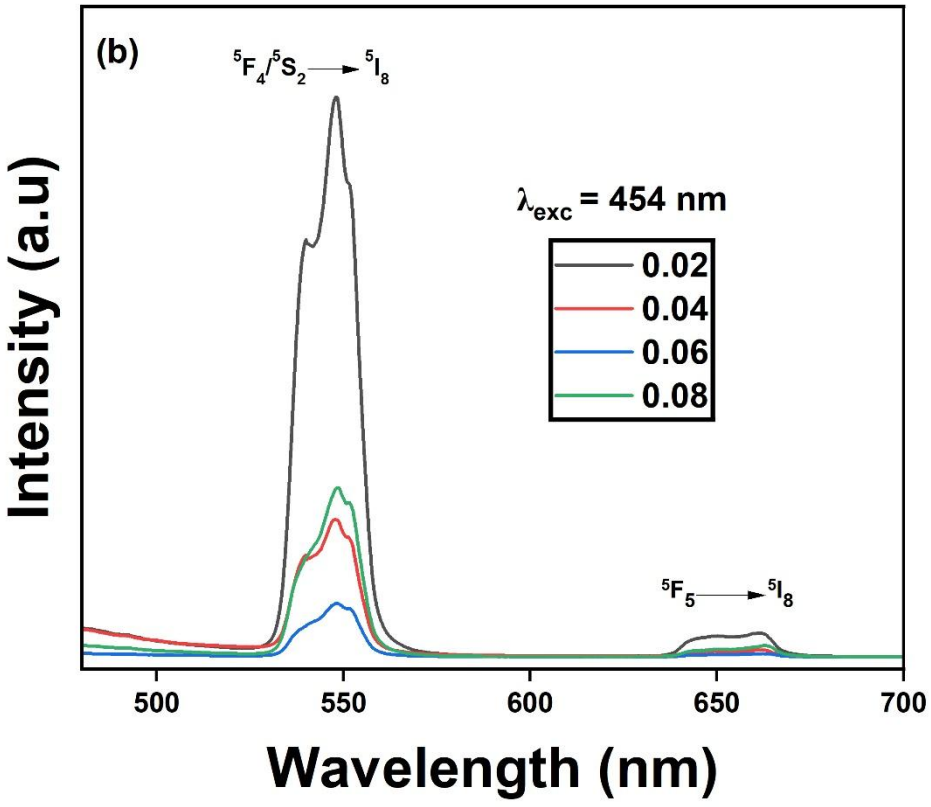

Fig 5: PL spectra of $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.02–0.08) under the excitation of 454 nm.

The optimal luminescence is observed at **y = 0.02**, suggesting this as the ideal concentration for downconversion applications.

The downconversion process exhibited by these materials renders them promising candidates for use in photonic devices, solid-state lighting, and solar energy conversion, where transforming high-energy photons into visible light offers significant advantages.

3.8.5 UV-Vis Diffuse Reflectance Spectroscopy Analysis

The optical properties of pure $BaBi_2Nb_2O_9$ (BBN) and Ho^{3+}-doped BBN samples ($BaBi_{2-\gamma}Nb_2Ho_\gamma O_9$, where y = 0.00, 0.02, 0.04, 0.06, and 0.08) were investigated using UV-Vis spectroscopy in the wavelength range of 200–900 nm. The corresponding reflectance spectra are presented in Figure 6.

The reflectance curves exhibit distinct features corresponding to both the host matrix (BBN) and the effects of Ho^{3+} doping:

- **Baseline behavior of pure BBN (y = 0.00):**
  The undoped BBN sample shows a relatively high reflectance in the visible region beyond ~500 nm, with a pronounced dip in the reflectance centered around 330–400 nm. This dip corresponds to the fundamental band gap absorption edge of the BBN matrix, typically associated with charge-transfer transitions between O 2p and Nb 4d orbitals.

- **Effect of Ho^{3+} substitution:**

Upon doping with holmium, a noticeable modification in the spectral profile is observed. With increasing Ho content The overall reflectance in the visible region (400–800 nm) decreases for intermediate concentrations (y = 0.02 to 0.06), indicating enhanced light

absorption. A series of small reflectance minima or inflections appear around 450–650 nm, which are absent or less pronounced in the undoped sample. These features are likely attributed to the intra-4f transitions of Ho^{3+} ions (Laporte-forbidden but partially allowed due to mixing with host lattice orbitals), such as $^5I_8 \rightarrow {}^5G_6$, $^5F_4$, $^5S_2$ transitions. At higher doping levels (y = 0.08), there appears to be a partial recovery of reflectance, suggesting possible saturation effects or the onset of secondary phase formation or clustering, which can reduce the efficiency of dopant-lattice interaction.

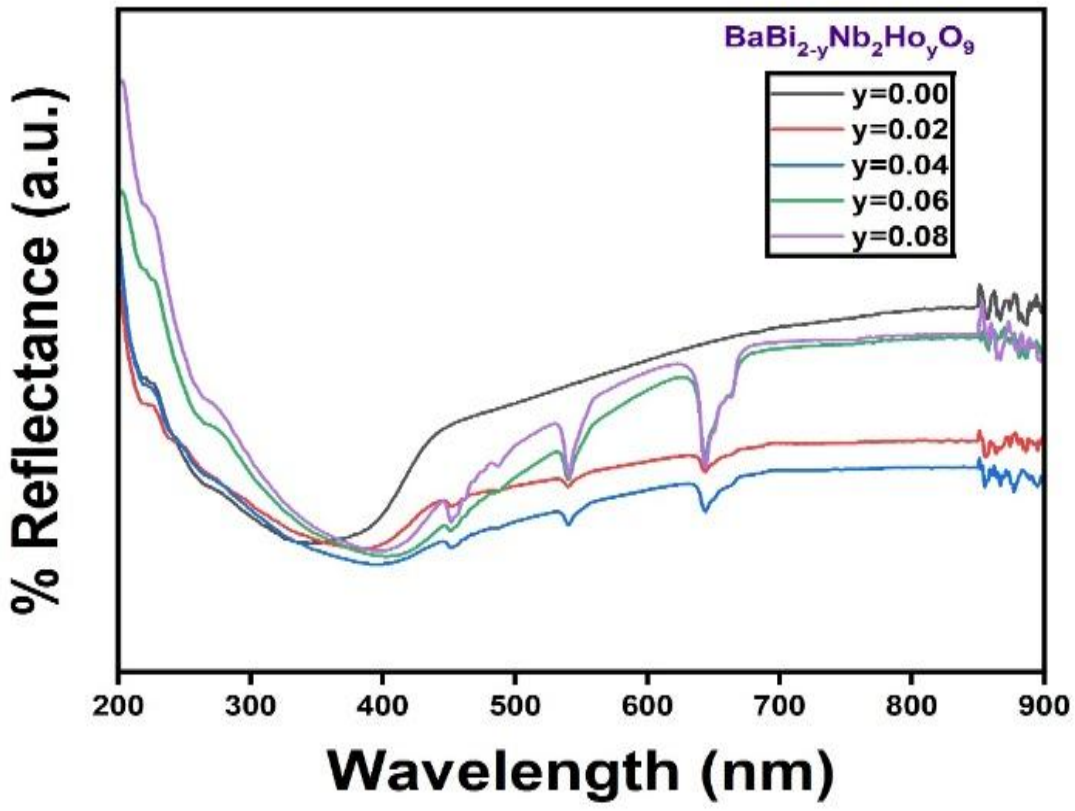

Fig 6: UV-Vis absorption spectra of undoped and Ho-doped $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.00, 0.02, 0.04, 0.06, and 0.08) ceramics with varying Ho concentrations (y = 0.00 to 0.08).

All samples show strong absorption below 400 nm, indicating that the band edge of BBN remains in the UV region. However, a slight redshift in the absorption edge can be inferred

with increasing Ho^{3+} content, suggesting a narrowing of the optical band gap (Bokolia et al., 2017).

This behaviour may result from the incorporation of Ho^{3+} ions into the B-site of the perovskite structure, causing localized electronic states within the bandgap or altering the Nb–O bonding network. The observed trend in the reflectance spectra implies that Ho^{3+} doping effectively modifies the optical absorption properties of BBN. The gradual decrease in reflectance and emergence of new absorption features in the visible range suggest the potential to tailor BBN for applications requiring visible light activity, such as photocatalysis or optoelectronic devices.

3.8.6 Ferroelectric Properties: P–E Hysteresis Loop Analysis

Ferroelectric characteristics of undoped and Ho^{3+}-substituted $BaBi_{2-\gamma}Nb_2Ho_\gamma O_9$ ceramics (where y = 0.00 to 0.08) were analyzed using P–E hysteresis loop measurements. These loops were obtained at ambient conditions under an applied electric field of ±70 kV/cm, as depicted in Figure X. The pristine BBN sample (y = 0.00) displayed a distinct and closed hysteresis loop, confirming its ferroelectric nature. Key parameters such as P_r and P_{max} were evident, indicating the ability of the material to exhibit reversible spontaneous polarization.

The loop is slightly rounded, which is characteristic of BBN ceramics due to their layered perovskite structure and moderate leakage current(Swami et al., 2020). As the holmium concentration increases, a notable change in the shape and area of the hysteresis loops is observed. At y = 0.02 and 0.04, the loops remain open and slightly enhanced compared to the undoped sample, particularly at y = 0.04, where the largest loop area and highest polarization (~6.2 $\mu C/cm^2$) are seen, suggesting improved ferroelectric properties. This improvement may be attributed to optimal substitution of Ho^{3+} at the Bi^{3+} site, leading to enhanced lattice distortion and local dipole alignment. At higher doping levels (y = 0.06 and 0.08), the loops

become slimmer and more linear, approaching a lossy dielectric-like behaviour. This reduction in loop area indicates decreased remnant polarization and possible degradation of long-range ferroelectric ordering.

High Ho^{3+} content might introduce excessive lattice strain, point defects, or oxygen vacancies, which can pin domain walls and suppress polarization switching. Ho^{3+} ions, having a smaller ionic radius than Bi^{3+}, cause local structural distortion when substituted into the A-site of the perovskite layers.

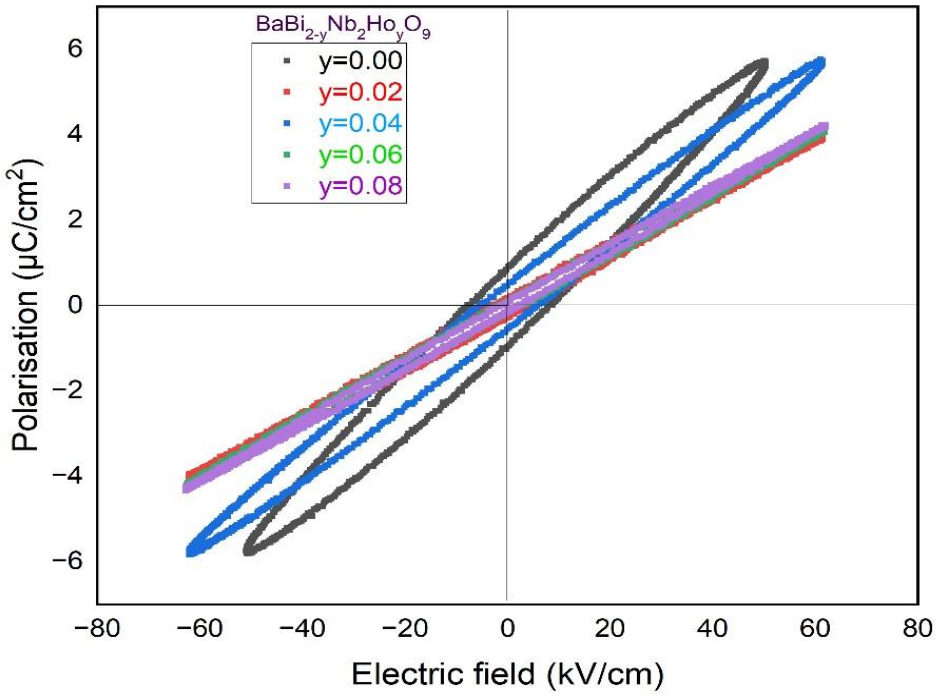

Fig 7: Polarization v/s Electric Field (P-E) curve of $BaBi_{2-y}Nb_2Ho_yO_9$ (y = 0.00,0.02,0.04,0.06,0.08)

At lower concentrations, this distortion can enhance local dipole alignment and increase polarizability. However, beyond a critical doping limit (y > 0.04), defect-induced disorder and potential non-ferroelectric secondary phase formation start to dominate, reducing the net switchable polarization.

CHAPTER 4

CONCLUSION AND FUTURE SCOPE

4.1 **Conclusion**

This research explored how incorporating holmium (Ho^{3+}) influences the structural and luminescence characteristics of $BaBi_2Nb_2O_9$ (BBN) ferroelectric ceramics. The X-ray diffraction results verified that the orthorhombic Aurivillius-type layered perovskite structure remained intact across all compositions, with no evidence of impurity phases. A slight shift in diffraction peaks and changes in lattice parameters indicated successful substitution of Bi^{3+} ions by Ho^{3+} ions, leading to minor lattice distortions. The crystallite size was slightly influenced by holmium doping, and phase stability was preserved across all doping concentrations.

SEM analysis revealed that holmium doping promoted grain growth, with the average grain size increasing with higher doping levels. The doped ceramics showed enhanced densification and reduced porosity, which are critical for improving the functional properties.

FTIR spectra showed the presence of characteristic vibrational modes related to Nb–O, Bi–O, and Ho–O bonds, confirming the structural integrity of the doped ceramics.

PL analysis showed a notable increase in emission intensity for the Ho^{3+}-doped specimens, which can be linked to the characteristic intra-4f electronic transitions of holmium ions. UV-Vis measurements demonstrated a gradual redshift in the absorption edge with higher Ho^{3+} content, suggesting a narrowing of the optical band gap. This behaviour is likely a result of dopant-induced localized energy states within the band structure, enhancing light absorption in the visible range—an effect potentially beneficial for solar energy conversion and photocatalytic systems.

Polarization–electric field (P–E) loop measurements demonstrated that the P_r and coercive field values varied with Ho doping, suggesting that dopant concentration influences domain wall motion and defect dipole interaction. Improved ferroelectric behaviour at moderate doping concentrations indicates possible applications in non-volatile memory devices and dielectric components.

Holmium doping improved the microstructure and luminescence properties of BBN ceramics, making them suitable for potential applications in optoelectronic devices, sensors, and photonic materials.

4.2 Future Scope

The findings of this study open up several opportunities for further research and development in holmium-doped BBN ceramics:

1. Optimization of Doping Levels:

Further studies can explore doping levels beyond the range studied here to identify the optimal concentration for maximizing luminescent and dielectric properties.

2. Dielectric and Ferroelectric Studies:

Comprehensive investigations on the dielectric, ferroelectric, and piezoelectric properties of doped BBN ceramics are needed to evaluate their suitability for memory and actuator applications.

3. Temperature-Dependent Behaviour:

Analysis of structural and luminescent properties at varying temperatures could provide insights into the thermal stability of holmium-doped BBN ceramics.

4. Integration in Devices:

Research on fabricating thin films or composites of doped BBN ceramics could advance their application in miniaturized electronic and optoelectronic devices.

5. Energy Applications:

The improved luminescent properties make these materials candidates for applications in energy-harvesting devices, such as solar cells and photocatalysts.

6. Multi-Dopant Systems:

The effects of co-doping with other rare-earth ions, such as Eu^{3+} or Dy^{3+}, can be explored to further enhance the optical and dielectric properties of BBN ceramics.

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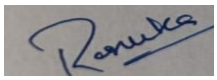

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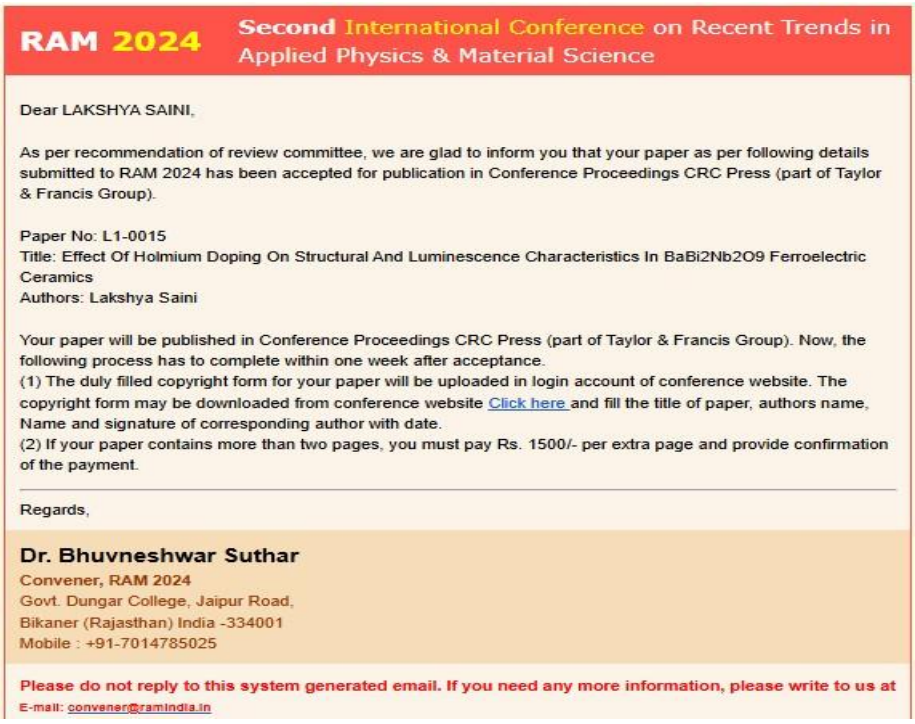

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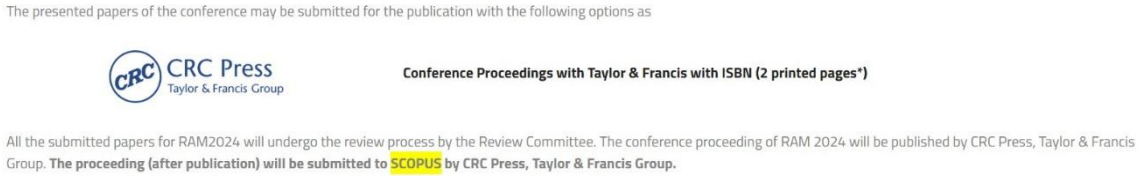

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