JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Ferroelectric And Structural Behavior of Bismuth Layered Structured Ferroelectric Ceramics Prepared Via High-Energy Ball Milling

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ABSTRACT

$SrBi_4Ti_4O_{15}$ (SBT) is a Bismuth layered (Aurivillius) ferroelectric ceramic valued for its stable polarization and high curie temperature. SBT powders were prepared using high-energy ball milling and sintered into dense ceramics. X -ray diffraction confirmed the layered orthorhombic phase, while SEM showed well-sintered plate-like grains. Ferroelectric measurements (P-E hysteresis) at room temperature revealed typical polarization, coercive field, and good reversibility, influenced by grain orientation and homogeneity. The results confirm SBT stability and suitability for high-temperature ferroelectric and piezoelectric applications. This study establishes a clear link between processing, structure, and ferroelectric behavior, providing a foundation for further improvements through doping or microstructural optimization.

Keywords: $SrBi_4Ti_4O_{15}$, Aurivillius ceramics, XRD, SEM, Ferroelectric properties, Hysteresis.

1. INTRODUCTION

Dielectric materials are essential in modern electronics because they can store and release electrical energy under an applied field. This makes them widely used in capacitors, sensors, actuators, and memory devices. Their performance mainly depends on two key parameters: dielectric constant, which measures the ability to store charge, and dielectric loss, which reflects energy dissipation. For practical application, materials with high dielectric constant, low loss, and stability across temperature and frequency ranges are preferred.

Bismuth-layered structured ferroelectrics (BLSF), part of the Aurivillius family, are a special class of ferroelectric oxides. Their structure consists of perovskite like slabs separated by Bi_2O_2 layers, giving them strong anisotropy and multifunctional behaviour. They are valued for their high curie temperature, fatigue resistance, lead-free nature, and stable dielectric and piezoelectric properties, making them suitable for advanced devices.

$SrBi_4Ti_4O_{15}$ (SBT) is an n=4 member of this family. its crystal structure has four perovskite-like slab stacked along the c-axis, sandwiched between Bi_2O_2 layers. At room temperature, SBT crystallizes in an orthorhombic phase, which changes to tetragonal above ~500-500 ^{0}C. These features make SBT a promising material for high-temperature capacitors, piezoelectric actuators, and non-volatile memory applications. SBT ceramics gained attention due to their promising dielectric and ferroelectric properties, which are strongly influenced by their microstructure. To study these materials, techniques such as X-ray diffraction (XRD) and scanning electron microscopy milling has emerged as an effective processing method, as it improves the uniformity of the materials, lowers the calcination temperature, and supports better densification and grain size control. These improvements directly contribution to enhanced device performance. However, despite these advantages there is still limited research that systematically compares the effects of tradition preparation methods, leaving an important gap for future investigation.

2. SYNTHESIS OF THE MATERIAL

The synthesis of ceramic materials, particularly for Aurivillius type layered perovskite like $SrBi_4Ti_4O_{15}$ (SBT), greatly influences their structural and electrical properties. For this study, a solid-state reaction by planetary ball milling was used to synthesize rare earth doped SBT ceramics.

RAW MATERIALS:

High purity powders were used

- Strontium carbonate ($SrCO_3$,99.9%)
- Bismuth oxide (Bi2O3,99.9%)
- Titanium dioxide (TiO_2,99.9%)

Rare earth Oxides (Nd_2O_3, Ho_2O_3) were added for doping.

Synthesis by Ball Milling

Planetary ball milling enhanced powder mixing and reduced particle size:

- Ball to powder ratio: ~10.1
- Speed: ~300 rpm
- Duration :12 hours (with pauses)
- Medium: Isopropanol, dried at 100 ^{0}C after milling.

The milling powders were calcined at 800-850 ^{0}C for 4 hour in alumina crucibles to initiate phase formation. The calcined powders were then pressed into pellets using PVA binder.

Sintering:

Pellets were sintering at 1100-1500 ^{0}C for 2-4 hour with controlled heating and cooling to achieve densification.

This simplified version retains all the essential details while being more concise.

3. Characterization Techniques

- **X-ray Diffraction (XRD):**

Used to assess phase purity, crystal structure, and lattice parameters of the synthesized ceramics. Data were collected in the 2θ range of 10°–80° using CuKα radiation (λ = 1.5406 Å) and compared with JCPDS references to confirm the formation of the Aurivillius phase.

- **Scanning Electron Microscopy (SEM):**

Performed on thermally etched sintered pellets to examine microstructure, including grain size, porosity, and grain boundary features.

- **X-Ray Diffraction (XRD) Analysis**

  XRD was performed to study the phase formation, crystallinity, and structural stability of pure and rare-earth substituted $SrBi_4Ti_4O_{15}$ (SBT) ceramics using Cu Kα radiation (λ = 1.5406 Å) over 2θ = 10°–80°. The diffraction peaks matched JCPDS data, confirming the formation of a single-phase orthorhombic Aurivillius structure without noticeable secondary phases.
- Rare-earth substitution caused slight peak shifts due to lattice distortions from ionic radius differences. At low doping levels, peaks shifted to lower angles (lattice expansion), while higher doping caused shifts to higher angles (lattice contraction). These variations verify dopant incorporation into the lattice.
- Refined lattice parameters showed small changes consistent with ionic substitution. Crystallite size, calculated using the Debye–Scherrer formula, was in the nanometer range, indicating fine-grained ceramics. Overall, rare-earth doping preserved the layered perovskite structure while introducing minor structural modifications that can influence dielectric and ferroelectric behavior.

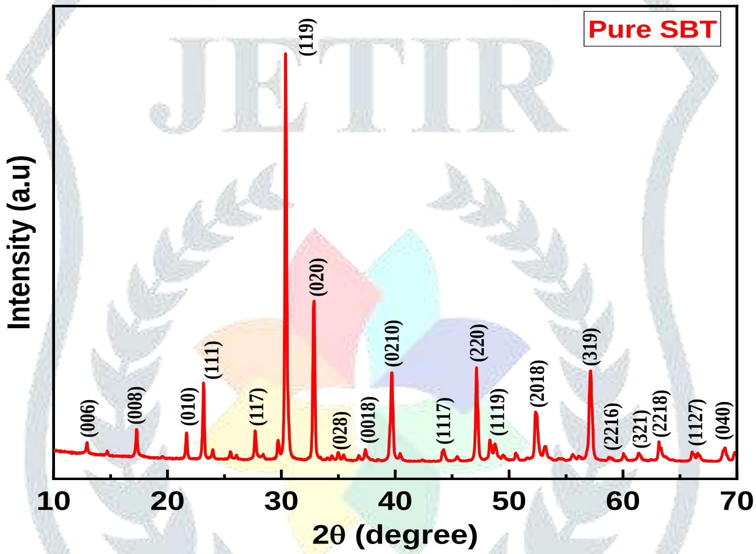

Figure 1: X-ray diffraction pattern of pure $SrBi_4Ti_4O_{15}$ ceramic prepared by the ball milling method, confirming the orthorhombic Aurivillius layered perovskite structure

Scanning Electron Microscopy (SEM) Analysis:

SEM was used to study the microstructure of pure and rare-earth doped $SrBi_4Ti_4O_{15}$ (SBT) ceramics, focusing on grain shape, size distribution, porosity, and densification. The micrographs show a dense structure with plate-like grains, typical of Aurivillius layered oxides, caused by preferential growth along the a–b plane. Grain boundaries are clearly defined, and pores are minimal, indicating effective sintering.

Grain size generally falls between sub-micron to a few micrometres. Pure SBT exhibits relatively larger grains, while rare-earth substitution refines grain size by restricting boundary mobility. This refinement improves dielectric stability and lowers leakage by suppressing domain wall motion. The dense microstructure with few pores enhances both dielectric constant and ferroelectric polarization. The morphology observed in SEM aligns with the layered phase confirmed by XRD.

SEM of $SrBi_4Ti_4O_{15}$ Ceramics:

Figure 2 shows the fracture surface of pure SBT prepared by high-energy ball milling. The grains are plate-like (1–5 µm), closely packed, and display a mixed size distribution due to milling and subsequent anisotropic growth.

Limited porosity and well-connected grain boundaries suggest good densification, beneficial for dielectric and ferroelectric performance.

The fine plate-like grains restrict domain wall motion, reducing losses, while the dense structure improves polarization and insulation. Thus, SEM confirms that ball milling effectively produces dense, plate-like microstructures, favourable for enhanced dielectric and ferroelectric behavior in SBT ceramics.

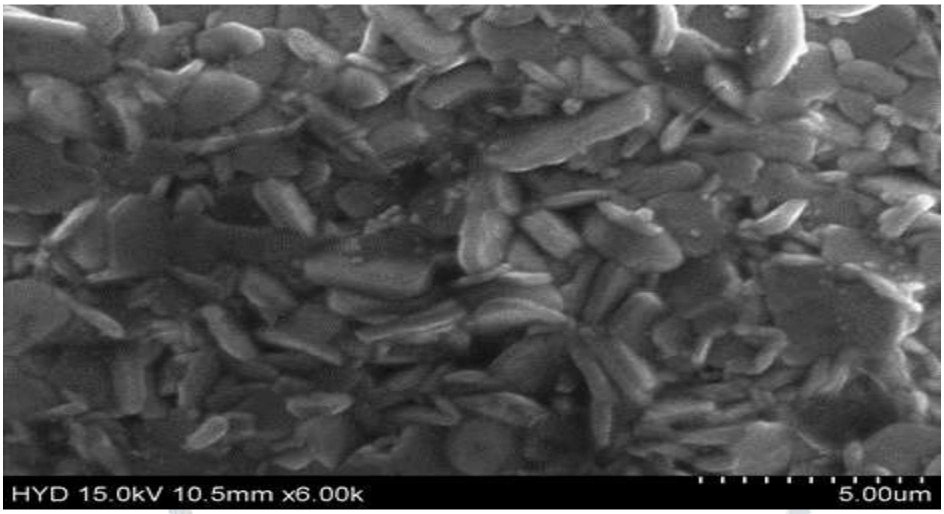

Figure 2: SEM micrograph of pure $SrBi_4Ti_4O_{15}$ ceramic prepared by the ball milling method, showing dense plate-like grains typical of Aurivillius layered perovskite oxides

Ferroelectric properties:

Ferroelectricity is a key feature of bismuth-layered structured ferroelectrics (BLSFs) like $SrBi_4Ti_4O_{15}$ (SBT). These materials exhibit reversible spontaneous polarization, typically analyzed using the polarization–electric field (P–E) hysteresis loop. This loop provides information on remanent polarization, coercive field, and switching behavior. In SBT, the Aurivillius-type layered structure, with perovskite slabs separated by Bi_2O_2 layers, induces strong anisotropy. As a result, switching requires higher fields, producing slim loops compared to conventional perovskites such as $BaTiO_3$ or $PbTiO_3$.

P–E Hysteresis:

Ferroelectric measurements of ball-milled and sintered SBT ceramics were carried out at room temperature under ±150 kV/cm. The obtained P–E loop verifies ferroelectric behavior but appears slender and elongated rather than square, a typical trait of Aurivillius phases. This response arises from anisotropic structure and domain wall pinning, which restrict polarization switching.

Analysis of Ferroelectric Parameters:

From the P–E loop, the following observations were made:

- **Remanent Polarization (Pr):**
  The polarization retained in the absence of an electric field was found to be about 7–8 µC/cm². This value is moderate compared to classical ferroelectrics but is in agreement with reported values for SBT ceramics.

- **Coercive Field (Ec):**
  The electric field required to reverse the polarization direction was about 70–80 kV/cm, which is relatively high compared to perovskite ferroelectrics. This high coercive field arises from the strong anisotropy of the layered structure and defect-related pinning of domain walls.
- **Saturation Polarization (Ps):**
  At the maximum applied field (±150 kV/cm), the polarization approached about 12 μC/cm², indicating that full polarization saturation was not achieved. This is common in SBT ceramics due to the difficulty of aligning all dipoles under an applied field.
- **Loop Shape and Slimness:**
  The slim nature of the hysteresis loop reflects hard ferroelectric behavior, meaning that the material has lower dielectric losses and improved fatigue resistance, which is desirable for high-temperature piezoelectric devices but less suitable for ferroelectric memory applications.
- **Asymmetry of Loop:**
  A slight asymmetry was observed in the P–E loop, which may be attributed to space charge effects, oxygen vacancies, grain boundary contributions, or internal bias fields introduced during ball milling and sintering.

Correlation with Structure and Microstructure:

The ferroelectric response of SBT is strongly influenced by its structural and microstructural features. The orthorhombic Aurivillius structure confirmed by XRD explains the anisotropic switching, while SEM shows dense plate-like grains that support layered growth and domain alignment. Defects such as oxygen vacancies and Bi loss during sintering act as pinning centers, leading to slim loops and high coercive fields.

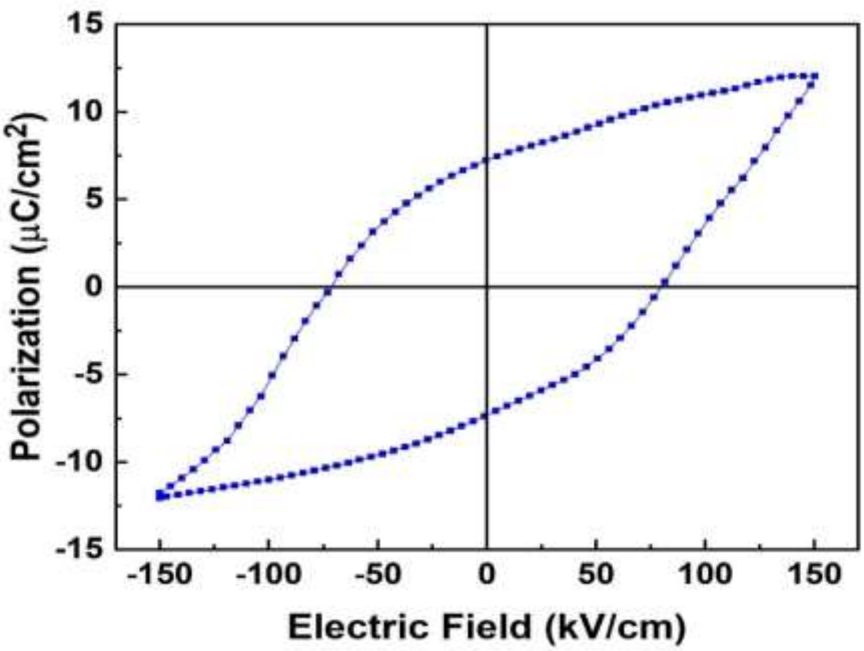

Figure 3: Polarization–electric field loop of pure SBT

- The closed loop verifies ferroelectric switching with clear remanent polarization (~7–8 μC/cm²).
- The coercive field is relatively high (~70–80 kV/cm), typical of Aurivillius compounds.
- At ±150 kV/cm, the polarization approaches ~12 μC/cm² but does not fully saturate, showing incomplete domain alignment.

- The loop is slim and slightly asymmetric, reflecting anisotropy, oxygen vacancies, and internal bias from processing.

Conclusion

$SrBi_4Ti_4O_{15}$ ceramics were successfully synthesized through high-energy ball milling followed by solid-state sintering. The main outcomes are:

- Single-phase orthorhombic SBT (space group A21am) was obtained with sharp peaks indicating good crystallinity and no secondary phases, confirming the effectiveness of the milling route.
- The samples showed a dense, layered morphology with plate-like grains in the submicron–micron range. The observed anisotropic growth is typical of Aurivillius ceramics, with slight agglomeration from high reactivity.
- SBT displayed a clear hysteresis loop with Pr ≈ 7–8 μC/cm², Ec ≈ 70–80 kV/cm, and Ps ≈ 12 μC/cm². The slim loop reflects hard ferroelectric behavior arising from structural anisotropy and defect pinning.

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