

# Structural and electrical investigation in Pr modified SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> Ceramics

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## Abstract

*SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (SBT) and SrBi<sub>3.9</sub>Pr<sub>0.1</sub>Ti<sub>4</sub>O<sub>15</sub> (SBPT) polycrystalline ceramics were prepared using a planetary ball mill and the solid-state sintering technique. Stoichiometric amount of precursor powders were grinded for 10 hour. The XRD results confirmed single phase formation. At Bragg angle of 30°, the highest peak (119) was visible. The use of Pr<sup>+3</sup> in place of Bi<sup>+3</sup> resulted in smaller cells and orthorhombic distortion, according to X-ray diffraction results. Scanning electron microscope revealed existence of microstructures grains with variation in particle size. At frequencies of 10kHz, 15kHz, 25 kHz, 50kHz and 100kHz, the LCR dielectric analyzer was used to measure the dielectric properties between 100°C temperature and 700°C. When SBT doped with Praseodymium, the Curie temperature rose while the dielectric constant and loss decreased.*

**Keywords:** Solid state sintering; X-Ray diffraction; scanning electron microscopy; Curie temperature, dielectric constant; dielectric loss.

## 1. Introduction

The Bismuth Layer-Structured Ferroelectrics (BLSFs) are very interesting materials because of their many applications. Lead-free piezoelectric materials, Bismuth Layered Structured Ferroelectrics (BLSFs), are excellent for sensors. These sensors work at high temperatures and show a lot of stability. The BLSFs materials have high Curie temperatures and low dielectric constant; they could be utilized as alternatives to PZT, which is widely used these days. Several researchers have studied Bismuth Layer-Structured Ferroelectrics (BLSFs).<sup>[1-3]</sup> Recently, research of the ferroelectric family has been more focused on non-volatile ferroelectric random access memory (FeRAM) applications<sup>[4-5]</sup>. BLSF materials offer a viable alternative to PZT materials for high-temperature piezoelectric sensor applications. Since the Curie temperature of the Aurivillius family is above 500 °C, these BLSF materials are suitable to lead free piezoelectric materials. The presence of bismuth ions increases the Curie temperature<sup>[6-7]</sup>. The standard formula for BLSFs is  $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})_2$ <sup>[8]</sup>, where A is monovalent, divalent, or trivalent, or a combination of these, B is a transition element, and m is the number of octahedra between Bismuth oxide layers. m is usually an integer that ranges from 1 to 5<sup>[9]</sup>.  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  (SBT) is a material with good electrical characteristics<sup>[10]</sup>. SBT, a BLSF with m=4, has been explored by a number of researchers<sup>[11]</sup>. The dielectric characteristics of Rare-Earth doped ceramics, synthesized using the solid-state reaction technique, are described in this paper.

## 2. Experimental Procedure

### 2.1. Sample preparation

$\text{SrCO}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Pr}_2\text{O}_3$  and  $\text{TiO}_2$  (Sigma Aldrich 99%) are taken as raw precursor to make the ceramic compounds SBT and SBPT in a ball mill. The stoichiometry powder ratios are milled for 5 hours in a ball mill in distilled water medium, then calcined for 2 hours at 800 °C<sup>[12-13]</sup>. The calcined powder is processed further for 5 hours in ball mill. The specimens were pressed and 1 percent polyvinyl alcohol was used as a binder at a pressure of 10MPa, resulting in pellets with a thickness of 1 mm and a diameter of 1cm, which were then sintered at 1160 °C for 2 hours<sup>[14-18]</sup>. The densities are calculated using the Archimedes principle and a density tool kit.

### 2.2. Characterization

The Pan analytical X 'pert plus Diffractometer was used to study X-Ray Diffractogram data at room temperature. The Archimedes method was used to determine the densities of sintered ceramics using distilled water (density 0.91 g/cm<sup>3</sup>) as the liquid media. The Archimedes rule is used to calculate the experimental densities. HITACHI S4300SE/N was used to take SEM micrographs of the ceramic compounds. Dielectric properties measured using LCR meter.

Table 1.

S.NO	Compound	Nomenclature
1	$\text{SrBi}_4\text{Ti}_4\text{O}_{15}$	SBT
2	$\text{SrBi}_{3.9}\text{Pr}_{0.1}\text{Ti}_4\text{O}_{15}$	SBPT

### 3. Results and Discussions

#### 3.1. X-Ray Diffraction

Figure 1 shows the XRD results. With  $m=4$ , this shows the presence of a pure Bismuth oxide layer type structure. The results revealed that the crystal symmetry is orthorhombic, and that a single phase is generated, with no evidence of a second phase. Using JCPDS information card no. 43-0973, the peaks and corresponding intensities are compared to standard data. At room temperature, the SBT and SBPT phase are evaluated using a Pan analytical X' pert plus Diffractometer. The XRD analyses demonstrate that a pure single phase of perovskite of ferroelectrics with  $m=4$  was formed. It should be noted that substituting Pr ions for Bi ions didn't impact on the phase formation, no additional peaks have been reflected and structural modifications. The maximum intensity peak observed at (1 1 9), indicated BLSFs structure [23].

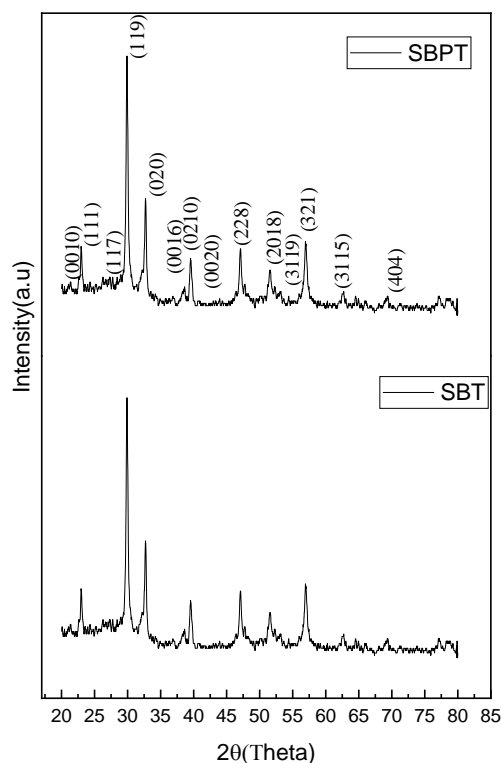
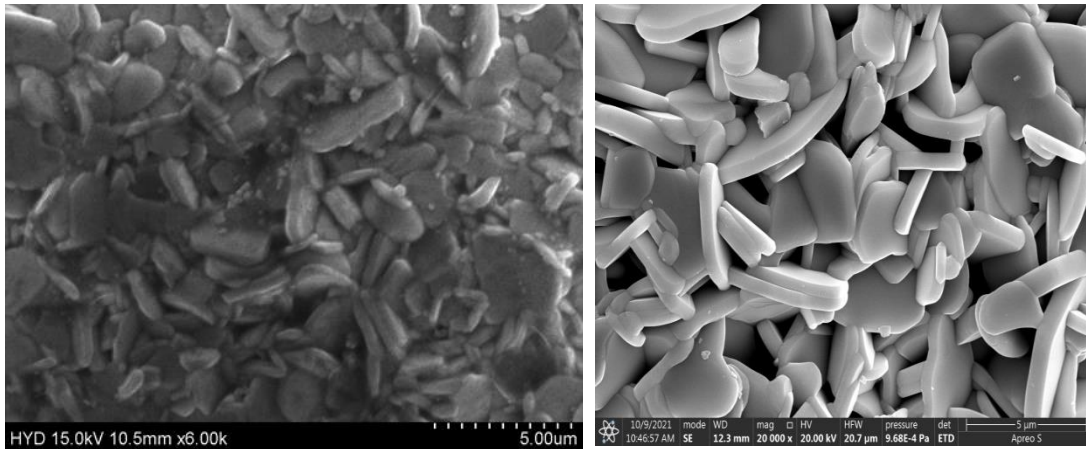


Figure 1. XRD pattern of SBT and SBPT

### 3.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) images of SBT and SBPT ceramics are shown in Figure 2. A SEM employs a focused electron beam to reveal the complete surface characteristics of a samples as well as information about its three-dimensional structure. It is made up of plate like grains with irregular plate force directions <sup>[19]</sup>. It is realized that plate-like grain arrangement is a standard characteristic of BLSF, which as shown on the sintered surface dense structure.



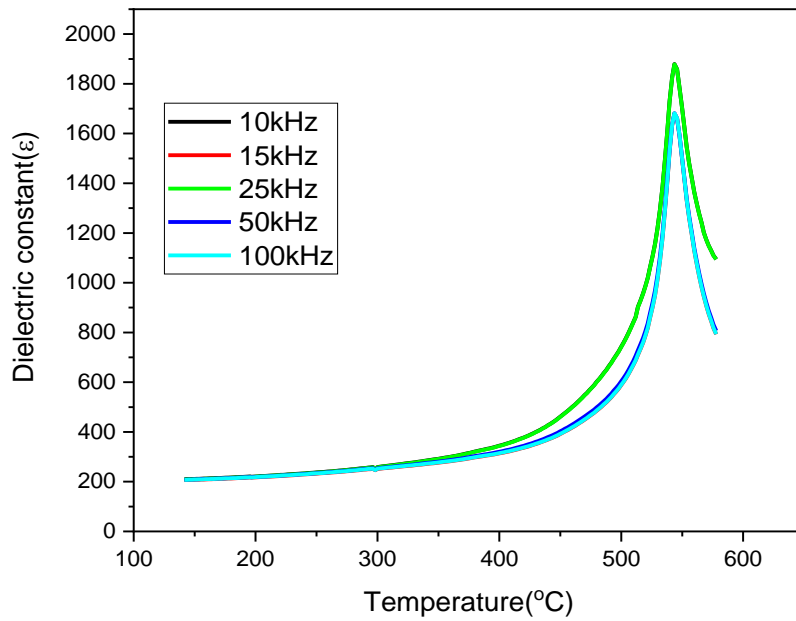
**Figure 2. Scanning electron microscope (SEM) images SBT and SBPT**

### 3.3 Dielectric Properties

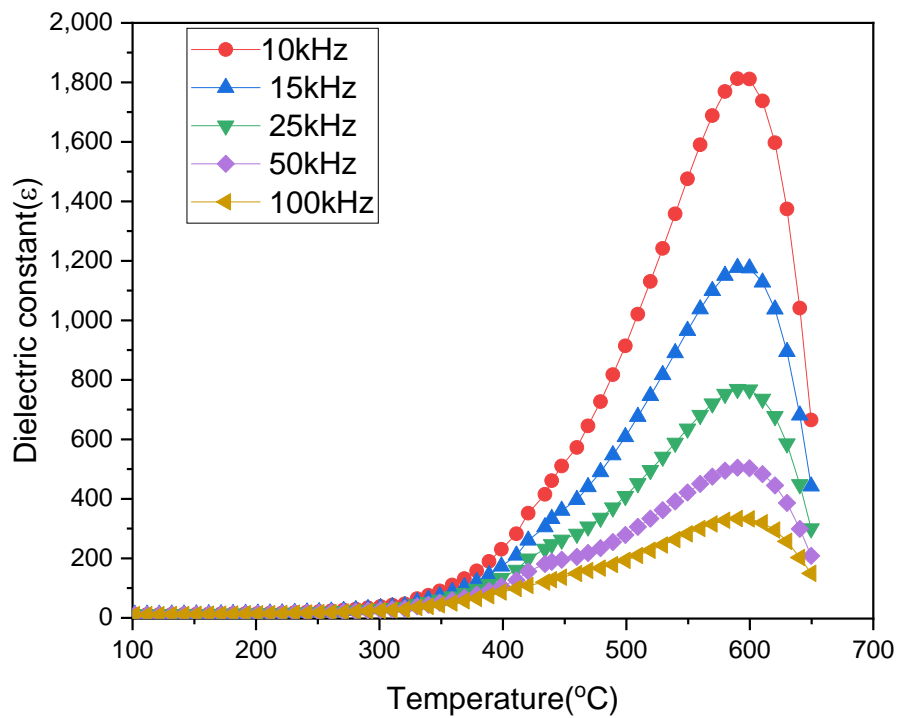
The figure3 and 4 show dielectric constant at distinct frequencies (10 kHz, 15 kHz, 25 kHz, 50kHz and 100 kHz) from 100 °C to 700 °C for SBT and SBPT ceramics. The dielectric constant and Curie temperature in SBT and SBPT improve with increasing temperature. The connection acquired between dielectric constant and temperature as function of frequency shows that the dielectric constant reduces with replacement of Praseodymium of SBT. The Curie temperature ( $T_c$ ) for SBT was found to be 535 °C <sup>[20-22]</sup> by prior reports. In the current work, Curie temperature was found at 544 °C for SBT and 593 °C for SBPT. The Curie temperature increased from 544 °C to 593 °C by adding of Praseodymium with ionic radii 1.013Å, individually twisting of oxygen octahedra. The raised  $T_c$  affirms bending of oxygen octahedral. The Curie temperature is generally related to the tolerance factor ( $t$ ). The tolerance factor is correlated to the size of A-site cation. Tolerance factor ( $t$ ) relation given by

$$t = \frac{R_A + R_O}{2(R_B + R_O)} \text{-----(1)}$$

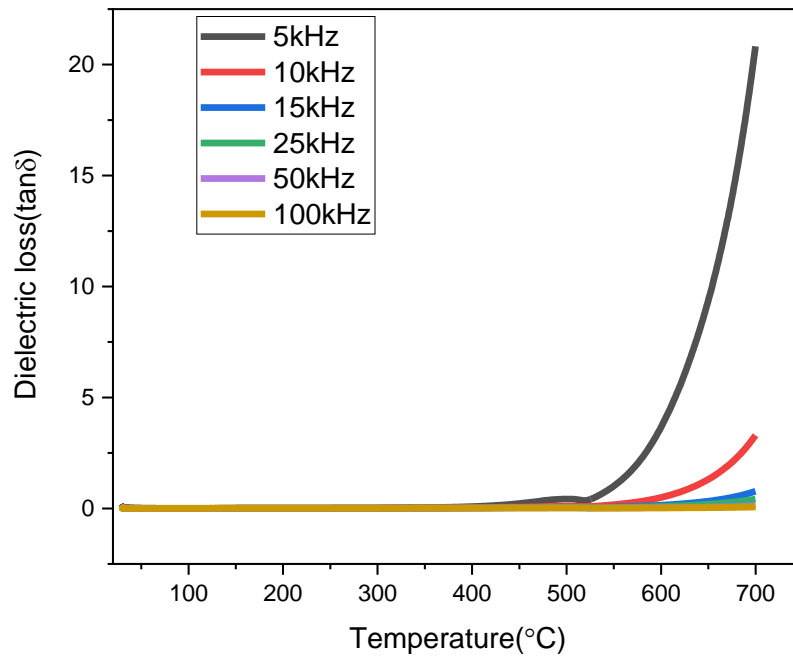
Here  $R_A$  is ionic radii belonging to A- site,  $R_B$  is ionic radii belonging to B- site cations and  $R_O$  oxygen ions respectively. The tolerance factor of pure SBT was 0.938. The tolerance factor was found to decrease with substitution in place of Bismuth. This allows improved rotation of  $TiO_6$  in a-b plane and higher Curie temperature.



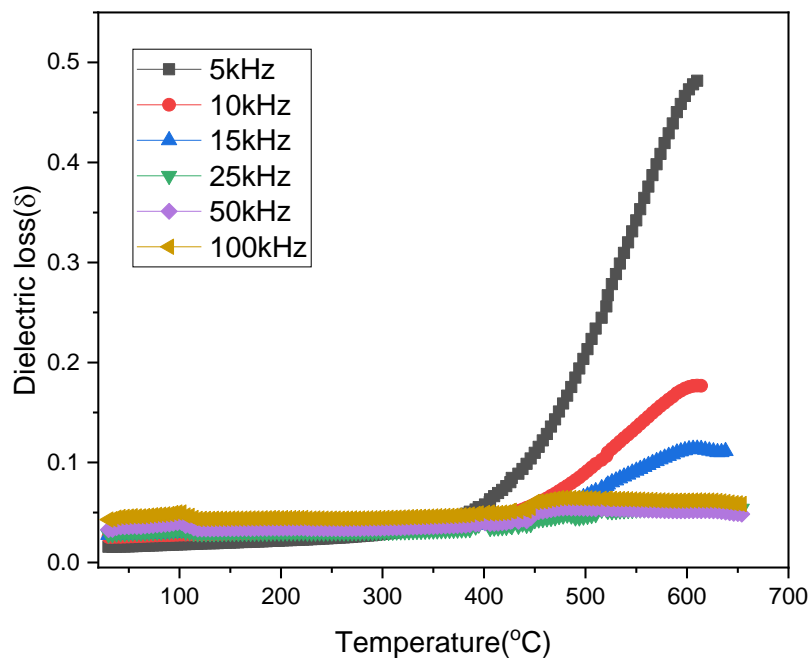
**Figure3. Dielectric constant of SBT as a function of temperature at different frequencies.**



**Figure4. Dielectric constant of SBPT as a function of temperature at different frequencies.**



**Figure 5. Dielectric loss (Tanδ) of SBT with temperature**



**Figure 6. Dielectric loss (Tanδ) of SBPT with temperature**

## 5. Conclusion

In summary, SrBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>(SBT) and SrBi<sub>3.9</sub>Pr<sub>0.1</sub>Ti<sub>4</sub>O<sub>15</sub> (SBPT) have been prepared by solid state sintering method, utilizing ball mill for 10 hours. The specimens were calcined at a temperature of 800°C and pellets were sintered at 1160°C for 2 hours. X-ray diffraction analysis revealed that the Pr-doped SBT ceramics had a pure phase, and SEM was used to obtain plate-like, grain structures. The dielectric characteristics were measured. The Curie temperature increased from 544°C to 593°C by introducing Praseodymium in place of Bismuth. With increasing frequency, the dielectric constant decreased. The dielectric loss was stable up to 410°C. The dielectric constant and loss tangent of the ceramics decreased with increasing frequency. Pr-doped SBT ceramics were improved compared to those of pure SBT ceramics. These results suggest that Pr doping can effectively enhance the electrical properties of SBT ceramics, making them suitable for use in various electronic devices such as capacitors, piezoelectric transducers, and sensors. Further studies are needed to optimize the doping concentration and processing conditions to achieve even better performance. As a result, the SBPT piezoelectric ceramics developed and examined in this study are suitable for high temperature applications.

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