# Dielectric studies of Niobium Modified $SrBi_4Ti_4O_{15}$ Ceramics

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## Abstract

*$Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$ (SBNBT) polycrystalline ceramics were prepared using a planetary ball mill*

*This work investigates the structural and dielectric properties of $Nb^{5+}$-doped $SrBi_4Ti_4O_{15}$ ceramics synthesized through the conventional solid-state reaction method. The incorporation of $Nb^{5+}$ ions into the $SrBi_4Ti_4O_{15}$ lattice was confirmed by X-ray diffraction (XRD), which revealed a layered perovskite structure. A noticeable shift in XRD peak positions was observed, reflecting changes in lattice parameters due to the modifications with $Nb^{5+}$ ions. Microstructural analysis using scanning electron microscopy (SEM) demonstrated a uniform and dense morphology with well-defined grain boundaries. Dielectric properties were characterized over a wide range of frequencies and temperatures, showing a substantial enhancement in dielectric constant and a reduction in dielectric loss with increasing $Nb^{5+}$ concentration. The Curie temperature was found to shift to higher values upon $Nb^{5+}$ doping, indicating improved thermal stability of the material. These results suggest that $Nb^{5+}$-doped $SrBi_4Ti_4O_{15}$ ceramics hold promise for high-temperature dielectric applications and advanced electroceramic devices.*

*At frequencies of 10kHz, 15kHz,25 kHz,50kHz and 100kHz, the LCR dielectric analyzer was used to measure the dielectric properties between 100$^oC$ temperature and 700$^oC$. 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

Bismuth Layer-Structured Ferroelectrics (BLSFs) have garnered significant attention due to their wide range of applications, particularly as lead-free piezoelectric materials. These materials are highly suitable for use in high-temperature sensors due to their remarkable thermal stability. BLSFs exhibit high Curie temperatures and low dielectric constants, making them promising alternatives to lead-based piezoelectric materials like PZT, which is commonly used today. Numerous studies have investigated the properties of BLSFs, highlighting their potential in various applications [1-3].

Recently, research within the ferroelectric family has increasingly focused on their potential for non-volatile ferroelectric random access memory (FeRAM) applications [4-5]. In particular, BLSFs have emerged as a viable substitute for PZT in high-temperature piezoelectric sensor technologies. With Curie temperatures typically exceeding 500°C, these materials are well-suited for lead-free piezoelectric applications. The presence of bismuth ions in the structure plays a crucial role in elevating the Curie temperature, thus enhancing the thermal stability of the material [6-7].

The general structural formula for BLSFs is given as $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$ [8], where "A" can be a monovalent, divalent, or trivalent ion, or a mixture thereof, and "B" is a transition metal ion. The variable "m" represents the number of octahedral units between the bismuth oxide layers, with typical values for "m" ranging from 1 to 5 [9]. $SrBi_4Ti_4O_{15}$(SBT), a member of the Aurivillius family with m=4, has been widely studied due to its favorable electrical properties [10]. Various researchers have explored the characteristics of SBT, focusing on its potential for practical applications in piezoelectric and ferroelectric devices [11].

In this study, we examine the dielectric properties of rare-earth doped BLSFs, synthesized using the conventional solid-state reaction method. This approach allows for precise control over the doping concentrations and phase formation, leading to materials with optimized dielectric and ferroelectric characteristics. The results provide valuable insights into the impact of rare-earth doping on the structure and properties of these ceramics, further establishing BLSFs as promising candidates for lead-free, high-performance electro ceramic applications.

# 2. Experimental Procedure

## 2.1. Sample preparation

To synthesize the ceramic compound $Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$ (SBNBT) high-purity precursor materials $SrCO_3$, $Bi_2O_3$, $Nb_2O_5$ and $TiO_2$ (Sigma Aldrich 99%) were utilized. The stoichiometrically measured powders were mixed and milled in a planetary ball mill for 5 hours using distilled water as the milling medium to ensure thorough homogenization. After milling, the mixture was subjected to calcination at 800 °C for 2 hours to promote the formation of the desired phase [12-13]. Following the initial calcination, the calcined powder was further milled for an additional 5 hours to achieve fine particle size and improved material uniformity.

The processed powder was then compacted into pellet form using 1% polyvinyl alcohol (PVA) as a binder to aid in the pressing process. The powder was pressed at a pressure of 10 MPa, producing pellets with a thickness of 1 mm and a diameter of 1 cm. These pellets were subsequently sintered at 1160 °C for 2 hours to enhance their structural integrity and densify the material [14-18].

Finally, the density of the sintered pellets was determined using the Archimedes principle, with a density toolkit employed for precise measurement. This method allowed for accurate calculation of the materials' bulk densities, providing valuable data for further analysis of their physical and dielectric properties.

### 2.2. Characterization

The characterization of the ceramic samples involved multiple analytical techniques to ensure a comprehensive understanding of their structural, microstructural, and electrical properties. X-ray diffraction (XRD) measurements were conducted at ambient room temperature using a Panalytical X'Pert Plus Diffractometer. This instrument allowed for detailed analysis of the crystalline phases and structural arrangement within the ceramic materials.

To determine the density of the sintered ceramic samples, the Archimedes method was applied, utilizing distilled water as the immersion medium, which has a density of 0.91 g/cm$^3$. By carefully following Archimedes' principle, the experimental densities were calculated, providing insights into the porosity and compactness of the ceramics.

Further microstructural examination was performed using a HITACHI S4300SE/N Scanning Electron Microscope (SEM), which provided high-resolution images of the ceramic samples. These SEM images were analyzed to evaluate grain size, morphology, and overall surface structure, which are critical for understanding the physical characteristics that can impact the material's performance.

In addition to structural analysis, the dielectric properties of the ceramic samples were investigated using an LCR meter. This instrument allowed for precise measurement of the ceramics' electrical properties, providing valuable data on their dielectric behavior, which is essential for applications that rely on such electrical characteristics. Through this thorough characterization, a complete profile of the ceramic samples' properties was established, contributing to a deeper understanding of their suitability for practical applications.

**Table 1.**

| S.NO | Compound | Nomenclature |
|---|---|---|
| 1 | $Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$ | SNBBT |

## 3. Results and Discussions

### 3.1. X-Ray Diffraction

Figure 1 illustrates the X-ray diffraction (XRD) patterns of the synthesized ceramic samples, providing clear evidence for the successful formation of a pure Bismuth oxide-based layered structure, specifically characterized by an m=4 value in its composition. The detailed analysis of these patterns confirmed that the crystal structure of the samples is orthorhombic and that a single-phase material was achieved, as no secondary phases were detected. This absence of additional peaks indicates high phase purity, a critical factor for the material's intended functional applications.

The peak positions and intensities in the XRD patterns were rigorously matched with the standard Joint Committee on Powder Diffraction Standards (JCPDS) data, particularly JCPDS card no. 43-0973, which serves as a reference for phase validation. This comparison further confirmed the accuracy of the structural formation, emphasizing the material's purity.

Room-temperature XRD patterns for $Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$samples were obtained using a Panalytical X'Pert Plus Diffractometer. The results confirmed the successful formation of a single-phase perovskite structure, typical of ferroelectric materials with m=4. This layered perovskite structure is characteristic of Bismuth Layered Structured Ferroelectrics (BLSFs), which are known for their applications in dielectric and piezoelectric devices due to their stable structural and electrical properties.

Notably, the Nb ion substitution for Sr and Bi ions in the structure did not impact the phase formation, as evidenced by the lack of any additional peaks or detectable structural modifications in the XRD data. The presence of a high-intensity peak corresponding to the (1 1 9) crystallographic plane is indicative of the characteristic BLSFs structure, aligning with existing research on similar layered structures in ferroelectric materials【23】. This thorough phase analysis confirms the material's suitability for advanced applications requiring stable ferroelectric properties.

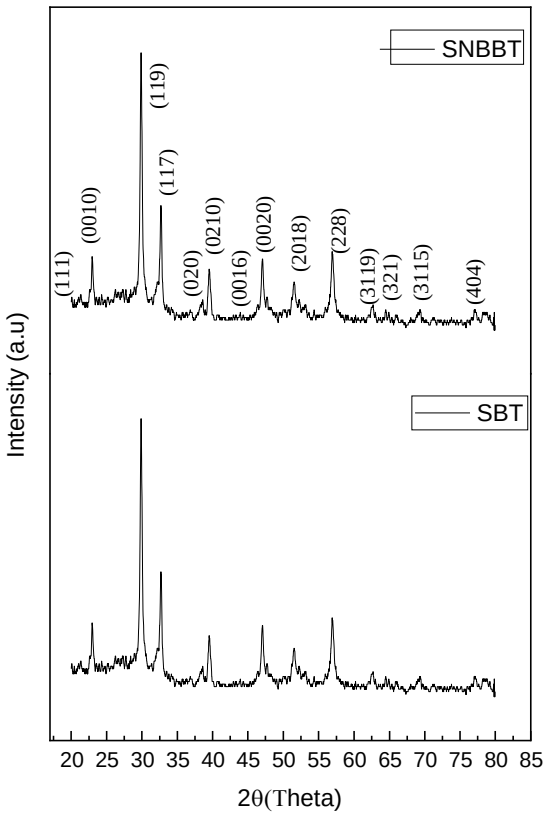


**Figure 1. XRD pattern of SBT and SBPT**

### 3.2 Scanning Electron Microscopy

Figure 2 presents scanning electron microscope (SEM) image of $Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$ ceramics, offering a detailed examination of their surface morphology and grain structure. SEM, by employing a finely focused electron beam, allows for precise imaging of the ceramic surfaces, revealing key aspects of their three-dimensional structures and contributing significantly to the analysis of material properties.

The SEM micrographs display that both SBT and the Na- and Nb-doped ceramics consist of distinctive plate-like grains arranged in an irregular orientation, a hallmark of Bismuth Layer-Structured Ferroelectrics (BLSF) materials. This unique grain morphology, with the plates randomly oriented across the surface, is typical of BLSF ceramics, contributing to their functional properties. The dense and tightly sintered surfaces shown in the images further confirm the high quality of the grain formation achieved during the sintering process, indicative of optimal densification for these materials【19】.

This dense microstructure not only highlights the successful synthesis and sintering of the ceramics but also suggests potential durability and stability in applications that rely on BLSF materials. Such structural characteristics are particularly advantageous in dielectric and piezoelectric applications, where well-formed, densely packed grains can enhance performance. The observed plate-like structure and dense surface morphology affirm the high

quality and structural integrity of these ceramics, aligning with expectations for BLSF materials used in advanced functional applications.

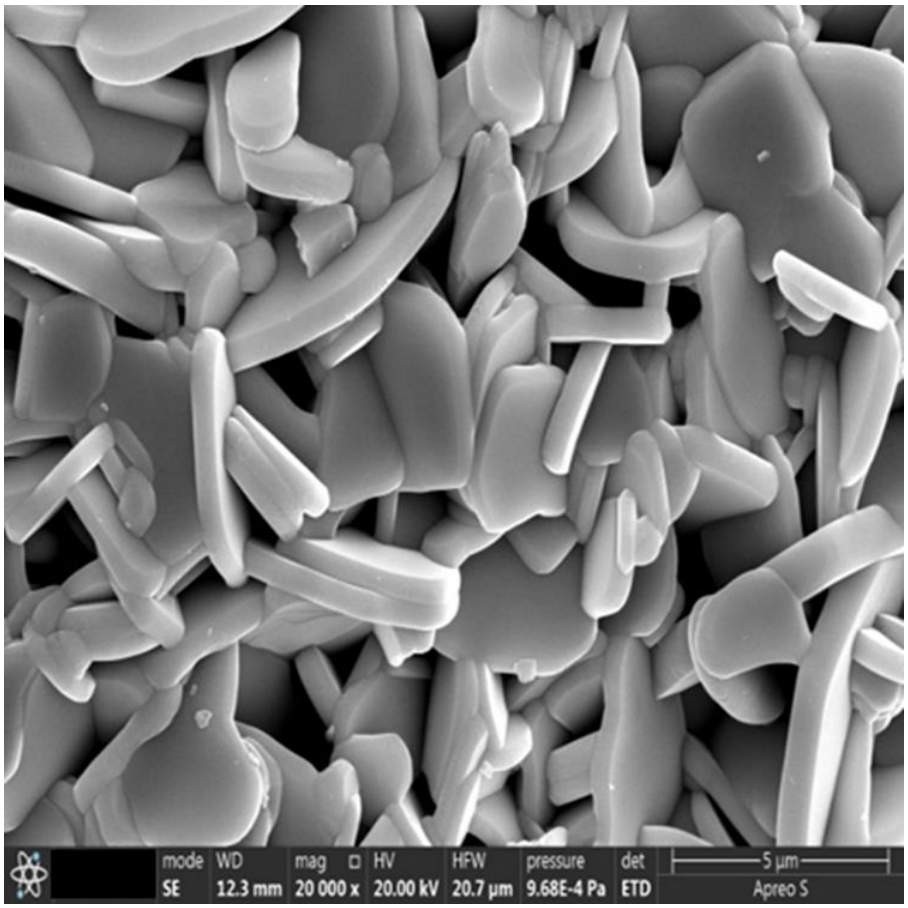


**Figure 2. Scanning electron microscope (SEM) images SNBBT**

### 3.3 Dielectric Properties

Figures 3 and 4 depict the dielectric constant of SNBBT ceramics at multiple frequencies (10 kHz, 15 kHz, 25 kHz, 50 kHz, and 100 kHz) across a temperature range from 100 °C to 700 °C. The data show that both the dielectric constant and Curie temperature for SBT and SBPT increase with rising temperature, indicating a positive correlation between these properties and thermal energy.

The relationship between dielectric constant and temperature across different frequencies reveals that the substitution of Niobium (Nb) in SBT results in a reduction of the dielectric constant. According to previous studies【20-22】, the Curie temperature (Tc) for SBT is approximately 535 °C. However, in the present study, a slight increase in Curie temperature was observed, with Tc for SNBBT at 553 °C above. Notably, the addition of Niobium, which has an ionic radius of 0.64 Å, led to an increase in Curie temperature to values exceeding 553 °C. This rise in Tc is attributed to the individual twisting and increased stability of the oxygen octahedra in the crystal lattice, confirming the presence of a more rigid octahedral framework.

Curie temperature (Tc) is closely linked to the tolerance factor (t), a parameter that describes the structural stability of perovskite-like materials. The tolerance factor is directly influenced by the sizes of A-site and B-site cations. It is defined by the equation:

$$t = \frac{RA+RO}{2(RB+RO)} \text{ ----------(1)}$$

Here $R_A$ is ionic radii belonging to A- site, $R_B$ is the ionic radius of the B-site cation, and  is the radius of the oxygen ions. For pure SBT, the tolerance factor was found to be 0.938. With the substitution in the Bismuth sites, a reduction in the tolerance factor was observed. This decrease in ( t ) facilitates enhanced rotation of the $TiO_6$ octahedra within the a-b plane, leading to an elevated Curie temperature. Such structural modifications due to the change in the tolerance factor are essential in understanding the thermal stability and electrical performance of BLSF ceramics.

Is ionic radii belonging to B- site cations and Ro 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.

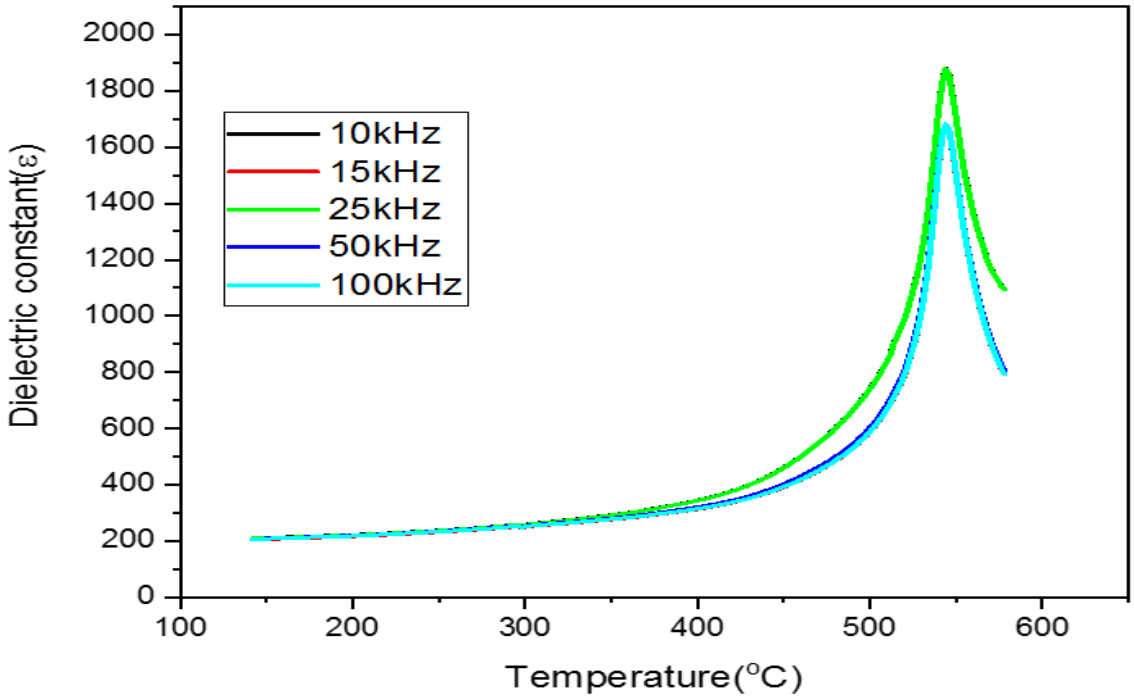


**Figure3.Dielectric constant of SNBBT as a function of temperature at different frequencies.**

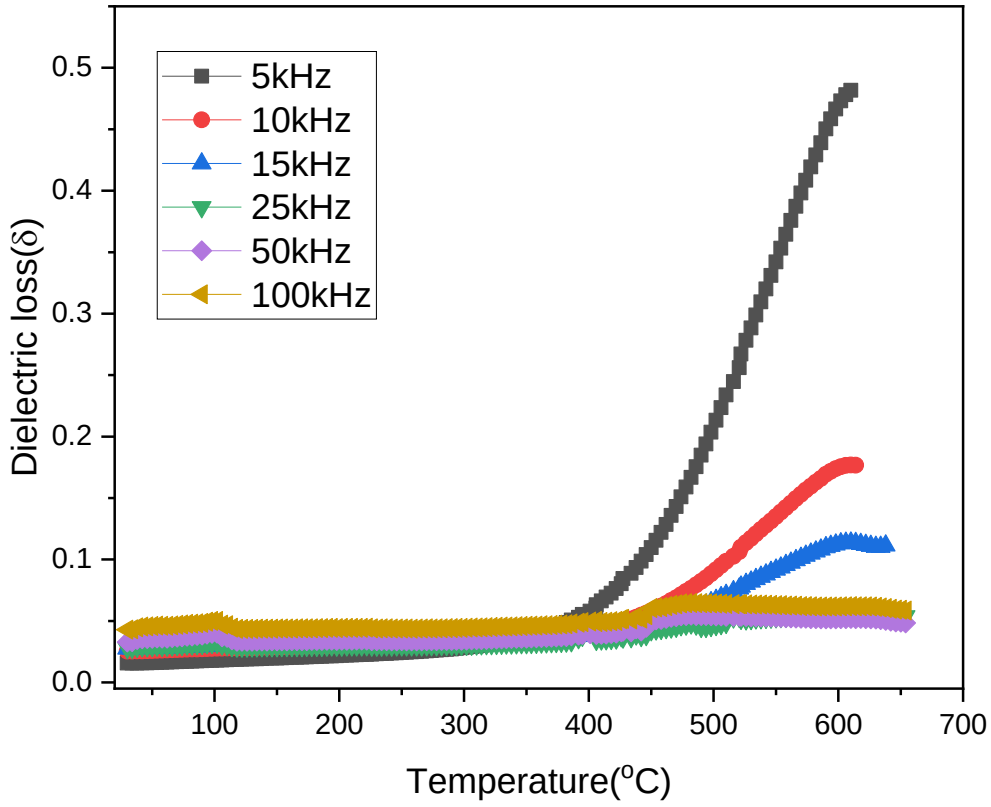


**Figure 4. Dielectric loss (Tanδ) of SNBBT with temperature**

## 5. Conclusion

In summary, $Sr_{0.2}Na_{0.4}Nb_{0.4}Bi_4Ti_4O_{15}$ ceramics were successfully synthesized using the solid-state sintering method, with an initial ball milling for 10 hours. The samples were calcined at 800 °C, and the resulting pellets were sintered at 1160 °C for 2 hours. X-ray diffraction analysis confirmed the formation of a pure phase in the Nb-doped SBT ceramics, while SEM imaging revealed plate-like grain structures. Dielectric properties were characterized, and it was observed that introducing Niobium in SBT Modification raised the Curie temperature from 544 °C to 593 °C above.

As frequency increased, the dielectric constant exhibited a decreasing trend, and dielectric loss remained stable up to 410 °C. Both the dielectric constant and loss tangent decreased with rising frequency, indicating improved dielectric properties in Nb-doped SBT ceramics compared to undoped SBT. These enhancements suggest that Nb doping can effectively improve the electrical performance of SBT ceramics, making them suitable for electronic applications such as capacitors, piezoelectric transducers, and sensors. Further research is needed to optimize the doping concentration and processing parameters to achieve even better performance. Consequently, the SNBBT ceramics developed and analyzed in this study demonstrate suitability for high-temperature applications.

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## References:

1. *Aurivillius B "A family of mixed-layer type bismuth compounds",Ark.Kemi, 463; 1, 499, (1949).*
2. *Aurivillius B, Mixed Oxides with Layer Lattices. 3. Structure of BaBi4Ti4O15: Ark.Kemi, 2, 519, (1950).*
3. *Arrivillius B, The structure of Bi2NbO5F and isomorphous compounds: Ark.Kemi, 5, 39 (1952).*
4. *J.F Scott, C.A Araujo, Ferroelectric memories, Science. 246, 1400, (1989).*
5. *Chung-Hsin Lu, Chung-Han Wu. Preparation, sintering, and ferroelectric properties of layerstructured strontium bismuth titanium oxide ceramics, Journal of the European Ceramic Society. 22, 707, (2002).*
6. *G. A. Geguzina, E. G. Fesenko, and E. T. Shuvayeva, On problems of search for novel Bicontaininglayeredperovskite-like high-Tc, Ferroelectrics 167 (1), 311, (1995).*
7. *D. Damjanovic, Materials for high temperature piezoelectric transducers, Curr. Opin. SolidState Mater. Sci. 3 (5), 469, (1998).*
8. *G.S White, A.S Raynes, M.D Vaudin, S.W Freiman, Fracture behaviour of cyclically loaded PZT, J. Am. Ceram. Soc. 77, 2603,(2005).*
9. *H. Haertling Gene, Ferroelectric ceramics history and technology, J. Am. Ceram. Soc. 82, 797, (1999).*
10. *M. Raghavendar, G. S. Kumar, M. Vithal and G. Prasad, Ferroelectrics.324, 145(2005)*
11. *E.C Subbarao, Int.Ferroelectr. 12,33,(1996).*
12. *B. Mamatha, M. B. Suresh, A. R. James, M. Vithal and P. Sarah, Phys. Scr. 84,55704, (2016) .*
13. *G. Rajashekhar, Rizwana, and P. Sarah, P-E studies of nd modified SrBi4Ti4O15 ceramics, Rasayan j. chem. 11(1), 361. (2018).*
14. *U. Ravikiran, Elizabeth Zacharias, G. Rajashekhar, P. Sarah, "Impedance spectroscopy studies on samarium and sodium substituted strontium bismuth titanate (SBTi)," Ceramics International,Vol. 45, 15188-15198 (2019).*
15. *G. Rajashekhar, T. Sreekanth, U. Ravikiran, and P. Sarah, "Dielectric properties of Na and Pr doped SrBi4Ti4O15 ceramics," Mater. Today Proc., vol. 33, pp. 5467–5470. (2019) .*
16. *G. Rajashekhar, T. Sreekanth, A. R. James, U. R. Kiran, and P. Sarah, "Dielectric properties of sodium and neodymium substitute to A-Site SrBi4Ti4O15 ceramics," Ferroelectrics, vol. 558 (1), 79–91. (2020).*
17. *G. Rajashekhar, T. Sreekanth, N. Tripathy, P. Sarah "Structural and dielectric investigation of rare earth modified SrBi4Ti4O15 ceramics synthesized by high energy ball milling method"Materials today proceedings. (2023).*
18. *G. Rajashekar, T. Sreekanth, Srinivas Pattipaka , P. Sarah "Structural, microstructural, dielectric and ferroelectric properties of Ho3+ doped SrBi4Ti4O15 ceramics" Ferroelectrics, Vol. 598, 187–196. (2022).*

19. *Huiling Du, Xiang Shi and Huilu Li, Bull. Mater. Sci., 34, 1201, (2011).*
20. *Shimakawa Y., Kubo Y., Tauchi Y., Kamiyama T., Asano H. and Izumi F.,Appl. Phys. Lett. 77, 2749,(2000).*
21. *Park B. H., Kang B. S., Bu S. D., Noh T. W., Lee J. and Jo W., Nature401, 682,(1999).*
22. *Watanable T., Funakubo H., Osada M., Noguchi Y. and Miyayama M.,Appl. Phys. Lett. 80, 10. (2012).*