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Processing and study of dielectric and ferroelectric nature of $BiFeO_3$ modified $SrBi_2Nb_2O_9$

A. Srinivas [a,*], F. Boey [a], T. Sritharan [a], Dong Wan Kim [b], Kug Sun Hong [b]

[a] *School of Materials Engineering, Nanyang Technological University, Singapore 639798, Singapore*
[b] *School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul 151-744, South Korea*

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Abstract

The solid solution of $BiFeO_3$ (BF)–$SrBi_2Nb_2O_9$ (SBN) prepared at a concentration of 1:1 ratio, shows significant changes in the structure and the physical properties. A solid-state double sintering route was adopted in synthesizing the material. X-ray diffraction (XRD) measurements show a single-phase formation. The dielectric measurements showed anomalies at higher temperatures. Polarization versus electric field measurement indicates the compound consists of ferroelectric ordering. Significant changes are observed when BF is added to SBN in the various physical properties.

Keywords: A. Sintering; C. Ferroelectric properties; C. Dielectric properties; C. Electrical conductivity

1. Introduction

Bismuth layer structured ferroelectric materials (BLSF) have good structural stability, high curie temperatures, anisotropic characteristics, and properties suitable for use as memory devices. Strontium bismuth niobate (SBN) is a common ferroelectric material in many electronic applications. In order to design a material consisting of both ferroelectric and magnetic ordering, i.e. to take advantage of the same material in both electronic and magnetic based applications, $BiFeO_3$ (BF), which is reported to have both ferroelectric and ferromagnetic natures, is chosen. BF is added to SBN to obtain $SrBi_3Nb_2FeO_{12}$ (SBNF).

BLSF belongs to Aurivillius family of compounds with a general formula of $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$, where $A = Bi^{3+}$, La^{3+}, and Sr^{2+}; $B = Fe^{3+}$and Ti^{4+}; and '*m*' refers to the number of perovskite-like layers between Bi_2O_2 layers [1]. These BLSFs are characterized by a high ferroelectric transition temperatures and therefore they are excellent candidates for substituting PZT and PZT-based materials in NvRAM applications, due to their excellent fatigue resistance, and the fact that they can operate at relatively low voltage and have less of a thickness dependence in ferroelectric properties [2].

The present compound has three perovskite layers between the Bi_2O_2 layers. This reflects the fact that there exists a good possibility for mutual dopings within these various elements or with some other ions to BLSFs. Generally, the doping could be in bismuth oxide layer or in perovskite-like units (A- or B-sites). Within the perovskite-like units, partial substitution of strontium ions by bismuth ions would increase the Curie temperature and improve the dielectric properties in both SBN and SBT (strontium bismuth tantalate) [3]. Although the recent reports of these bismuth layer compounds are studies, not much data is available in the present solid solution system, xBF–$(1 - x)$SBN with $x = 0.5$, which is equivalent to a three layered Aurivillius phase. With the BFs T_c at 840 °C, it is possible to expect a high T_c and with excess Bi in the lattice, the polarization could also be high with improved dielectric properties. In addition, the presence of Fe^{3+} with three unpaired electrons in the lattice gives rise to magnetic ordering and the interaction between the ferroelectric and magnetically ordered phase may lead to magnetoelectric effect, which is known to occur in materials having the presence of simultaneous magnetic and ferroelectric ordering [4]. The present study

* Corresponding author.
E-mail address: sadiraj@ntu.edu.sg (A. Srinivas).

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aims at the synthesis and characterization of the solid solution system xBiFeO$_3$–$(1-x)$SrBi$_2$Nb$_2$O$_9$ with $x = 0.5$, to understand the structure, dielectric and ferroelectric nature.

2. Experimental procedure

Solid-state, double sintering route was adopted in synthesizing the material at different sintering temperatures. Stoichiometric amounts of Bi_2O_3, $SrCO_3$, Nb_2O_5, and Fe_2O_3 were weighed and ground thoroughly. The pre-sintering was done at 900 °C for 2 h and the final sintering was performed at 950, 1000, 1050, and 1100 °C, respectively for 2 h with intermediate grindings. X-ray diffractograms were collected on model M18XHF, Macscience Instruments, Japan. Scanning electron micrographs are collected on Philips XL20, Eindhoven, Netherlands. Electrical resistivity measurements are carried out using Keithley electrometer for measuring the electrical resisitivity. Dielectric measurements were made at a frequency of two different frequencies from room temperature to 700 °C, using HP 4194A Impedance Analyzer. The polarization versus electric field (P versus E) measurements were made at room temperature using modified Sawyer–Tower circuit loop tracer.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns at 950, 1000, 1050, and 1100 °C. Interestingly, XRD showed peak splitting in the diffractograms (at 950–1100 °C), which indicates structural changes in the compound. A single phase is confirmed with the XRD data. There is no indication of second phase in the system indicates that a single-phase layered perovskite structure was formed. The lattice parameters obtained in the present compound are $a = 5.488$, $b = 5.416$, and $c = 29.62$, respectively. The addition of $BiFeO_3$ has apparently improved the sinterability of SBN.

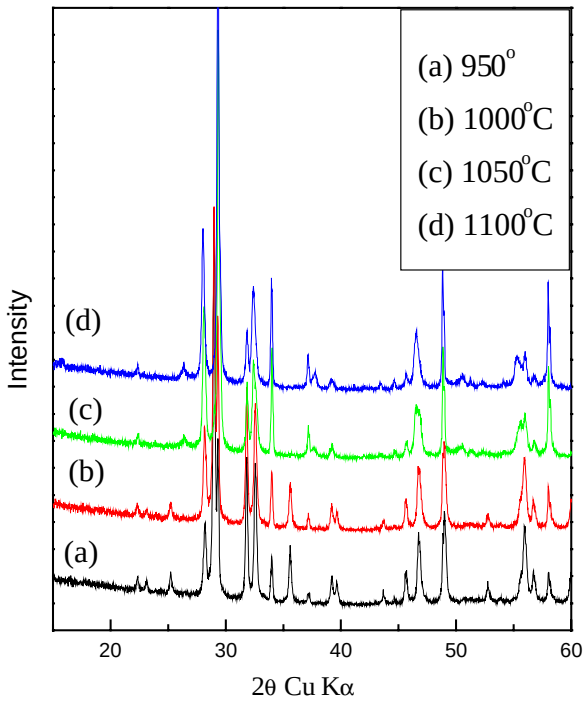

Fig. 1. X-ray diffraction patterns of $SrBi_3Nb_2FeO_{12}$ at different sintering temperatures.

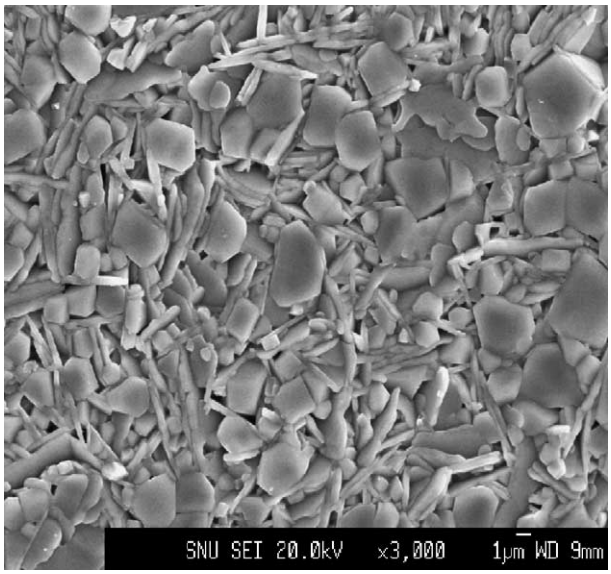

Fig. 2. Scanning electron micrograph of $SrBi_3Nb_2FeO_{12}$ at 3000× magnification.

Fig. 2 shows the scanning electron micrograph of the title compound at 3 K× magnification. It revealed the homogenious grain growth similar to other bismuth layer perovskites. From the micrograph it can be observed that the grains are in the form of needles along the long axis. Doping or substitution with alternate cations often resulted

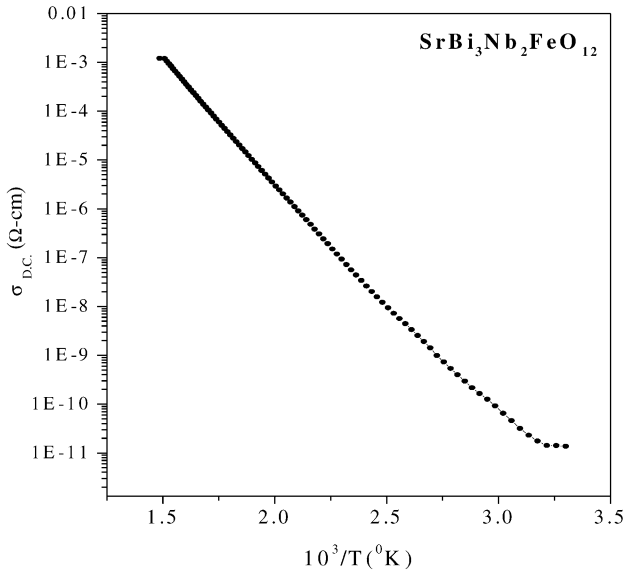

Fig. 3. $\log\sigma$ vs. $10^3/T$ plot of $SrBi_3Nb_2FeO_{12}$.

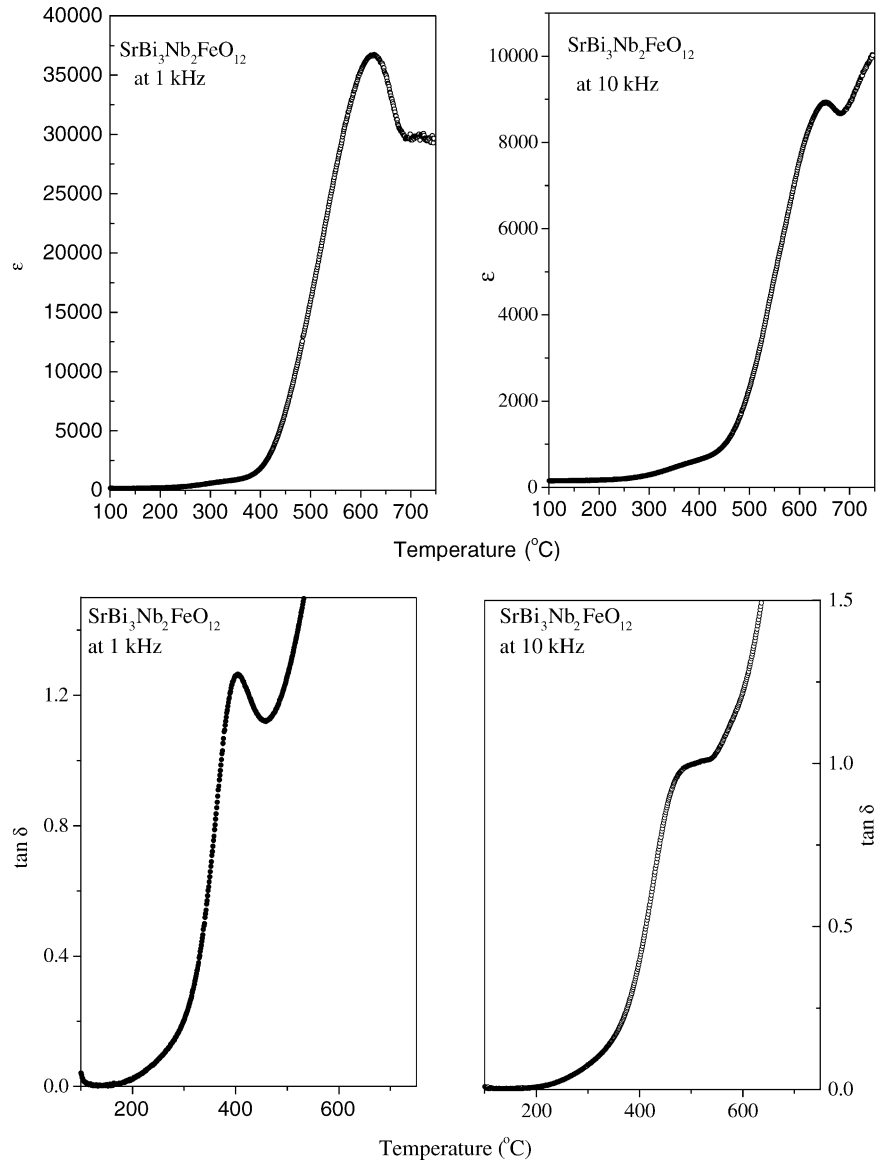

Fig. 4. ε and $\tan\delta$ vs. temperature plot at (a) 1 kHz of $SrBi_3Nb_2FeO_{12}$ and (b)10 kHz of $SrBi_3Nb_2FeO_{12}$.

in a reduction in grain size in isotropic ferroelectric ceramics, because the alternate cations may hinder the diffusion across grain boundaries during sintering and thus, retard the grain growth, resulting in a fine grained microstructure.

Fig. 3 shows the $\log\sigma$ versus $10^3/T$ plot. The electrical resistivity studies indicate that this material is an insulator at room temperature with a high order of resistivity. The dc conductivity at higher temperatures of the SBFN compound decreased with the addition of BF. In these bismuth layer compounds the conduction mechanism is likely due to the migration of oxygen vacancies. The experimental results observed in this study suggests that the effect of A-site i.e. Sr/Bi and B-site Nb/Fe dopings on the dc conduction are complex, and further analysis like ac conductivity and impedance analysis are required to achieve a better understanding.

The dielectric measurements show a single transition at around 620 °C, which is higher than SBN (~420 °C). Prior to the dielectric measurement, electrical poling was done on the ceramic samples in the field of 30 kV/cm at 120 °C for 30 min. The real part of dielectric constant as a function of temperature shows a sharp rise and shows a transition around 620 °C at a frequency of 1 kHz, and at a frequency of 10 kHz, the transition was observed around 650 °C from the Fig. 4. The value of dielectric constants at peak temperatures are around 37 000 and 9000 at 1 and 10 kHz, respectively, where as for pure SBN, the values are in hundreds. The plots between $\tan\delta$ versus temperature, peaks are noted at 410 and 490 °C at 1 and 10 kHz, respectively.

The structure of SBN consists of $(SrNb_2O_7)^{2-}$ perovskite layers which is interleaved between the two $(Bi_2O_2)^{2+}$ lay-

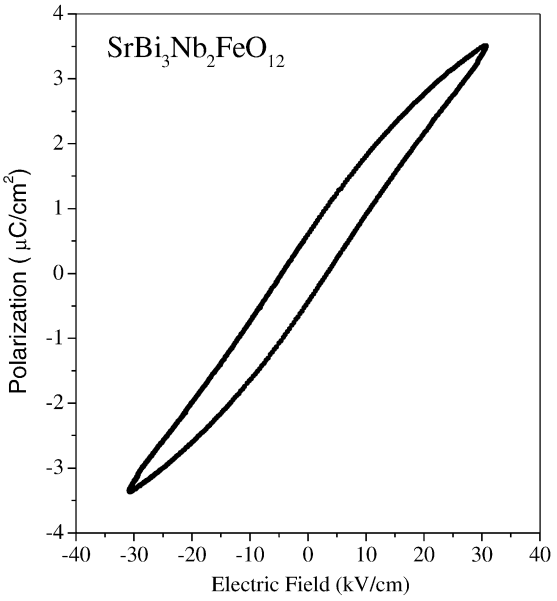

Fig. 5. Polarization vs. electric field of $SrBi_3Nb_2FeO_{12}$ at room temperature.

ers. The incorporation of smaller ions like Fe^{3+} in these bismuth layer perovskites causes shrinkage in the lattice along the long direction. The cationic vacancies introduced by the addition of $BiFeO_3$ to SBN causes a tensile stress in the $(Bi_2O_2)^{2+}$ layers, by which the perovskite-like unit is under compressive stress. The oxygen octahedra undergo a large distortion due to these stresses, resulting in the increase of transition temperature. The addition of BF content to SBN causes some mismatch in the ionic radii of Fe^{3+} and Nb^{5+} as the Fe^{3+} ionic radii is smaller than Nb^{5+}. The mismatch caused by the substitutions of different sizes in the lattice introduces significant distortion in the oxygen octahedra, showing significant variation in the dielectric property.

To confirm the ferroelectric nature of the compound Polarization verus electric field measurement was performed at room temperature. Fig. 5 shows a slim hysteresis loop. The maximum value of polarization observed at a field of 30 kV/cm was around 3.48 $\mu C/cm^2$. Application of higher fields was restricted by the high conductivity of the sample. Ferroelectricity in bismuth layer compounds is attributed due to the tilt of octahedra (NbO_6). The amount of polarization depends on the extent of the tilt of octahedra. The decrease of value of polarization in this material when compared to SBN may be attributed to the addition of Fe to the lattice. No loop was observed for the $BiFeO_3$. [5].

4. Conclusions

$SrBi_3Nb_2FeO_{12}$, a three-layered bismuth layered Aurivillius structure was synthesized, when BF and SBN were mixed in 1:1 ratio. The structure appears to be closer to SBN. The important factor that should be noted is the value of dielectric constant is high for SBN–BF compound, when compared to SBN compound and BF compound. The ferroelectric nature of the material was confirmed by P verus E measurements. In the light of the earlier results it becomes extremely necessary to further investigate the entire solid solution system between SBN–BF for a possible application.

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