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Effect of rare earth ion doping on the structural, microstructural and diffused phase transition characteristics of $BaBi_2Nb_2O_9$ relaxor ferroelectrics

B. Rajesh Kannan, B. Harihara Venkataraman*

Department of Physics, Birla Institute of Technology and Science (BITS) – Pilani, Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, R. R. District 500078, Andhra Pradesh, India

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Abstract

Barium bismuth samarium niobate $Ba(Bi_{1-x}Sm_x)_2Nb_2O_9$ ($x=0$, 0.03, 0.05, and 0.10) ceramics have been fabricated successfully via molten salt synthesis route. The X-ray diffraction analysis revealed the existence of bismuth layered perovskite phase with orthorhombic crystal structure in all the compositions studied. The dielectric and electrical conductivity properties were carried out in the 100 Hz to 1 MHz frequency range at 300 K. The dielectric constant and dielectric loss were found to decrease from 186 to 180 and 0.0966 to 0.0755 with increase in samarium content at 100 kHz. A decrease in dielectric constant maximum (ε_m) and a shift in the temperature of dielectric maximum (T_m) from 438 K to 393 K with the increase in the samarium concentration had been observed.

Keywords: A. Sintering; B. Microstructure; C. Dielectric properties; C. Electrical conductivity

1. Introduction

In recent years, bismuth layered structured ferroelectric materials (BLSFs) have been widely exploited for non-volatile random access memory (NVRAM) device applications owing to their high polarization fatigue resistance combined with low switching field [1,2]. The general formula of BLSFs is $(Bi_2O_2)^{2+}(A_mB_{m-1}O_{3m+1})^{2-}$, where A is a 12-coordination site and B is an octahedral coordination site with "m" indicating the number of octahedrons stacked along the c-axis between two neighboring $(Bi_2O_2)^{2+}$ layers [3]. Most of the layered ferroelectric materials that include $SrBi_2Ta_2O_9$, $SrBi_2Nb_2O_9$ and $Bi_4Ti_3O_{12}$ belong to normal ferroelectrics whereas their barium based counterparts ($BaBi_2Ta_2O_9$ and $BaBi_2Nb_2O_9$) are relaxors in nature. These relaxor ferroelectric ceramics characterized by the diffused phase transition possess high fatigue endurance and polarization retention characteristics [4,5]. However, the drawbacks of these materials are high processing temperature and low remnant polarization [6]. In addition, the dc conductivity of these layered ferroelectric oxides are higher than that of perovskite materials. A proper substitution in $BaBi_2Ta_2O_9$ (BBT) and $BaBi_2Nb_2O_9$ (BBN) is expected to provide this material with enhanced physical properties that meets the requirements for its application in NVRAM devices [7,8]. It is widely accepted that the Bi_2O_2 layers have a significant influence on the polar and electrical conductivity properties of bismuth based layered structures [9]. There has been a lot of research conducted to enhance their properties by the substitution of the Bi^{3+} ions by alternate cations. Recently, trivalent rare earth ions doping in the layered ferroelectric structures have been paid considerable attention due to their profound influence on the physical properties [10,11]. For instance, doping with La^{3+} ions in $SrBi_2Nb_2O_9$ ceramics resulted in decrease in the Curie temperature and also an appreciable decrease in the dc conductivity [12]. It is expected that by substituting Bi^{3+} ion with the large difference in the eightfold coordination ionic radii of Sm^{3+} ion in the crystal lattice of BBN relaxor ferroelectrics could enhance its physical properties.

Most of the layered ferroelectric compounds are fabricated based on the conventional solid state reaction route which often leads to the compositional and structural inhomogeneities owing to the high calcination and sintering temperatures and thus worsening the microstructural and subsequently the

*Corresponding author. Tel.: +91 040 66303557.
E-mail address: tut.hari@gmail.com (B.H. Venkataraman).

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electrical properties of the ferroelectric materials [13]. Molten salt synthesis (MSS) is proved to be of one of the effective fabrication routes for synthesizing ceramic powders at relatively lower temperatures [14,15]. Since there seems to be no attempts made to synthesize samarium ion doped barium bismuth niobate compound via molten salt synthesis route, we have reported the effect of Sm^{3+} doping (on Bi^{3+} sites) on the structural, microstructural, diffused phase transition and electrical conductivity characteristics of BBN ceramics in this paper.

2. Experimental

The polycrystalline barium bismuth samarium niobate (BBSmN) ceramic powders in the composition $Ba(Bi_{1-x}Sm_x)_2Nb_2O_9$ with x ranging from 0 to 0.10 (10 mol%) were synthesized by the molten salt synthesis route using KCl as a flux material. The starting reactants barium carbonate ($BaCO_3$), bismuth oxide (Bi_2O_3), samarium (III) oxide (Sm_2O_3) and niobium pentaoxide (Nb_2O_5) were thoroughly mixed with KCl in the molar ratio of 1:5. An excess amount of 5 wt% bismuth oxide was added to the initial mixture to compensate bismuth vaporization at high temperatures. This admixture was calcined at 1073 K for 4 h in air with the heating and the cooling rate of 3 K/min and subsequently these calcined powders were washed with hot deionized water for several times to remove the alkali metal salt. Further these powders were cold pressed at 300 K for few minutes at the pressure of 225 kg/cm^2 and subjected to the conventional sintering process at 1323 K for 10 h. The densities of the sintered ceramic samples were determined by the liquid displacement/Archimedian method. The structural phase formation of the calcined powders and sintered ceramic samples was confirmed via powder X-ray diffraction (XRD) using CuKα radiation (Pan Analytical XPERT – PRO diffractometer). The surface morphological features of ceramic samples were monitored by scanning electron microscope (SEM; JSM-6390). These ceramic samples were bonded with silver paste on both the sides and the dielectric and electrical conductivity property studies were carried out as a function of frequency (100 Hz to 1 MHz) using Waynekerr LCR meter with a signal strength of 1 V_{rms} at 300 K. The thickness and the area of the ceramic samples were 1.5 mm and 95 mm^2 respectively.

3. Results and discussion

3.1. Structural analyses

Fig. 1 shows the XRD patterns obtained for the various compositions of calcined $Ba(Bi_{1-x}Sm_x)_2Nb_2O_9$ (where $x=0$, 0.03, 0.05 and 0.10) polycrystalline powders. These XRD patterns revealed the presence of single phase layered perovskite structure associated with few impurity peaks that correspond to the unreacted Bi_2O_3 reactant. All the remaining crystalline peaks of the layered perovskite BBN crystal structure could be indexed to an orthorhombic unit cell [16].

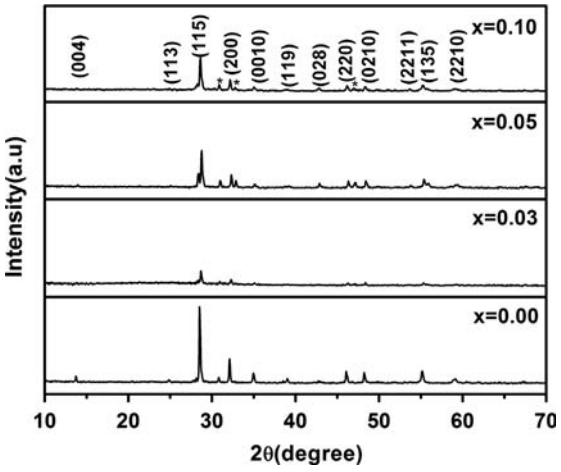

Fig. 1. XRD patterns recorded for the polycrystalline powders of various concentrations of samarium.

Table 1
Unit cell parameters derived from X-ray powder diffraction data.

Composition	a (Å)	b (Å)	c (Å)	V (Å^3)
$x=0.00$	5.5677	5.5672	25.6404	794.7582
$x=0.03$	5.5471	5.5477	25.5488	786.2304
$x=0.05$	5.5355	5.5410	25.5356	783.2311
$x=0.10$	5.5587	5.5568	25.5828	790.2102

The obtained lattice parameters of all the compositions of the synthesized polycrystalline powders are listed in Table 1. It is observed that the values of lattice parameters (a, b and c) decrease slightly with increase in samarium content until $x=0.05$, which could be attributed to the ionic size difference between Sm^{3+} and Bi^{3+} ions. The incorporation of smaller cation (Sm^{3+}) into the crystal lattice has also led in the shrinkage of the unit cell as indicated by the decrease in the magnitude of cell volume.

The XRD patterns recorded for the polycrystalline BBN ceramic samples containing different content of samarium sintered at 1323 K for 10 h are depicted in Fig. 2. The d-spacings that are associated with all these XRD patterns of the sintered samples are found to be corresponding to the layered perovskite BBN crystal structure without any detectable impurity phase indicating the formation of solid solution between samarium and bismuth ions. The full width at half maximum (FWHM) of the Bragg peaks of these sintered samples are sharper compared to that of the respective BBSmN powder samples which reveals that there is an occurrence of grain growth during the sintering process.

3.2. Microstructural analyses

The scanning electron micrographs obtained for the sintered samples of BBN and BBSmN ceramics are shown in Fig. 3. The SEM recorded for pure BBN ceramic samples reveals the existence of plate shaped grains with an average grain size of