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Dielectric and pyroelectric properties of Sr-modified $(Na_{0.5}Bi_{0.5})\,Bi_4Ti_4O_{15}$ ceramics

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Abstract

Polycrystalline $(Na_{0.5}Bi_{0.5})\,Bi_4Ti_4O_{15}$ (NBT) ceramics were prepared by the solid-state reaction method with the Sr substitution in place of divalent pseudo-cation (Na^+, Bi^{3+}) with $Sr = 0.1, 0.2, 0.3$. X-ray diffraction measurements indicate an increase in the orthorhombic distortion and cell volume with the increase of Sr content in the ceramics. Dielectric measurements show the diffuse type transitions with the change in composition. The reduction in Curie temperature can be attributed to the increased tolerance factor due to the substitution of relatively bigger ion in the pseudo cation- (Na^+, Bi^{3+}). Pyroelectric data indicate that the samples with $x = 0.2$ exhibits the better pyroelectric activity than other components of the series. Pyroelectric figures of merit are calculated from the pyroelectric coefficients.

Keywords: Ferroelectrics; Sintering; Dielectric response; X-ray diffraction

1. Introduction

Aurivillius [1] reported that the family of Bismuth layer structured ferroelectrics (BLSF) with a general formula show interesting physical properties. Compounds of this group such as $SrBi_2Ta_2O_9$, $Bi_{4-x}La_xTi_3O_{12}$ and $SrBi_4Ti_4O_{15}$ have attracted much attention due to their applications in non-volatile ferroelectric random access memory (NVFRAM). BLSFs are important from the application viewpoints for electronic materials such as dielectrics, piezoelectrics and pyroelectrics under high frequencies, high temperature due to their high Curie temperature, low dielectric constant, and larger anisotropy in electromechanical coefficients (K_{33}, K_{31}) as compared to those of lead-based materials [2–4].

BLSF materials are generally formulated as $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$. The 12-fold coordinated perovskite A sites can be occupied by mono or di or trivalent cations such as Na^+ Ba^{2+}, Ca^{2+}, Sr^{2+}, Bi^{3+} and the six-fold coordinated B sites are usually occupied by smaller cations such as Ti^{4+}, Ta^{5+}, Nb^{5+}, and W^{6+}, leading to BO_6 octahedra. In these crystals, perovskite blocks $(A_{n-1}B_nO_{3n+1})$ are sandwiched between bismuth oxide (Bi_2O_2) layers, where n denotes the number of BO_6 octahedral layers in the perovskite blocks. Many of the compounds with this structure are ferroelectric, and the spontaneous polarization arises from different modes of simultaneous rotation of the oxygen octahedra. The displacements of the ions, in the perovskite B-sites contribute a major component of polarization in the *a*–*b* plane of the perovskite-like layers. Bi_2O_2 layers act as insulating paraelectric layers and control the electronic response such as electrical conductivity, band gap, etc. [5,6], while the ferroelectricity arises mainly in the perovskite blocks [7–9]. The crystal structure, dielectric and ferroelectric anisotropy of BLSFs depend strongly on the value of n [10].

$(Na_{0.5}Bi_{0.5})\,Bi_4Ti_4O_{15}$ (NBT) belongs to this family of compounds with $m = 4$. At room temperature, NBT is orthorhombic with $a = 0.5427$ nm, $b/a = 1.006$ and $c = 4.065$ nm and undergoes a ferroelectric ($A2_1am$) to paraelectric ($I4/mmm$) transition at $T_C = 655\,°C$ [2,11]. NBT is a classical ferroelectric with a sharp maximum of thermal variation in dielectric constant close to T_C. Takenaka and Sakata studied Ca-doped NBT ceramics and reported that the system exhibit good piezoelectric and pyroelectric properties to be useful in pyroelectric applications

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[4,12,13]. Dynamic pyroelectric studies on hot forged NBT-CBT samples exhibited higher values of pyroelectric parameters. Ramasastry et al. [14] reported low dielectric constant (143), dielectric loss (0.0015) and moderate pyroelectric coefficient (90 pC cm^{-2} °C^{-1}) at room temperature in calcium doped NBT. They have attributed the increase in pyroelectricity of Ca-doped NBT to the formation of locked-up charge complexes, which at higher temperatures contribute to the pyroelectricity. The necessary parameters for good pyroelectric detection are low dielectric constant, low dielectric loss and high pyroelectric coefficients [15]. Since these BLSF compounds have high T_C, they exhibit good thermal stability. The impurity doping seems to have improved the pyroelectric coefficient [13]. Replacement of Ca^{2+} results in increase of Curie temperature and decrease in density. Calcium has the lower polarizability compared to the ions like Sr^{2+} or Ba^{2+}.

Present study describes the dielectric and pyroelectric properties of Sr-modified sodium bismuth titanate. The dependence of the dielectric and pyroelectric properties on the amount of doping has been investigated.

2. Experimental

$(Na_{0.5}Bi_{0.5})_{1-x}Sr_xBi_4Ti_4O_{15}$ (SNBT) ceramic samples with $x = 0.1, 0.2, 0.3$ (01SNBT, 02SNBT, 03SNBT, respectively), were prepared by conventional solid state double sintering technique. Reagent grades of Na_2CO_3, Bi_2O_3, TiO_2 and $SrCO_3$ were used as the starting raw materials. The raw materials were ground to obtain a fine powder. The powder was uniaxially pressed into cylindrical discs of 2.54 cm diameter. These discs were pre-sintered in a temperature range of 800–850 °C for 2 h. The pre-sintered discs were again crushed to fine powder and pressed into cylindrical discs of diameter 1 cm and thickness 1 cm using uniaxial pressing. These discs were sintered at 1000–1100 °C for 2 h in air. Most suitable firing temperature was determined by studying the density obtained under different firing schedules. The sintered cylindrical discs were diamond cut into discs of thickness 0.5–0.8 mm. X-ray diffraction patterns for the final sintered samples were obtained using the Panalytical (X'Pert) diffractometer.

Sputtered gold thin film electrodes were used for the dielectric and pyroelectric measurements. The samples were poled under a dc field of 3–4 kV mm^{-1} at room temperature for 3 h, by keeping the sample in a silicon oil bath. The temperature dependence of dielectric constant and loss tangent was measured at different frequencies ranging from 10 to 1000 kHz using HP4192A Impedance analyzer interfaced to a computer. The dielectric measurements were made in the temperature range from room temperature to 650 °C at a heating rate of 1 °C/min. The pyroelectric coefficient and spontaneous polarization were measured by the static pyroelectric method (Bayer–Roundy) [16] by heating the samples at a rate of 5 °C/min. All the samples after poling were heated to a temperature about 200 °C less than the transition temperature for about 1 h under short circuit condition prior to pyroelectric measurements. This was to ensure that the thermal depolarization effects were minimized during the pyroelectric measurements. The specific heat of the samples was obtained using differential scanning calorimetry.

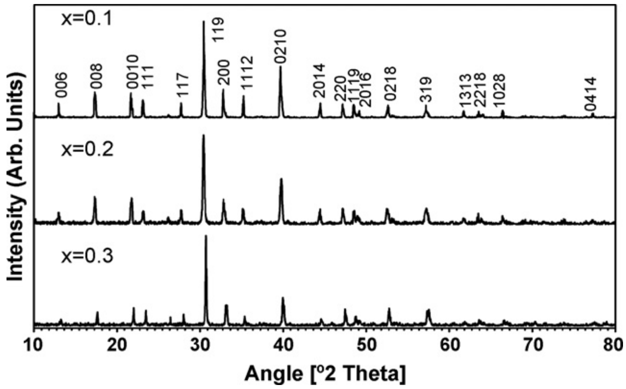

Fig. 1. XRD pattern of $(Na_{0.5}Bi_{0.5})_{1-x}Sr_xBi_4Ti_4O_{15}$ ceramics.

3. Results and discussion

According to XRD in Fig. 1, the sintering conditions lead to the formation of single phase with no detectable phase within the experimental range for all compositions of Sr. All the peaks could be indexed on the basis of orthorhombic symmetry with $a = 0.5427$ nm, $b = 0.5459$ nm, and $c = 4.065$ nm. Lattice parameters calculated indicate the orthorhombic structure of the samples at room temperature (Table 1). As the content of Sr increases, cell volume as well as the lattice parameters increases. One possible explanation is that the ionic radius of Sr^{2+} (0.144 nm) is more than that of the mean ionic radii of Na^{+} and Bi^{3+} (0.135 nm) [17]. Similar behavior was observed in the case of Ba^{2+} replacement for (Na^{+}, Bi^{3+}) [18]. Table 1 also gives the information regarding the tetragonal distortions and strain on the axis with the addition of Sr^{2+} in place of the divalent pseudo-cation (Na^{+}, Bi^{3+}).

Lattice parameters are calculated from the obtained values of d-spacings and 2θ using the XLAT software after several iterations. These values are tabulated in Table 1. A slight increase in the values of a and c is observed while no significant change could be detected in the values of b. Orthorhombic distortion (b/a) decreases with the increase of Sr^{2+} and no systematic change in the value of tetragonal strain (c/a) is observed. Hence, even after the substitution of Sr^{2+} in the present study, the system retains the orthorhombic symmetry. According to Cohen and other workers [19,20], the substitution of Pb^{2+} in A-site increases the tetragonal strain due to the covalent nature of Pb–O bonds while Sr^{2+} forms ionic bonds with the neighboring oxygen ions, which favors the orthorhombicity. As the BLSF compounds are known to coexist in tetragonal and orthorhombic phases [21], from Table 1, addition of Sr^{2+} releases the tetragonal strain keeping the present ceramics in orthorhombic symmetry.

Table 1
Lattice parameters of SNBT system

x	*a* (nm)	*b* (nm)	*c* (nm)	Volume	*b*/*a*	*c*/*a*
0.0*	0.5427	0546	4.065	1204.52	1.006	7.490
0.1	0.5431 ± 0.007	0.5442 ± 0.007	4.064 ± 0.143	1206.33	1.002	7.483
0.2	0.5437 ± .004	0.5445 ± 0.004	4.067 ± 0.203	1209.20	1.001	7.480
0.3	0.5494 ± 0.008	0.5491 ± 0.010	4.114 ± 0.055	1241.05	0.999	7.489