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Structural and Electrical Characterization of Pb and La Co-substituted $SrBi_2Nb_2O_9$

SAMEER JAIN and A.K. JHA*
Department of Applied Physics, Delhi College of Engineering
Bawana Road, Delhi-110 042, India
E-mail: dr_jha_ak@yahoo.co.in

In the present study, effects of Pb and La co-substitution on the structural and dielectric properties have been investigated in $SrBi_2Nb_2O_9$ layered ferroelectric ceramics. Samples were synthesized using solid-state reaction technique. X-ray diffraction analysis reveals the formation of single-phase layered perovskite structure. Dielectric properties have been investigated in a broad range of temperature (300-800 K).

Key Words: Ferroelectrics, Dielectric constant, Dielectric loss, Curie temperature, Tetragonal strain.

INTRODUCTION

$SrBi_2Nb_2O_9$ (SBN) is one of the most promising fatigue free ferroelectric ceramic with potential of being used for high-density non-volatile ferroelectric random access memories[1-8]. Among bismuth layered ferroelectric materials, SBN/SBT have gained more importance because of their high remnant polarization, low coercive field and low leakage current. Bismuth Layered Aurivillius type structured compounds have a general formula $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ consisting of peroviskite $[A_{n-1}B_nO_{3n+1}]^{2-}$ layers sandwiched between $[Bi_2O_2]^{2+}$ layers. Here A can be Ba^{2+}, Sr^{2+}, Pb^{2+}, *etc*. and B can be Nb^{5+}, Ta^{5+}, *etc*. These ceramics are very sensitive to the compositional variations. Changing the stoichiometry or doping with various elements remarkably influences crystal structure and ferroelectric properties. It has been reported that partial substitution of Sr^{2+} by Pb^{2+} has a profound influence on the dielectric and ferroelectric properties of SBN ferroelectrics[9]. In the present work, the structural and electrical studies on the influences of Pb^{2+} and La^{3+} doping on SBN ferroelectric ceramics is reported. Dielectric constant and dielectric loss of $Sr_{0.9}Pb_{0.1}Bi_{1.9}La_{0.1}Nb_2O_9$ ferroelectric ceramics have been studied as a function of temperature at a frequency of 100 kHz.

EXPERIMENTAL

The samples of compositions $SrBi_2Nb_2O_9$ (SBN) and $Sr_{0.9}Pb_{0.1}Bi_{1.9}La_{0.1}Nb_2O_9$ (SPBLN) were prepared by solid-state reaction method. The starting powders $SrCO_3$, PbO, Bi_2O_3, La_2O_3, Nb_2O_3 (all from Aldrich of 99.9% purity) mixed in stoichiometric proportions were

ground and then calcined in air for 2 h at 900°C. The calcined powders were ground and mixed with about 1.5 wt. % polyvinyl alcohol (Aldrich) as a binder and pressed to form pallets by applying uniaxial pressure of *ca.* 270 MPa. These pellets were sintered at 1200°C for 2 h in air. XRD diffractograms were recorded using CuK_α radiations (range $10° \leq 2\theta \leq 70°$). For dielectric property measurement, the sintered pellets were polished to a thickness of *ca.* 1 mm and silver pasted on both sides and cured at 550°C for 30 min. The dielectric measurements were carried out from room temperature to 500°C using Aplab MT 4080A LCR meter at oscillations amplitude of 1V.

RESULTS AND DISCUSSION

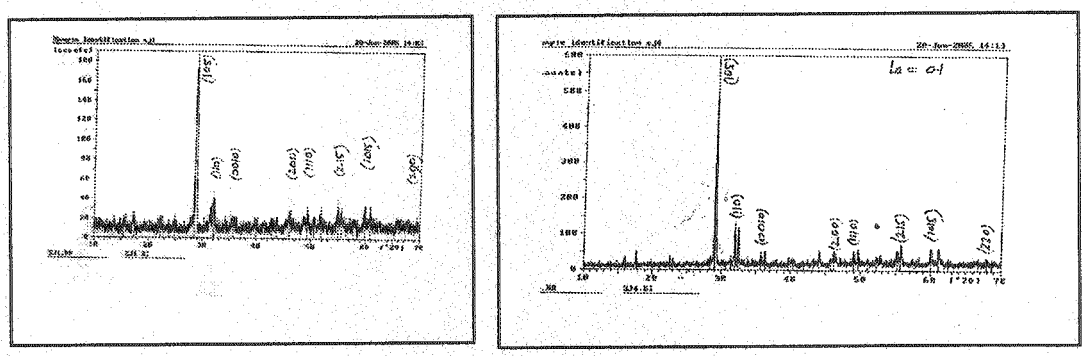

Fig.1. X-ray Diffractograms (a) $SrBi_2Nb_2O_9$ (b) $Sr_{0.9}Pb_{0.1}Bi_{1.9}La_{0.1}Nb_2O_9$

Fig. 1 shows the X-ray diffractograms of SBN and SPBLN. XRD analysis indicates that both $SrBi_2Nb_2O_9$ (SBN) and $Sr_{0.9}Pb_{0.1}Bi_{1.9}La_{0.1}Nb_2O_9$ (SPBLN) ceramics have a perovskite single-phase orthorhombic structure. This implies that the layered perovskite structure of SBN is preserved in $Sr_{0.9}Pb_{0.1}Bi_{1.9}La_{0.1}Nb_2O_9$. The intensity of few peaks is observed to increase in SPBLN indicating an increase in perovskite phase in this sample. Also, SPBLN show a decrease in background noise of the sample indicating enhanced crystallinity of the structure. XRD analysis shows a decrease in peak width in Pb and La doped samples. The peak positions shift to the right on doping *e.g.*, the most intense peak (105) is at $2\theta = 28.510°$ for pure SBN which shifts to $2\theta = 28.930°$ for SPBLN sample. This peak shift signifies the change in lattice parameters. Lattice parameters have been calculated from the obtained d-values. Pb and La added sample shows small changes in the lattice parameters. The values of calculated lattice parameters for SBN are a = 3.8708 Å, b = 4.016 Å, c = 26.812 Å and that for x = 0.1 are a = 3.9358 Å, b = 3.892 Å, c = 24.693 Å. Tetragonal strain (c/a) of the samples was calculated from the obtained lattice parameters. Tetragonal strain of SPBLN sample shows a decrease compared to that of undoped SBN. Lattice distortions have significant influence on the dielectric

properties of BLSF and hence the change observed in c/a ratio is worth noting.

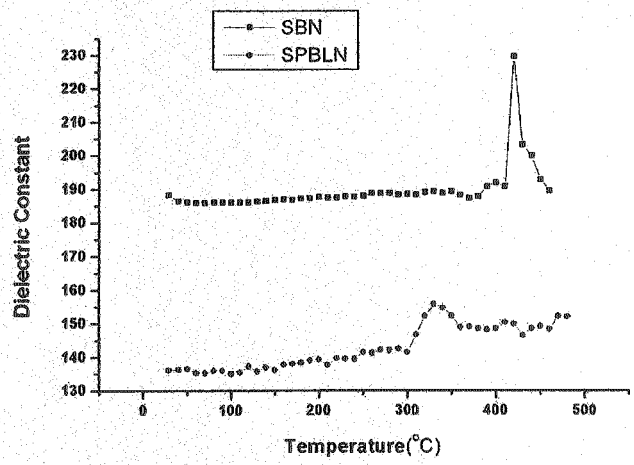

Fig.2. Dielectric constant *vs.* Temperature curve

Fig. 2 shows dielectric constant as a function of temperature. These observations have been plotted using microcal origin 5.1. Curie temperature was determined using the dielectric constant *vs.* temperature curve. The temperature at which phase transition occurs corresponds to Curie temperature of the sample. Curie temperature is observed to decrease from 420°C for SBN to 330°C for SPBLN sample. The decrease in Curie temperature is attributed to reduce tetragonal strain. Dielectric constant of pure SBN is more than Pb and La doped sample. Large number of vacancies in SBN at Bi site is expected because of Bismuth Oxide evaporation at higher temperature[12]. Replacement of Bi by La not only stabilizes the crystal structure but also creates fewer vacancies at Bi site. This is possibly the cause for the lower dielectric constant of SPBLN than that of SBN.

The subsequent increase of dielectric constant in SPBLN at higher temperature is due to the increase in conductivity[8]. Dielectric relaxation observed in BLSF may be due to either of two reasons: (i) substitution of different ions may result in the formation of heterogeneous domains due to compositional inhomogeneities[8,10] and (ii) creation of oxygen vacancies also plays an important role in electrical polarization of perovskite ceramics[11]. In the present case, XRD data analysis indicates that the single layered perovskite structure SBN is preserved in SPBLN. Since no secondary phase is observed in SPBLN, the possibility of heterogeneous domain formation is unlikely while the increase in dielectric constant at higher temperature may be correlated to the higher concentration of oxygen vacancies, which may have created more mobile charges. Fig. 3 shows dielectric loss as a function of temperature at 100 kHz. The dielectric loss of SBN at Curie temperature is 1.19 and that of SPBLN at Curie temperature is 0.965.The decrease in dielectric loss at Curie temperature may be attributed to the less structural

distortions and low charge concentration in La doped materials. Dielectric loss increases with increase in temperature and the increase is sharp at higher temperature. This is also possibly due to higher concentration of charge carriers in specimens at higher temperature.

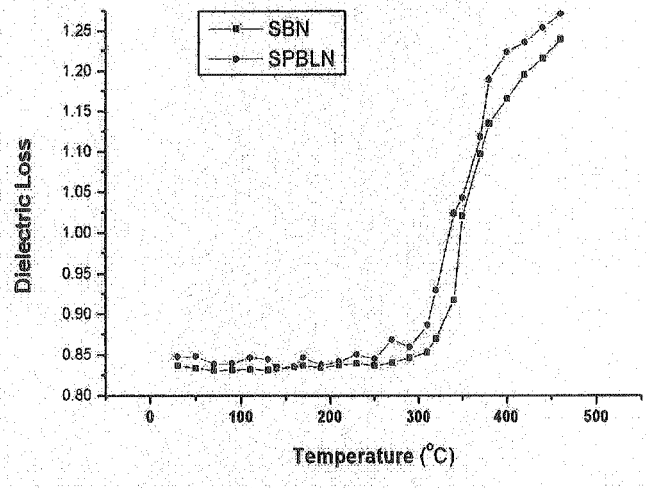

Fig. 3. Dielectric loss *vs.* Temperature curve

Conclusion

It is concluded from the present work that Pb and La co-substitution in SBN at Sr and Bi sites respectively reduces lattice parameters and tetragonal strain. This results in the reduction of Curie temperature, Dielectric constant and dielectric loss.

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