Conduction phenomenon of Al3+ modified lead free (Na0.5Bi0.5)0.92Ba0.08TiO3 electroceramics

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Conduction Phenomenon of Al^{3+} Modified Lead Free $(Na_{0.5}Bi_{0.5})_{0.92}Ba_{0.08}TiO_3$ Electroceramics

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Abstract. Choice of proper dopants at A or B-site of ABO_3 perovskite structure can modify the morphotropic phase boundary (MPB), and hence functional properties of polar systems. The chemical nature of donor or acceptor will significantly influence the fundamental properties. Lead-free ferroelectrics have vast potential to replace the lead-based ceramics. The $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ (NBT-BT) (at x=0.08) near MPB with small substitution of trivalent cations (Al^{3+}) has been synthesized by solid state reaction route. The aim to choose the trivalent cations (Al^{3+}) was its relatively smaller radii than that of Bi^{3+} cations to develop the antipolar phases in the ferroelectric ceramic. Structural, morphological and elemental compositional analyses were studied by X-ray diffraction (XRD), Secondary electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDAX), respectively. Ferroelectric studies were carried out on various compositions of $(Na_{0.46}Bi_{0.46-x}Al_xBa_{0.08})TiO_3$ (NBAT-BT) (x=0, 0.05, 0.07, 0.10) electroceramics. It was observed that with increase in concentration of Al the ferroelectricity state changes from soft to hard. Temperature dependent dielectric spectroscopy shows broad dielectric dispersion. The Al doping diminishes the relaxor behavior of NBT-BT ceramics. Impedance spectroscopy shows that electrical resistivity and relaxation frequency decreases with increase in Al-concentration. Modulus spectra indicate that Al significantly change the bulk capacitance of NBT-BT.

Keywords: Ferroelectrics, Dielectrics, Impedance and Modulus.
PACS: 77.80.Dj, 77.22.Gm

INTRODUCTION

On considering environmental issue, worldwide ferroelectric laboratories have placed much attention on replacing lead based materials for future devices [1-3]. Previous studies have shown that several perovskite-type lead-free ceramics, including sodium bismuth titanate (NBT) systems, have the potential for replacing commercialized PZT-based devices [4]. The NBT based compositions are one of the most preferable ceramics due to their excellent dielectric, ferroelectric and piezoelectric performances [5]. Doping of modest concentrations has an effective method to enhance the fundamental as well as functional properties of lead-based or lead free ceramics. Appropriate cation modifications like Al^{3+} or light elements influenced both the structural and functional properties of ceramics [6]. Trivalent cations (Al^{3+}) doped NBT-BT was studied, which produces local distortion in crystal structure and domain orientation [7]. The leakage current, dielectrics, impedance, and polarization properties were notably changed after cations substation [8]. Being ionic radius of Bi^{3+} larger than of Al^{3+}, the substitution develops the antipolar phases in ferroelectric ceramic. The Al^{3+} is randomly distributed on A-site of perovskite materials, and its relaxation behavior was also reasonably modified which produces positional disorder. Due to modification in composition, changes in structural, morphological and dielectric phase transitions have been reported.

EXPERIMENTAL PROCEDURE

The conventional solid state reaction method was used to prepare Al doped NBT-BT ceramics. Raw materials of Na_2CO_3, Bi_2O_3, $BaCO_3$, Al_2O_3 and TiO_2 with higher than 99.9% purity were used as starting materials, mixed according to series of composition $(Na_{0.44}Bi_{0.44-x}Al_xBa_{0.08})TiO_3$ (NBAT-BT) (x=0, 0.05, 0.07, 0.10). Calcination was done at 1000 ^oC for 4 hrs. The calcined powder was reground then pelletized using binder (polyvinylalcohol), and latter sintering was carried out at 1200 ^oC for 8 hrs. Sintered ceramic pellets were painted with silver paste and dried at 250 ^oC for 2 hrs. further electrical characterizations were carried out. Room temperature polarization was measured by precision multiferroics tester from radiant

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technology and temperature dependent dielectric spectra were recorded over wide range of temperature (30-400 ^{o}C) by LCR 3532-50 HiTESTER from HIOKI.

RESULTS AND DISCUSSION

Dielectric Properties

Figure 1(a,b) shows dielectric constant (ε) and tangent loss (tan δ) as function of temperature at 10 kHz of compositional series $(Na_{0.46}Bi_{0.46-x}Al_xBa_{0.08})TiO_3$ (NBAT-BT) (x=0, 0.05, 0.07, 0.10) respectively. In composition x=0 well-defined phase transition was observed near 110 ^{o}C and 290 ^{o}C and dielectric loss was also very low as compared to Al doped ceramics [8]. In Al doped ceramics, the first phase transition vanishes completely and second phase transition becomes broad around 290-310 ^{o}C. The Al^{3+} cationic distribution formed A-site disorder in perovskite structure. It attributes an enhancement in the degree of disorder with cations occupying at lattice site. The magnitude of dielectric constant and loss increases with increase in concentration as function of temperature and frequency.

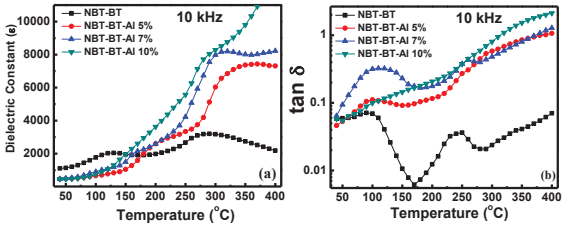

FIGURE 1. (a) Temperature dependence dielectric spectra, (b) loss tangent for NBAT-BT electroceramics at 10 kHz.

Ferroelectric Properties

Polarization-electric field (P-E) hysteresis loops were performed on electrically poled electrceramics [9]. Figure 2 shows changes in polarization at 10 Hz with Al concentration. The change in values of coercive field and polarization obtained from P-E loops evidenced the changes from soft to hard ferroelectrics with increase in Al doping concentration. The formation of hard ferroelectricity is because of Al doping develop the antipolar phases in the ferroelectric ceramic. The nature of hard ferroelectric is due to dopants associated defects which influence the domains and domain walls. This type of doping leads to hardening of ferroelectricity, which may be due to polar defect dipoles orientation along polarization vector in individual domains effectively clamping domain walls.

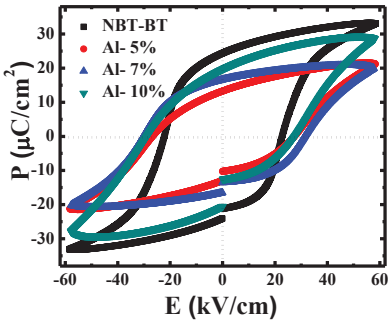

FIGURE 2. Ferroelectric polarization of NBAT-BT poled electroceramics at 10 Hz.

Impedance and Modulus Formalism

Large variation of imaginary part of impedance as function of frequency was observed at 300 ^{o}C as shown in figure 3 (a). It can also observed from figure 3(a) that resistivity decreases as increase in dopant concentrations. These data suggest that mobile charge carriers were highly active at elevated temperature in Al doped NBAT-BT electroceramics. These results confirmed that addition of Al cations lowered its resistivity and generates a large no of charge carries in electroceramics.

Complex modulus have specialty to find out small capacitance in matrix. Figure 3 (b) shows variation of imaginary part of electrical modulus of electroceramics at 300 ^{o}C. It shows that dielectric relaxation peaks observed for Al-doped ceramics but not for simple NBAT-BT at x=0. The shifting of modulus relaxation peak towards higher frequency gives small relaxation time. Modulus data provide information regarding migration of charge carriers responsible for the conductivity. It indicates that Al doping significantly affects the bulk capacitance of electroceramics due to formation of long range conductivity and fast oscillation of charge carriers.

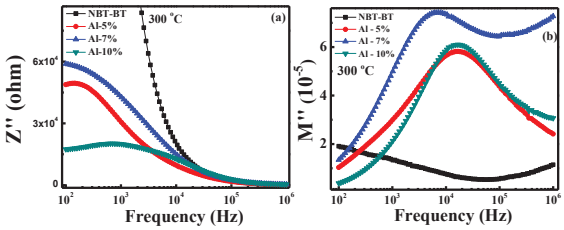

FIGURE 3. (a) Imaginary part of Impedance spectra as function of frequency, (b) modulus spectra as function of temperature at 300 ^{o}C.

CONCLUSIONS

In summary we have successfully studied dielectric and ferroelectric behavior of $(Na_{0.46}Bi_{0.46-x}Al_xBa_{0.08})TiO_3$ (NBAT-BT) (x=0, 0.05, 0.07, 0.10). It was observed that with increase in concentration of Al the ferroelectricity changes from soft to hard ferroelectric states on electrically poled electroceramics. Temperature dependent dielectric spectroscopy shows broad diffused dielectric dispersion in highly doped NBAT-BT. Impedance spectroscopy shows that electrical resistivity and relaxation times decreases with increase in Al-concentration. Modulus spectra indicate that Al significantly change the bulk capacitance of NBT-BT.

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