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Piezoelectric properties and dielectric behavior of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ lead-free piezoelectric ceramics

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Abstract New lead-free piezoelectric ceramics of ABO_3 perovskite type, $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$, were synthesized by conventional solid state reaction. The effect of the replacement of complex ions of $(Sb_{1/2}Nb_{1/2})^{4+}$ in the B cationic site on structural and electrical properties was investigated. The XRD analysis showed that all samples exhibited a single phase of perovskite structure. Piezoelectric and dielectric measurement revealed that the substitution of $(Sb_{1/2}Nb_{1/2})^{4+}$ ions lead to an increase in piezoelectric constant(d_{33}), electromechanical coupling factor(k_t), relative dielectric constant(ε_r),and loss tangent (tanδ), while excess of $(Nb_{1/2}Sb_{1/2})^{4+}$ ions results in a decrease in d_{33}, k_t, ε_r, but an increase in tanδ. Temperature dependence of dielectric constant ε_r measurement indicated these compounds were relaxor ferroelectric. At low frequency and high temperature, dielectric constant increased sharply attributed to the super-paraelectric clusters after $(Sb_{1/2}Nb_{1/2})^{4+}$ ions substitution.

Keywords Ferroelectrics · Dielectric response · Phase transition · Piezoelectricity

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1 Introduction

The piezoelectric properties play an important role for electronics and mechatronics materials. The most widely used piezoelectric materials are Pb(Zr, Ti)O_3(PZT)-based three component system. However, volatilization of toxic PbO during high temperature sintering not only causes environmental pollution but also generates unstability of composition and electrical properties of products. Therefore, it is necessary to develop environment-friendly lead-free piezoelectric ceramics to replace PZT based ceramics.

Among the lead-free compounds, bismuth sodium titanate ($Bi_{1/2}Na_{1/2}TiO_3$, abbreviate as BNT), is interesting as BNT shows a strong ferroelectricity and high Curie temperature T_c=320 °C [1]. This material belongs to the peroskite family ABO_3, which has drawbacks such as high conductivity and large coercive field of 73 kV/cm, to cause problems in poling process. As a result of those, a lot of work to modify and improve piezoelectric properties of BNT ceramics have been done by substitution of $BaTiO_3$ [2], $K_{1/2}Bi_{1/2}TiO_3$ [3], $NaNbO_3$, [4], $BiFeO_3$ [5], La_2O_3 [6]. However, the modification was heterovalent and homovalent ions substitution, there were few reports on substitution of compensation valent of complex ions. Therefore, the present work was to prepare and to characterize $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics of perovskite type derived from $Bi_{1/2}Na_{1/2}TiO_3$ by complex ions of compensation valent substitutions. The study mainly describes the complex ions of $(Sb_{1/2}Nb_{1/2})^{4+}$ substitution on improving the electrical properties of BNT ceramic. The effect on microstructure, relaxor behavior, phase transition characteristics were also investigated.

2 Experimental

The $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ (x=0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.4 mol%) ceramics were prepared by the conventional ceramic fabrication technique. Bi_2O_3, Na_2CO_3, TiO_2, Sb_2O_3, and Nb_2O_5 with the purity of over 99.5% were used as starting materials. The powders were ball-milled for 12 h and calcined at 950 °C for 2 h. After calcinations, the mixture was ball-milled for 24 h, dried and granulated with PVA as a binder. The granulated powders were pressed into disc. The compacted discs were sintered at 1190 °C for 2 h in air. Silver paste was fired on both faces of the discs at 650 °C for 30 min as electrodes. The specimen for measurement piezoelectric properties was poled in silicon oil at 80 °C under 4–6 kV/mm for 15 min. After 24 h, piezoelectric properties were measured by resonant and anti-resonant method according to IEEE standards using an impedance analyzer (Agilent 4294A), and crystal structure were measured by X-ray diffractometer (Bruker D8-Advance). Piezoelectric constant d_{33} was measured using a d_{33} meter (ZJ-3A) and the temperature dependence of dielectric constant were investigated using an impedance analyzer (Agilent 4294A) in the temperature range 20–500 °C.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of sintered samples in the 2θ ranges 20–80°. A pure perovskite structure without any secondary impurity phases could be confirmed. The splitting peaks observed is Kalpha1 and Kalpha2 type splitting because two X-ray wavelengths hit the sample. It indicated $(Sb_{1/2}Nb_{1/2})^{4+}$ ions have diffused into the BNT lattice to form a solid solution.

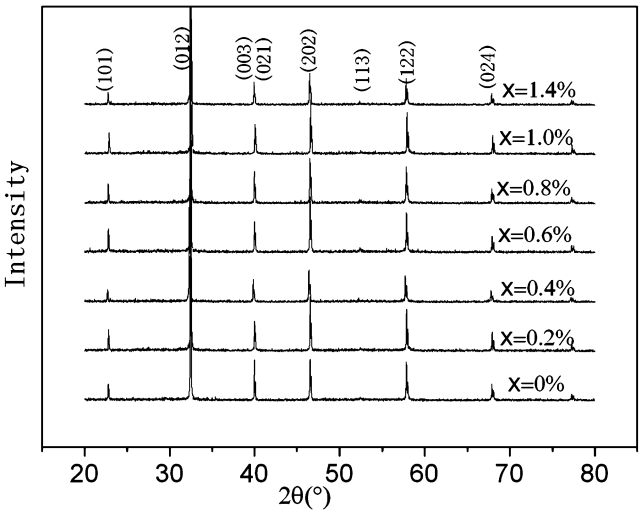

Fig. 1 XRD pattern of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics sintered at 1190 °C for 2 h

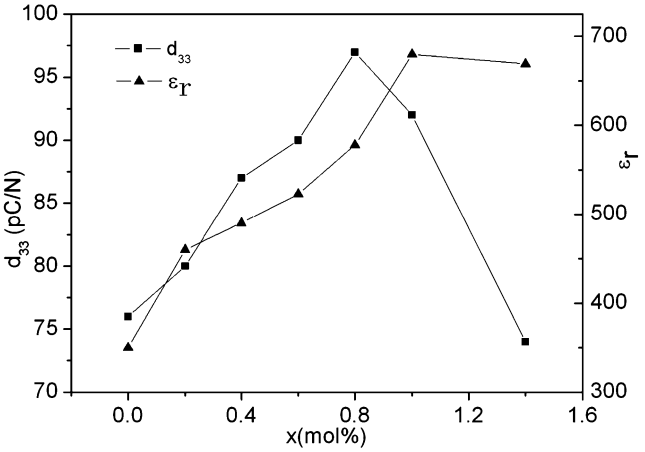

Fig. 2 Piezoelectric constant d_{33} and relative dielectric constant ε_r of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics as a function of $(Sb_{1/2}Nb_{1/2})^{4+}$ concentration x

Figure 2 shows the piezoelectric constant d_{33} and the dielectric constant ε_r at room temperature of the $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics as a function of x. Piezoelectric constant d_{33} increases with increasing $(Sb_{1/2}Nb_{1/2})^{4+}$ fraction up to 0.8% with d_{33}=97 pC/N and then decreases. The dielectric constant changes as a function of composition similarly to the piezoelectric constant.

The electromechanical coupling factor k_t and dissipation factor tanδ of the $Bi_{1/2}Na_{1/2}Ti_{1-x}(Sb_{1/2}Nb_{1/2})_xO_3$ ceramics as a function of x are showed in Fig. 3. It can be seen that k_t first slightly increase, reaching maximum k_t=0.50, then decrease as the x increase. The dissipation factor tanδ linearly increase with increasing of $(Sb_{1/2}Nb_{1/2})^{4+}$ concentration.

It seemed that the electrical properties change were caused by complex ions of $(Sb_{1/2}Nb_{1/2})^{4+}$ substitution in the B site of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ perovskite structure

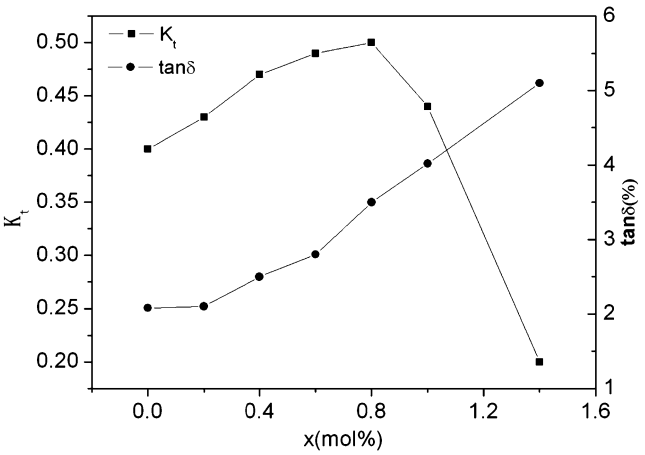

Fig. 3 Electromechanical coupling factor k_t and dissipation factor tanδ of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics as a function of $(Sb_{1/2}Nb_{1/2})^{4+}$ concentration x

ceramics. That is because the additives in BNT-based composition cause defects such as vacancies, lattice deformation and they facilitate the domain movement leading to higher piezoelectric and dielectric properties [7, 8].

Figure 4 shows the temperature dependence of dielectric constants ε_r and dielectric loss tanδ for x=0, 0.2, 0.8 mol% of the $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics between room temperature and 500 °C at 1, 10, 100 kHz. From the dielectric constant versus temperature curves, it can be evidently seen that there are two abnormal dielectric peaks with the increasing temperature. The two dielectric peaks can attribute to the reason caused by the phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric phase, which is consistent with the previous reports of NBT, NBT-BT, NBT-KBT lead-free ceramics

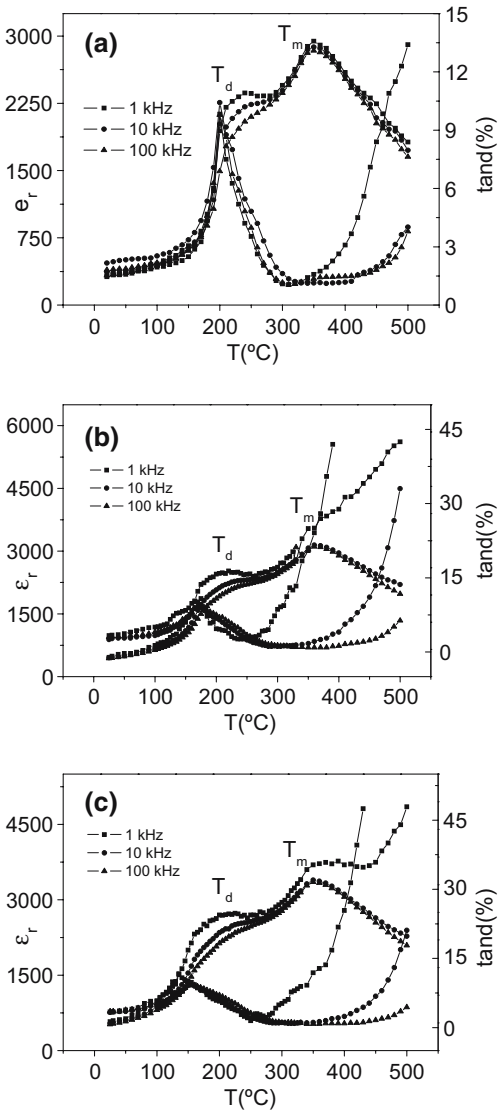

Fig. 4 The dielectric constant ε_r and the dielectric loss tanδ of $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics with x=0% (**a**), 0.2% (**b**), and 0.8% (**c**) as a function of temperature

system [9–11]. Here, the temperature where the transition between ferroelectric phase and anti-ferroelectric phase is called as depolarization temperature (T_d) and the temperature corresponding to maximum value of dielectric constant is named as maximum temperature (T_m). The dielectric loss tanδ versus temperature curves indicate one loss peak corresponds with T_d. The dielectric loss tanδ achieves the minimum value before the temperature T_m. In ferroelectric phase, the dielectric loss probably comes from domain wall movement. When phase transition from ferroelectric to anti-ferroelectric occurred at T_d, the domain wall movement enhancement brings to the loss peak. Then, the sharp dielectric loss increase was caused by the high conductivity of ceramics at high temperature. The dielectric constant present in Fig. 4 indicates another phenomenon that the dielectric constant increase sharply at low frequency and high temperature after $(Sb_{1/2}Nb_{1/2})^{4+}$ was added. This phenomenon is consistent with previous results [12] and has been explained by Tu et al. in term of superparaelectric clusters existing in the tetragonal phase of the BNT ceramics [13–15]. According to superparaelectric model [16, 17], superparaelectric clusters are the microregions of nano-size and the size of superparaelectric clusters and related potentials are assumed to be temperature dependent. The volume of superparaelectric clusters is different under different temperature, which is corresponding with different relaxation time. In the $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$ ceramics, the Bi^{3+}, and Na^+ are randomly distributed at the A sites, and the $(Sb_{1/2}Nb_{1/2})^{4+}$ doped at B site, causing randomly local electric fields and elastic distortions. As a result, the ferroelectric ordering of the ceramics as a whole is inhibited and unit dipoles are divided into superparaelectric clusters. The reorientation of the cluster polarization in the applied electric field is governed by the relaxation time required for the redistribution of charge carries around the cluster. Accordingly, the cluster polarization is 'frozen' under a high-frequency electric field, whereas the reorientation of the cluster polarization under low-frequency electric field and high temperature is allowed, leading to a large dielectric constant value.

It can be also found from Fig. 4 that the ceramics have relaxor ferroelectric characteristics. The dielectric constant ε_r at T_d, transition temperature T_d are strong depended on the measurement frequency. The value of relative dielectric constant ε_r decrease as the measuring frequency increases, Also, the fact that the T_d increase with measurement frequency increase shows the evidence of a diffusion phase transition with a frequency dispersion occurring around the temperature T_d. For most ABO_3 type peroskite ferroelectric, it has relaxor feature caused by A or B site cations substitutions. In present work, $(Sb_{1/2}Nb_{1/2})^{4+}$ ions substitute at B site induce the ions disorder at lattice which lead to relaxor behavior.

4 Conclusion

Lead-free piezoelectric ceramics $Bi_{1/2}Na_{1/2}[Ti_{1-x}(Sb_{1/2}Nb_{1/2})_x]O_3$, a new member of the BNT-based group, was prepared by conventional solid state reaction and their dielectric, piezoelectric properties were investigated. All samples exhibit a single phase perovskite structure without detectable secondary phase. The piezoelectric constant d_{33} and the electromechanical coupling factor k_t increased with the increasing content of $(Sb_{1/2}Nb_{1/2})^{4+}$, showed the maximum value of 97 pC/N and 0.50 at x=0.8 %, respectively, and rapidly decreased when x over 0.8 %. The loss tangent tanδ linearly increased with the increasing amount of $(Sb_{1/2}Nb_{1/2})^{4+}$. Temperature dependence of dielectric constant ε_r measurement indicated these compounds were relaxor ferroelectric. At low frequency and high temperature, dielectric constant increased sharply attributed to the superparaelectric clusters after $(Sb_{1/2}Nb_{1/2})^{4+}$ ions substitution.

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