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Dielectric and piezoelectric properties of bismuth-containing complex perovskite solid solution of $Bi_{1/2}Na_{1/2}TiO_3$–$Bi(Mg_{2/3}Nb_{1/3})O_3$

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Abstract New lead-free bismuth-containing complex perovskite solid solution, $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-x\ Bi(Mg_{2/3}Nb_{1/3})O_3$, were synthesized by conventional solid state reaction method. Effect of $Bi(Mg_{2/3}Nb_{1/3})O_3$ on crystal structure, dielectric and piezoelectric properties were investigated. The XRD analysis showed that all compositions can form single perovskite phase with rhombohedral symmetry. Addition of small amount of $Bi(Mg_{2/3}Nb_{1/3})O_3$ improves piezoelectric properties and the optimal piezoelectric properties of $d_{33} = 94$ pC/N and $k_t = 0.46$ were obtained at $x = 0.7\%$ and $x = 0.9\%$, respectively. Temperature dependence of dielectric constant ε_r measurement indicated these compounds were typical relaxor ferroelectric.

Introduction

Currently, piezoelectric ceramics based on lead zirconate titanate (PZT) system dominate piezoelectric ceramics applications. In processing, volatilization of toxic PbO during high-temperature sintering causes environmental pollution. Besides, piezoelectric components may cause continuous damage to environment after they are discarded. 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 ($(Bi_{1/2}Na_{1/2})TiO_3$, abbreviated as BNT), is one of the important lead-free piezoelectric materials as BNT shows a strong ferroelectricity and high Curie temperature Tc = 320 °C [1]. This material belongs to the perovskite family ABO_3, which has drawbacks such as high conductivity and large coercive field of 73 kV/cm, to cause problems in poling process. BNT-solutions that can be poled easily have been reported recently [2–10]. From these reports, it is assumed that the large ferroelectricity of BNT-based solid solutions is attributed to $(Bi_{0.5}Na_{0.5})^{2+}$ ions, especially Bi^{3+} ions, in the A sites of ABO_3 perovskite structure. Bismuth lies next to lead in the periodic table and its atomic weight is as large as that of lead. Moreover, the electronic configuration of Bi^{3+} is identical to that of Pb^{2+}. Major advances have been achieved in simple perovskite $(Bi_{1/2}Na_{1/2})TiO_3$–$BaTiO_3$ and related material. However, few researches on bismuth-containing complex perovskites have been conducted. The effect of $Bi(Mg_{2/3}Nb_{1/3})O_3$ doping on dielectric and piezoepectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramics was investigated by R. Wang et al. [11]. Therefore, in this article, we have prepared bismuth-containing complex perovskite solid solution of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3$–$xBi(Mg_{2/3}Nb_{1/3})O_3$ and have investigated its dielectric and piezoelectric properties, relaxor behavior and phase transition characteristics.

Experimental procedure

The $(1-x)$ $(Bi_{1/2}Na_{1/2})TiO_3$–$xBi(Mg_{2/3}Nb_{1/3})O_3$($x = 0$, 0.1, 0.3, 0.5, 0.7, 0.9, 1.5 mol%) ceramics were prepared by the conventional ceramic fabrication technique. Bi_2O_3,

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Na_2CO_3, TiO_2, $MgCO_3$, 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 850∼900 °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 disk. The compacted disks were sintered at 1,170∼1,190 °C for 2 h in air. Silver paste was fired on both faces of the disks at 650 °C for 30 min as electrodes. The specimen for measurement of piezoelectric properties was poled in silicon oil at 80 °C under 4∼5 kV/mm for 15 min. After 24 h, piezoelectric properties were measured using an impedance analyzer (Agilent 4294A) by resonant and anti-resonant method, and crystal structure was measured by X-ray diffractometer (Bruker D8-Advance). Silicon is used as an internal standard for calibration. Piezoelectric constant d_{33} was measured using a d_{33} meter (China of Acoustics ZJ-3A) and the temperature dependence of dielectric constant was investigated using an impedance analyzer (Agilent 4294A) in the temperature range 30–500 °C at 1 kHz.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of sintered samples in the 2θ ranges 20–80°. A pure perovskite structure with rhombohedral symmetry could be confirmed, which indicate $Bi(Mg_{2/3}Nb_{1/3})O_3$ can diffuse into the lattice of BNT ceramics. The lattice parameter, density, theoretical density, and density ratio of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ solid solutions are shown in Table 1. It can be seen that lattice constant and density of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ solid solutions

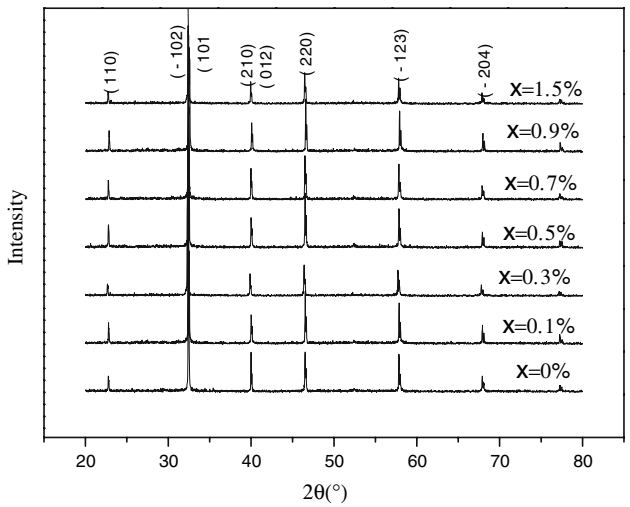

Fig. 1 XRD pattern of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics sintered at 1,170∼1,190 °C for 2 h

Table 1 The lattice parameter, density, theoretical density, and density ratio of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ solid solutions

x (%)	A (nm)	α (^{0})	ρ_{th} (g/cm^3)	ρ (g/cm^3)	ρ_{re} (%)
0	3.887	89.60	5.996	5.654	94.3
0.1	3.890	89.64	5.998	5.698	95.0
0.3	3.900	89.58	6.001	5.749	95.8
0.5	3.905	89.66	5.998	5.788	96.5
0.7	3.909	89.53	5.998	5.800	96.7
0.9	3.913	89.59	5.995	5.833	97.3
1.5	3.913	89.55	5.993	5.855	97.7

increase with the increasing x. All samples have high density over 94% of theoretical density. The effective radius of Ti^{4+} and $(Mg_{2/3}Nb_{1/3})^{3+}$ is 0.061 and 0.069 nm (6 C.N.). The lattice constant of the solid solutions increases due to $(Mg_{2/3}Nb_{1/3})^{3+}$ substituting Ti^{4+}. Also, the increase of the density of sintered samples attributed to the addition of $Bi(Mg_{2/3}Nb_{1/3})O_3$, which significantly improves the sintering performance and greatly assists in densification of the ceramics.

Figure 2 shows the piezoelectric constant d_{33} and the dielectric constant ε_r at room temperature of $(1-x)$ $(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics as a function of substituting amount x. The piezoelectric constant d_{33} and dielectric constant ε_r display a similar variation, enhancing with the increasing of x through a maximum value and then tending to decrease. The piezoelectric constant d_{33} attains maximum value of 94 pC/N at $x = 0.7\%$ and the dielectric constant ε_r reaches to maximum value of 469 at $x = 0.5\%$.

The thickness electromechanical coupling factor k_t and dissipation factor tanδ of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics as a function of x are showed in Fig. 3. It can be seen that k_t tend to increase slightly from 0.40 at

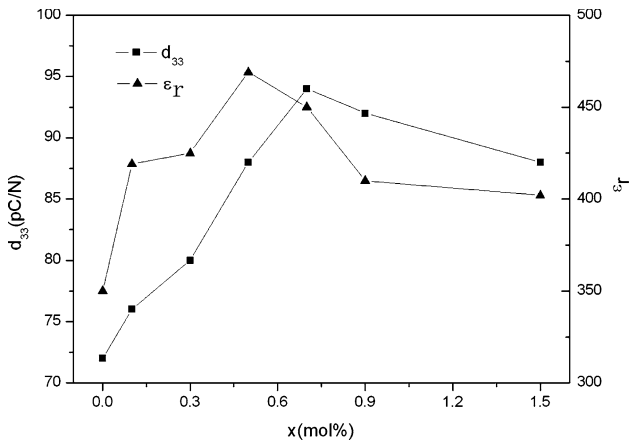

Fig. 2 Room-temperature piezoelectric constant d_{33} and relative dielectric constant ε_r of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics as a function of x

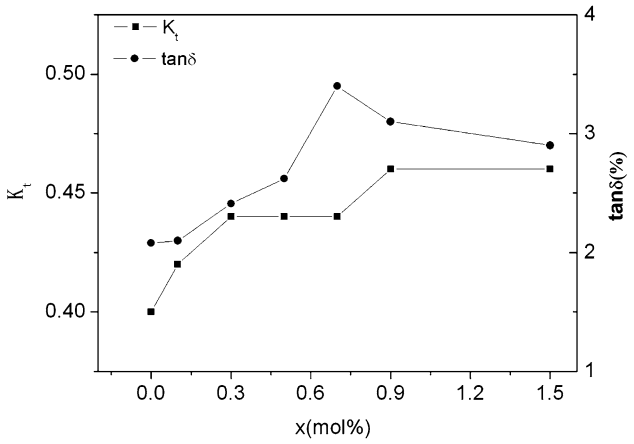

Fig. 3 The thickness electromechanical coupling factor k_t and dissipation factor tanδ of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics as a function of x

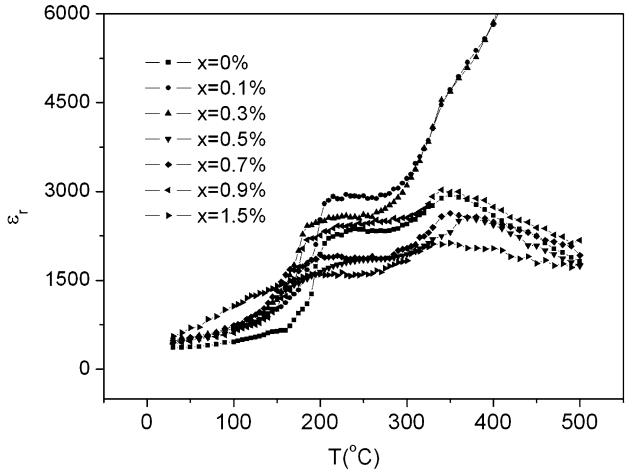

Fig. 4 The dielectric constant ε_r of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics as a function of temperature

$x = 0\%$ up to 0.46 at $x = 0.9\%$. The dissipation factor tanδ increases with increasing x concentration initially, reaches the maximum value of 3.4% at $x = 0.7\%$ and then decrease with more x.

It seemed that the piezoelectric property changes was caused by $Bi(Mg_{2/3}Nb_{1/3})O_3$ addition. That is because the large piezoelectricity of BNT-based solid solutions is attributed to Bi^{3+} ions which easily volatilizes during high-temperature sintering, but Bi^{3+} ions of $Bi(Mg_{2/3}Nb_{1/3})O_3$ can compensate the volatilization and improve the piezoelectric properties. Moreover, complex ions of $(Mg_{2/3}Nb_{1/3})^{3+}$ of $Bi(Mg_{2/3}Nb_{1/3})O_3$ can get into B site of BNT-based solid solutions substituting Ti^{4+}, which cause oxygen vacancies because the charges between $(Mg_{2/3}Nb_{1/3})^{3+}$ and Ti^{4+} are not in equilibrium. The low concentration vacancies can facilitate the domain movement leading to higher piezoelectric properties and dielectric constant. However, with the increasing of $Bi(Mg_{2/3}Nb_{1/3})O_3$ addition, the high-concentration vacancies would order into chain fragments around domain boundaries and pin the domain leading to the decreasing of d_{33}, k_t, and ε_r [12].

Figure 4 shows the temperature dependence of dielectric constants ε_r of the $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics between room temperature and 500 °C at 1 kHz. From the curves, it can be evidently seen that the dielectric constant increase sharply at high temperature when $x = 0.1$ and 0.3%. This phenomenon is consistent with previous results and has been explained in term of superparaelectric clusters [13–15]. Additionally, at lower $Bi(Mg_{2/3}Nb_{1/3})O_3$ concentration, there are distinct hump (T_f) around 200 °C. Such humps were also reported in BNT, BNT–$NaNbO_3$, BNT–$PbTiO_3$ lead-free ceramics system [16–19]. This can be regarded as the manifestation of phase transition between ferroelectric and anti-ferroelectric phases. As $Bi(Mg_{2/3}Nb_{1/3})O_3$ concentration becomes higher, this distinct humps evolve into obscure bumps.

Figure 5 shows the temperature dependence of dielectric constants ε_r for $x = 0$, 0.1, 0.9 mol% of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics between room temperature and 500 °C at 1, 10, 100 kHz. It can be found from Fig. 5 that the ceramics have evidently relaxor ferroelectric characteristics. The dielectric constant ε_r, transition temperature (T_f) are strongly dependent on the measurement frequency. The value of relative dielectric constant ε_r decreases and the transition temperature T_f increases as the measuring frequency increases. For most ABO_3 type perovskite ferroelectric, it has relaxor feature caused by A or B site cations disorder. In the present work, Bi^{3+} ions substituting A site and $(Mg_{2/3}Nb_{1/3})^{3+}$ ions substituting B site induce the ions disorder at lattice which lead to relaxor behavior.

Conclusion

Lead-free piezoelectric ceramics $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$, a new member of the BNT-based group, was prepared by conventional solid state reaction method 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 thickness electromechanical coupling factor k_t increased with the increasing content of $Bi(Mg_{2/3}Nb_{1/3})O_3$, showed the maximum value of 94 pC/N and 0.46 at $x = 0.7\%$, 0.9%, respectively. Temperature dependence of dielectric constant ε_r measurement indicated these compounds were typical relaxor ferroelectric.

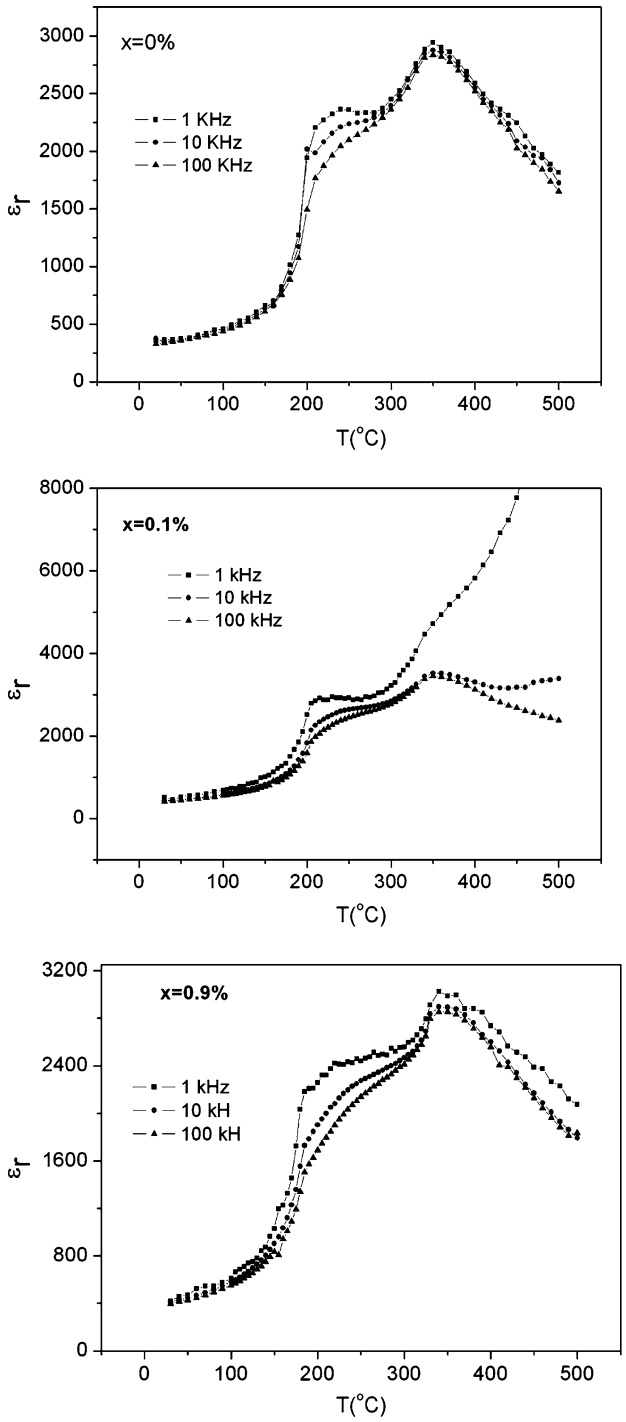

Fig. 5 The dielectric constant ε_r of $(1-x)(Bi_{1/2}Na_{1/2})TiO_3-xBi(Mg_{2/3}Nb_{1/3})O_3$ ceramics with $x = 0\%$, 0.1%, and 0.9% as a function of temperature at 1, 10, and 100 kHz

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