Effect of substitution of titanium by magnesium and niobium on structure and piezoelectric properties in $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics

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Abstract. To develop new $(Bi_{1/2}Na_{1/2})TiO_3$-based ceramics with excellent piezoelectric properties, the similarities and the differences between PZT and $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics were analysed. Based on the analysis, a new $(Bi_{1/2}Na_{1/2})TiO_3$-based piezoelectric ceramic of B-site substitution of complex ions $(Mg_{1/3}Nb_{2/3})^{4+}$ for Ti^{4+} was prepared by a conventional ceramic technique, and effect of complex ions $(Mg_{1/3}Nb_{2/3})^{4+}$ addition on the micro-structure, dielectric and piezoelectric properties was investigated. The results show that all compositions are mono-perovskite phase and the grain size increases with increasing content of $(Mg_{1/3}Nb_{2/3})^{4+}$. The piezoelectric constant, d_{33}, first increases and then decreases, and electromechanical coupling factor, k_p, varies insignificantly with increasing content of $(Mg_{1/3}Nb_{2/3})^{4+}$.

Keywords. Lead-free piezoelectric ceramics; perovskite structure; substitution.

1. Introduction

Pb(Zr, Ti)O_3(PZT) and related compositions have been the mainstay for high performance actuators and transducers, owing to their superior dielectric, piezoelectric and electromechanical coupling coefficients (Jaffe *et al* 1971). In the past, innovations in actuators and ultrasonic transducers have been the driving force for new developments in piezoelectric ceramics (Xiao *et al* 2006). Currently, the driving force is the result of environmental regulations. 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) with ABO_3 type perovskite structure has been considered to be a promising candidate for lead-free piezoelectric materials as BNT shows a strong ferroelectricity ($P_r = 38 \mu C/cm^2$) and high Curie temperature($T_c = 320°C$) (Smolenski *et al* 1961). However, this ceramic has drawbacks such as high conductivity and large coercive field ($E_c = 73$ kV/cm), which cause problems in poling process. As a result of these, a lot of work to modify and improve piezoelectric properties of BNT ceramics has been done by substitution of BaTiO$_3$ (Takenaka *et al* 1991), $(Bi_{1/2}K_{1/2})TiO_3$ (Sasaki *et al* 1999), NaNbO$_3$ (Li *et al* 2004), BiFeO$_3$ (Nagata *et al* 1999a), Ba(Cu$_{1/2}$W$_{1/2}$)O$_3$ (Elkechai *et al* 1996), PbTiO$_3$

(Kuharuangrong and Schulze 1996), and so on. Based on the binary BNT system, some ternary systems with good piezoelectric properties such as $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$–BaTiO$_3$ (Chen and Lu 2007), $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$–NaNbO$_3$ (Li *et al* 2005a), $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$–KNbO$_3$ (Li *et al* 2005b), $(Bi_{1/2}Na_{1/2})TiO_3$–BaTiO$_3$–BiFO$_3$ (Nagata *et al* 1999b) were also studied. However, the piezoelectric properties of these ceramics are not high enough for most practical uses.

In order to further enhance the properties of BNT ceramics and meet the requirements for practical uses, it is necessary to develop new BNT-based ceramics. To develop new BNT-based ceramics, the similarities and the differences between BNT ceramics and PZT ceramics were analysed. Firstly, compared with BNT-based ceramics, the high piezoelectric properties are attributed to Pb because the Pb $6s$ and O$2p$ state are strongly hybridized in PZT ceramics (Cohen and Krakauer 1992). Then, bismuth lies next to lead in the periodic table, its atomic weight is as large as that of lead and the electronic configuration of Bi^{3+} is identical to that of Pb^{2+}. Therefore, it is assumed that the large ferroelectricity of BNT-based solid solutions is attributed to $(Bi_{1/2}Na_{1/5})^{2+}$ ions, especially Bi^{3+} ions, in the A sites of ABO_3 perovskite structure (Nagata and Takenaka 1997). Besides, in PZT-based ceramics, the Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$–PbTiO$_3$ ceramics with B-site substitution of complex ions of $(Mg_{1/3}Nb_{2/3})^{4+}$ have excellent piezoelectric properties (Chen *et al* 2000). Based on the above discussion, it is assumed that the B-site substitution of complex ions of $(Mg_{1/3}Nb_{2/3})^{4+}$ for

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Ti^{4+} in BNT ceramics should have excellent piezoelectric properties. Therefore, the lead-free ceramics of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ have been prepared and the effect of complex ions substitution of (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ for Ti^{4+} in the B-sites for (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ perovskite lattice on structure and piezoelectric properties was investigated.

2. Experimental

High purity Bi$_2$O$_3$, Na$_2$CO$_3$, TiO$_2$, MgCO$_3$ and Nb$_2$O$_5$ (purity over 99·5%) powders were used as starting materials. Our preliminary experiments found that (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics were not well synthesized by mixing and calcinating all these above powders as used in the conventional oxide mixing process. Therefore, the (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics were prepared by using a modified two-step calcination approach, in which MgCO$_3$ and Nb$_2$O$_5$ powders were first calcinated at 1100°C for 4 h to be compound of MgNb$_2$O$_6$, then MgNb$_2$O$_6$ was blended with other powders and calcined at 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 discs with diameter 18 mm and thickness 1·2 mm. 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 specimens for measurement of piezoelectric properties were poled in silicon oil at 80°C under 4 ~ 7 kV/mm for 15 min. After 24 h, piezoelectric properties were measured using an impedance analyser (Agilent 4294A) by the resonant and anti-resonant method. The microstructure of sintered samples was observed by a scanning electron microscope (JSM-5610LV), and crystal structure was measured by X-ray diffractometer (Bruker D8-Advance). Piezoelectric constant, d_{33}, was measured with a d_{33} meter (China of Acoustics ZJ-3A).

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics in the 2θ range of 20–80°. It is clear that all compositions exhibit typical ABO$_3$ perovskite diffraction peaks, and no trace of secondary phases is detectable. The lattice parameter and angle parameter of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics are shown in table 1. The lattice and angle parameters were indexed to be a rhombohedral symmetry structure, implying that (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ ions dissolved into the BNT lattice and does not cause an obvious change in the phase structure. It can be seen that lattice dimensions of the (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics increase with the increasing content of (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$. According to Shannon's effective ionic radius with a coordination number of six (Shannon 1976), (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ has an average radius of 0·67 Å, which is close to that of Ti^{4+} (0·61 Å). There-

fore, (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ ionic should enter into the six-fold coordinated B site of the perovskite structure to substitute for Ti^{4+} because of radius matching, which leads to the increase of lattice dimensions.

Figure 2 shows typical microstructures of sintered (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics. With the substituting content of x increasing, the grain size increases, and then a high dense microstructure is obtained. Examination of the microstructure in the samples with high level substituting revealed the presence of needle-like grains throughout the samples. Similar microstructure containing needle-like grains has been reported by Nagata and Takenaka (2001) in Mn doped (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$. They attributed this phenomenon to the presence of non-stoichiometry due to the rejection of Bi by Mn. The formation of needle-shape phase may be attributed to the vacancies which were produced by vapourizing of Bi during the high temperature sintering process.

Figure 3 shows the piezoelectric constant, d_{33} and the planar electromechanical coupling factor, k_p, of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics as a function of x. The piezoelectric constant, d_{33}, first increases sharply with x increasing from 0·005 to 0·015, and then decreases with x further increasing with the maximum value of 105 pC/N at $x = 0·015$. However, the planar electromechanical coupling factor, k_p, has no evident change with increase of x.

Figure 4 shows the dielectric constant, ε_r and the dielectric loss, tan δ, at room temperature of the (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics as a function of x. The dielectric constant, ε_r, increases with increasing (Mg$_{1/3}$Nb$_{2/3}$)$^{4+}$ fraction up to $x = 0·015$ with $\varepsilon_r = 435$ and then decreases. The dielectric loss tan δ increases linearly with increasing x. Owing to the ion radius of (Mg$_{2/3}$Nb$_{1/3}$)$^{4+}$ which is larger than that of Ti^{4+}, (Mg$_{2/3}$Nb$_{1/3}$)$^{4+}$ substituting
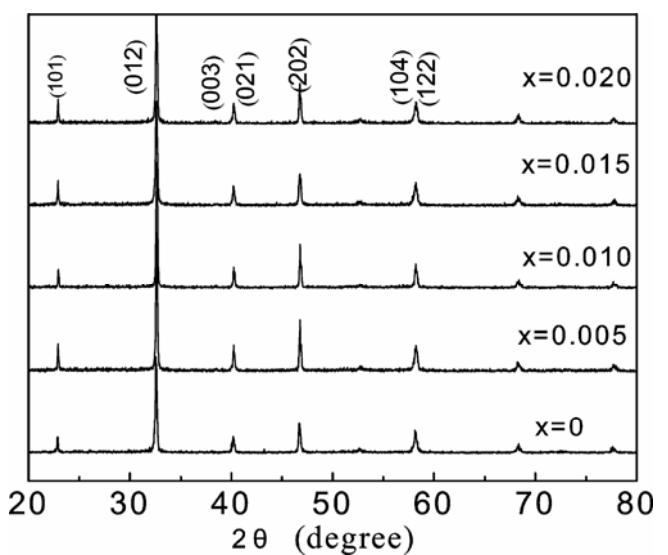

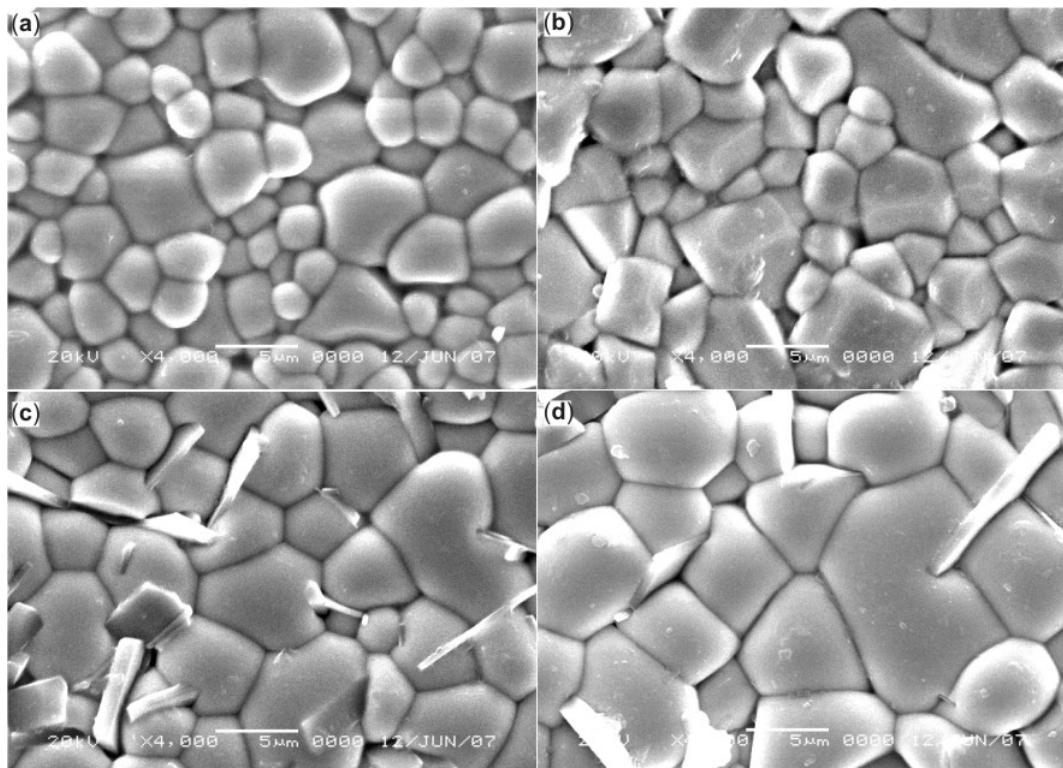**Figure 1.** XRD patterns of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics.

Figure 2. SEM micrographs of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics with (**a**) $x = 0.005$, (**b**) $x = 0.010$, (**c**) $x = 0.015$ and (**d**) $x = 0.020$.
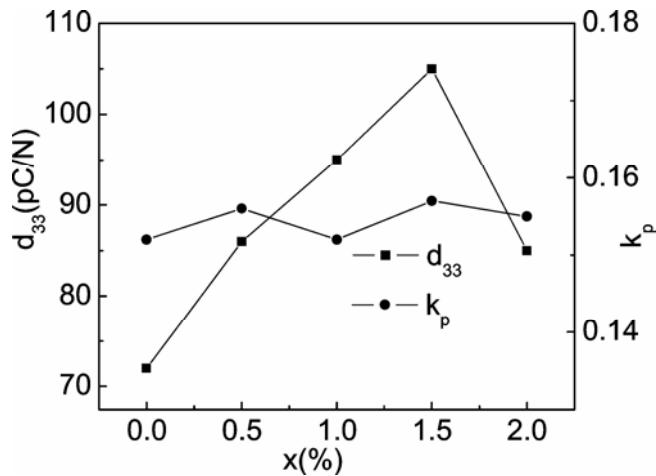

Figure 3. Piezoelectric constant, d_{33} and planar electromechanical coupling factor, k_p, of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics as a function of x.

Table 1. The lattice parameter and angle parameter of (Bi$_{1/2}$Na$_{1/2}$)Ti$_{1-x}$(Mg$_{1/3}$Nb$_{2/3}$)$_x$O$_3$ ceramics.

x	a (nm)	$\alpha(0)$
0	3·887	89·66
0·005	3·892	89·63
0·010	3·892	89·63
0·015	3·895	89·60
0·020	3·897	89·58

Ti^{4+} leads to the lattice deformation. The lattice deformation facilitates the reorientation of ferroelectric domains and causes the increase in dielectric constant and dielectric loss. With further increasing content of (Mg$_{2/3}$Nb$_{1/3}$)$^{3+}$, the decrease of dielectric constant may be the presence of the needle-shaped phase.

The above result is different from the assumption we concluded from the analysis between PZT and BNT ceramics. Many theories have been proposed to explain the piezoelectric properties change in the modified piezoelectric ceramics. Yamashita *et al* (2000) indicated that the electromechanical coupling factor (k_p) tended to increase with the mass difference between the perovskite A-site and B-site cations by studying the effects of the molecular mass of the B-site cations on k_p of lead-based perovskite piezoelectric materials. Yan *et al* (2005) exhibited that the comprehensive factor (containing the ionic size, atomic weight and electric negative) is related to the piezoelectric properties by studying the effects of the differences of the ionic size, atomic weight and electric negative of the A-site and B-site ions of ABO$_3$ perovskite (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based solid solutions. Wang *et al* (2005) showed that the change of random field by doping was a predominant factor affecting the dielectric and piezoelectric properties by studying the bismuth-containing complex perovskite. These indicate that the mechanism of the high piezoelectric activity is complex. The unexpected low piezoelectric properties of the B-site substituting BNT-
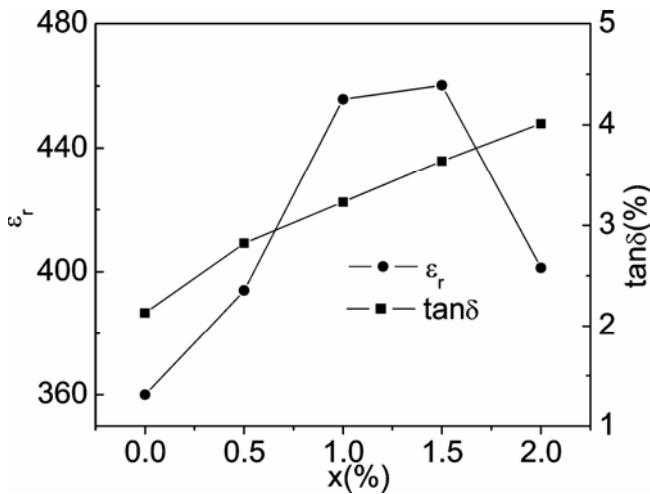
Figure 4. Dielectric constant, ε_r and dielectric loss tanδ of $(Bi_{1/2}Na_{1/2})Ti_{1-x}(Mg_{1/3}Nb_{2/3})_xO_3$ ceramics as a function of x.

based ceramics may be attributed to the deference between the A-site complex ions of $(Bi_{1/2}Na_{1/2})^{2+}$ in BNT ceramics and single ions of Pb^{2+} in PZT ceramics. Also, the morphotropic phase boundary(MPB) is an important factor and further study is in progress.

4. Conclusions

Lead-free piezoelectric ceramics of $(Bi_{1/2}Na_{1/2})Ti_{1-x}$ $(Mg_{1/3}Nb_{2/3})_xO_3$ with x = 0, 0·005, 0·015, 0·020 and 0·025 have been synthesized by a two-step calcination approach. The effect of cationic substitution of magnesium and niobium for titanium in the B sites for $(Bi_{1/2}Na_{1/2})TiO_3$ perovskite lattice on structure and piezoelectric properties were investigated. X-ray diffraction and SEM analysis show that the materials are mono-perovskite phase and grain size increases with increasing x. The piezoelectric constant, d_{33}, first increases and then decreases with increasing x, showing the maximum value of 105 pC/N at x = 0·015. The planar electromechanical coupling factor,

k_p, has no evident change with increasing x. The results indicate that the mechanism of the high piezoelectric activity is complex and the low piezoelectric properties of the B-site substituting BNT-based ceramics may be due to the A-site complex ions of $(Bi_{1/2}Na_{1/2})^{2+}$.

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