Microstructure and properties of lead-free $(Bi_{1/2}Na_{1/2})TiO_3$ based piezoelectric ceramics doped with different cations

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Abstract Different cations doped lead-free piezoelectric $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics with the general formula $Na_{0.4995}Bi_{0.4995}Ba_{0.001}Ti_{0.998}M_{0.002}O_3$ (M = Nb, Ta, and Sb) were fabricated. The effects of processing parameters and doping on phase content, microstructure, dielectric and piezoelectric properties of the materials were discussed. Experimental results show that Nb doped $(Bi_{1/2}Na_{1/2})TiO_3$ exhibits superior polarization performance over the existing lead-free ceramics with a d_{33} value of 122 pC/N obtained when poled at 60 kV/cm at room temperature. The best piezoelectric properties were achieved in $(Bi_{1/2}Na_{1/2})TiO_3$ doped with Ta having a measured d_{33} value of 164 pC/N for samples poled at 100 °C under the applied field of 50 kV/cm.

Introduction

In the last few years, there has been a renewed interest in the development and fabrication of bismuth sodium titanate, $(Bi_{1/2}Na_{1/2})TiO_3$, one of the promising candidates to replace lead-based piezoelectrics. Despite its potentially useful piezoelectric properties such as rela-tively high Curie temperature (Tc~320 °C) and a large remnant polarization (~38 $\mu C/cm^2$) [1–4], bismuth sodium titanate has high coercive field (Ec~73 kV/cm) and high electrical conductivity at room temperature, which creates problems during the poling process [1]. Recent results concerning the effect of doping on ferroelectric properties of BNT-based solid solutions have indicated that the large ferroelectricity of BNT-based solid solutions is associated with Bi^{3+} ions at the A-site in the perovskite structure [5–7] and poling performance was improved by forming solid solutions with $BaTiO_3$ [8], $BiFeO_3$ [9], $NaNbO_3$ [10] or doping with different oxides such as CeO_2 [11], Sc_2O_3 [12], La_2O_3 [13], and MnO_2 [14] in both A-site and B-site.

In the present study, doping cations Ba^{2+}, Nb^{5+}, Ta^{5+} and Sb^{5+}, usually used in PZT system, were introduced into $(Bi_{1/2}Na_{1/2})TiO_3$ with an attempt to modify its polarizability. More precisely, the intention here was to partially substitute Na and Bi by Ba, and Ti by Nb, Ta and Sb, respectively, as expressed by the general formula $Na_{0.4995}Bi_{0.4995}Ba_{0.001}Ti_{0.998}M_{0.002}O_3$ where M = Nb, Ta or Sb, Dielectric constant (ε) and loss tangent (tanδ) were measured by impedance analysis. The effects of processing parameters and doping cations on the microstructure and electric properties were examined. The polarization behaviour under different DC poling fields were investigated, the dependence of electric displacement-poling field (D-E) hysteresis loop behaviour on an AC field at low frequency were studied.

Experimental

$Na_{0.4995}Bi_{0.4995}Ba_{0.001}Ti_{0.998}M_{0.002}O_3$ (M = Nb, Ta and Sb respectively) powders were synthesized by the

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conventional chemical reaction process. A mixture of reagent grade Na_2CO_3, Bi_2O_3, TiO_2, $BaCO_3$, Nb_2O_5, Ta_2O_5 and Sb_2O_5 powders, corresponding to a designed final stoichiometry $Na_{0.4995}Bi_{0.4995}Ba_{0.001}$-$Ti_{0.998}M_{0.002}O_3$ (M = Nb, Ta and Sb respectively), were ball milled with ZrO_2 balls in a DI water in a polyethylene bottle for 6 h. The mixtures were dried at 105 °C and calcined at temperatures ranging from 800 to 1100 °C for 2 h. The calcined powders were then mixed with PEG (1–5 wt%) and ball milled with 5 mm ZrO_2 balls in DI water in a polyethylene bottle for 2 h. The as-granulated powders were then dry pressed into disc shape samples with a diameter of 12.5 mm and thickness of ~2 mm under 50 MPa followed by isostatic pressing at 200 MPa to achieve a higher green body density. The green bodies were sintered at 1150–1280 °C for 2 h depending on the composition. It was found that the weight loss from the sample at 1200 °C was <1%. The phase present in the BNT based powders and bulk ceramics was analyzed using a Rigaku Miniflex X-ray diffractometer with CuK_α radiation. The surface morphologies and grain sizes of the pellets were studied using a JEOL JSM-840 scanning electron microscope (SEM). To minimize the impact of this nonstoichiometry on the properties, at least 250 μm of material was removed from the top and bottom surfaces before measurements. The surface of the sample was first ground and fine polished followed by coating with Ag for electrical property measurements. Dielectric constant at frequencies between 1 Hz and 1 MHz and its dependence on temperature were measured using a Solartron Impedance Analyser (1260/1296 dielectric interface) in conjunction with a Eurotherm controlled temperature chamber. Samples were heated and cooled at 2 °C/min. The samples were poled by applying an electric field from 20 kV to 70 kV/cm at room temperature and 100 °C for 10 and 30 min followed by cooling to room temperature while maintaining the field. The d_{33} measurements were made on the poled samples using a d_{33} meter at frequencies of 100 Hz and 200 Hz for comparison purpose. Simultaneous polarization (P) and strain (S) hysteresis curves were generated using a computer-controlled modified Sawyer Tower system and a linear variable displacement transducer (LVDT) sensor. Electric fields as high as 70 kV/cm were applied using an amplified sine wave form at 0.2 Hz, using a Trek high voltage DC amplifier. During testing, the samples were submerged in silicon oil, as an insulating liquid, to prevent arcing.

Results and discussion

X-ray diffraction analysis

Figure 1 shows the X-ray diffraction patterns of Nb, Ta, and Sb-doped powders synthesized at 800 °C and the bulk materials sintered at 1200 °C.

It was reported that ferroelectric $(Na_{1/2}Bi_{1/2})TiO_3$-$BaTiO_3$ with low $BaTiO_3$ concentrations has rhombohedral symmetry (R3c) with a small rhombohedral distortion (90°–α < 0.05°) at room temperature. The structure of $(Na_{1/2}Bi_{1/2})TiO_3$-$BaTiO_3$ solid solution becomes tetragonal with increasing $BaTiO_3$ concentration. The morphotropic phase boundary (MPB) is located at ~5.5 mol% $BaTiO_3$. In the present study, low level of doping with Ba (x = 0.001) was employed to ensure a less distorted crystal structure. X-ray diffraction patterns show that the powder and sintered ceramics consist predominantly of perovskite phase with traces of Sb_2O_5 phase as shown in Fig. 1. The Sb_2O_5 appears to come from the incomplete reaction and inability of Sb to dissolve fast into the perovskite structure. Also, it is noticed that both Nb and Ta doped
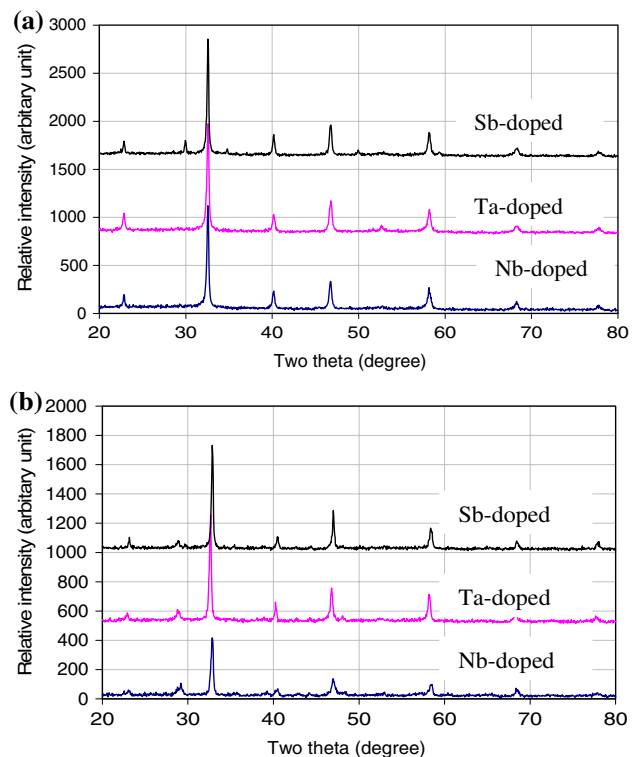
Fig. 1 X-ray diffraction patterns of Nb, Ta and Sb-doped $Na_{0.4995}Bi_{0.4995}Ba_{0.001}Ti_{0.998}(Nb,Ta,Sb)_{0.002}O_3$. (a) as-synthesized powders and (b) sintered bulk ceramics

$(Na_{1/2}Bi_{1/2})TiO_3$ powders showed rhombohedral symmetry whereas Sb doped powder showed a tetragonal structure. However, all sintered samples showed a tetragonal structure.

Figure 2 shows typical microstructures of sintered $(Bi_{1/2}Na_{1/2})TiO_3$ materials doped with Nb.

A highly dense microstructure is obtained with the expected increase in grain size as the sintering temperature is increased. For example, the average grain size for samples sintered at 1160 °C was 2 μm and that for samples sintered at 1200 °C was 8 μm. Although most of the grains are equiaxed, some of them are elongated with a rather large aspect ratio. In samples sintered at lower temperatures, the elongated grains are longer, with smaller diameters, whereas, samples sintered at higher temperatures the elongated grains are shorter with a larger diameter.

The effect of Nb, Ta, and Sb addition on microstructure is shown in Fig. 3 for samples sintered at 1180 °C.

It is evident that the doping elements cause a significant change in microstructure. For example, samples doped with Ta have a more dense and homogeneous microstructure with a smaller grain size (~2 μm), whereas samples doped with Nb and Sb have much coarser microstructure and signs of abnormal grain growth as evidenced in Fig. 3(a, c). Also, doping with Nb and Sb resulted in the creation of large pores in the microstructure, which appear to have significant effect on the piezoelectric properties of the resultant ceramics. Another interesting microstructural feature observed in the samples is the growth of the elongated grains in both Ta and Nb doped ceramics. Examination of the microstructure in the samples doped with Ta revealed the presence of needle-like grains throughout the samples. Similar microstructure containing needle-like grains has been reported by Nagata and Takenaka [14] in Mn doped $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics. They attributed this phenomenon to the presence of non-stoichiometry due to the rejection of Bi by Mn. Whether these elongated grains have the same structure as $(Bi_{1/2}Na_{1/2})TiO_3$ is not clear at this time. Additional research is required to determine their composition and their effect on piezoelectric properties.

Dielectric properties

All dielectric properties were measured at frequencies ranging from 1 Hz to 1 MHz. The variation of dielectric constant and loss tangent, tanδ, with frequency before poling is shown in Fig. 4 for the $(Bi_{1/2}Na_{1/2})TiO_3$ doped with Nb, Ta and Sb sintered at different temperatures.

As expected, the experimental data reveal that both the frequency and sintering temperature have a strong effect on dielectric properties (Fig. 4).

A higher dielectric constant (at 1 KHz) was achieved in $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics sintered at lower

Fig. 2 SEM micrographs showing the microstructure evolution of $(Na_{1/2}Bi_{1/2})TiO_3$ doped with Nb and sintered at various temperatures. (**a**) 1160 °C, (**b**) 1180 °C, and (**c**) and (**d**) 1200 °C
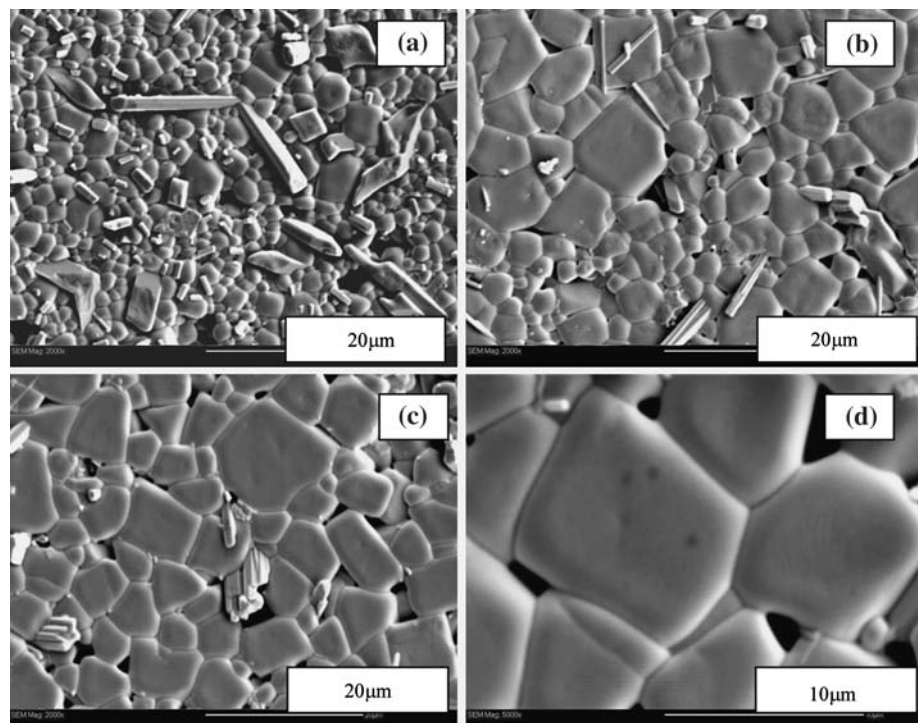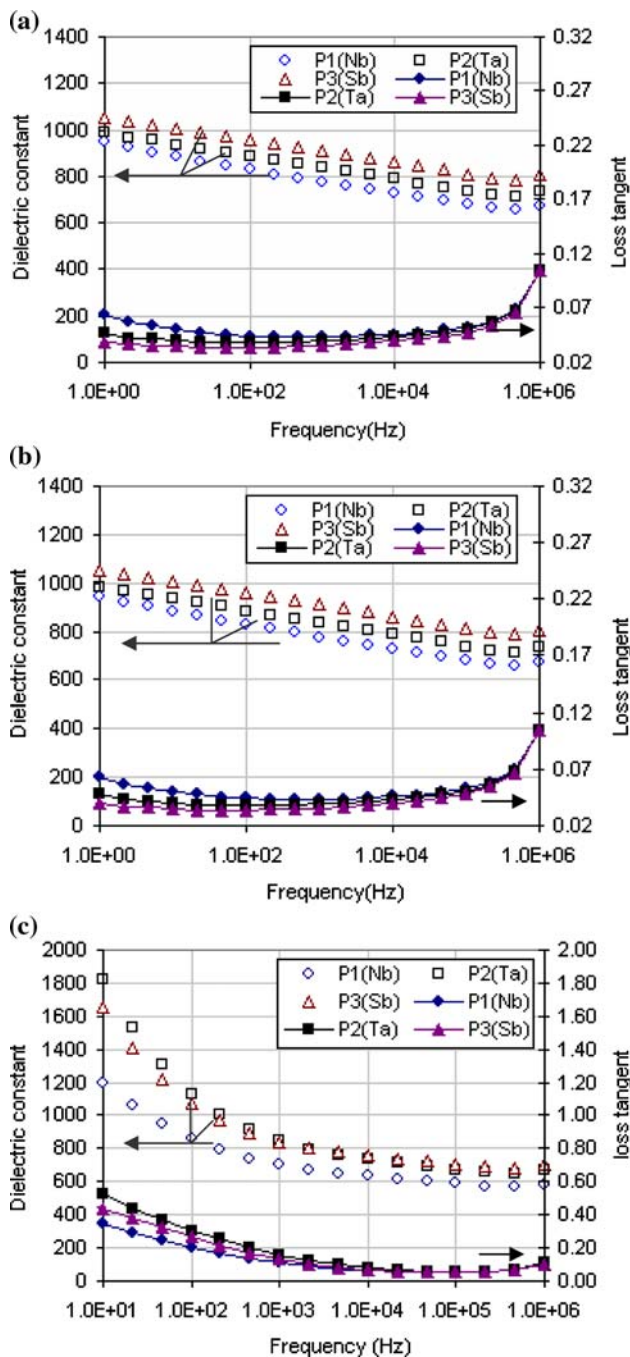
Fig. 3 SEM micrographs of the $(Na_{1/2}Bi_{1/2})TiO_3$ doped with Nb, Ta and Sb and sintered at 1180 °C. (**a**) and (**b**) Nb doped, (**c**) and (**d**) Ta doped and (**e**) and (**f**) Sb doped
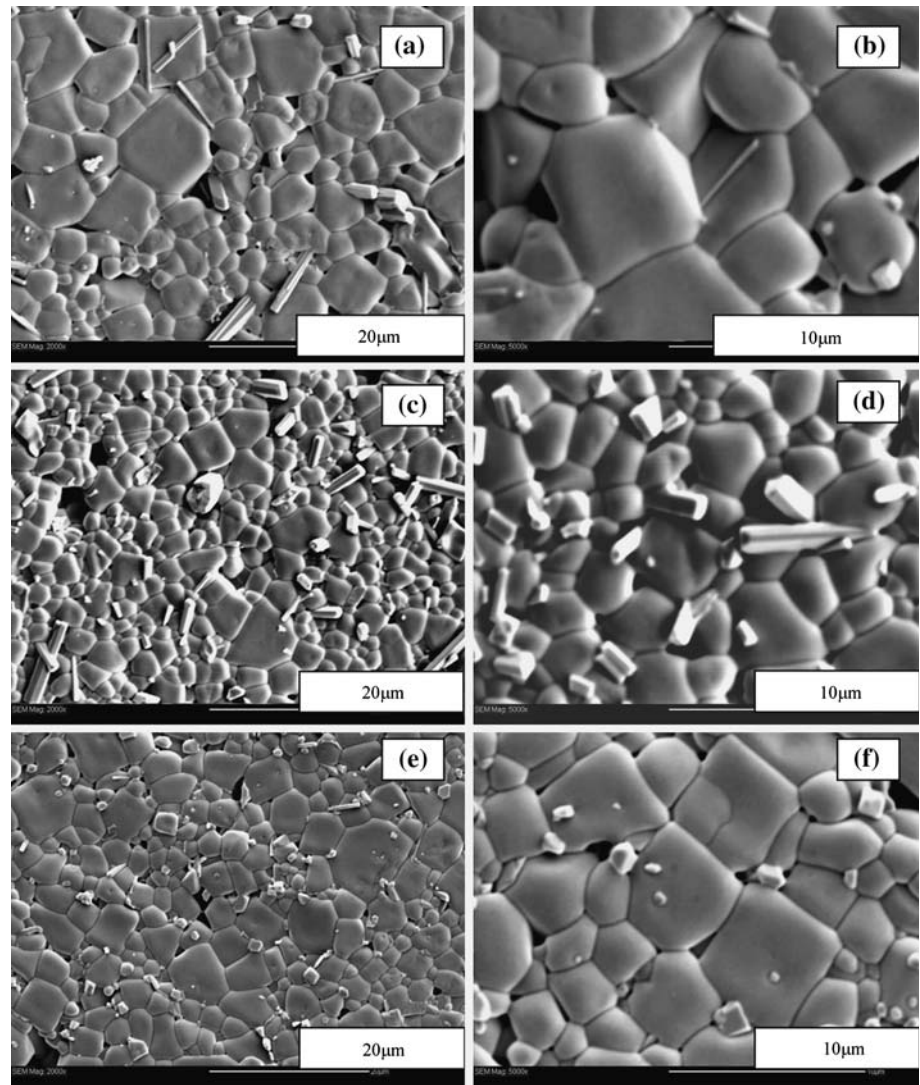
temperatures. For example, the Sb doped $(Bi_{1/2}Na_{1/2})$ TiO_3 exhibits the highest dielectric constant of ~872 while Nb doped ceramics show the lowest value of 776. The same trend was observed with loss tangent $(\tan\delta)$. The lowest loss was obtained in samples doped with Sb (3.33%) and the highest with Nb (4.35%). When it comes to sintering, it appears that the effect of sintering temperature on dielectric properties of doped $(Bi_{1/2}Na_{1/2})TiO_3$ stems from the volatilization of the bismuth-rich phase, resulting in space charges in the grain boundaries. This view is further reinforced by the relatively high dielectric loss of the materials sintered at higher temperatures when measured at lower frequencies, as depicted in Figs. 4(b) and (c). Additional investigations involving the field dependence of dielectric and piezoelectric properties of $(Na_{1/2}Bi_{1/2})$ TiO_3 lead to the same conclusion.

Temperature characteristics, such as Curie temperature (T_c), temperature corresponding to the maximum dielectric constant (T_m), dielectric constant (ε) and loss tangent $(\tan\delta)$ are present in Table 1 for $(Na_{1/2}Bi_{1/2})$ TiO_3 doped with different cations. All measurements were done at 1 KHz.

It is interesting to note that all materials exhibit the highest dielectric constant at $T_m \cong 240$ °C. In absolute terms, the highest dielectric constant of 2890 was achieved in Nb doped $(Na_{1/2}Bi_{1/2})TiO_3$ (showing an increase from 785 at room temperature to 2890 at 240 °C) and the lowest value of 2240 in materials doped with Sb. Overall, the prepared materials show rather similar trend in the dielectric constant (ε) and loss tangent $(\tan\delta)$ with temperature even though the doping elements are different. A typical variation of dielectric constant and loss tangent with depolarization

Fig. 4 Dielectric constant and loss tanδ of $(Bi_{1/2}Na_{1/2})TiO_3$ piezoelectric ceramics doped with Nb, Ta and Sb and sintered at: (**a**) 1180 °C, (**b**) 1190 °C and (**c**) 1200 °C

Table 1 Temperature characteristics of BNT doped with different cations at 1 KHz

| Doping element	ε (25 °C)	tanδ (25 °C)	ε_{max} (240 °C)	tanδ (240 °C)	T_c (°C)	T_m (°C)
Nb	785	0.064	2890	0.0087	~240	240
Ta	834	0.039	2740	0.0068	~240	240
Sb	872	0.033	2240	0.0058	~220	220

in the temperature range 180–240 °C and then goes up for all frequencies used ranging from 10 Hz to 100 kHz. However, no measurable change in loss was observed for samples tested at 1 MHz at temperatures above ~240 °C. The dielectric constant vs. temperature curve in Fig. 5(a) exhibits a broad peak with maximum value at T_m ~ 240 °C. This differs from generally observed behaviour in the normal ferroelectrics, in which the depolarization temperature (T_d) and the maximum temperature (T_m) usually coincide with each other and are named Curie temperature (T_c). It is believed that the Curie point (T_c) in this system should be in the vicinity of T_m which cannot be simply regarded as a Curie point according to the recent report in the BNT-BT system by Chu et al. [15]. They suggest that the phase transition between ferroelectric phase and paraelectric in doped $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics cannot be expected to occur at a specific temperature.

High DC field electrical properties of $Na_{(1-x)/2}$ $Bi_{(1-x)/2}Ba_xTi_{(1-y)}(Nb,Ta,Sb)_yO_3$ Ceramics

A series of tests were carried out on doped BNT ceramics where polarization was measured as a function of poling field. Typical polarization behaviour in terms of d_{33} at room temperature is given in Fig. 6.

Figure 6 shows that all BNT ceramics doped with different cations exhibit an increase in d_{33} with the electric field. The highest increase was found in BNT doped with Nb, reaching a value of 122 pC/N when poled under an electric field of 60 kV/cm. The strong field dependence of d_{33} shown in Fig. 6 suggests active contribution of non-180° domain walls in these ceramics. It is estimated that the switching of this non-180° domain starts at ~20 kV/cm. This result is important for it indicates that low concentration of A- and B-site doping does not inhibit displacement of domain walls; i.e. it does not render material piezoelectrically too "hard", thus suggesting that the "soft" cations play similar roles as in the classical PZT based system. The terms "soft" and "hard" were borrowed from the PZT piezoelectrics in order to characterize the poling ability of the BNT ceramics. The polarization results of the Nb doped BNT ceramics showed the

temperature (T_d) for Ta doped $(Na_{1/2}Bi_{1/2})TiO_3$ is shown in Fig. 5.

Clearly, there is a broad maximum in the dielectric constant at ~240 °C followed by a decrease in ε with a further increase in temperature. Unlike dielectric constant, the loss tangent shows an opposite trend. Initially, tanδ goes down to a minimum value of ~0.3%

Fig. 5 Temperature dependence of dielectric constant (**a**) and loss tangent tanδ (**b**) of $Na_{0.4995}Bi_{0.4995}Ba_{0.001}Ti_{0.998}Nb_{0.002}O_3$ ceramics at the frequency regime 10 Hz to 1 MHz
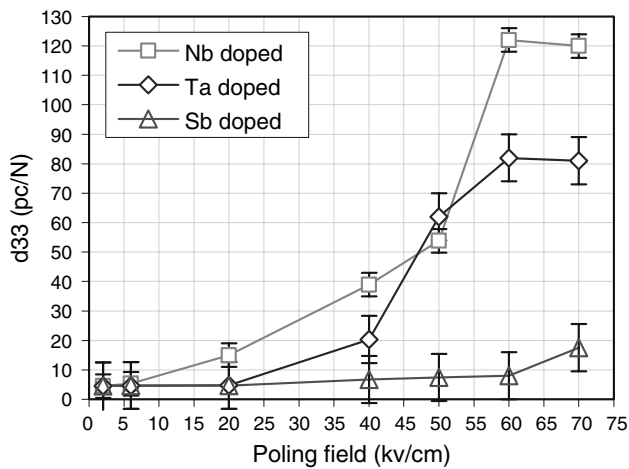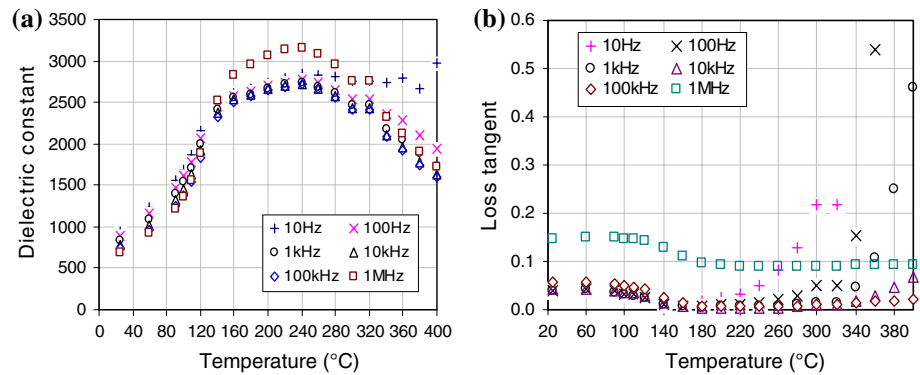
Fig. 6 Variation of d_{33} with poling field at room temperature for BNT ceramics doped with Nb, Ta, and Sb respectively and sintered at 1190 °C

d_{33} coefficient to vary from 15 pC/N when poled under 20 kV/cm to 122 pC/N when poled under 60 kV/cm. In the case of Ta doped BNT, the d_{33} piezoelectric coefficient increases from 5 pC/N to 80 pC/N and for Sb doped BNT the d_{33} increases from 5 pC/N to 20 pC/N. At room temperature, the highest d_{33} value of 122 pC/N was obtained in BNT ceramics doped with Nb when polarized at the electric field of 60 kV/cm. Further increase in poling field (over 60 kV/cm) did not lead to an increase in d_{33} for ceramics doped with Nb and Ta, indicating that the poling field applied has reached its saturation level. However, ceramics doped with Sb showed a slow increase in d_{33} with the poling field all the way to 70 kV/cm. A further increase in the applied field (>80 kV/cm) caused a breakdown of ceramics, presumably due to the presence of a minor amount of second phase particles.

Preliminary study of the polarization behaviour above room temperature (100 °C) was also conducted. The results are given in Table 2.

From Table 2, it is seen that, for samples doped with Nb, the value for piezoelectric coefficient (d_{33}) is similar to that obtained for samples poled at room temperature but under a higher electric field, suggesting that this material is "soft". Doping with Sb however did not produce a significant increase in polarization. Referring again to Table 2, it is clear that the largest d_{33} was achieved with samples doped with Ta. For example, with samples poled under an electric field of 40 kV/cm, the piezoelectric coefficient, d_{33}, increased from 20.3 pC/N at room temperature to 145 pC/N at 100 °C and for samples poled under an electric field of 50 kV/cm, the d_{33} increased from 62 pC/N for samples poled at room temperature to 164 pC/N when poled at 100 °C.

Ferroelectric behaviour

Typical polarization vs. electric field curves for prepared lead-free piezoelectric $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics doped with Ta are shown in Fig. 7.

It can be observed from Fig. 7(a) and (b), the D-E loops are not well-saturated under the low electric field (<40 kV/cm); however, under higher electric fields (>40 kV/cm), the ceramics showed a well-saturated hysteresis loop. Although the loops are not perfectly symmetrical, it is estimated that the remnant polarization (Pr) is around ~8.6 μC/cm^2. The small shift of the hysteresis loop toward the direction having |Ec(-)| >|Ec(+)| is caused by either the

Table 2 d_{33} values for $(Na_{1/2}Bi_{1/2})TiO_3$ poled at 100°C under different electric fields

Electric field	40 kV/cm	50 kV/cm
Nb doped BNT	108 pC/N	116 pC/N
Ta doped BNT	145 pC/N	164 pC/N
Sb doped BNT	25 pC/N	39 pC/N
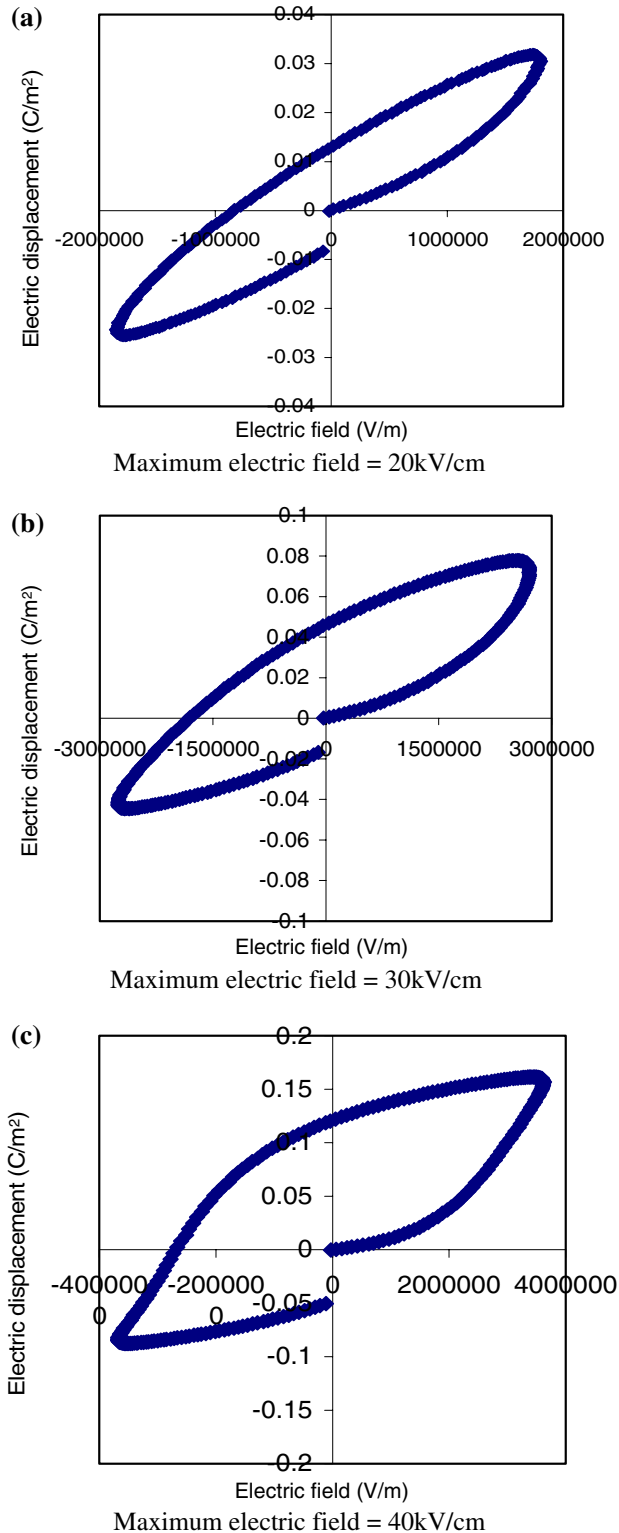
Fig. 7 Change of polarization with electric field for $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics doped with Ba and Ta

asymmetric top and bottom electrodes or ''self'' polarization of the materials. The total coercive field $(|Ec(+)| + |Ec(-)|)$ is approximately 43 kV/cm (with an average Ec of 22 kV/cm) which is markedly smaller than the reported ~76 kV/cm for pure $(Bi_{1/2}Na_{1/2})TiO_3$ [1]. This suggests that the introduction of so-called ''soft'' cations played an important role in improving the polarizability of $(Bi_{1/2}Na_{1/2})TiO_3$ materials.

Conclusions

''Soft'' cations doped lead-free piezoelectric $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics with general formula $Na_{(1-x)/2}Bi_{(1-x)/2}BaxTi_{(1-y)}M_yO_3$ (M = Nb, Ta, and Sb) with $x = 0.001$ and $y = 0.002$ were synthesized in the form of a single phase and sintered to a high density. The highest dielectric constant (872) and smallest loss (3.3%) was achieved in samples doped with Sb. The $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics doped with different cations showed a similar dielectric property-temperature characteristics with $T_m \cong 240$ °C. Among the three dopants used in the present study, Nb doped $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics demonstrated a superior polarization performance over the existing lead-free ceramics at room temperature, with a d_{33} value of 122 pC/N obtained in ceramics poled at 60 kV/cm. The best piezoelectric properties were achieved in $(Bi_{1/2}Na_{1/2})TiO_3$ doped with Ta with a d_{33} value of 164 pC/N when poled at 100 °C under the applied field of 50 kV/cm.

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