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Effects of Nb^{5+} doping on sintering and electrical properties of lead-free $(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

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Abstract The Nb^{5+} doped $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) ceramics were manufactured by a conventional solid state reaction method. The influence of Nb^{5+} doping on the sintering, microstructure and various electrical properties of BNT ceramics was investigated. The results of X-ray diffraction show that the solubility limit of Nb^{5+} in the BNT lattice is less than 3%. Additionally, Nb^{5+} doping produces significant effects on the densification and grain growth of BNT ceramics. Various electrical properties of BNT ceramics are obviously changed with doping a small amount of Nb^{5+}. The ferroelectric and piezoelectric properties display enhanced values at a low doping level. The formation of A-site vacancies is considered as the reason for the changed ferroelectric and electromechanical behavior.

1 Introduction

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) was discovered by Smolenskii et al. in 1960 [1] and have been considered as one of potential lead-free candidate ferroelectric materials. It is a rhombohedral perovskite ferroelectric with a relatively large remnant polarization, $P_r = 38\ \mu C/cm^2$ and has a Curie temperature, $T_c = 320\ °C$ and a phase transition point from ferroelectric to antiferroelectric, $T_p = 200\ °C$. However, because of its high coercive field, $E_c = 7.3$ kV/mm, and relatively large conductivity, pure BNT is difficult to be poled and cannot be a good piezoelectric material. These drawbacks limit its application for potential ferroelectric and electromechanical devices.

These problems were then improved by forming solid solutions [2–13] with $BaTiO_3$, $Bi_{0.5}K_{0.5}TiO_3$, $KNbO_3$, $NaNbO_3$, $(Sr_aPb_bCa_c)TiO_3$, $BiFeO_3$, $BiScO_3$, etc., accompanied by enhanced electromechanical coupling effects due to so-called morphotropic phase boundary. Another way to improve the electrical properties of BNT is by doping a small amount of rare-earth elements [14–19], such as La^{3+}, Co^{3+}, Mn^{2+}, etc. to decrease its conductivity and coercive fields by means of various lattice defects.

The purpose of this study is to demonstrate the influence of Nb^{5+} doping on the physical and electrical properties of the BNT composition. The A-site vacancies were considered as the charge compensation mechanism. The effect of the substitution of Nb^{5+} for Ti^{4+} on the sintering, microstructure and various electrical properties was discussed.

2 Experimental

Ceramics with compositions of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.10$, and 0.20) were prepared by a conventional mixed oxide route. High-purity oxides and carbonates, Na_2CO_3 (99.9%), Bi_2O_3 (99.97%), TiO_2 (99.9%) and Nb_2O_5 (99.9%) were used as raw materials. After weighing and mixing, the powders were calcined in a lidded alumina crucible at 820 °C for 2 h. Before compaction, the mixture was ball milled once again using anhydrous ethanol as the medium for 24 h. Green samples were placed in a

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platinum foil and simultaneously covered with an alumina crucible. Sintering was carried out in air in the temperature range of 1,100–1,200 °C for 2 h depending on x.

Densities of the sintered specimens were evaluated by the Archimedes method. The microstructure was observed on natural surfaces by means of a scanning electron microscope (SEM, JEOL6301F, Tokyo, Japan). The crystal structures were checked by a powder X-ray diffractometer (XRD, Rigaku, Japan) using a Cu*Ka* radiation.

Dielectric properties were measured at 10 kHz as a function of temperature by an LCR meter (Agilent 4980A, USA) equipped with a programmable temperature box. Polarization versus electric field hysteresis loops were measured in a silicone oil bath by applying an electric field of triangular waveform at a frequency of 50 mHz by means of a modified Sawyer–Tower bridge.

For piezoelectric and electromechanical measurements, samples were first poled at 50 °C in silicone oil at 6–7 kV/mm for 10 min, and then cooled to room temperature in the electric field. The planar electromechanical coupling factor kp was measured by a resonance-antiresonance method through an impedance analyzer (HP4192A, USA) on the basis of IEEE standards. The piezoelectric constant d_{33} was measured by a quasi-static Belincourt-meter (YE2730, SINOCERA, China).

3 Results and discussion

Figure 1 shows the effect of Nb^{5+} doping on the crystal structure of the BNT composition. The diffraction peaks belonging to the perovskite structure were indexed in the plot. When $x < 0.03$, only phases with a perovskite structure are detected. A second phase starts to appear at $x = 0.03$, meaning that the solubility limit of Nb^{5+} in the BNT lattice has been reached. With increasing the doping content of Nb^{5+}, the amount of the second phase becomes more and more.

Moreover, the partial substitution of Nb^{5+} for Ti^{5+} has an influence on the sintering of BNT ceramics, as seen in Fig. 2. The densification has been promoted by a small amount of Nb^{5+} up to approximately 2%. It can be thought that the formation of A-site vacancies contributes to the improved sinterability based on enhanced mass transportation ability. However, due to the solubility limit, excess niobium oxide is expelled off the BNT lattice to form second phases, thus degrading the sintering properties of BNT ceramics. The optimal concentration of Nb^{5+} for improving densification seems to be 2%.

The microstructure of BNT ceramics doped with different amounts of Nb^{5+} is shown in Fig. 3. Pure BNT ceramics sintered at 1,150 °C for 2 h has an average grain size of ~13 μm. It decreases dramatically to ~5 μm when doped with 1 mol% Nb^{5+}. The average grain size continues to decrease till 2 mol% Nb^{5+} is doped. After this doping level, the grain size does not significantly change, as confirmed by comparing Fig. 3c, d. The reduction in grain size is believed to be the result of the formation of A-site vacancies. The vacancies can retard grain boundary movement, but promote the mass transportation, leading to improved densification. In addition, the excessive Nb^{5+} dispersed at the grain boundary tends to pin the boundary motion.

The addition of niobium oxide not only influences the sintering behavior of BNT but also modifies its electrical properties. Comparable densities of all samples (>96% theoretical densities) were obtained for the electrical measurement by optimizing the sintering conditions. Figure 4 shows the dielectric properties of the Nb^{5+} doped BNT ceramics as a function of temperature. The dielectric maxima declines with doping Nb^{5+} and the dielectric constants versus temperature curves become more and more flat. This indicates that niobium oxide plays a role like a "repressor". At the same time, the loss tangents in

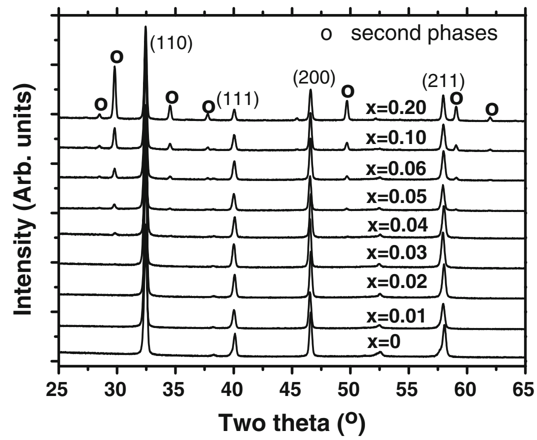

Fig. 1 X-ray diffraction patterns of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics sintered at 1,150 °C

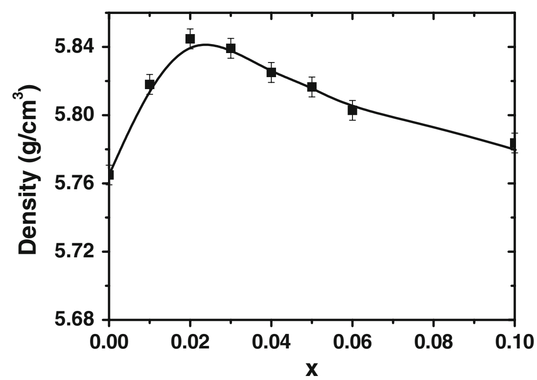

Fig. 2 Densities of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics as a function of x; each sample was sintered at 1,150 °C for 2 h

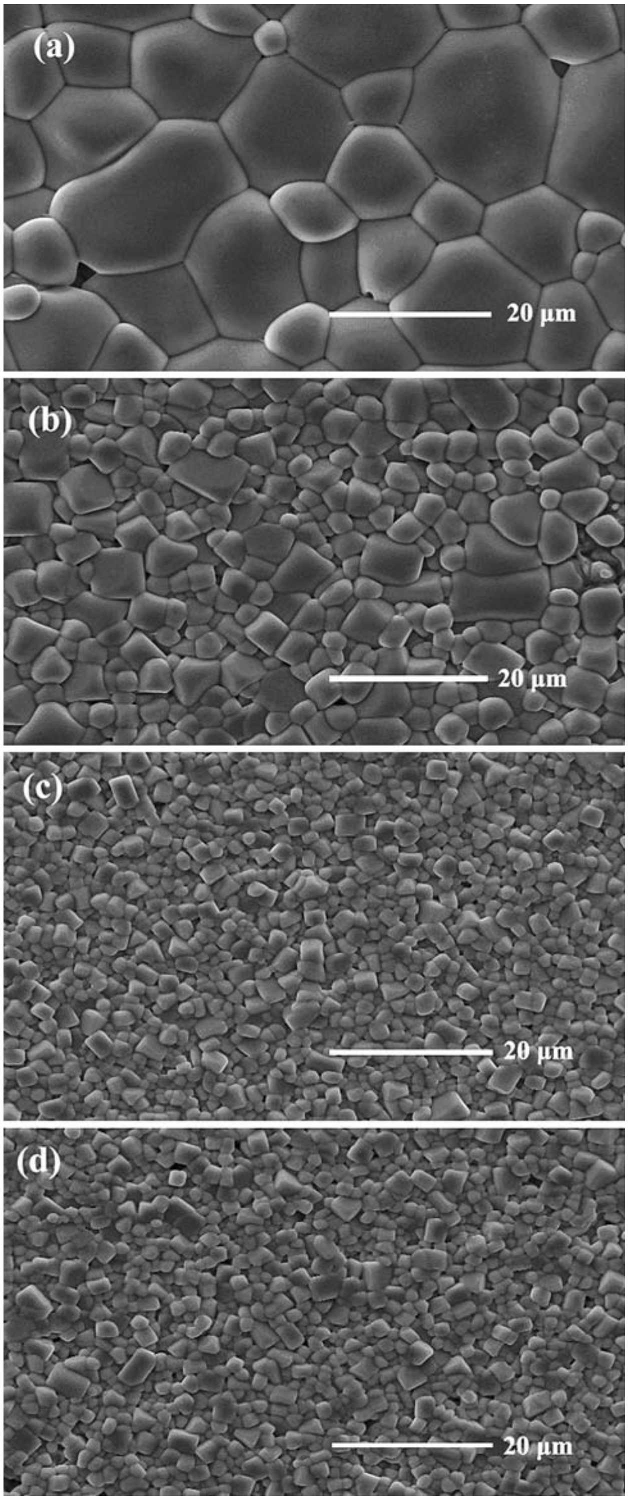

Fig. 3 Grain morphology of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics sintered at 1,150 °C for 2 h: **a** $x = 0$, **b** $x = 0.01$, **c** $x = 0.02$ and **d** $x = 0.06$

Fig. 4b are slightly reduced, particularly below 200 °C. Therefore, the conductivity problem of this system as mentioned in the introduction can be somewhat improved.

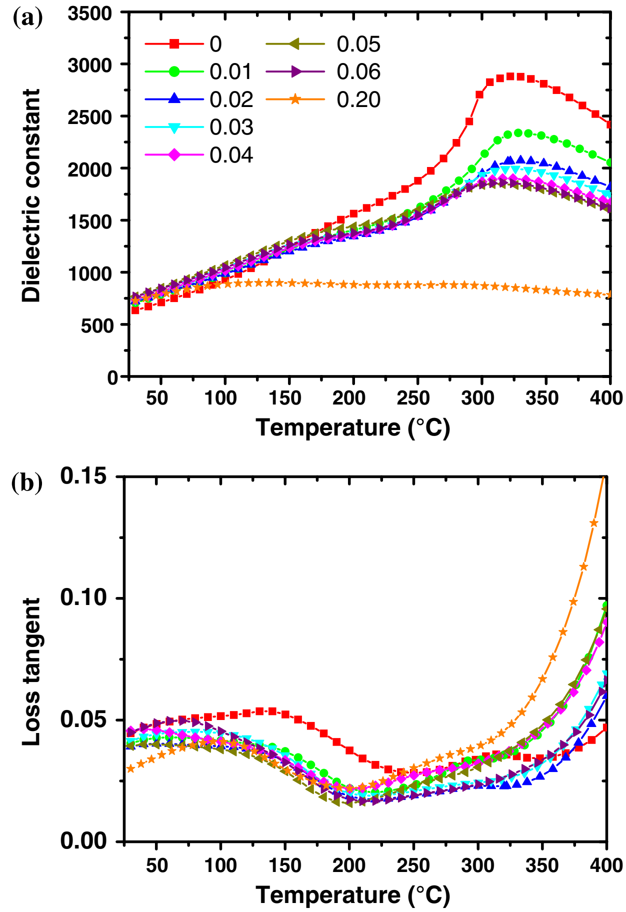

Fig. 4 Dielectric constants (**a**) and losses (**b**) at 10 kHz of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics as a function of temperature

Figure 5 shows polarization versus electric field hysteresis loops for Nb^{5+} doped BNT ceramics. Pure BNT ceramics seem to have relatively high leakage current. However, fairly saturated hysteresis loops for BNT

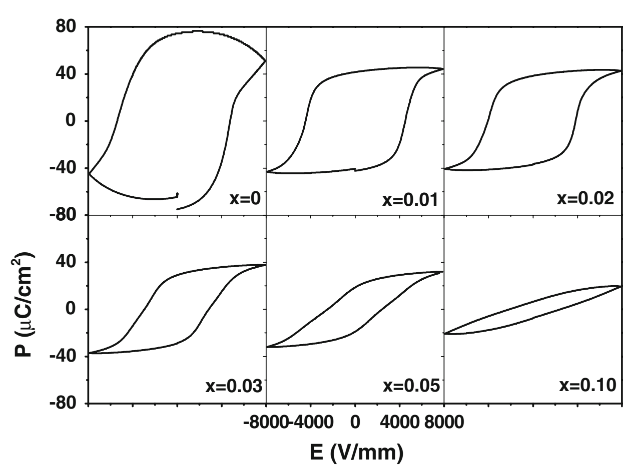

Fig. 5 Hysteresis loops of polarization versus electric field for $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics

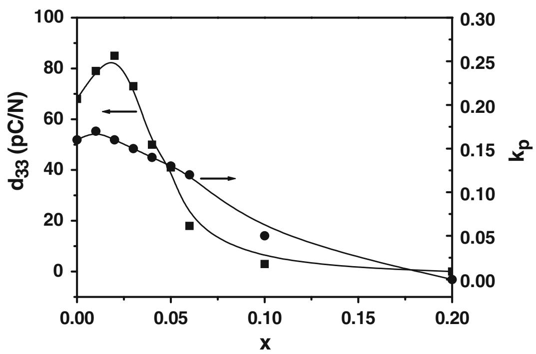

Fig. 6 Piezoelectric and electromechanical properties of $(Bi_{0.5}Na_{0.5})_{1-x/2}(Ti_{1-x}Nb_x)O_3$ ceramics

ceramics doped with Nb^{5+} are achieved under the same driving conditions. This can be attributed to the improved conductivity characteristic as mentioned above. Moreover, both the remanent polarization P_r and coercive field E_c decrease simultaneously with doping more Nb^{5+}. The ferroelectricity of BNT compositions becomes weaker and weaker. The second phases formed due to more Nb^{5+} doping may cause the continuing decreased dielectric and ferroelectric properties. It can be found that the optimal doping level for improving the electrical properties of BNT ceramics seems between 1 and 2% where saturated hysteresis loops can be achieved with a relatively large P_r. The 1 mol% Nb^{5+} doped BNT ceramics have a P_r of 41.5 μC/cm^2 and a E_c of 4.5 kV/mm. The E_c value is reduced and P_r is increased by doping Nb^{5+} compared to those of pure BNT [1], indicating a softening effect.

The piezoelectric and electromechanical properties of the Nb^{5+} doped BNT ceramics are shown in Fig. 6. It can be seen that only a small amount of Nb^{5+} doping tends to enhance piezoelectric responses. The formation of A-site vacancies leads to an increased resistivity and an enhanced densification, thus contributing to both an improved poling condition and a relatively easy domain orientation. As a result, the weak dielectric and ferroelectric properties for BNT doped with more Nb^{5+} bring about a low electromechanical response. Microstructure may have a minor contribution to the decreased electrical properties in this case because all samples for the electrical measurement have close density values. Moreover, the grain sizes no longer decrease when the Nb^{5+} doping level is above 2%. Therefore, BNT ceramics can be improved by substituting Nb^{5+} for Ti^{4+} in a small amount.

4 Conclusion

$(Bi_{0.5}Na_{0.5})TiO_3$ ceramics have been modified by doping a small amount of Nb_2O_5, exhibiting not only changed sintering behavior and microstructure, but also improved electrical properties. The average grain size of BNT ceramics is reduced by doping Nb^{5+} up to 3 mol%. The increased resistivity and enhanced densification due to the formation of A-site vacancies contributes to the improved ferroelectric and electromechanical response. However, more Nb^{5+} doping tends to induce the weak dielectric and ferroelectric properties.

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