Influence of A-site nonstoichiometry on sintering, microstructure and electrical properties of $(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

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ABSTRACT

Lead-free $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ ceramics ($x = -0.02, -0.01, -0.005, 0, 0.005$ and 0.01) were prepared by ordinary sintering. The effect of A-site stoichiometry on the densification, microstructure, dielectric properties, high-temperature impedances, and piezoelectric properties was explored. It was found that the high conductivity of $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) ceramics should be mainly attributed to the formation of A-site cation vacancies during sintering. Improved physical and electrical properties can be achieved in the sample with A-site cation excess. The control of the stoichiometry proves to be an effective way to improve BNT ceramics for possible application.

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1. Introduction

Since $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) was discovered by Smolenskii et al. in 1960 [1], it has gained a lot of attentions from various aspects. It is a ferroelectric with an ABO_3 perovskite structure of A-site complex occupation, possessing a relatively large remnant polarization, $P_r = 38\,\mu C\,cm^{-2}$, a Curie temperature, $T_c = 320\,°C$, and a phase transition point from ferroelectric to antiferroelectric, $T_p = 200\,°C$. It is thus considered as one of potential lead-free piezoelectric candidate materials. However, because of its high coercive field, $E_c = 7.3\,kV\,mm^{-1}$, and relatively large conductivity, pure BST is difficult to be poled and cannot be a good piezoelectric material. These drawbacks limit its application for potential ferroelectric and electromechanical devices. Although these problems were improved by forming solid solutions [2–9] or by doping rare-earth elements [10–13], the mechanism for its high conductivity has been rarely pointed out. As known, the conductivity of a material may be attributed to various kinds of structure defects, for example, free electrons or charged vacancies. Considering that both Bi and Na at A-site tend to evaporate during sintering at high temperature, A-site vacancies should be easily formed in a pure BNT ceramic.

The goal of this work is to investigate the effect of A-site stoichiometry on the physical and electrical properties of the BNT composition. This can be done by making a few compositions with initially different A-site stoichiometry. The relationship between the stoichiometry and the densification, microstructure and various electrical properties was discussed.

2. Experimental

A conventional mixed oxide processing route was used to make $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ ($x = -0.02, -0.01, -0.005, 0, 0.005, 0.01$) ceramics using high-purity metal oxides and carbonates as raw materials: Bi_2O_3 (99.9%, Guoyao Chemical Company, Shanghai), TiO_2 (99.9%, Xilong Chemical Factory, Guangdong), and Na_2CO_3 (99.8%, Hongguang Chemical Factory, Shanghai). The powders weighed according to the above formula were mixed thoroughly in ethanol using zirconia balls for 12 h. After drying, the calcination was carried out at 820 °C for 3 h. After the calcined powder underwent a second ball-milling for 24 h, it was pressed into disk samples. Sintering was performed in air in the temperature range of 1000–1120 °C for 2–4 h. Densities of the sintered samples were measured by the Archimedes method. Silver electrodes were made on two major surfaces of polished samples. The samples were poled at 50 °C in stirred silicone oil under a dc field of 6 kV mm^{-1} for 15 min.

The microstructure was observed on natural surfaces of the sintered specimens by means of scanning electron microscopy (SEM, JEOL 6301F, Tokyo, Japan). The crystal structures were examined by a powder X-ray diffractometer (XRD, Rigaku) using a Cu Kα radiation. The dielectric properties were measured as a function of temperature and frequency using an impedance analyzer (HP 4192A) 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 300 mHz by means of a modified Sawyer-Tower bridge. The planar electromechanical coupling factor k_p was measured by a resonance-antiresonance method through an impedance analyzer (HP 4192A) on the basis of IEEE standards. The piezoelectric constant d_{33} was measured by a quasi-static Belincourt-meter (YE2730, Yangzhou, SINOCERA).

3. Results and discussion

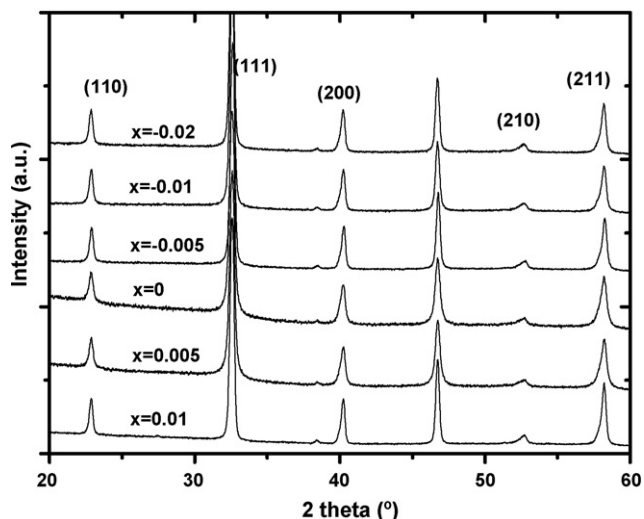Fig. 1 shows the XRD patterns of BNT ceramics with different stoichiometry ratios at A-site. All compositions show a pure perovskite

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Fig. 1. X-ray diffraction patterns of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics with A-site nonstoichiometry as indicated.

Fig. 2. Sintering profiles of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics as a function of A-site stoichiometry (x) and temperature.

structure with a rhombohedral symmetry at room temperature. The change in stoichiometry at A-site does not induce the instability of the perovskite structure. For stoichiometric compositions or those in excess of A-site cations, there are nearly the same lattice parameters as seen from the position of diffraction peaks (2 0 0). Howeve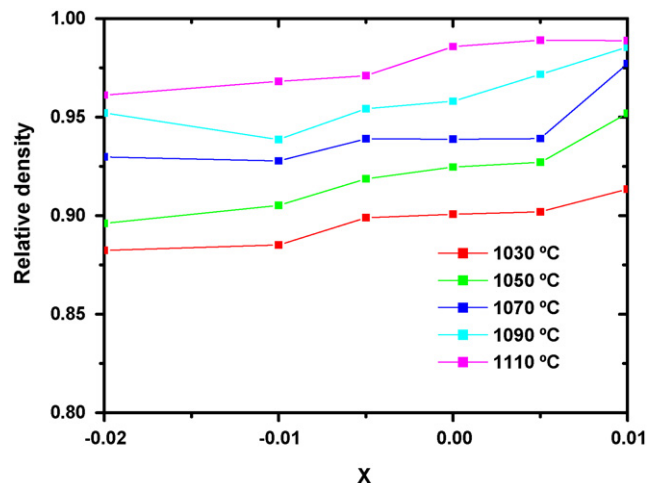r, the diffraction peaks shift slightly toward high angles when A-site cations are deficient, meaning that unit cells shrink. The A-site deficiency corresponds to the formation of A-site vacancies, thereby probably inducing a change in various properties.

An influence of A-site stoichiometry on sintering behavior can be expected, as shown in Fig. 2. The change in stoichiometry at A- or B-site of a perovskite structure usually has an effect on the densification, particularly for compositions containing volatile elements
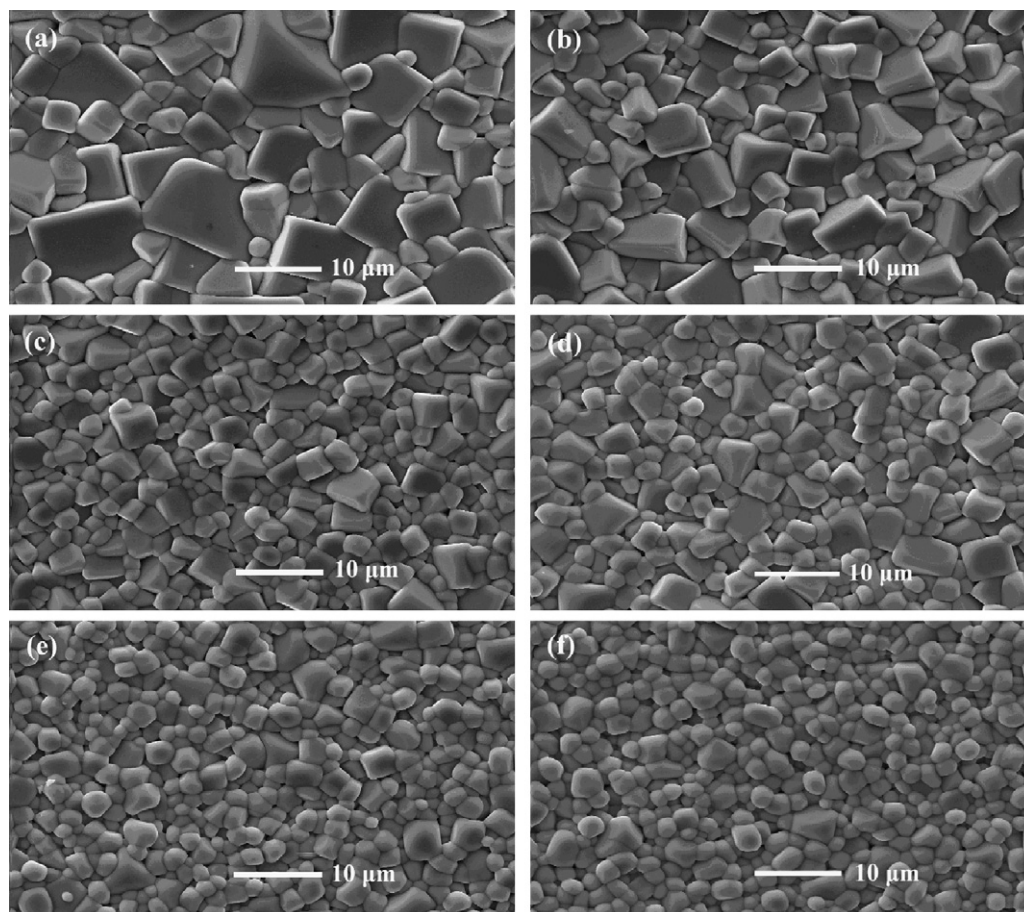

Fig. 3. Surface morphology of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics with A-site nonstoichiometry: (a) $x = 0.01$, (b) $x = 0.005$, (c) $x = 0$, (d) $x = -0.005$, (e) $x = -0.01$ and (f) $x = -0.02$.

such as Pb-based perovskite materials [14,15]. With increasing x, relative density of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ ceramics increases at each temperature (theoretical density of BNT 5.998 g cm^{-3} roughly used for all compositions) [16]. The A-site cation deficiency degrades the densification to a certain degree. On the contrary, the A-site cation excess promotes sintering. The excess of A-site ($Bi_{0.5}Na_{0.5}$), on the one hand, compensates for the loss of Bi and Na at high temperature. On the other hand, these two metal oxides in samples with A-site cation excess can serve as sintering aids by forming liquid phases due to their relatively low melting points. Consequently, the microstructure will be then changed, as shown in Fig. 3. All samples for SEM observation were sintered at 1100 °C for 3 h. The excess A-site elements promote the grain growth, relative to the A-site deficiency. The sample of a stoichiometric composition has an average grain size of ∼3 μm. It increases to ∼8 μm for the sample with 1 mol% A-site cations excess. Only a slight decrease in grain size was seen in the sample with 2 mol% A-site deficient, compared to the stoichiometric BNT compositions. The excess A-site Bi and Na elements form liquid phases at high temperature, promoting the grain growth and densification simultaneously.

Fig. 4 shows the polarization versus electric field hysteresis loops of BNT ceramics with different A-site stoichiometric ratios. All compositions show almost the same remanent polarization P_r, 38 μC cm^{-2}, and coercive field E_c, 5.1 kV mm^{-1}. This result indicates that the A-site stoichiometry produces an ignorable effect on the ferroelectricity of BNT ceramics.

The dielectric constants of BNT ceramics with A-site nonstoichiometry as a function of temperature and frequency are shown in Fig. 5. The results indicate that the composition with A-site deficiency shows more frequency dependency of relative permittivities. The dielectric constants of the stoichiometric BNT composition are still frequency dependent to a certain degree. However, nearly frequency independent relative permittivities at temperatures below the Curie points can be achieved in com-
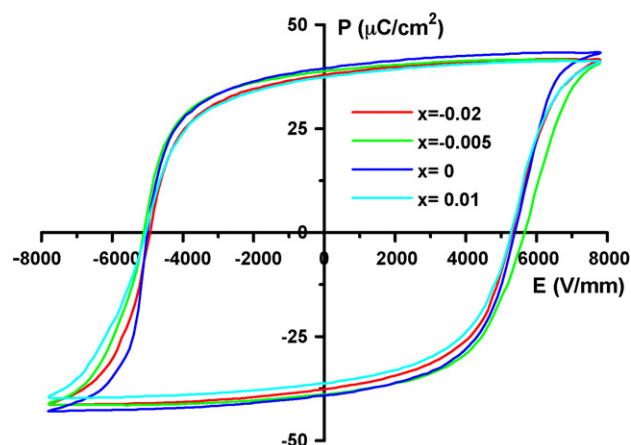

Fig. 4. Polarization versus electric field hysteresis loops of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics with A-site nonstoichiometry under an ac field of 300 mHz.

positions with 1 mol% A-site excess. As known, higher relative permittivity at lower frequency is usually attributed to space charges. This kind of space charges exists in BNT compositions with A-site deficiency serving as charged vacancies. The A-site vacancies can still exist in the stoichiometric composition as A-site cations evaporate at high temperature. However, the evaporated A-site elements can be offset by the excess addition of Bi and Na. Therefore, there should be no A-site vacancies in the sample with 1 mol% A-site cation excess. This processing procedure has been often used in Pb-based perovskite ferroelectric materials, such as Pb(Zr, Ti)O$_3$. The same phenomenon can be reflected in Fig. 6 where loss tangents at an equal frequency are much larger for A-site deficient samples.
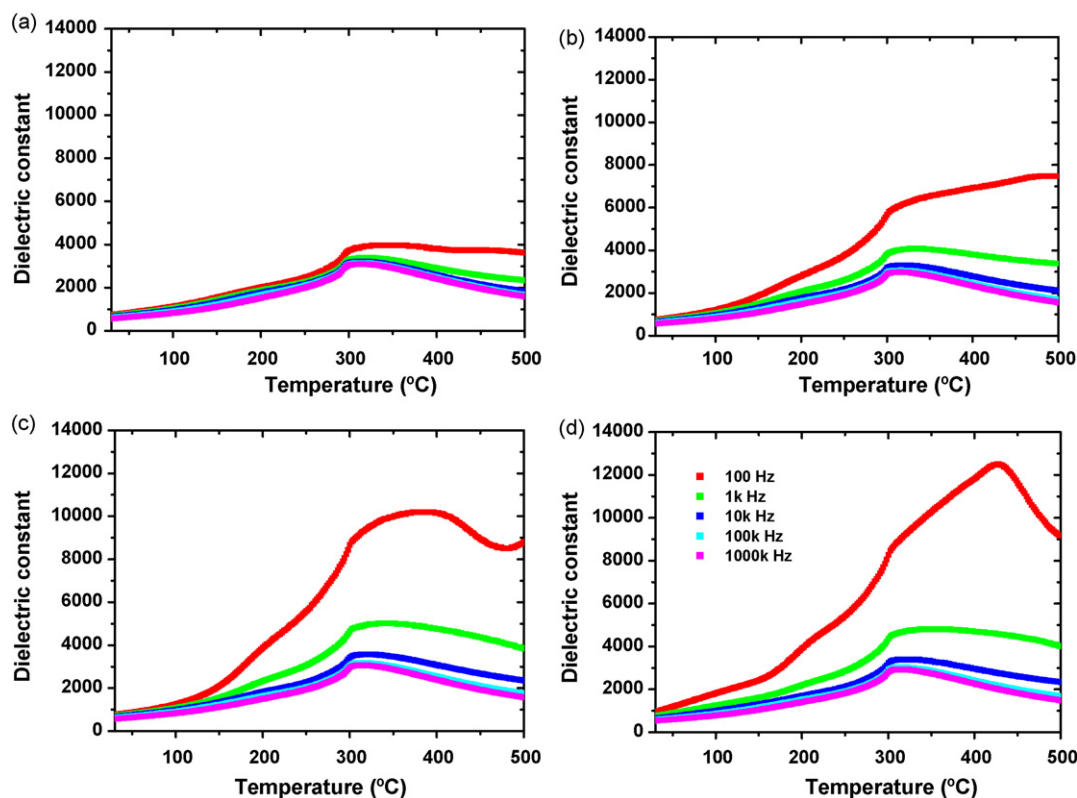

Fig. 5. Dielectric constants of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics sintered at 1100 °C: (a) $x = 0.01$, (b) $x = 0$, (c) $x = -0.005$ and (d) $x = -0.02$.

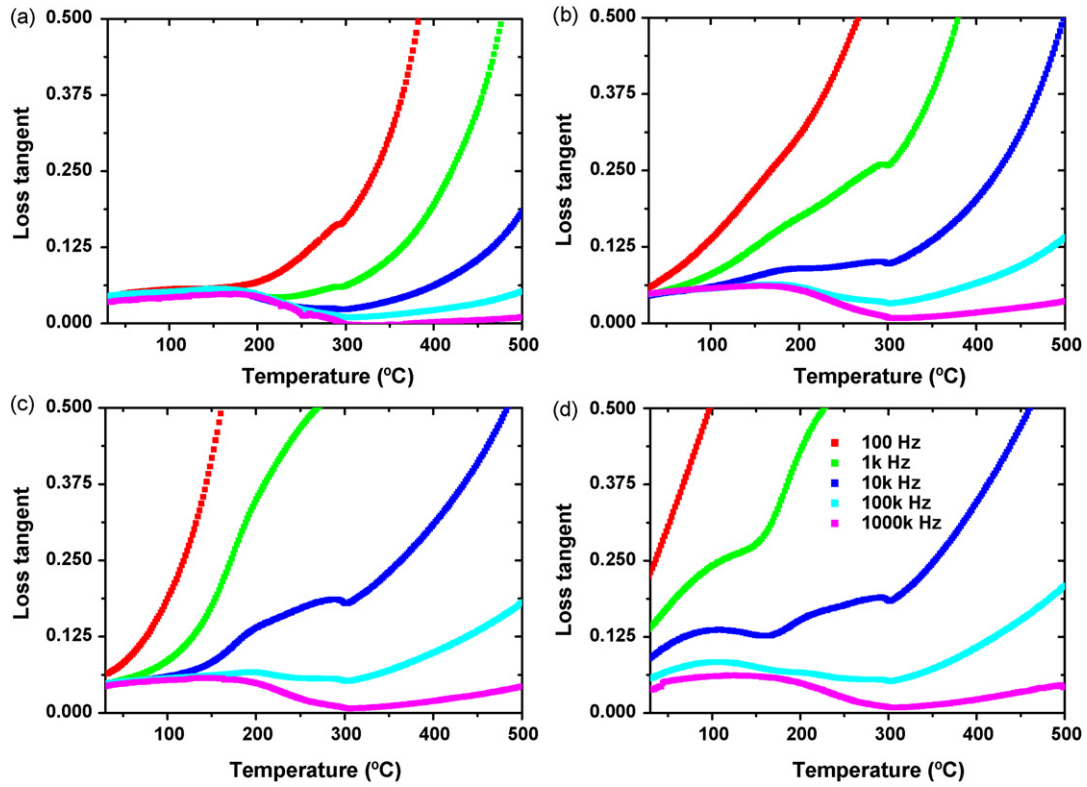**Fig. 6.** Loss tangents of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics sintered at 1100 °C: (a) $x = 0.01$, (b) $x = 0$, (c) $x = -0.005$ and (d) $x = -0.02$.
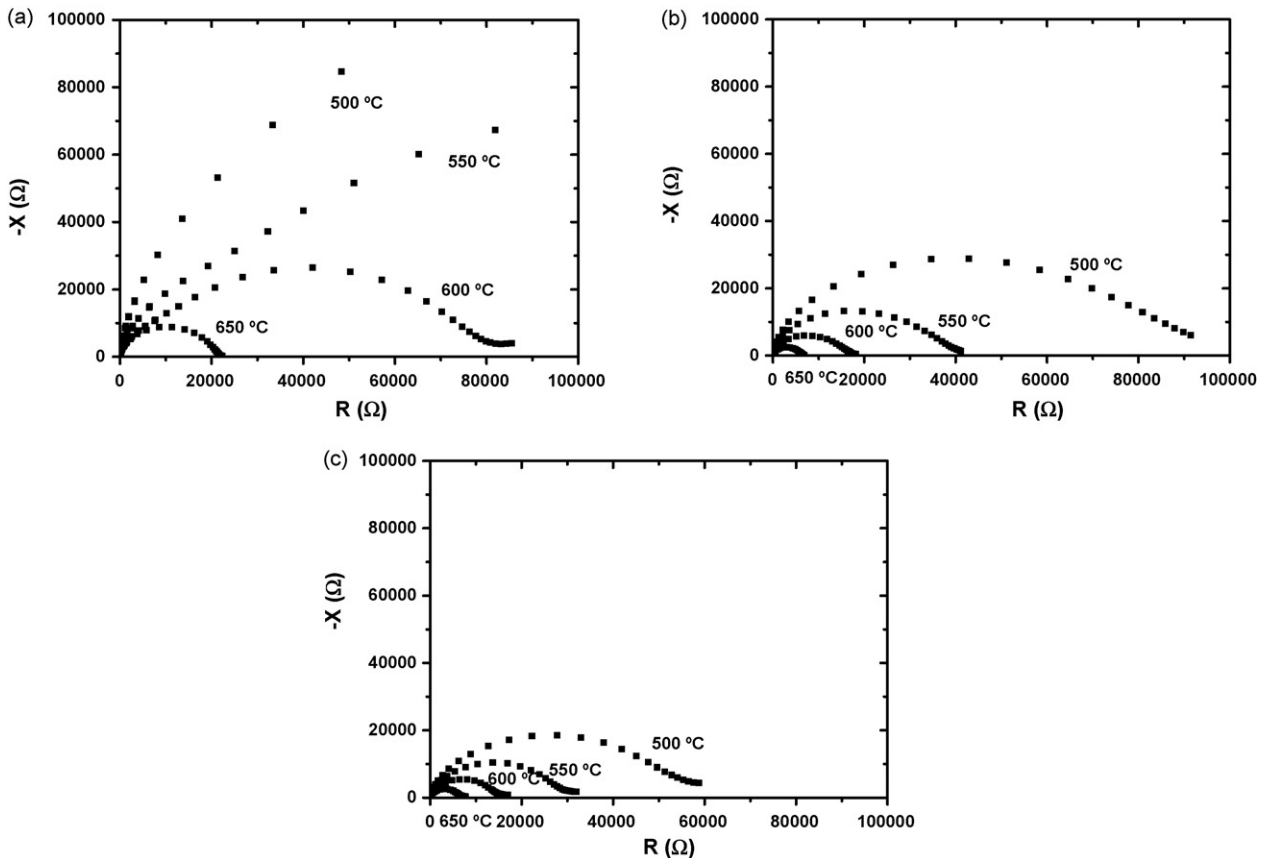

Fig. 7. AC impedance spectra of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics: (a) $x = 0.01$, (b) $x = 0$ and (c) $x = -0.02$.

Table 1
Various properties of $(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ lead-free ferroelectric ceramics sintered at 1100 °C for 3 h

	x					
	−0.02	−0.01	−0.005	0	0.005	0.01
Relative density (%)	95.6	95.9	96.8	97.1	97.9	97.6
Dielectric permittivity at 1 kHz	742	696	695	682	665	664
Loss tangent at 1 kHz	0.135	0.0546	0.0483	0.0447	0.044	0.0399
Piezoelectric constant, d_{33} (pC N^{-1})	50	54	58	75	84	83
Coupling factor, k_p (%)	12.3	13.0	14.0	15.4	17.2	17.3

Fig. 7 shows high-temperature impedance spectra of BNT ceramics with different stoichiometric ratios. The results indicate that all compositions are characteristic of grain conductivity, as there is only one semicircle even till high temperature (650 °C). Moreover, the A-site deficient samples (Fig. 7c) show much lower resistivity at different temperatures. The activation energies for the conductivity are evidently reduced by the formation of A-site vacancies. As we know, one of drawbacks for BNT compositions is that there are higher conductivities as mentioned above. From our results, this is probably due to the formation of A-site vacancies during sintering. The above results indicate that A-site excess to some degrees can overcome this problem. Therefore, the control of stoichiometry during manufacturing is an effective way for improving the characteristic of conductivity of BNT ceramics.

Various physical and electrical properties of BNT ceramics are summarized in Table 1. As discussed above, the density can be improved by the A-site excessive addition. The A-site deficiency leads to the degraded densification. The dielectric constants at 1 kHz are slightly reduced with increasing x; however, the loss tangents exhibit a larger improvement. The piezoelectric and electromechanical properties are slightly enhanced probably due to an enhanced densification behavior and a smaller leakage current during poling.

4. Conclusions

$(Bi_{0.5}Na_{0.5})_{1+x}TiO_3$ ceramics with different A-site stoichiometric ratios were made by means of conventional ceramic preparation processing. The change of A-site stoichiometry exhibits a significant effect on the densification, microstructure and electrical properties. The results indicate that the formation of A-site vacancies during

sintering is responsible for the high conductivity of BNT ceramics. The excess of A-site $(Bi_{0.5}Na_{0.5})$ can effectively improve sintering, decreases loss tangent, and further enhance various electrical properties.

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