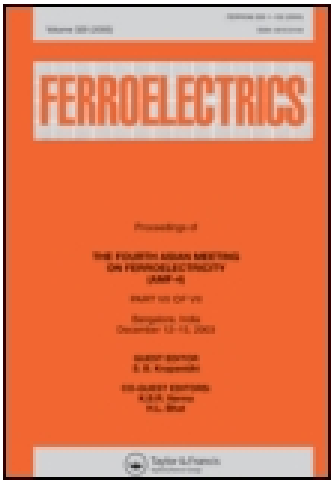

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Bismuth Sodium Titanate Lead-Free Piezoelectric Ceramics Fabricated by Using Novel Low-Temperature Solid-State Synthesis Method

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$0.94Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$ (BNT-06) lead-free piezoelectric ceramic has been prepared by using a novel low-temperature solid-state synthesis method. The relationship between the calcine conditions and the electrical properties of the ceramics was systematically studied. The results show that a small amount of the activated assistant additives in the raw materials by using the novel low-temperature solid-state synthesis method decreases the calcine temperature of the BNT-06 powder from 900°C to 600°C. The BNT-06 ceramics prepared by using this powder presents good properties with ρ = 5.86 g/cm^3, d_{33} = 122 pC/N, k_p = 0.24, Q_m = 109, T_C = 271.2°C, ε_r = 1656, tan δ = 0.05, P_r = 32.6 μC/cm^2, and E_c = 32.1 kV/cm respectively, which is comparable to that of the ceramics prepared by using ordinary solid-state method.

Keywords Lead-free piezoelectric ceramics; $0.94Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$; low-temperature solid-state synthesis method; piezoelectric properties

Introduction

Lead-free materials have received considerable attention recently [1–8], in which $Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated as BNT) ceramics are considered to be one of the excellent candidates for lead-free piezoelectric ceramics because of their relatively large remanent polarization ($P_r = 38\ \mu C/cm^2$) and a higher Curie temperature ($T_C = 320°C$). However, BNT ceramics are difficult to be poled due to their relatively large coercive field ($E_c = 73$ kV/cm) and high electrical conductivity [3]. Therefore, most researches focused on how to modify and improve the electrical properties of BNT ceramic [3–8]. Among the researches, the $0.94Bi_{0.5}Na_{0.5}TiO_3$–$0.06BaTiO_3$ (BNT-06) ceramics, which are rhombohedral-tetragonal morphotropic phase boundary (MPB) composition, show good electrical properties.

The fabrication techniques and their relations to the properties of the materials related are overall one of the main research topics for ceramics. The author's group

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of present paper has developed and patented a fabrication method for the powders of multi-component alkaline metal niobate-based lead free piezoelectric ceramics, namely activated assistant additive (3″A″) in the raw material, and the KNN-based lead-free ceramics were prepared by using the novel low-temperature solid-state synthesis method. The results show that the powders of the KNN-based ceramics with favorable piezoelectric properties can be synthesized at temperature as low as 450°C for 4–5 hours, and KNN-based ceramics prepared by using this novel method show good ferroelectric properties [9].

Could the novel low-temperature solid-state synthesis method be used for BNT-based lead-free piezoelectric ceramics? The question should be answered with facts. In present study, the BNT-06 ceramics have been prepared by using the novel low-temperature solid-state synthesis method, and the properties of BNT-06 ceramics have been systematically studied.

Experimental

Bi_2O_3 (99%), Na_2CO_3 (99.8%), $BaCO_3$ (99%), TiO_2 (98%) and activated assistant were used as starting raw materials. The $0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$ ceramics were prepared by the ordinary solid-state method (BNT-06-1#) and a novel low-temperature solid-state synthesis method (BNT-06-2#, with 5 wt.% activated assistant additive in the starting raw materials). The stoichiometric powders were mixed by ball milling for 24 h with zirconia balls media in anhydrous ethanol and then dried. The dried powders of BNT-06-1# and BNT-06-2# were calcined at 900°C and 600°C for 5 h. The calcined powders were milled again for 24 h, and pressed into disks with diameters of 15 mm and thicknesses of 1.1∼1.3 mm at 20 MPa using polyvinyl alcohol (PVA) as a binder. After burning off PVA, the ceramic disks were sintered at 1150°C for 2 h in air.

The phase structure were examined by the X-ray diffraction using Cu K_α radiation ($\lambda = 1.54178$ Å) in the θ-2θ scan mode (DX1000, Dandong, China). The density of the fired samples was determined by the Archimedes method. Silver paste was sintered on both sides of the specimens at 700°C for 10 min to form electrodes for electrical measurements.

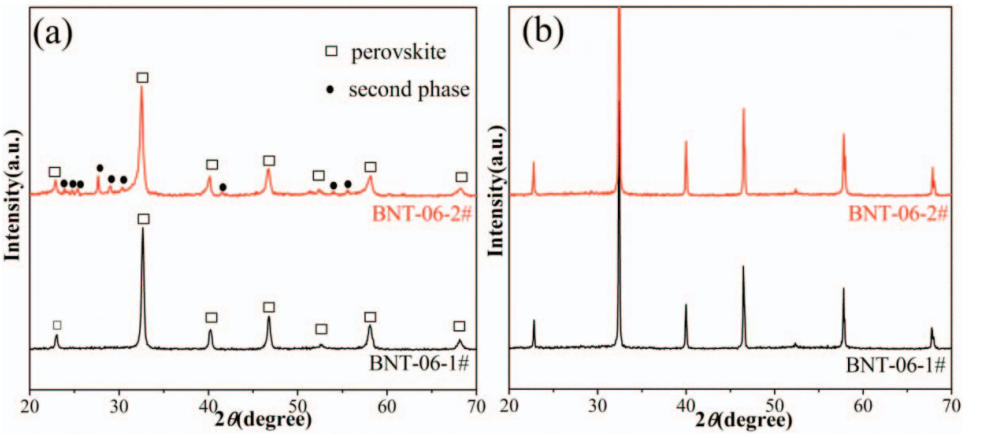

Figure 1. (a) XRD patterns of calcined powders of BNT-06-1# and BNT-06-2# ceramics; (b) XRD patterns of BNT-06-1# and BNT-06-2# ceramics sintered at 1150°C for 2 h respectively.

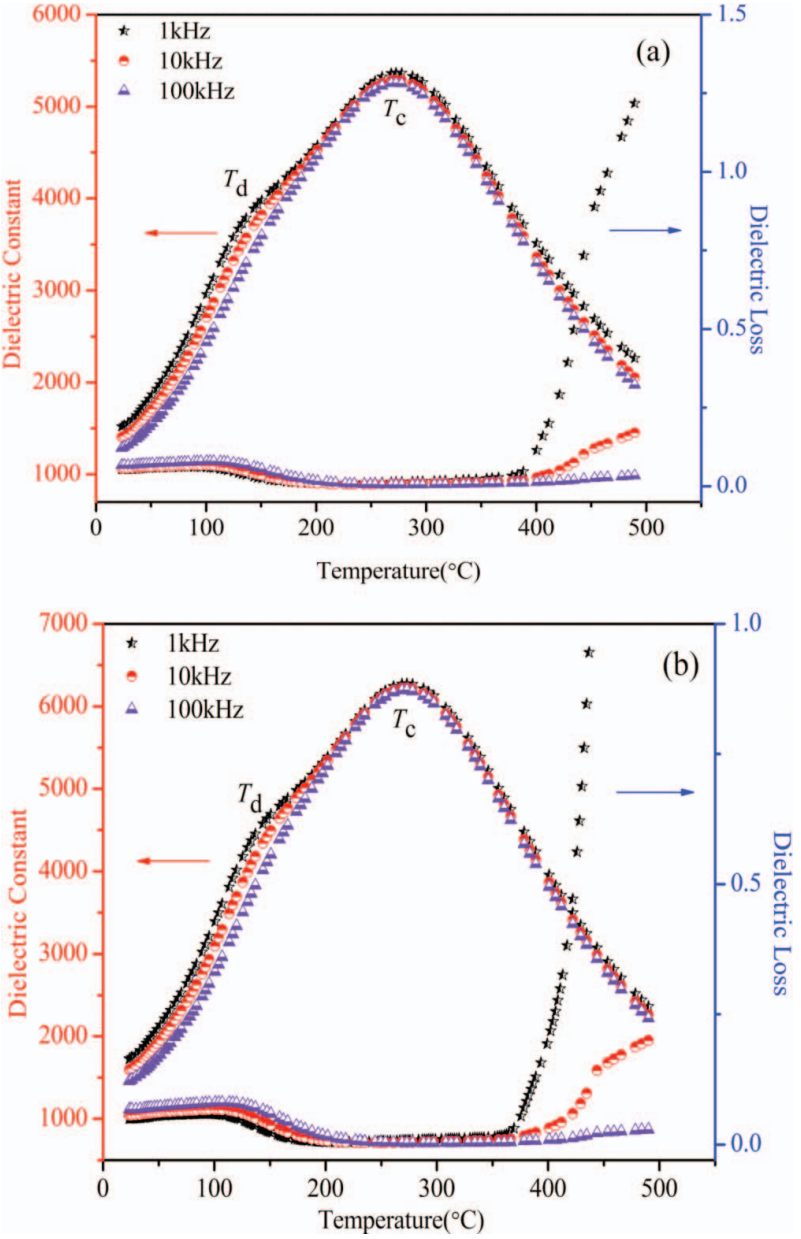

Figure 2. Temperature dependences of ε_r and tan δ for (a) the BNT-06-1# and (b) BNT-06-2# ceramics at frequencies from 1 kHz to 100 kHz respectvely. (See Color Plate VIII)

The specimens were poled in silicon oil bath at 60°C by applying a *dc* electric field of 4.5 kV/mm for 20 minutes. The piezoelectric constant was measured using a piezo-d_{33} meter (ZJ-3A, China). The dielectric constant as a function of temperature was obtained using an *LCR* meter (Agilent 4980A, U.S.A.). The hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA) at 10 Hz.

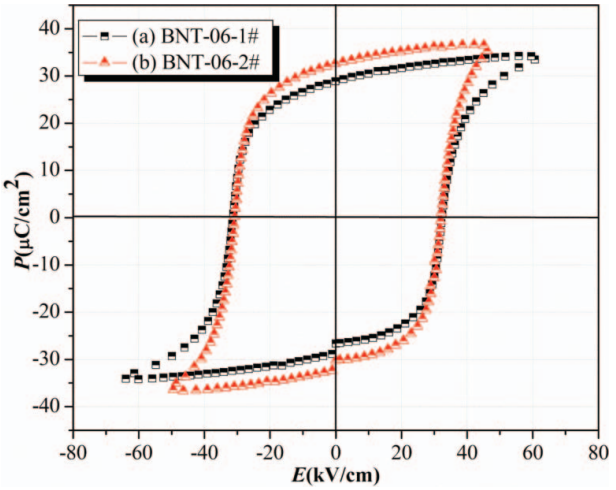

Figure 3. *P-E* hysteresis loops of (a) the BNT-06-1# and (b) BNT-06-2# ceramics at room temperature respectively. (See Color Plate IX)

Results and Discussion

Figure 1(a) shows the X-ray diffraction (XRD) patterns for calcined powders of BNT-06-1# and BNT-06-2# ceramics, which were calcined at 900°C and 600°C respectively. The calcined powder of BNT-06-1# ceramics exhibit a pure perovskite structure, while the calcined powder of BNT-06-2# ceramics form a primary perovskite structure as well as a small amount of second phase. As mentioned in Reference [10], calcination causes the constituents to interact by inter diffusion of their ions and so reduces the extent of the diffusion that must occur during sintering in order to obtain a homogeneous body. The required final phases may not be completely formed but the remaining chemical gradients may assist sintering. Therefore, the calcination temperature of the powder of BNT-06-2# ceramics was much decreased by introducing the activated assistant additive (3″A″). It may be because that the additive could provide a mass of energy for the system during calcination.

The XRD patterns of the BNT-06-1# and BNT-06-2# ceramics sintered at 1150°C for 2 h were shown in Figure 1(b). All the ceramics exhibit a single perovskite structure with no trace of any secondary phase, and a rhombohedral-tetragonal MPB exists in BNT-06-1# and BNT-06-2# ceramics. As mentioned in Reference [4], the XRD of the composition at MPB is characterized with separated presence of two peaks to (003)/(021) at around 39° and splitting of the peak to (202) planes at around 46°. The results indicate that the activated assistant additive (3″A″) in the starting raw materials couldn't change the crystal structure of BNT-06 ceramics.

Figure 2 shows the temperature dependences of ε_r and tan δ for (a) the BNT-06-1# and (b) the BNT-06-2# ceramics at frequencies ranging from 1 kHz to 100 kHz respectively. All the ceramics exhibit the similar dielectric properties-temperature curves, which have two dielectric anomalous peaks during the heating process. As shown in Fig. 2, it can be seen that the BNT-06-1# and BNT-06-2# ceramics have the same Curie temperature regardless of the different preparation method. Moreover, it is also clearly observed the T_C peak of the BNT-06-1# and BNT-06-2# ceramics are relatively broad, suggesting that the phase

Table 1
The piezoelectric, electromechanical, dielectric, and ferroelectric properties of the BNT-06-1# and BNT-06-2# ceramics

Sample	Calcination	ρ (g/cm^3)	d_{33} (pC/N)	k_p	Q_m	T_C (°C)	ε_r	tanδ	P_r (μC/cm^2)	E_c (kV/cm)
BNT-06-1#	900°C/5h	5.65	113	0.21	105	272.7	1457	0.05	28.9	32.3
BNT-06-2#	600°C/5h	5.86	122	0.24	109	271.2	1656	0.05	32.6	32.1

transition at T_C is a diffuse phase transition, and the piezoelectric ceramics is a typical relaxor ferroelectric with A-site complex ions [6, 7]. All these results indicated that the BNT-06 lead-free piezoelectric ceramics prepared by using different solid-state synthesis methods have similar dielectric properties.

Figure 3 shows the *P-E* hysteresis loops of the BNT-06-1# and BNT-06-2# ceramics measured at 10 Hz and room temperature. All the ceramics possess well-saturated *P-E* hysteresis loops. The detailed electrical properties of BNT-06-1# and BNT-06-2# ceramics are summarized in Table I. It can be concluded that the BNT-06-2# ceramics possess better electric properties due to their higher density.

Conclusions

The comparative studies of the phase structure and electrical properties of the BNT-06-1# and BNT-06-2# ceramics prepared by the ordinary solid-state method and a novel low-temperature solid-state synthesis method respectively are investigated. The results show that the calcine temperature (600°C) of the powder of BNT-06-2# ceramics is much lower than that (900°C) of the BNT-06-1# ceramics. The 5 wt% activated assistant additive in the starting raw materials couldn't change the phase structure of the ceramics but improve their electrical properties. The BNT-06-2# ceramics present good properties with ρ of 5.86 g/cm^3, d_{33} of 122 pC/N, k_p of 0.24, Q_m of 109, T_C of 271.2°C, ε_r of 1656, tan δ of 0.05, P_r of 32.6 μC/cm^2, and E_c of 32.1 kV/cm respectively. These results indicate that the novel low-temperature synthesis method developed by the author's group can be used for BNT-based lead-free ceramics.

Acknowledgment

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