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Journal of the European Ceramic Society 32 (2012) 1481–1484

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Short communication

Phase transition behavior and electrical properties of $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Na_{0.53}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ lead-free ceramics

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Received 22 October 2011; received in revised form 7 January 2012; accepted 10 January 2012
Available online 10 February 2012

Abstract

$(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Na_{0.53}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ (BNT–xNKLNST) with $x = 0$–0.10 lead-free piezoelectric ceramics were prepared by a solid state method, and the structure and electrical properties were investigated in this study. It is found that a morphotropic phase boundary (MPB) of rhombohedral (R) and tetragonal (T) phase exists in the range of $0.03 \leq x \leq 0.05$ and the structure changes to paraelectric phase when $x > 0.07$. The samples with $x = 0.05$ exhibit improved electrical properties owing to the formation of MPB, which are as follows: piezoelectric constant $d_{33} = 120$ pC/N, remnant polarization $P_r = 39.4$ μC/cm^2 and coercive field $E_c = 3.6$ kV/mm. These results indicate that the enhanced piezoelectric properties for BNT can be achieved by forming the coexistence of R and T phase.

Keywords: Dielectric properties; Ferroelectric properties; Piezoelectric properties; Perovskites; Lead-free

1. Introduction

In recent years, perovskite lead-free piezoelectric ceramics have been attractive in fields of applied electronic devices such as actuators, transducers and sensors.[1] $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based and $K_{0.5}Na_{0.5}NbO_3$ (KNN)-based ceramics are currently two main systems with perovskite structure.[2–5] Generally speaking, there are two basic ways to improve the properties of piezoelectric ceramics. One way is seeking for the morphotropic phase boundary (MPB) which enhances the piezoelectric properties,[6–13] for example $(Na_{0.5}Bi_{0.5})TiO_3$–$BaTiO_3$ (BNT-BT) system. The other way to improve the electrical properties is to add a small amount of rare-earth elements.[14–17] For KNN systems, a lot of previous researches focus on the polymorphic phase boundary (PPT) between orthorhombic (O) and tetragonal phase with the addition of Li, Ta and Sb ions, which brings enhanced piezoelectric and electromechanical properties.[11–13,18–22] The researches for the dependence of properties on composition and temperature reveal that the electrical property is the consequence of PPT shifted to room temperature.

As we know, the classical MPB usually is formed between T and R phase, such as $PbZrO_3$–$PbTiO_3$ and BNT-BT systems. However, there are few reports on MPB between BNT ceramics with R phase and KNN-based ceramics with T phase, and most of researches focus on O–T phase or R–O phase.[9,23] In this study, we tried to design a new solid solution between BNT and NKLNST, possessing rhombohedral (R) and tetragonal phase (T), respectively. The reason for choosing NKLNST composition is due to its excellent properties ($d_{33} > 350$ pC/N) and its O–T phase transition temperature is much lower than the pure KNN ceramics because of the doping of Li, Ta and Sb ions.[19] Moreover, the solid solution ceramics between these two typical lead-free perovskite materials were investigated for their phase transition behavior and electrical properties.

2. Experimental procedure

$(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Na_{0.53}K_{0.44}Li_{0.04})(Nb_{0.88}Sb_{0.08}Ta_{0.04})O_3$ piezoelectric ceramics ($x = 0$, 0.01, 0.03, 0.05, 0.07

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0955-2219/$ – see front matter.
doi:10.1016/j.jeurceramsoc.2012.01.008

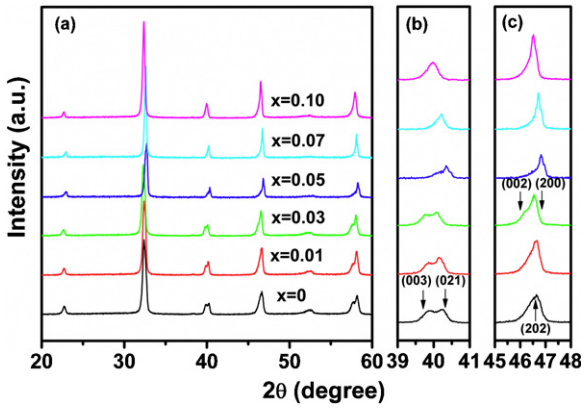

Fig. 1. XRD patterns of BNT–xNKLNST ceramics sintered at 1140 °C.

and 0.10 mol) were prepared by a conventional solid-state reaction method. The raw materials used in this study are K_2CO_3 (99.0%, Sinopharm Chemical Reagent Co., Ltd.), Na_2CO_3 (99.8%, Sinopharm Chemical Reagent Co., Ltd.), Li_2CO_3 (99.9%, Sinopharm Chemical Reagent Co., Ltd.), Nb_2O_5 (99.5%, Zhuzhou Mingri Cemented Carbide Co, Ltd.), Ta_2O_5 (99.9%, Alfa Aesar), Sb_2O_3 (99.99%, Sinopharm Chemical Reagent Co., Ltd.), Bi_2O_3 (99.0%, Sinopharm Chemical Reagent Co., Ltd.) and TiO_2 (99.0%, Sinopharm Chemical Reagent Co., Ltd.). The powders were weighed according to the stoichiometry of BNT–xNKLNST and then ball mixed in nylon jars with ZrO_2 balls for 8 h using ethanol as the medium. Mixtures were dried and calcined at 850 °C for 4 h. After that, the calcined powders were milled again for 12 h and granulated by adding polyvinyl butyral (PVB) as a binder. The obtained powders were subsequently pressed into green disks with a diameter of 13 mm. These compacts were sintered in air at 1140 °C for 3 h. Fired-on silver paste was used as electrodes for the measurement of electrical properties. The ceramics were poled in silicone oil under a dc electric field of 5–7 kV/mm at 60 °C for 20 min.

The crystal structures of the sintered BNT–xNKLNST ceramics were determined by an X-ray diffractometer (XRD, D/Max2500, Rigaku, Tokyo, Japan). The microstructures of sintered samples were observed using a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). The piezoelectric constant d_{33} was measured by a d_{33} meter (PM300, PIEZOTEST, London, U.K.). Dielectric properties were obtained using a LCR meter (HP4284A, Hewlett-Packard, Palo Alto, CA) at 1 kHz as a function of temperature under 1 V measuring voltage. Polarization hysteresis loops were measured using a ferroelectric measuring system (Precision LC, Radiant Technologies, Inc. USA).

3. Results and discussion

Fig. 1 shows XRD patterns of BNT–xNKLNST ceramics sintered at 1140 °C. It is clear that all samples have pure perovskite structure without any detectable impurity phases, which indicates that a series of continuous solid solutions between BNT and NKLNST were formed. As we know, the pure BNT possess a rhombohedral symmetry, which is characterized by a (0 0 3)/(0 2 1) peak splitting between 39° and 41° and a single (2 0 2) peak between 45° and 48°. From Fig. 1(b), it can be seen that the (0 0 3)/(0 2 1) peak splitting can be distinguishable until $x = 0.05$. In Fig. 1(c), a distinct (0 0 2)/(2 0 0) peak splitting is observed at $x >= 0.03$, corresponding to the tetragonal symmetry. However, the (0 0 3)/(0 2 1) peaks splitting changes into a single peak when $x \geq 0.07$. Therefore, it can be referred that a MPB between rhombohedral and tetragonal phase of BNT–xNKLNST ceramics exists in the composition range of $0.03 \leq x \leq 0.05$. Furthermore, when $x = 0.10$, all become single peak and the phase changes into cubic phase.

Fig. 2 shows SEM morphology of BNT–xNKLNST ceramics with various NKLNST contents sintered at 1140 °C for 3 h. It is observed that all the samples possess high densities of about 5.72–5.84 g/cm^3, which are more than 95% of the theoretical values. Moreover, it can be also found that there is a significant evolution in grain shape with the NKLNST addition. The grain morphologies change from square pillar shape to polyhedral shape, which can be attributed to the phase transition with the compositional change.

The P–E hysteresis loops of BNT–xNKLNST ceramics sintered at 1140 °C are displayed in Fig. 3. Saturated loops for all the investigated composition range are obtained under an electrical field of 6 kV/mm. As we all know, the pure BNT ceramics have high coercive field E_c, corresponding to 5.1 kV/mm in our study. An increasing amount of NKLNST leads to a decrease in the coercive field E_c and an increase in the remnant polarization P_r. For $x = 0.05$ ceramics, $P_r = 39.4\ \mu C/cm^2$ and $E_c = 3.6$ kV/mm are observed in Fig. 3, which means that incorporation of a proper amount of NKLNST in BNT composition enhances the ferroelectric properties significantly. However, the P_r of BNT–xNKLNST ceramics decreases rapidly when $x = 0.07$. Even at $x = 0.10$, the P–E hysteresis loop becomes very narrow and exhibits the phenomenon of paraelectric phase.

The relative permittivity at 1 kHz of BNT–xNKLNST ceramics as a function of temperature is displayed in Fig. 4(a). It is found that two dielectric anomalies exist for ceramics with $x = 0$, 0.01, 0.03 and 0.05, where the dielectric peaks occurring at higher temperatures correspond to phase transitions from anti-ferroelectric to paraelectric (at T_m, temperature with the maximum relative permittivity), while the dielectric anomaly before T_m relates to the occurrence of a ferroelectric to anti-ferroelectric phase transition (at T_d, depolarization temperature), at which the ceramics lose their piezoelectric activities. With the increasing x content, both of T_m and T_d shift to lower temperature. The dielectric maxima are found to decrease significantly, and the dielectric peaks become more diffuse. The addition of NKLNST introduces more ions into the A-site and B-site of BNT perovskite structure, leading to cation disorder and diffuseness. Moreover, it can be found that there is only one dielectric anomaly observed for the compositions with $x = 0.07$ and 0.10, and the result of XRD shows near cubic phase at room temperature because of the diffuseness and smeared dielectric peak. The dielectric loss of BNT–xNKLNST ceramics is shown

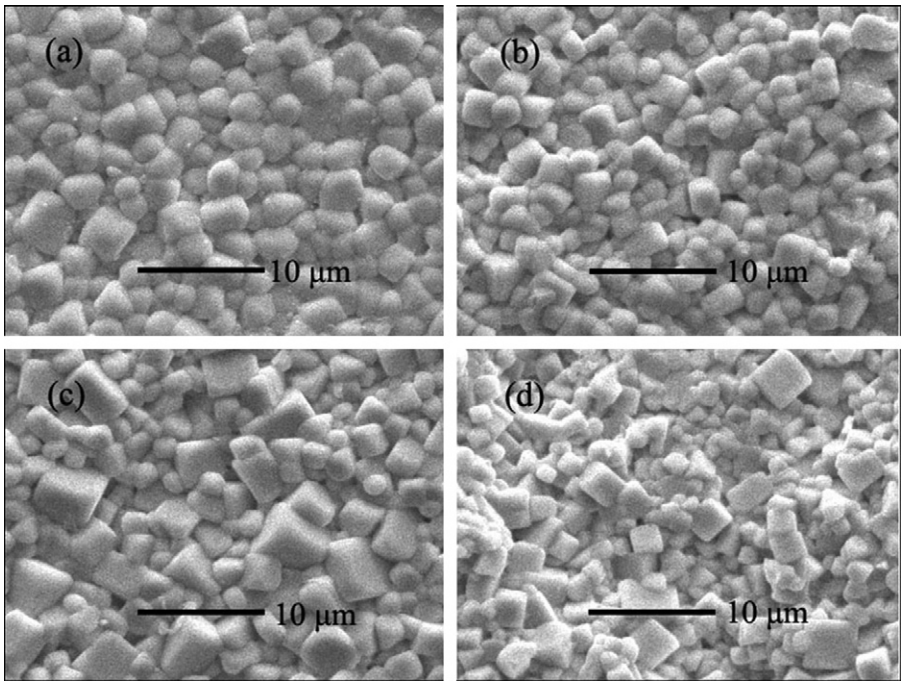

Fig. 2. SEM morphology of BNT–xNKLNST ceramics with various KN contents sintered at 1140 °C for 3 h: (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.05$ and (d) $x = 0.10$.

in Fig. 4(b). It can be seen that there are anomalies close to T_d for different x, showing the same tendency as the relative permittivity.

Fig. 5 shows the piezoelectric constant, remnant polarization and coercive field of BNT–xNKLNST ceramics as a function of x. The piezoelectric constant d_{33} increases from 72 pC/N to 120 pC/N with the content of NKLNST increasing from $x = 0$ to $x = 0.05$. The remnant polarization P_r has the same trend with d_{33}, while the coercive field E_c decreases with increasing NKLNST content. The significant improvement in electrical properties of BNT–xNKLNST ceramics should be attributed to the formation of the MPB between R and T phase, larger P_r and lower E_c. However, for the $x = 0.10$ ceramics, d_{33} decreases to 20 pC/N due to the phase transition and the decrease of T_d and T_m.

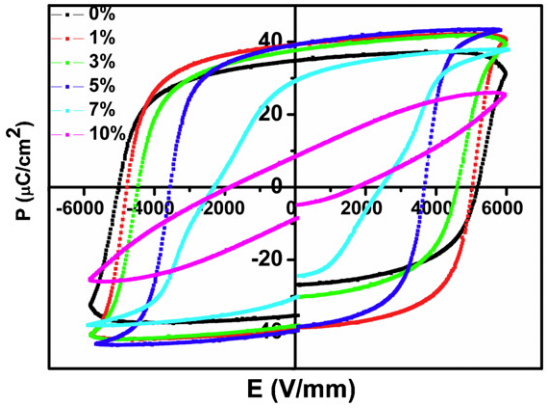

Fig. 3. P–E hysteresis loops of BNT–xNKLNST ceramics sintered at 1140 °C.

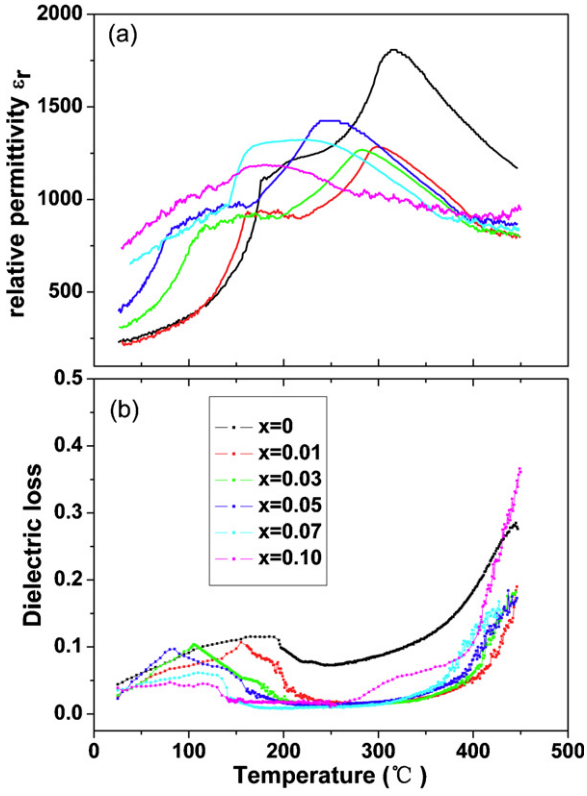

Fig. 4. Relative permittivity (a) and dielectric loss (b) of BNT–xNKLNST ceramics as a function of temperature at 1 kHz.

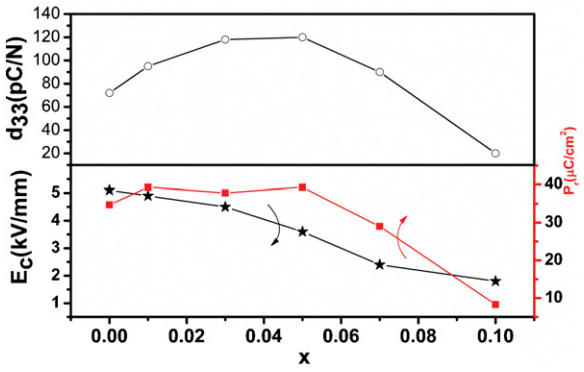

Fig. 5. Piezoelectric properties, remnant polarization and coercive field of BNT–*x*NKLNST ceramics as a function of *x*.

4. Conclusions

The BNT–*x*NKLNST piezoelectric ceramics were investigated to determine phase structure and electrical properties. It is found that the rhombohedral–tetragonal MPB of the ceramics is close to $x = 0.05$ at room temperature. The phenomenon of grain morphologies changed from the square pillar shape to the polyhedral shape with the increase of NKLNST could be observed. The resulting BNT–*x*NKLNST ceramics exhibit superior piezoelectric properties of d_{33} up to 120 pC/N near the rhombohedral–tetragonal MPB at $x = 0.05$. These results indicate that the BNT–NKLNST ceramic is a promising candidate material for lead-free piezoelectric ceramics.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (51102175), a Ph.D. Programs Foundation of Ministry of Education of China (20100032120020), Seed Foundation of Tianjin University and the State Key Laboratory of New Ceramics and Fine Processing of Tsinghua University.

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