Vertical morphotropic phase boundary in lead-free piezoelectric ceramics (K,Na,Li)NbO₃–BaZrO₃–(La,Na)TiO₃ system

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Received 11 December 2015; Revised 7 January 2016; Accepted 8 February 2016; Published 14 April 2016

A morphotropic phase boundary (MPB) with temperature-independent behavior, the so-called vertical MPB was investigated in lead-free (K,Na,Li)NbO₃–BaZrO₃–(La,Na)TiO₃ ternary ceramic system. The specimens were synthesized by a conventional solid-state reaction method, and their crystal structures as well as their MPB were determined from X-ray diffraction patterns measured from room temperature to 300°C. The vertical MPB composition was determined to be 0.9025(K_{0.45}Na_{0.5}Li_{0.05})NbO₃–0.09BaZrO₃–0.0075(La,Na)TiO₃ and the Curie temperature was found to be about 195°C. It was successfully confirmed that ceramic samples of this system could be sintered in a reducing atmosphere. For lead-free piezoceramic applications of multilayer actuators using Ni inner electrodes, the results obtained in this work have important practical implications.

Keywords: Lead-free piezoceramics; vertical morphotropic phase boundary; reducing atmosphere; high-temperature XRD; phase transition.

1. Introduction

Piezoelectric materials are widely used in modern electronic devices. Among them, lead-based piezoelectric ceramics, Pb(Zr,Ti)O₃ (PZT) system ceramics, are widely used as actuators and transducers because of their excellent piezoelectric properties. The PZT system has a morphotropic phase boundary (MPB) between rhombohedral phase and tetragonal phase. It is well known that dielectric and piezoelectric properties show their maximum values around the MPB composition.¹ Additionally, in composition–temperature phase diagram of the PZT the MPB is almost perpendicular to the composition axis, indicating that the PZT ceramics have a high performance in a wide temperature range with high stability. Therefore, the vertical MPB is very important for the piezoelectric applications.

Because of the harmful lead contained in the PZT, research and development of lead-free piezoelectric materials have attracted much attention. In particular, lead-free BaTiO₃-based, (Bi,Na)TiO₃-based, and (K,Na)NbO₃-based piezoelectric ceramics have been considered as replacement candidates for the PZT ceramics.^{2–17} The BaTiO₃-based, (Bi,Na)TiO₃-based, and (K,Na)NbO₃-based system ceramics have the same perovskite structure as the PZT, and the MPB compositions were also formed/discovered in those systems. In our early work, one of the lead-free piezoceramics with vertical MPB has been successfully developed by adjusting the MPB slope of (K_{0.45}Na_{0.5}Li_{0.05})NbO₃–BaZrO₃ (KNLN–BZ) binary system using the rhombohedral (Bi,Na)TiO₃ (BNT) as a third component.¹⁸

Recently, multilayer actuators were required for engine-injector applications. To reduce the total cost, Ni inner electrode was selected. In this case, the Ni electrode and the ceramics have to be co-sintered in a reducing atmosphere to prevent oxidation of the Ni.^{19–22} However, the vertical MPB composition developed in our early work, lead-free KNLN–BZ–BNT, contains very small amount of Bi. The Bi₂O₃ was metalized and evaporated during the sintering process in the reducing atmosphere. Chean *et al.* reported that Bi in BNT could be replaced by small amount of La and a single perovskite structure was kept.²³ The La has the same ionic valence and almost same ionic radius as Bi. Furthermore, the La₂O₃ can be sintered in reducing atmosphere without metallization nor evaporation. In this study, the MPB formation and the slope of KNLN–BZ binary system adjusted by (La,Na)TiO₃ (LNT) were investigated.

2. Experimental Procedure

(1–x–y)KNLN–xBZ–yLNT (0.07 ≤ x ≤ 0.1) (y = 0.0075, 0.01) ternary system ceramics with compositions denoted by numbers 1–10, as shown in Fig. 1, were prepared by a conventional solid-state synthesis method. Carbonate and oxide powders of K₂CO₃, Na₂CO₃, Li₂CO₃, BaCO₃, La₂O₃, TiO₂, ZrO₂, and Nb₂O₅ were used as raw materials. Stoichiometrically weighed powders were mixed by planetary ball milling with zirconia balls and ethanol for 4 h. After drying, the mixtures were calcined at 1000°C in air for 2 h, and then the powders were crushed and ball-milled again for 15 h. The

Fig. 1. (Color online) Ternary ceramic compositions investigated in this work.

final ceramic powders with submicron size particles were mixed with a polyvinyl alcohol binder and then formed into pellets by pressing at 170 MPa. After burning out the binder, the pellets were sintered at 1190°C for 5 h. The sintered specimens were lapped to 1 mm thickness and then silver-electroded on both surfaces at 650°C for 2 h. The bulk ceramics were poled with an electric field of 4.0 kV/mm in silicone oil at 150°C for 15 min.

Powder X-ray diffraction (XRD) analysis was carried out using Cu K α radiation. Specimens of sintered powders were measured by XRD analysis in the range $2\theta = 20\text{--}60^\circ$ at room temperature (RT) to confirm their perovskite structure. The pseudocubic perovskite indication was used in our work. The $(200)_{\text{pc}}$ reflections of selected specimens were measured by XRD analysis from RT to 300°C for phase transition determination. For perovskite structure materials, weak-left and strong-right double $(200)_{\text{pc}}$ reflections indicate the tetragonal phase, strong-left and weak-right double $(200)_{\text{pc}}$ reflection indicates the orthorhombic phase, and a single $(200)_{\text{pc}}$ reflection indicates the rhombohedral or cubic phase.¹⁸ The Curie temperature T_C was determined at the peak value from the curve of the temperature dependence of the dielectric constant at 1 kHz. Electromechanical coupling factor k_p was measured by the resonance-antiresonance method using a Poisson's ratio of 0.3.

3. Results and Discussion

Figure 2(a) shows XRD patterns of numbers 1–10 specimens at RT. The XRD patterns show that all the samples had single perovskite phase. The $(200)_{\text{pc}}$ reflection peaks located at $2\theta = 44.5\text{--}46^\circ$ are magnified in Fig. 2(b). It could be clearly seen that numbers 1 and 2 specimens had weak-left and strong-right double $(200)_{\text{pc}}$ reflections indicating tetragonal phase and number 10 specimen had a rhombohedral phase. However, numbers 3–9 specimens had nonbissymmetry

Fig. 2. XRD patterns of numbers 1–10 specimens at RT (a) from $2\theta = 20^\circ$ to 60° and (b) $(200)_{\text{pc}}$ refraction.

single reflections. After peak-separating and peak-fitting treatment, it was determined that numbers 3–9 specimens had a tetragonal phase. From the above, MPB in this ternary system at RT could be determined between numbers 8 and 10, as the solid line shown in Fig. 1.

High-temperature XRD patterns of numbers 1, 4, and 7, 8 and 10 specimens at $2\theta = 44.5\text{--}46^\circ$ and their fitted peaks are shown in Figs. 3(a)–3(e). The double $(200)_{\text{pc}}$ reflection changed to single $(200)_{\text{pc}}$ reflection at 200°C for number 7, and at 250°C for numbers 1 and 4 specimens, respectively. The Curie temperatures of all the specimens were determined at the peak value from the curve of temperature dependence of dielectric constant at 1 kHz. Some of them, curves of numbers 1 and 7 specimens are shown in Fig. 4. The T_C of numbers 1 and 7 specimens were 235°C and 205°C, which agreed with the results observed in Figs. 3(a) and 3(c). At line of $y = 0.0075$ (Fig. 1), the T_C decreased at 20°C/mol% with increase of BZ. The T_C of specimens at $y = 0.0075$ line were little higher than that at $y = 0.01$ line. Near the MPB composition, the T_C of numbers 8, 9 and 10 specimens were determined as around 202°C, 195°C and 190°C, respectively. The T_C of this ternary system is lower than that BNT one of KNLN-BZ-BNT system.¹⁸ Considering the T_C determined from the dielectric constant curve and the XRD date in Fig. 3(b), lattice constant change of number 4 specimen was obtained, as plotted in Fig. 5.

To investigate the slope of the MPB, numbers 8 and 10 specimens were also analyzed by the high-temperature XRD. Figures 3(d) and 3(e) show the high-temperature XRD measurement results. It could be clearly seen that the number 10 specimen had a rhombohedral phases from RT to the T_C , and then the perovskite phase changed to cubic phase. Number 8 specimen had tetragonal phases from RT to the T_C , and had a cubic phase above the T_C . Considering the composition difference between the two specimens, we could suggest an almost vertical MPB existing near the composition of 0.9025KNLN–0.09BZ–0.0075LNT with the T_C of about

Fig. 3. (Color online) High-temperature XRD patterns of (200)_{pc} reflections and fitted peaks of (a) number 1, (b) number 4, (c) number 7, (d) number 8 and (e) number 10 specimens.

195°C. Electromechanical coupling factor k_p of a poled number 8 specimen was measured from RT to 210°C. As a result, $k_p = 40\%$ at RT and $k_p = 6\%$ at 200°C were obtained.

Fig. 4. Temperature dependence of dielectric constant of numbers 1 and 7 specimens.

Fig. 5. Temperature dependence of lattice constants of number 4 specimen.

Therefore, it was confirmed that number 8 specimen had the piezoelectricity until the T_C and there was no phase transition from RT to the T_C . Figure 6 shows the phase diagram of $(1-x-y)\text{KNLN}-x\text{BZ}-y\text{LNT}$ ($y = 0.0075$) ceramic system nearby the vertical MPB. The k_p values of number 8 specimen, however, were smaller than those expected. It was considered that the specimen had not been well prepared and manufacturing process needed an improvement. Further investigation of the above lead-free piezoceramics with good performance in terms of piezoelectric properties is in progress.

One of number 8 specimens was tested to be sintered in reducing atmosphere. $\text{N}_2\text{-}2\%\text{H}_2$ gas was used and the oxygen partial pressure was about 1×10^{-6} Pa. After sintered in the reducing atmosphere at 1190°C for 4 h, the specimen was thermal-treated in air at 1000°C for 3 h. This specimen had

Fig. 6. Phase diagram of $(1-x-y)\text{KNLN}-x\text{BZ}-y\text{LNT}$ ($y = 0.0075$) ceramics nearby MPB.

high density ($> 97\%$) and d_{33} about 270 pC/N at RT (measured by a d_{33} meter).

4. Conclusions

In KNLN–BZ–LNT ternary ceramic system, there is a temperature-independent MPB, the so-called vertical MPB located around composition of 0.9025KNLN–0.09BZ–0.0075LNT with a T_C of about 195°C. The piezoelectric properties were confirmed from RT to the T_C , indicating that there is no phase transition in the temperature range. Compared with the KNLN–BZ–BNT system reported by our group, there is no Bi element in the component, so that the ceramic sample was successfully sintered in a reducing atmosphere. For lead-free piezoceramic applications of multilayer actuators using Ni inner electrodes, such as engine-injector, the results obtained in this work have important practical implications.

Acknowledgment

This work was partly supported by the CAS/SAFEA International Partnership Program for Creative Research Teams.

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