High Performance Lead-free Piezoelectric Material

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Abstract

Lead has recently been expelled from many commercial applications and materials (for example, from solder, glass and pottery glaze) owing to concerns regarding its toxicity. Lead zirconium titanate (PZT) ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices; they contain more than 60 weight per cent lead. Although there has been a concerted effort to develop lead-free piezoelectric ceramics, no effective alternative to PZT has yet been found.\(^1\)\(^-\)\(^14\) Here we report a lead-free piezoelectric ceramic with an electric-field-induced strain comparable to typical actuator-grade PZT. We achieved this through the combination of the discovery of a morphotropic phase boundary in an alkaline niobate-based perovskite solid solution, and the development of a processing route leading to highly \(<001>\) textured polycrystals. The ceramic exhibits a piezoelectric constant \(d_{33}\) (the induced charge per unit force applied in the same direction) of above 300 picocoulombs per newton (pC N\(^{-1}\)), and texturing the material leads to a peak \(d_{33}\) of 416 pC N\(^{-1}\). The textured material also exhibits temperature-independent field-induced strain characteristics.

Keywords

Piezoelectrics, Perovskite structure, Pseudo-illmenite structure, Morphotropic phase boundary, Texture orientation, Electric-field induced strain, Templated grain growth, Topochemical reaction
1. Material design

1.1 Compositional design

The piezoelectric properties of PZT materials can be improved by the formation of a morphotropic phase boundary (MPB) between the tetragonal and rhombohedral phases in solid solutions of perovskite-type PbTiO₃ and PbZrO₃ (Refs. 15-17). For the development of new, lead-free piezoelectric materials, we designed a compositional formation of MPB between a different pair of crystal structures—namely, the pseudo-ilmenite-type and perovskite-type structures, having rather different lattice forms and unit sizes from each other. We anticipated the formation of a new MPB in the perovskite-rich region by the dissolution of a small amount of the pseudo-ilmenite-structured material, causing a lattice distortion for the structural phase transition. The general need for stable piezoelectric characteristics over a wide temperature range made us select high Curie-temperature (T_C >250 °C) end members: orthorhombic perovskite-type (K₀.₅Na₀.₅)NbO₃ (T_C = 415 °C) and hexagonal pseudo-ilmenite-type LiTaO₃ (T_C = 615 °C). Besides the formation of a MPB, we also exploited the hybridization of covalency onto ionic bonding for further improvement in piezoelectricity, on the basis of Cohen's calculation for the titanate-perovskite system. In addition to LiTaO₃, we also used LiSbO₃ as an end member for the compositional study with (K₀.₅Na₀.₅)NbO₃, because the higher electronegativities of Sb and Ta compared to Nb were expected to make the alkaline niobate-based perovskite more covalent.

Figure 1a shows the result of the MPB study: a phase diagram determined by X-ray diffraction (XRD) measurements at room temperature (25 °C) for conventionally sintered and unpoled ceramic specimens, and d₃¹ (the induced charge per unit force applied in the perpendicular direction) values for the specimens poled (given a macroscopic polar Curie-temperature (T_C >250 °C) end members: orthorhombic perovskite-type (K₀.₅Na₀.₅)NbO₃ (T_C = 415 °C) and hexagonal pseudo-ilmenite-type LiTaO₃ (T_C = 615 °C). Besides the formation of a MPB, we also exploited the hybridization of covalency onto ionic bonding for further improvement in piezoelectricity, on the basis of Cohen's calculation for the titanate-perovskite system. In addition to LiTaO₃, we also used LiSbO₃ as an end member for the compositional study with (K₀.₅Na₀.₅)NbO₃, because the higher electronegativities of Sb and Ta compared to Nb were expected to make the alkaline niobate-based perovskite more covalent.

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axis by altering the direction of the spontaneous polarization with an applied high electric-field) at 5 kV mm\(^{-1}\).

The compositions with high \(d_{33}\) values, shown in Fig. 1 as LF1, LF2 and LF3, are found in a tetragonal phase area near the MPB formed between orthorhombic and tetragonal phases in the alkaline niobate-based perovskite system. The Curie temperature is controllable between 170 and 500 °C in this compositional range, such that additions of Li and Ta elements shift the Curie temperature higher and lower, respectively. The highest piezoelectric charge sensor \(d_{33}\) constant in the (K, Na)NbO\(_3\)-LiTaO\(_3\) system was found to be 230 pC N\(^{-1}\) with a Curie temperature of 323 °C at the LF3 composition. The introduction of the solid solution in the (K, Na)NbO\(_3\)-LiTaO\(_3\)-LiSbO\(_3\) pseudo-ternary system further enhanced the piezoelectric performance, including a \(d_{33}\) constant up to as high as 300 pC N\(^{-1}\), with a Curie temperature of 253 °C (at the LF4 composition, which is also a tetragonal phase at 25 °C in the unpoled state; Fig. 1b). These excellent piezoelectric properties exceed the composition, which is also a tetragonal phase at 25 °C in the unpoled state; Fig. 1b).

1. Texture orientation

By additional engineering of the microstructural design, we developed a novel processing route for producing textured polycrystals of the alkaline niobate-based compositions, LF3 and LF4. The \(d_{33}\) constants and Curie temperatures are shown in Fig. 1b for the textured ceramics LF3T and LF4T, of which the Lotgering's factors\(^{19}\) of the <001> orientation are 92% and 91%, respectively. The enhanced \(d_{33}\) constants are 373 and 416 pC N\(^{-1}\) for LF3T and LF4T, respectively, which are 1.8 and 1.6 times as large as those of non-textured ceramics, LF3 and LF4, respectively.

For the successful fabrication of textured ceramics with high \(d_{33}\) values, one of the most important technologies is the preparation of plate-like particles, which are used as a template. The hot-working (hot-forging\(^{20}\) and hot-pressing\(^{21}\)) method cannot give a texture to such a pseudo-isotropic system, and no proper template materials have been available for the templated grain growth and reactive-templated grain growth (RTGG\(^{22-27}\)) of the alkaline niobate-based perovskite. We have developed a new synthesis technique for plate-like NaNbO\(_3\) particles as templates for <100> oriented (K, Na)NbO\(_3\)-based ceramics. This process comprises three steps as follows: (1) Bismuth layer-structured plate-like Bi\(_2.5\)Na\(_3.5\)Nb\(_5\)O\(_{18}\) (BiNN\(_5\)) particles (shown in Fig. 1b and c) are synthesized as a precursor by the molten-salt synthesis method. (2) Using this precursor, plate-like NaNbO\(_3\) particles (Fig. 2d and e), identified by JCPDS powder diffraction file card No.33-1270, are synthesized through a topochemical reaction, in which NaNbO\(_3\) is formed by ion exchange of Na for Bi ions on BiNN\(_5\) with

![Fig. 2 Schematic diagram of topochemical conversion from bismuth layer-structured BiNN5 particles to plate-like NaNbO3 particles. a, Crystal structures of plate-like BiNN5 and NaNbO3 particles. b, c, SEM image and X-ray diffraction profile of plate-like BiNN5 particles used as precursor. d, e, SEM image and X-ray diffraction profile of plate-like NaNbO3 particles. X-ray diffraction profile of NaNbO3 particles is characterized by pseudotetragonal Miller indices. BiNN5 particles are completely converted into the regular perovskite-structured NaNbO3 particles with a preserved plate-like shape.](image)
preserved particle morphology and a developed \{001\} plane of the perovskite (Fig. 2a). (3) This NaNbO₃ platelet is used as a reactive template, and textured (K,Na)NbO₃-LiTaO₃(-LiSbO₃) polycrystals are synthesized by the RTGG method.

Figure 3a and b shows the scanning electron micrograph (SEM) image and X-ray diffraction (XRD) profile of textured (K₀.₄₄Na₀.₅₂Li₀.₀₄) (Nb₀.₈₄Ta₀.₁₀Sb₀.₀₆)O₃ ceramic (LF4T) in comparison to those of the non-textured ceramic (LF4) with the same composition. It should be noted that the textured ceramic give brick-layer-like quadrangular grains, which align parallel to the tape-casting plane, and the \{001\} diffraction peaks of the textured ceramic in the XRD pattern are clearly high compared to those of the non-textured ceramic. In addition, the XRD patterns show that the phases of the textured and non-textured ceramics in the unpoled state are tetragonal at 25 °C. From this result, it is considered that the transformation from a low-temperature orthorhombic phase to a high-temperature tetragonal phase occurs below 25 °C.

2. Piezoelectric actuator performance

In order to examine the applicability of the developed materials for high-power devices, actuator performances were evaluated. The electric-field-induced strain was measured for the textured LF4T, non-textured LF4 and the conventional PZT ceramic (PZT4) for actuator application under a high electric field from 0 to 2,000 V mm⁻¹ with a triangular wave.

For the non-textured LF4 (Fig. 4a), the electric-field-induced strain was unstable within this...
temperature range, and had an anomaly: the highest value occurred at 40 °C. It is considered that this anomaly is related to the electric-field-induced tetragonal-to-orthorhombic phase transformation, shifting the phase transformation temperature from below 25 °C in the unpoled specimen to 40 °C under a high electric field. In order to clarify the origin of this anomaly, morphotropic phases need to be determined under high electric-field driving. However, this evaluation is very difficult to perform, and is left for future studies.

On the other hand, it is obvious in Fig. 4a that the textured LF4T, which is the <001> orientated ceramic, exhibited a large strain nearly double of that of the non-textured LF4 ceramic, and the strain was even larger than the field-induced strain for PZT4. In addition, we discovered that the texture given to LF4 not only enhanced the field-induced strain but also improved the temperature coefficient of normalized strain ($S_{\text{max}}/E_{\text{max}}$), as shown in Fig. 4a, where $S_{\text{max}}$ and $E_{\text{max}}$ denote the maximum strain and the maximum electric field strength, respectively. That is to say, the texture stabilizes the temperature-dependent strain characteristic of LF4T, even though its transformation temperature between orthorhombic and tetragonal phases is the same as that of non-textured LF4 in the unpoled state. Furthermore, it should be noted that the flat, temperature-independent characteristic of LF4T is even more prominent than PZT4, since the strain deviation value of 6.5% for LF4T between RT to 160 °C is smaller than that of 15% for PZT4. This piezoelectric strain behaviour of LF4T is of great importance for temperature-independent actuator devices.

The temperature-independent strain characteristics (for a given texture) are the result of changes in the amplitude of, and in the ratio between, two strain components; one from a lattice motion and the other from domain wall motion.28-30) Those two field-induced strain components must be dependent on temperature and microstructure (that is, textured or non-textured). In order to clarify the underlying mechanism, a measurement system needs to be developed for the separate evaluation of strain components from the two different origins.

3. Conclusions

The overall performance of the developed LF4T ceramic is listed in Fig. 4b with that of the typical high-performance PZT ceramic (PZT4). It is clear that most of the piezoelectric properties are comparable to those of the PZT. This high performance leads us to expect that the developed materials are leading candidates for environmentally friendly piezoelectric devices.

Supplement: Methods

Bi$_{2.5}$Na$_{3.5}$Nb$_5$O$_{18}$ (BiNN5) platelet was synthesized at 1100 °C using a molten salt as a flux. NaNbO$_3$ platelet was synthesized in a flux at 950 °C, and Bi$_2$O$_3$, by-product, was removed. The NaNbO$_3$ platelets as reactive templates and complementary reactants, equiaxed NaNbO$_3$, KNbO$_3$, KTaO$_3$, LiSbO$_3$ and NaSbO$_3$ particles, were mixed, tape-cast and stacked. The textured (K$_{0.44}$Na$_{0.52}$Li$_{0.04}$) (Nb$_{0.84}$Ta$_{0.10}$Sb$_{0.06}$)O$_3$ polycrystal was prepared by sintering the stacked tape at 1135 °C.

The piezoelectric $d_{31}$ constants were measured by the resonance anti-resonance method with an impedance analyzer (Agilent, HP4194A). The piezoelectric $d_{33}$ constants were measured by the converse piezoelectric method using a piezo-$d_{33}$ meter (Institute of Acoustic Academia Sinica, model ZJ-4B). The degree of tetragonal <001> axis orientation, $F$, was evaluated by the Lotgering’s equation using the X-ray diffractmeter (Rigaku, Rint TTR2, CuKα radiation).

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