Enhanced piezoelectric response of BaTiO$_3$–KNbO$_3$ composites

Ichiro Fujii,[1] Shigehito Shimizu,[1] Kenta Yamashita,[1] Kouichi Nakashima,[1] Nobuhiro Kumada,[1] Chikako Moriyoshi,[2] Yoshihiro Kuroiwa,[2] Yoshinori Fujikawa,[3] Daisuke Tanaka,[3] Masahito Furukawa,[3] and Satoshi Wada[1,a)]

[1]*Interdisciplinary Graduate School of Medical and Engineering, University of Yamanashi, Kofu, Yamanashi 400-8510, Japan*
[2]*Department of Physical Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan*
[3]*Materials and Process Development Center, TDK Corporation, 570-2 Matsugashita, Minamihatori, Narita, Chiba 286-8588, Japan*

The piezoelectric response of solvothermally synthesized BaTiO$_3$ (BT)–KNbO$_3$ (KN) composites (the nominal BT/KN ratio was 1) with distinct interfaces was investigated. The x-ray diffraction pattern showed two distinct peaks began to merge into a singular broad peak at a two-theta position between (200) and (002) tetragonal-related peaks of BT. The transmission electron microscopy observation showed a heteroepitaxial interface region between BT single-crystal particles and deposited KN crystals. The large-field piezoelectric constant was 136 pC/N, which was three times larger than that of a sintered 0.5BT–0.5KN composite. The enhanced piezoelectric response was attributed to the strained epitaxial interface region. © 2011 American Institute of Physics. [doi:10.1063/1.3662397]

Lead-free piezoelectric materials are important due to environmental concerns.[1] However, the piezoelectric properties are lower than those of currently utilized Pb(Zr,Ti)O$_3$ (PZT) ceramics.[2,3] One of the approaches to increase the piezoelectric response may be use of an artificial superlattice structure, as large dielectric constant and remanent polarization were reported in BaTiO$_3$ (BT)–SrTiO$_3$ (ST) artificial superlattices.[4,5] Although the dielectric and piezoelectric responses seem to decrease due to the interfaces (boundaries) of each layer which could act as pinning centers for domain wall motion,[6] first principle calculations and an experimental result of BT–ST artificial superlattices explain that the enhancements are attributed to an increased lattice constant ratio, c/a, of BT caused by the lattice mismatch stress.[7,8] Moreover, a polarization rotation observed experimentally and theoretically at the interfaces of the superlattices[9,10] could, in part, be attributed to the enhancement,[11] as proposed for PZT ceramics with morphotropic phase boundary compositions.[12]

To make use of such an artificial superlattice structure and potential polarization rotation in a bulk form, solvothermally synthesized BT–KNbO$_3$ (KN) composites with strained or crystal-structurally distorted interfaces between a compact of BT single-crystal particles and deposited KN crystals (see Fig. 1(a)) are studied.[11] Such composites differ, in concept, from conventional ferroelectric/polymer composites in terms of the strained epitaxial interfaces. The work reported some structural results: epitaxial-like strained interfaces between BT and KN crystals, with a low relative density of the composite (~65%). In this study, BT–KN composites with the strained epitaxial interfaces were prepared with a higher Nb source concentration to achieve a

higher density, and the structural, dielectric, and piezoelectric properties were investigated.

BT–KN composites were prepared by a solvothermal method.[11] BT powder (BT03, particle size of approximately 300 nm, Sakai Chemical Industry Co., Ltd.) and Nb$_2$O$_5$ powder (the particle size: approximately 1 μm, Rare Metallic Co., Ltd), with a Nb$_2$O$_5$/BT molar ratio of 0.5, were ball-milled for 16 h with zirconia balls and ethanol. After 2 wt. % polyvinyl butyral was added, the ethanol was dried at 80 °C. The mixture was ground, screened through a 250 μm mesh, and then pressed into green compacts using a uniaxial press. After binder burnout at 500–600 °C for 10 h, the density of the compacts was measured by an Archimedes method with ethanol. To calculate the theoretical and relative density, the
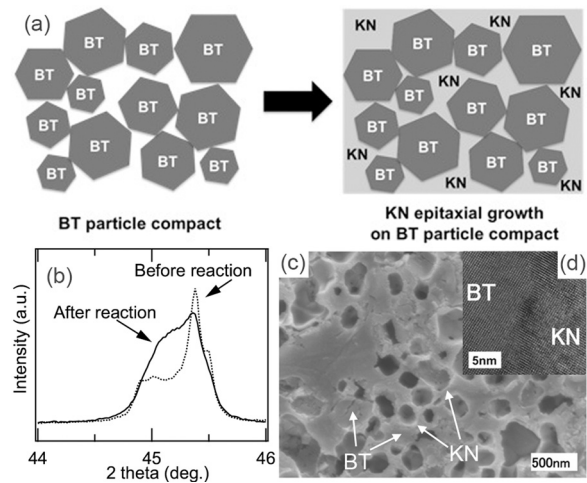

FIG. 1. (a) Schematic procedure for the preparation method of the BT–KN composite with heteroepitaxial interface regions between BT and KN. (b) XRD patterns of the (200) and (002) peaks for the crushed powders of the compacts before and after the reactions. SEM (c) and TEM (d) micrographs of a cross section of the compact after the reaction.

a)Electronic mail: swada@yamanashi.ac.jp.

following was assumed: (1) all the Nb_2O_5 particles of the compact react with the potassium source to $KNbO_3$, (2) all the Nb ions remain in the composite as $KNbO_3$ after the reaction, and (3) $BaTiO_3$ and $KNbO_3$ do not make a solid-solution. The compact was crushed to powder and the crystal structure of the powder was investigated by x-ray diffraction (XRD, Rigaku, Ultima IV) with Cu Kα radiation. The BT–Nb_2O_5 compacts were placed in a Teflon-coated auto-clave container with ethanol, KOH, and K_2CO_3, with a ratio of 20 *l* of ethanol, 2 mol of KOH, and 9 mol of K_2CO_3 per 1 mol of Nb_2O_5 of the BT–Nb_2O_5 compact. They were heated to 230 °C for 20 h without stirring. The details of the KN formation were described elsewhere.[11,13] After the reaction, the composites were washed with ethanol and dried at 200 °C. The density of the composites and the crystal structure were remeasured. The microstructure was observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For electric measurements, the composites were polished and sawed to a size of $2 \times 2 \times 0.5$ mm^3. Gold electrodes were sputtered on the top and bottom surfaces with an area of 2×2 mm^2. The room temperature dielectric properties were measured at the frequencies between 40 Hz and 10 MHz using an impedance analyzer (Agilent, HP4294A). Temperature dependence of the dielectric properties was measured at temperatures from room temperature to 480 °C using an LCR meter (Wayne Kerr, 6440B). The strain vs. electric-field (S-E) curves were measured at room temperature and 0.1 Hz using a ferroelectric character evaluation system. The samples were not poled due to a large leakage. A large-field piezoelectric constant (d_{33}^*) was calculated as the maximum strain over the applied field amplitude of the S-E curve measured at 30 kV/cm, 0.1 Hz.

An XRD pattern of the solvothermally synthesized BT–KN composite showed only perovskite peaks and the absence of peaks associated with Nb_2O_5 within the detection limits, which means that the Nb_2O_5 particles of the compact reacted with KOH and K_2CO_3 to KN, and the BT/KN molar ratio of the composite was expected to be 1. Figure 1(b) shows XRD patterns of (200) and (002) peaks of BT for crushed powders of the unreacted compact and the reacted composite. For the compact, a clear splitting of (002) and (200) peaks of BT particles was observed. This is typical of tetragonal BT. For the composite, on the other hand, the splitting became weaker, and a broad peak at a specific two-theta value between the (200) and (002) peaks was developed. Such a "bridge structure" was previously reported for samples with strained or crystal-structurally distorted interfaces.[14–16] The samples have two categories. One is layered particles such as BT particles with approximately 100-400 nm particle sizes[14] and BT-coated ST particles.[15] For the BT particles, Rietveld analyses of the XRD patterns of the "bridge structure" suggested that the particles consisted of the core of the tetragonal phase, the surface of the cubic phase, and the intermediate, interface region between the two, of which the tetragonal distortion gradually relaxed.[14] The other is samples with large domain wall density.[16] An example of this is BT ceramics. It was reported that the broad peak developed as the domain size decreased.[16] This was ascribed to an increase in a density of the domain walls,

of which the crystal structure extended to connect the neighboring domains. Thus, the "bridge structure" is caused by strained or crystal-structurally distorted interface region, and the "bridge structure' observed in this study can be attributed to the distorted interface region between grown KN crystals and the BT single-crystal particles.

The density of the unreacted compact was 3.530 g/cm^3 (relative density: 61.90%), which increased to 4.013 g/cm^3 (relative density: 70.36%) after the reaction. The increase was attributed to a summation of the two phenomena: (1) dissolution of Nb_2O_5 particles and (2) KN formation on the surface of the BT particles. Note that the relative density of the composite increased compared to that of the composite prepared from a compact with a Nb_2O_5/BT molar ratio of 0.25.[11]

The microstructure was studied by SEM and TEM. A cross-sectional SEM image of the composite is shown in Fig. 1(c). It can be seen that the BT particles were connected with KN crystals. A high resolution TEM image was taken to see the interface, as shown in Fig. 1(d). This image shows a heteroepitaxial interface region where the fringe patterns between the two grains were matched. There, it is believed that lattices of both BT and KN grains at the interface region were gradually deformed to reduce the lattice mismatch and the interface region was not seen as a line.

The room temperature dielectric constant (ε_r) and loss tangent (tanδ) of the composite were measured as a function from 40 Hz and 10 MHz (not shown). With increasing frequency, both the properties decreased, and the ε_r and tanδ were nearly constant above 1 MHz, with $\varepsilon_r = 370$ and tan$\delta = 0.10$ at 1 MHz. For KN porous ceramics with the porosity ∼30%, the ε_r was reported to be about 50,[17] while for the BT03 particle compact with the porosity ∼30%, the ε_r was reported to be about 62.[18] As compared to the ε_r of 50 and 62 for each component, the ε_r of the BT–KN composite was much higher, which suggested that the interface region between BT and KN crystals was contributed to the dielectric enhancement.

Figure 2 shows the temperature dependence of the dielectric properties of the composite. Two kinds of phase transition peaks were observed, i.e., (1) the Curie temperature of BT ∼130 °C and (2) a broad dielectric peak near 330 °C (a phase transition temperature related to KN). KN experiences phase transitions at temperatures of −50 °C (between the orthorhombic and rhombohedral phases), 230 °C (between the tetragonal and orthorhombic phases), and 430 °C (between the cubic and tetragonal phases).[2,3]
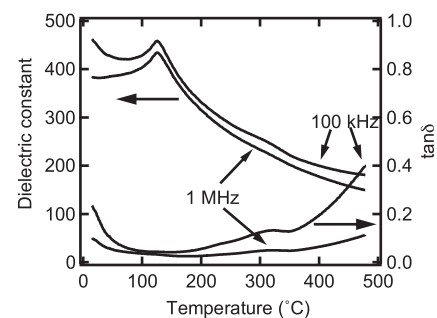
FIG. 2. Temperature dependence of the dielectric constant and loss tangent of the BT–KN composite.
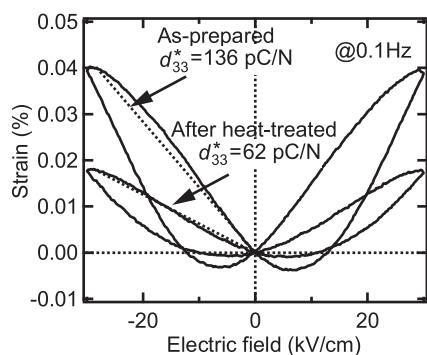
FIG. 3. Strain vs. electric-field curves of the BT–KN composite of the as-prepared state and the heat-treated state.

At present, the broad dielectric peak near $330\,°C$ cannot be assigned to the phase transition either between tetragonal and orthorhombic phases or between cubic and tetragonal phases.

The S-E curves of BT–KN composites are shown in Fig. 3. The S-E curve of the composite (of the as-prepared state) was a typical ferroelectric butterfly-curve behavior, and the large-field piezoelectric constant d_{33}^* was calculated to $136\,pC/N$. Previously, for the 0.5BT–0.5KN dense ceramics with both the tetragonal phase of BT and the orthorhombic phase of KN, the large-field d_{33}^* was reported to be $40\,pC/N$.[19] Therefore, the d_{33}^* value obtained in this study was three times larger than that of the 0.5BT–0.5KN dense ceramics. A potential mechanism of the piezoelectric enhancement is the following. The TEM observation showed the heteroepitaxial interface region between BT and KN crystals, and the XRD pattern of the composite showed a distortion in the lattices at the interface region of the BT–KN composite. This may result in, at least, an extension of the lattice constant along the polar axis of BT near the interfaces and an subsequent increase in c/a of BT,[3] as calculated and observed for BT–ST superlattices,[7,8] which increased polarization. Moreover, the polarization at the interface region likely rotates since the polar axes of BT and KN are different, which could lead an additional contribution to the piezoelectric response through the polarization rotation mechanism.[12]

To confirm this hypothesis, the BT–KN composite was ground after removal of the electrodes, and a compact prepared from the powder was sintered at $1000\,°C$ for $10\,h$. A S-E curve of the compact electroded with Au is shown in Fig. 3. The d_{33}^* value was calculated to $62\,pC/N$, which was almost the half of that of the as-prepared composite. Therefore, the strained interface region of the BT–KN composite significantly contributed to the piezoelectric enhancement. On the other hand, the ε_r and $\tan\delta$ measured at room temperature and $1\,MHz$ were 390 and 0.10, respectively. The dielectric properties were similar to the permittivity of the as-prepared composite, which suggests that the dielectric response was not sensitive to the diffuseness of the interface region. Further study is necessary to understand the difference.

In conclusion, a large piezoelectric response was observed for solvothermally synthesized BT–KN composites. It was found that the interfaces between BT and KN crystals were strained and epitaxial. A possible mechanism for the large response was suggested in terms of the strained interface region and polarization rotation.

[1]M. D. Maeder and D. Damjanovic, in *Piezoelectric Materials in Devices*, edited by N. Setter (N. Setter, Lausanne, 2002), p. 389.

[2]B. Jaffe, W. R. Cook, and H. L. Jaffe, *Piezoelectric Ceramics* (R.A.N., Marietta, Ohio, 1971).

[3]F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962).

[4]T. Shimuta, O. Nakagawara, T. Makino, S. Arai, H. Tabata, and T. Kawai, J. Appl. Phys. **91**, 2290 (2002).

[5]T. Harigai, D. Tanaka, H. Kakemoto, S. Wada, and T. Tsurumi, J. Appl. Phys. **94**, 7923 (2003).

[6]D. Damjanovic, Rep. Prog. Phys. **61**, 1267 (1998).

[7]J. B. Neaton and K. M. Rabe, Appl. Phys. Lett. **82**, 1586 (2003).

[8]W. Tian, J. C. Jiang, X. Q. Pan, J. H. Haeni, Y. L. Li, L. Q. Chen, D. G. Schlom, J. B. Neaton, K. M. Rabe, and Q. X. Jia, Appl. Phys. Lett. **89**, 092905 (2006).

[9]A. Q. Jiang, J. F. Scott, H. Lu, and Z. Chen, J. Appl. Phys. **93**, 1180 (2003).

[10]K. Johnston, X. Huang, J. B. Neaton, and K. M. Rabe, Phys. Rev. B **71**, 100103 (2005).

[11]S. Wada, S. Shimizu, K. Yamashita, I. Fujii, K. Nakashima, N. Kumada, Y. Kuroiwa, Y. Fujikawa, D. Tanaka, and M. Furukawa, Jpn. J. Appl. Phys. **50**, 09NC08 (2011).

[12]H. Fu and R. E. Cohen, Nature **403**, 281 (2000).

[13]G. K. L. Goh, C. G. Levi, J. H. Choi, and F. F. Lange, J. Crystal Growth **286**, 457 (2006).

[14]T. Hoshina, S. Wada, Y. Kuroiwa, and T. Tsurumi, Appl. Phys. Lett. **93**, 192914 (2008).

[15]T. Goto, K. Nakashima, I. Fujii, Y. Kuroiwa, Y. Makita, and S. Wada, Key Eng. Mater. **485**, 305 (2011).

[16]T. Hoshina, K. Takizawa, J Li, T. Kasama, H. Kakemoto, and T. Tsurumi, Jpn. J. Appl. Phys. **47**, 7607 (2008).

[17]S. Wada, Y. Mase, S. Shimizu, K. Maeda, I. Fujii, K. Nakashima, P. Pulpan, and N. Miyajima, Key Eng. Mater. **485**, 61 (2011).

[18]A. Yazawa, T. Hoshina, H. Kakemoto, T. Tsurumi, and S. Wada, Key Eng. Mater. **320**, 127 (2006).

[19]S. Wada, M. Nitta, N. Kumada, D. Tanaka, M. Furukawa, S. Ohno, C. Moriyoshi, and Y. Kuroiwa, Jpn. J. Appl. Phys. **47**, 7678 (2008).