Structural study of heat-treated BaTiO$_3$–KNbO$_3$ nanocomposites with heteroepitaxial interface by synchrotron radiation powder diffraction

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KnBO$_3$ (KN)/BaTiO$_3$ (BT) nanocomposite ceramics, in which a BT nanoparticle is thinly coated with KN crystals through the heteroepitaxial interface, are heat-treated at 1000°C for 10 h, and the crystal structures are investigated by synchrotron radiation powder diffraction. The Rietveld analysis based on the multicomponent models reveals that the volumes of gradually distorted tetragonal components of BT are significantly decreased and the BT-KN solid solutions emerge in the nanocomposites by the heat-treatment. The suppression of the piezoelectric response in the heat-treated nanocomposites compared with the as-synthesized ones is attributed to these changes in the crystal structure. The core/multishell structure model for the ceramic grain is proposed, and the changes in the crystal structure are revealed to be caused at the heteroepitaxial interface regain between BT and KN.

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1. Introduction

It is urgently necessary to replace lead-containing dielectric materials such as Pb(Zr,Ti)O$_3$ (PZT) with lead-free materials. The comprehensive dielectric properties of lead-free ceramics are basically insufficient compared with those of PZT ceramics when we consider applying them to practical use in electric devices. The origin of high-piezoelectricity of PZT with the morphotropic phase boundary (MPB) compositions has been discussed in terms of the so-called polarization rotation mechanism. The polarization responds sensitively under applied electric field, and changes its direction between (001), directions in the tetragonal phase and (111)$_c$, directions in the rhombohedral phase through the monoclinic-like distorted region between the two phases. This idea has been successfully applied to the thin film of BaTiO$_3$ (BT)/SrTiO$_3$ (ST) artificial superlattices, and the large dielectric constant and remanent polarization have been observed in the BT/ST superlattices. Such enhancements of dielectric properties have been attributed to the increased lattice strain of BT caused by the lattice mismatch stress.

We are currently examining to make good use of such an artificial superlattice structure in a bulk form, i.e., a ceramic form. In our previous study, we have synthesized KNBO$_3$ (KN)/BT nanocomposite ceramics by the solvothermal method. Each ceramic grain in the nanocomposite ceramics consists of a BT nanoparticle thinly coated with KN crystals through the heteroepitaxial interface between BT and KN. Synchrotron radiation (SR) powder diffraction pattern of the nanocomposites is not reproduced by a simply mixed structure model consisting of one tetragonal BT and one orthorhombic KN. To explain the diffraction pattern, the core/multishell structure model is proposed. The structure model consists of a BT core with a bulk-like tetragonal structure, distorted BT shells, and KN shells. By analyzing the SR powder diffraction pattern in the wide angular range based on this core/multishell model, it is revealed that the tetragonality of the distorted BT gradually decreases toward the cubic structure at the boundary between BT and KN. The volume ratio of the distorted BT region changed with increasing the molar ratio of the outer KN. The volume of the distorted BT region has a maximum at KN/BT molar ratio of 0.5, and at the same ratio the dielectric constant also has a maximum value. From these results, we have proposed that the distorted interface region of BT provides a crucial contribution to the dielectric constant through the electrically soft nature. The as-synthesized KN/BT nanocomposite ceramics with KN/BT molar ratio of 0.5, in spite of the relative density of ~70%, has the large-field piezoelectric constant $d_{33}$ of 136 pC/N, which is three times larger than that of the 0.5BT–0.5KN solid solution ceramics without a heteroepitaxial interface. The result demonstrates that the heteroepitaxial region also enhances the piezoelectricity of the ceramics. By heat-treating the nanocomposites with the heteroepitaxial interface at 1000°C for 10 h, on the other hand, $d_{33}$ decreases to 62 pC/N. It is essential to investigate the crystal structure of the heat-treated nanocomposites in understanding the suppression of the piezoelectric response. In this study, the core/multishell structure of the heat-treated KN/BT nanocomposites with KN/BT molar ratio of 0.5 is revealed using the SR powder diffraction data, and the structural characteristics are discussed related to the change in the piezoelectric properties.

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2. Experimental procedure and structural analysis

KN/BT nanocomposite ceramics with KN/BT molar ratio of 0.5 was prepared by the solvothermal method, in which the KN crystal was grown on a BT nanoparticle (BT03, particle size of approximately 300 nm, Sakai Chemical Industry Co., Ltd.) through the heteroepitaxial interface by reactions in liquid at 230°C.\(^7\) Utilizing the BT nanoparticles enables us to obtain nanocomposite ceramics with high-density interface regions. SEM and TEM observation showed that the BT and KN areas were well-separated, and the stoichiometric relationships Ba/Ti = 1 and K/Nb = 1 were kept in the BT and KN areas respectively even near the heteroepitaxial interface.\(^7\)–\(^9\) The large-field piezoelectric constant \(d_{33}\) of the nanocomposite ceramics has been obtained from the S-E curve for both as-synthesized ceramics and heat-treated ones at 1000°C for 10 h.\(^9\)

The details of the KN formation on BT nanoparticles, the fabrication of the KN/BT nanocomposite ceramics, and the measurement of the S-E curve are described elsewhere.\(^7\)–\(^9\) The original ceramic plates were gently crushed to small ceramics pieces of approximately 0.1 mm in size which can be put into a glass capillary of 0.2 mm internal diameter. High-energy SR powder diffraction patterns at 300 K were recorded on an imaging plate of the large Debye–Scherrer camera installed at BL02B2 in SPring-8.\(^8\)\(^,\)\(^9\) The energy of SR was 18.5 keV [wavelength \(\lambda = 0.066900(5)\) nm]. The particle sizes of BT in the as-synthesized and heat-treated samples were estimated to be approximately 300 nm, respectively, using Scherrer’s equation from the full-width at half-maximum values of the (111) diffraction peak. Hence, it was confirmed by SR powder diffraction that the original structural characteristics of the KN/BT nanocomposite ceramics were preserved after processing them for the diffraction measurements. The crystal structure of the heat-treated KN/BT nanocomposite ceramics was analyzed by the Rietveld method using the diffraction intensity data in the range of \(\sin \theta/\lambda < 8.6\) nm\(^{-1}\) \((d > 0.058\) nm) assuming the multicomponent model in the same way as the previous study for the as-synthesized ceramics.\(^10\)

3. Results and discussion

The Rietveld profile fitting results of the as-synthesized\(^10\) and heat-treated KN/BT nanocomposites are shown in Figs. 1(a) and 1(b), respectively. The peak profile around the tetragonal-related (002) and (200) diffraction peaks is enlarged and shown in the inset. A dip between the (002) and (200) peaks observed for the as-synthesized KN/BT nanocomposites disappears for the heat-treated KN/BT nanocomposites. In the previous study,\(^10\) the diffraction pattern of the as-synthesized nanocomposites is never fitted by a simple structure model of one tetragonal BT and one orthorhombic KN. To explain the peculiar pattern of the nanocomposites, a multicomponent model which is composed of five tetragonal BTs (BT-T0 to BT-T4) with different tetragonal lattice parameters, one cubic BT (BT-C), one orthorhombic KN (KN-O), and two cubic KNs (KN-C1 and C2) with different lattice parameters is proposed. The reliability factors (\(R\)-factors) based on the weighted profile \(R_{wp}\), the Bragg intensities \(R_I\), and the structure factors \(R_F\) are \(R_{wp} = 3.05\%\), \(R_I = 2.42\%\), and \(R_F = 1.44\%\), respectively.\(^10\) In this study, first, the same multicomponent model was employed for the profile fitting of the heat-treated nanocomposites, but the calculated intensities could not reproduce the observed intensity profile in the Rietveld analysis. By comparison of profiles between Figs. 1(a) and 1(b), the emergence of a new component which would be an intermediate between BT and KN should be taken into account in the heat-treated nanocomposites shown in Fig. 1(b) because the intensity between two tetragonal-related peaks rises enormously. The KN0.5-BT0.5 solid solution has been reported to have a cubic structure.\(^13\),\(^14\) Hence, by adding the component of KN0.5-BT0.5 solid solution (KNBT-C) to the multicomponent model, a good fitting result is obtained as shown in Fig. 1(b). One may think there is no significant difference among the cubic structure models of KN-C, BT-C and KNBT-C. But the Rietveld analysis enables us to distinguish the contribution from KNBT-C from the difference in the whole angular dependence of the diffraction intensity. Heat-treatment could give deviation from stoichiometry especially near the interface area, but in this study we adopted simple stoichiometric structure models to focus attention on the essential characteristics of the lattice distortion in the nanocomposites. Finally, we reveal that the heat-treated nanocomposites consists of five tetragonal components BT-T0 to BT-T4, one BT-C, one KNBT-C, one KN-O, and one KN-C. The \(R\)-factors are enough small: \(R_{wp} = 4.38\%\), \(R_I = 2.60\%\), and \(R_F = 1.68\%\), respectively.

Each structural component derived is assigned to the core and multishell components in a single grain of the KN/BT nanocomposite using the volume ratios derived from the intensity ratios (scale factors in the Rietveld analysis) of the structure components. No obvious change in the grain size is observed by scanning electron microscope; therefore the assignment is performed under the assumption of no change in the grain diameter.\(^10\)
The results of the as-synthesized nanocomposite and heat-treated one are shown in Figs. 2(a) and 2(b), respectively. In each figure, a schematic image of the lattice shape and the direction and magnitude of the spontaneous polarization $P_S$ in each unit cell by arrows is shown in the left. The lattice parameters of BT and KN, the unit cell volumes of BT and KN, and the lattice strain $c/a$ (tetragonal unit cell) and $c_O/a_O$ (orthorhombic unit cell) of BT and KN are shown as a function of the distance from center of particle $r$. Here, $a'$ and $c'$ ($=b'$) of KN-O are the primitive lattice parameters transformed from orthorhombic ones by $a'=|a_O|$ and $c'=b'=|b_O|+c_O/2(\alpha'<90^\circ)$, respectively. The bulk lattice parameters of tetragonal BT and orthorhombic KN are indicated by broken lines.

Fig. 2. Core/multishell structure model for the KN/BT grain of (a) as-synthesized and (b) heat-treated nanocomposites. Schematic image of the lattice shape and the direction and magnitude of the spontaneous polarization $P_S$ in each unit cell by arrows is shown in the left. The lattice parameters of BT and KN, the unit cell volumes of BT and KN, and the lattice strain $c/a$ (tetragonal unit cell) and $c_O/a_O$ (orthorhombic unit cell) of BT and KN are shown as a function of the distance from center of particle $r$. Here, $a'$ and $c'$ ($=b'$) of KN-O are the primitive lattice parameters transformed from orthorhombic ones by $a'=|a_O|$ and $c'=b'=|b_O|+c_O/2(\alpha'<90^\circ)$, respectively. The bulk lattice parameters of tetragonal BT and orthorhombic KN are indicated by broken lines.

The results of the as-synthesized nanocomposite and heat-treated one are shown in Figs. 2(a) and 2(b), respectively. In each figure, a schematic image of the lattice shape and the direction and magnitude of the spontaneous polarization $P_S$ in each unit cell by arrows is shown in the left. The lattice parameters of BT and KN, the unit cell volumes of BT and KN, and the lattice strain $c/a$ (tetragonal unit cell) and $c_O/a_O$ (orthorhombic unit cell) of BT and KN are shown as a function of the distance from center of particle $r$. Here, $a'$ and $c'$ ($=b'$) of KN-O are the primitive lattice parameters transformed from orthorhombic ones by $a'=|a_O|$ and $c'=b'=|b_O|+c_O/2(\alpha'<90^\circ)$, respectively. The bulk lattice parameters of tetragonal BT and orthorhombic KN are indicated by broken lines.

The heat-treated nanocomposites include the additional component of cubic KNBT-C. The KNBT-C component is assigned at the interface between BT and KN. This means that solid-state reaction occurs between BT and KN in the grain during the heat-treatment. The volume of each core and multishell component for the as-synthesized and heat-treated KN/BT nanocomposites is summarized in Table 1. It is reasonable to think from Table 1 that the KNBT-C component in the heat-treated grain is formed by the solid-state reaction between BT and KN near the interface.
the volume increased but the tetragonality $c/a$ decreased. In the strained BT region (BT-T1–T4), the volume and $c/a$ are decreased. These results indicate that the spontaneous polarization of BT and its spatial gradient in the grain are decreased by the formation of paraelectric KNBT-C.

The deformation of dielectric materials induced by the electric field ($E$) is described by the piezoelectric (proportional to $E$), electrostrictive (proportional to $E^2$), and higher-order terms. Generally the higher-order terms have less contribution to the $E$-induced deformation. The heat-treatment changes the structural symmetry of the fraction in the grain from the piezoelectric structure with point group $4mm$ for BT-Tn and $mm2$ for KN-O to the non-piezoelectric cubic structure with $m3m$ symmetry. This means that the leading term of the $E$-induced deformation is changed from the piezoelectric one to the higher-ordered electrostrictive one by the heat-treatment. Furthermore, the volume of distorted BT region (BT-T1–T4) which enhances the dielectric constant through the electrically soft nature\(^{(10)}\) is reduced by the heat-treatment. The suppression of the piezoelectric constant through the electrically soft nature\(^{(10)}\) is reduced by the heat-treatment. Furthermore, the volume and $c/a$ are decreased. These results indicate that the spontaneous polarization of BT and its spatial gradient in the grain are decreased by the formation of paraelectric KNBT-C.

### Table 1. Volumes of each core and shell for as-synthesized and heat-treated KN/BT grains

|                | As-synthesized | Heat-treated |
|----------------|----------------|--------------|
| $V_{BT-T0}$    | 1.7            | 2.4          |
| $V_{BT-T1–T4}$ | 11             | 9.8          |
| $V_{C}$        | 1.8            | 0.75         |
| $V_{KNBT-C}$   | —              | 2.4          |
| $V_{KN-O}$     | 0.66           | —            |
| $V_{KN-C1}$    | 5.0            | 4.3          |
| $V_{KN-C2}$    | 0.72           | 0.34         |

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