Fabrication of Ferroelectric Ceramics with Multi-Layered Structure by Solvothermal Solidification Method for Introduction of Internal Electric Field

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To increase the Curie temperature ($T_C$) of barium titanate (BaTiO₃; BT) ceramics, we tried to fabricate BT complex ceramics with an internal electric field. We propose that the electric field originating from poled potassium niobate (KNbO₃; KN) layers is applied on a BT layer by injecting the BT layer between the poled KN layers. Since such multi-layered ceramics is difficult to be fabricated without forming solid solution by a conventional sintering process, we fabricated the KN-BT multi-layered ceramics by a solvothermal solidification method at 230 °C. The $T_C$ of BT layer in the fabricated KN-BT multi-layered ceramics did not changed even after poling and it is attributed to insufficiently poling of the KN layers. Therefore, we intensively investigated the polarization of KN layers to optimize the microstructures and fabrication condition of the KN-BT multi-layered ceramics. We prepared the KN ceramics with various microstructures by the solvothermal solidification method, and the poling treatment was performed. The polarization of the KN ceramics can be improved by formation of strong necks and/or a densification of the ceramics.

Key words: barium titanate, Curie temperature, multi-layered ceramics, internal electric field, low temperature process.

1. INTRODUCTION

Lead zirconium titanium oxide (Pb(Zr,Ti)O₃)-related materials are applied to various piezoelectric devices because of their high-performance piezoelectric properties. On the other hand, lead-free piezoelectric materials recently have been in demand from the viewpoint of environmental protection [1]. However, lead-free piezoelectric materials with sufficiently high dielectric constant ($d_{33}$) and Curie temperature ($T_C$) have not been developed [2,3], and their applications are limited. Barium titanate (BaTiO₃; BT) is one of the lead-free piezoelectric materials, and the high $d_{33}$ values were reported for the textured BT ceramics [4-6]. In contrast, the $T_C$ of BT, which is approximately 130 °C [7], is required to be improved without reducing the piezoelectric responses. When an electric field is applied on a BT single crystal, the tetragonal BT phase was observed above the $T_C$ of BT measured without bias [8]. This result indicates that the $T_C$ of BT can be increased by applying the electric field. Hence, to improve the $T_C$ of BT, we attempt to fabricate BT complex ceramics with an internal electric field applying on BT layers. We propose use of the electric field originating from poled ferroelectric materials, and we selected potassium niobate (KNbO₃; KN) ceramics as this secondary phase. This is because the polarization of KN ceramics is maintained up to around 430 °C [9] and is assumed to generate the electric field above the $T_C$ of BT. We tried to apply the electric field on BT by injecting the BT layer between the poled KN layers, that is, we tried to fabricate KN-BT multi-layered ceramics. The multi-layered ceramics is frequently fabricated by a tape casting method and a subsequent sintering process. However, since such KN-BT multi-layered ceramics is difficult to be fabricated without forming solid solution by the sintering process, we employed a solvothermal solidification method to fabricate ceramics at a low temperature below 250 °C. We have reported a series of studies on fabrication of the KN/BT nanocomplex ceramics with epitaxial KN/BT interface by using the solvothermal solidification method [10-15]. In this study, the green sheets containing Nb₂O₅, and BT or KN nanoparticles were prepared by the tape casting and were stacked to construct the multi-layered structure. Then, they were converted into the KN-BT multi-layered ceramics by the solvothermal reaction at 230 °C. The poling treatment was performed for the resultant KN-BT multi-layered ceramics and their temperature dependence of electric properties was investigated. However, contrary to our expectation, the $T_C$ of BT layer in the multi-layered complex ceramics did not changed even after poling, and it may be attributed to an insufficient polarization of the KN layers. To improve the poled state of the KN layers, we intensively investigated the polarization of KN layers and tried to optimize microstructures of the KN ceramics. We prepared the KN ceramics with various microstructures by the solvothermal solidification method, and the poling treatment was performed. According to the results, the polarization of the KN layers can be improved by formation of strong necks and/or a densification of the ceramics.
2. EXPERIMENTAL PROCEDURE

2.1 Fabrication of KN-BT multi-layered ceramics

BT and KN layers were prepared by stacking green sheets containing BT and KN particles, respectively, and KN-BT multi-layered ceramics were fabricated from these stacked green sheets by the solvothermal solidification method [10-15]. The BT particles (BT03, particle size ≈ 300 nm, Sakai Chemical Industry Co., Ltd.), the KN particles (particle size ≈ 350 nm, Nippon Chemical Industrial Co., Ltd.), and the Nb2O5 particles (Rare Metallic Co., Ltd.) were used as starting materials. The green sheets were prepared by tape casting of slurries containing organic additives, and Nb2O5/BT mixture with a molar ratio of Nb2O5/BT = 1/4 or Nb2O5/KN mixture with a molar ratio of Nb2O5/KN = 1/4. The resultant green sheets prepared from the Nb2O5/BT slurry are designated as “Sheets A”, whereas the green sheets prepared from the Nb2O5/KN slurry are designated as “Sheets B”. The thickness of both the Sheets A and the Sheets B was around 40 μm. Four Sheets A were sandwiched between two sets of six Sheets B and pressed at 85 MPa at 95 °C. The resultant compacts (20 × 20 mm² in size and approximately 0.5 mm in thickness) were heated at 600 °C for 1 h to remove the binder and the plasticizer in the compacts. Then, the compact was placed in a Teflon container filled with KOH (Kanto Chemical Co., Inc.) and K2CO3 (Kojundo Chemical Laboratory Co., Ltd.) ethanolic solution with a molar ratio of KOH/K2CO3 = 0.22. The concentration of K⁺ ion in the solution was adjusted to 1 M and K/Nb atomic ratio was fixed to 10. The solvothermal treatment was performed at 230 °C for 20 h in an autoclave. The obtained complex ceramics were washed with water and ethanol and dried at 80 °C.

2.2 Fabrication of KN ceramics

We also fabricated three kinds of the KN ceramics by the solvothermal solidification method. The green sheets were prepared by tape casting of slurries containing organic additives and Nb2O5/KN mixture with a molar ratio of Nb2O5/KN = 1/4. The two kinds of green sheets designated as “Sheets B” and “Sheets C” were prepared by using KN particles with a size of approximately 350 nm and 450 nm (Nippon Chemical Industrial Co., Ltd.), respectively. The green compacts were prepared by hot-pressing the stacked Sheets B and Sheets C and were heated at 600 °C for 1 h to remove the organic additives. The solvothermal treatment was performed at 230 °C for 20 h in the KOH and K2CO3 ethanolic solution (KOH/K2CO3 = 0.22, [K⁺] = 1 M, K/Nb = 10), and the KN ceramics prepared from the stacked Sheets B and Sheets C are designated as KN350 and KN450 ceramics, respectively. Then, the KN350 ceramics was heated at 1000 °C for 10 h and “heated KN350” ceramics was obtained.

2.3 Characterization

The relative density of the samples was measured by an Archimedes method. Crystal structure of the samples were investigated by an X-ray diffraction (XRD: Rigaku, Ultima IV) analysis using Cu Kα radiation. For the XRD measurement, the sample powder was prepared by grinding the compacts. Microstructures of the samples were observed by a field-emission scanning electron microscope (FE-SEM: JEOL, JSM-6500F) equipped with a backscattered electron detector and a scanning electron microscope (SEM: JEOL, JSM-6510). To prepare samples for electrical measurements, gold electrodes were formed on the top and bottom surfaces of the polished samples, and they were cut to a size of 1.5 × 4.0 × 0.5 mm². After drying at 200 °C for 3 h in vacuum, the electrical measurements were performed. Polarization-electric field (P-E) curves were measured at room temperature at 100 Hz by a ferroelectric character evaluation system. The poling of samples was carried out under a DC electric field of 8 kV/mm at 120 °C for 30 min in a silicone oil bath. The poled state was judged by a resonance-antiresonance method using an impedance analyzer (Agilent, HP4294A). Temperature dependence of dielectric properties was recorded in the range from room temperature to 500 °C by an LCR meter (Wayne Kerr, 6440B). The Tc values of one KN-BT multi-layered ceramics in poled and depoled states were measured by the consequent temperature dependence measurement. In the first cycle, the temperature dependence of the dielectric properties in poled state was recorded up to 500 °C, and the sample was depoled. After cooling, the temperature dependence of the dielectric properties in depoled state was recorded in second cycle.

3. RESULTS AND DISCUSSION

3.1 Characterization of KN-BT multi-layered ceramics

The relative density of the complex compact before and after the solvothermal treatment was 62.2% and 68.6%, respectively. The mass of the compacts also increase by the solvothermal treatment, suggesting the Nb2O5 was reacted with K⁺ ions in the reaction solution and the synthesized KN was deposited inside the compact. Figure 1 shows XRD patterns of the complexes before and after the solvothermal treatment. While the diffraction peaks identified as Nb2O5 appear in the XRD pattern of complex before the solvothermal treatment, all the diffraction peaks are identified as the perovskite phase for the complex after the solvothermal
The results of the XRD measurements also indicate the conversion reaction of Nb$_2$O$_5$ into KN.

A backscattered electron image (BEI) of the KN-BT multi-layered ceramics obtained by the solvothermal solidification method is shown in Fig.2. From the result of an energy dispersive X-ray spectroscopy (EDX) mapping analysis (data not shown), we confirmed that the region with the brighter contrast indicates the BT layer and the region with the darker contrast indicates the KN layers. It is clearly observed that the multi-layered ceramics was successfully obtained. In addition, BT layer thickness before and after solvothermal treatment was almost the same.

We investigated the poled state of the KN-BT multi-layered ceramics after the poling treatment by the maximum phase $\theta_{\text{max}}$ of impedance in the inductance region between the resonance and antiresonance frequencies. The $\theta_{\text{max}}$ of the KN-BT multi-layered ceramics after poling is $\approx 82.3$°, suggesting the sample was unpoled and the internal electric field did not exist in the KN-BT multi-layered ceramics. Therefore, it is necessary to improve the polarization of the KN layers.

3.2 Characterization of KN ceramics

To improve the polarization of the KN layers, we investigated the KN ceramics prepared by the solvothermal solidification method. According to the results of the XRD measurements, all the diffraction peaks are identified as the perovskite phase for the KN350 and the KN450 ceramics, and thus the single-phase KN ceramics were obtained by the solvothermal solidification method.

After the solvothermal treatment, the relative density increases from 61.5% to 67.4% for the KN350 ceramics and from 63.9% to 67.6% for the KN450. It suggests the conversion of Nb$_2$O$_5$ into KN, in the solvothermal condition. The relative density of the KN350 ceramics heated at 1000 °C for 10 h is 80.9% because of sintering.

Figure 3 compares the temperature dependence of the dielectric constant and loss tangent measured at 1 MHz in the temperature range from room temperature to 500 °C for the KN-BT multi-layered ceramics in poled and depoled states.

Figure 4 shows SEM images of fracture cross-sections of (a) the KN350, (b) the KN450, and (c) the heated KN350 ceramics.

Figure 5 shows the $P-E$ curves measured at 100 Hz at room temperature for the KN ceramics.
Figure 4 shows SEM images of fractured cross sections of the KN350, the KN450, and heated KN350 ceramics. It can be observed that the particles size increases and strong necks were formed among KN particles for the heated KN350 ceramics (Fig.4(c)).

The P-E curves of the KN ceramics measured at 100 HZ at room temperature are shown in Fig.5. All of the hysteresis loops show the ferroelectric behavior, and a remanent polarization, \( P_r \), of the heated KN350 ceramics is larger than the other KN ceramics.

Table I \( \theta_{\text{max}} \) values of impedance in the inductance region between the resonance and antiresonance frequencies of the various KN ceramics after the poling treatment.

<table>
<thead>
<tr>
<th></th>
<th>KN350</th>
<th>KN450</th>
<th>Heated KN350</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \theta_{\text{max}} )</td>
<td>-82.2 °</td>
<td>-82.0 °</td>
<td>+0.3 °</td>
</tr>
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Then we investigated the poled state of these KN ceramics after the poling treatment. The \( \theta_{\text{max}} \) values of impedance in the inductance region between the resonance and antiresonance frequencies are summarized in Table I. The relatively large \( \theta_{\text{max}} \) value is obtained for the heated KN350 ceramics. Therefore, the polarization of the KN ceramics can be improved by formation of strong necks and/or a densification of the ceramics. For fabrication of the KN-BT multi-layered ceramics with the internal electric field, the microstructure of the KN layer should be modified by optimizing the fabrication process.

4. CONCLUSIONS

To increase the \( T_c \) of the BT layer, we tried to fabricate the KN-BT multi-layered ceramics from the stacked green sheets containing the Nb₂O₅, and BT or KN nanoparticles by the solvothermal solidification method at 230 °C. The Nb₂O₅ was completely converted into KN in the solvothermal condition, and the KN-BT complex ceramics with the multi-layered structure was successfully obtained. Although the poling treatment was performed, the \( T_c \) of BT layer in the KN-BT multi-layered ceramics did not change even after poling. It is attributed to an insufficient polarization of the KN layer. Therefore, we investigated the KN ceramics with various microstructures by the solvothermal solidification method. According to the result of the poled state investigation, the polarization of the KN ceramics can be improved by formation of strong neck and/or a densification of the ceramics.

Reference


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