Fabrication and electrical properties of potassium excess and poor (Bi₁/₂K₁/₂)TiO₃ ceramics

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Bismuth potassium titanate, (Bi₁/₂K₁/₂)TiO₃ (BKT), ceramics were fabricated using KHCO₃ as a starting material to control K amount precisely. Then, we fabricated (Bi₁/₂K(1+x/2)TiO₃ [BKT-10000x] ceramics to clarify an effect of poor or excess K ions in BKT ceramics for physical and electrical properties. The BKT-10000 ceramics were prepared by a conventional ceramic fabrication process, and then high density ratios of about 97% were obtained in all BKT-10000 ceramics (10000x = –10–100). The precise control of K amount did not strongly affect the sinterability for BKT ceramics. On the other hand, electrical properties such as ferroelectric, strain and piezoelectric behaviors of BKT ceramics are very sensitivity to the amount of K ions. Therefore, it is very important to control the amount of K in BKT ceramics.

Key-words : Lead-free, Bismuth potassium titanate, (Bi₁/₂K₁/₂)TiO₃, Density, Electromechanical coupling factor, Piezoelectric strain constant

1. Introduction

Currently, lead-free piezoelectric materials are required from the viewpoint of environmental protection. Bismuth potassium titanate, (Bi₁/₂K₁/₂)TiO₃ (BKT), is a typical ferroelectric material with a perovskite structure of tetragonal symmetry at room temperature (RT) and a relatively high Curie temperature \( T_C \) of 380°C.⁵,¹² This indicates that BKT has considerable promise as a candidate material for lead-free piezoelectrics in a wide working temperature range. Nevertheless, there are few reports on its electrical properties owing to its low sinterability and hygroscopicity of K raw material.⁵,⁶ To address these problems, there are few reports about BKT and BKT-based ceramics. For example, it has been reported that dense BKT ceramics were obtained by Li doping or solid solution with 10 mol % BaTiO₃.⁵,⁶ And, we have fabricated dense BKT ceramics with a single-phase perovskite structure by a hot-pressing (HP) method.⁷,⁸ Furthermore, we have fabricated dense BKT ceramic by conventional ceramic fabrication process using small-particle-size TiO₂ (~0.1 μm).⁹

As the next step of fabricating dense BKT ceramic without any special processing techniques, we focused on hygroscopicity of K raw material. Generally, K₂CO₃ powder is used as a starting raw material of K source.⁵,⁶ Owing to its highly hygroscopic property, it is very difficult to accurately take into account the water content of raw K₂CO₃ powder during the weighing process, even in a dry glove box. This causes the variation of the A/B ratio in perovskite unit cell, resulting in poor sinterability and electrical properties such as ferroelectric and piezoelectric activities. In this study, therefore, KHCO₃ powder was used as the starting material instead of K₂CO₃ powder. KHCO₃ powder is insensitive to moisture, and this enables us to weight KHCO₃ powder precisely, even in air, without any water absorption.¹⁰,¹¹ Also, the A/B ratio in BKT ceramics can be carefully controlled using KHCO₃ powder. Therefore, in this study, we attempted to fabricate (Bi₁/₂K(1+x/2)TiO₃ [BKT-10000x] ceramics to clarify the effect of the amount of K ions for BKT ceramic.

2. Experimental procedure

(Bi₁/₂K(1+x/2)TiO₃ ceramics were prepared using a conventional ceramic fabrication process. Reagent-grade Bi₂O₃ (99.99%), TiO₂ (~0.1 μm) (99.9%) and KHCO₃ (99.5%) were used as starting materials. These starting powders were mixed for 10 h in ethanol with 2-mm-diameter and 10-mm-diameter zirconia balls by ball milling, followed by calcination at 200°C for 4 h, 600°C for 5 h and 950°C for 4 h in an alumina crucible. The first stage at 200°C corresponds to the decomposition of KHCO₃ into K₂CO₃ and H₂O. The second stage at 600°C is for eliminating residual carbon. Finally, the pellets were heated to 950°C to complete the reaction for forming a perovskite structure. From our preliminary work about a DTA analysis, an endothermic reaction peak was observed at 900°C, so that the calcination temperature was determined at this temperature. After calcination, the ground powder was ball-milled for 20 h and then pressed into discs of 20 mm diameter and 5 mm thickness. The bulks formed were sintered by an ordinary firing (OF) method at 1000–1060°C for 20 h in an alumina crucible in air. The crystal structures and lattice constants of the sintered ceramics were determined using an X-ray diffractometer ( Rigaku; RINT2000). These ceramics were cut and polished for various physical and electrical measurements. For the obtained ceramics, densities were measured by the Archimedes method and microstructures were observed by scanning electron microscope (SEM: Hitachi S-2400). Fired-on silver paste was used as the electrode for the determination of the dielectric, ferroelectric and piezoelectric properties of the ceramics. Temperature dependences of the dielectric constants \( \varepsilon_{\infty} \) and loss tangent tan δ were measured at 1 MHz using an automated dielectric measurement system with a multifrequency LCR meter (Agilent 4285A). \( P-E \) hysteresis loops at 10 Hz were observed using a ferroelectric testing system (Toyo Corporation; Model 6252 Rev. C) at RT. The electrical properties such as ferroelectric, strain and piezoelectric behaviors of BKT ceramics are very sensitivity to the amount of K ions. Therefore, it is very important to control the amount of K in BKT ceramics.

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strains at RT were determined using a contact-type displacement sensor (Millitron; Model 1240) at 0.1 Hz. Specimens for piezoelectric measurements were poled in a stirred silicone oil bath by applying a dc electrical field of 4 kV/mm for 5 min at 200°C. The piezoelectric properties were measured by a resonance-antiresonance method based on EMAS-6100 standards using an impedance analyzer (YHP 4294A).

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of BKT-10000x ceramics. All compositions (10000x = −3.5–100) except BKT-(−10) had single-phase perovskite structures with tetragonal symmetries. In the case of K poor composition, Bi-rich phase was appeared and it was confirmed that the impurity peak in BKT-(−10) ceramic was identified to 117 of Bi4Ti3O12 phase. From the calculation of lattice parameters for all compositions in BKT-10000x ceramics, lattice anisotropies c/a were approximately 1.020 (±0.001). Figure 2 shows relative densities as a function of K amount 10000x in BKT-10000x ceramics sintered at 1040 and 1060°C. The BKT-0 ceramic sintered at 1060°C had the highest relative density of 99%. However, BKT-3.5 and 7 ceramics were dissolution when they were sintered at 1060°C. It is probably due to the liquid phase of excess K ions. Therefore, compositions of excess K ions were sintered at 1040°C. All BKT-10000x ceramics, sintered at 1040°C, indicated high relative densities about over 97%. From these results, relative densities of BKT-10000x ceramics were almost constant regardless of excess or poor K amount. Figure 3 shows SEM microstructures of BKT-0, 20 and 100 ceramics sintered at 1060 and 1040°C.

These pictures showed homogeneous and dense microstructures. Also, microstructures and average grain sizes for BKT-0 ceramics sintered at 1060 and 1040°C indicated similar to each other. On the other hands, the average grain sizes increased with increasing the excess K amount as shown in Fig. 4. This result suggests that excess K ions acted as liquid phase to increase their grain sizes. Y. Hiruma et al. reported8) that remanent polarization $P_r$ of BKT-based ceramics increased with increasing the grain size (<1μm). Therefore, it is expected that K excess compositions such as BKT-50 and 100 have larger $P_r$ value as compared with other compositions such as stoichiometric one.

Figure 5 shows $P$-$E$ hysteresis loops of BKT-3.5 and 50 ceramics at RT. The BKT-3.5 ceramic shows fully saturated $P$-$E$ hysteresis loop. The remanent polarization $P_r$ and the coercive field $E_c$ of BKT-3.5 ceramic were about 35 $\mu$C/cm² and 50 kV/cm², respectively, when the applied field $E_a$ was about 165 kV/cm. On the other hand, the $P$-$E$ hysteresis loop of the BKT-50 ceramic was not fully saturated. The maximum applied field $E_a$ to this ceramic was 100 kV/cm due to an electrical breakdown. Then, the $P_r$ and $E_c$ of BKT-50 were 19 $\mu$C/cm² and 49 kV/cm, respectively. Figure 6 shows the remanent polarization $P_r$ as a function of K amount in BKT-10000x ceramics. The BKT-3.5 indicated the maximum $P_r$ value and then the $P_r$ decreased with increasing the excess K amount. Considering the grain size, this result is contrary to the previous discussion. One of the possible reasons is a difficulty of domain wall switching because BKT-10000x ceramics have large tetragonality c/a of about 1.02.
However, there was no significant change in lattice anisotropies $c/a$ for BKT-10000x ceramics. As the second possible reason, we focused on the resistivities $\rho$ of BKT-10000x ceramics. Figure 7 shows resistivities $\rho$ as a function of K amount in BKT-10000x ceramics. BKT-0 and BKT-3.5 ceramics had higher resistivity than the other compositions. The tendency of the $P_r$ in Fig. 6 is almost similar to that of the $\rho$ in Fig. 7. From these results, higher electric field could be applied to the BKT-0 and 3.5 ceramics as compared with other compositions, and this goes to higher $P_r$ values in these compositions.

Figure 8 shows the longitudinal strain behavior under unipolar driving of BKT-0, 3.5 and 50 ceramics. Unipolar driving is critical for the actuator driving. The longitudinal strain of BKT-3.5 ceramic was about 0.17% of the electrical field from 0 to 90 kV/cm. The normalized $d_{33}^*$ was calculated using

$$d_{33}^* \text{ [pm/V]} = \frac{\text{Strain [%]}}{E \text{ [kV/mm]}} \times 10^6$$

The normalized $d_{33}^*$ of BKT-3.5 ceramic determined from this result was 184 pm/V. Figure 9 shows compositional dependence of normalized piezoelectric strain constant $d_{33}^*$ for BKT-10000x ceramics. The normalized $d_{33}^*$ showed the highest value at BKT-3.5 and decrease with changing the K amount in BKT-10000x. From these results, normalized $d_{33}^*$ has strong compositional dependence and the precise control of K amount is important for obtaining the large $d_{33}^*$ value. This compositional tendency of $d_{33}^*$ is also similar to those of the $P_r$ and $\rho$. From these results, it is thought that the electrical charge neutrality is quite important for $d_{33}^*$ and $\rho$ in this system. In other words, this is probably related to the defect structure near by domain walls. Then, a tiny amount of excess K ions plays an important role as liquid phase for improving the sinterability and reducing the oxygen vacancies at BKT-3.5. Therefore, it seems that the BKT-3.5 showed the highest $d_{33}^*$. Figure 10 shows the frequency dependences of the impedance $|Z|$ and phase $\theta$ of the BKT-3.5 ceramic. Poling treatment was carried out under the electrical field of 4 kV/mm for 5 min at 200°C. The electromechanical coupling factor $k_{33}$ and piezoelectric constant $d_{33}$ of BKT-3.5 ceramic were 0.367 and 84.8 pC/N, respectively. The $d_{33}$ value is almost half of $d_{33}^*$. 

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**Fig. 5.** $P$-$E$ hysteresis loops of BKT-3.5, and 50 ceramics at RT.

**Fig. 6.** Remanent polarization $P_r$ as a function of K amount in BKT-10000x ceramics.

**Fig. 7.** Resistivities $\rho$ as a function of K amount in BKT-10000x ceramics.

**Fig. 8.** Longitudinal strain behavior under unipolar driving of BKT-0, 3.5 and 50 ceramics.

**Fig. 9.** Compositional dependence of normalized piezoelectric strain constant $d_{33}^*$ for BKT-10000x ceramics.
Therefore, the field induced strain and $d_{33}$ value includes the much contribution from 90° domain wall switching. The maximum phase $\theta_{\text{max}}$ of BKT-3.5 was approximately 70° in Fig. 10. BKT-based ceramics have large lattice anisotropy $c/a$ of 1.02, so that it is considered that it is very difficult for BKT to obtain a full poling state by the poling treatment. The BKT-0 indicated similar piezoelectric properties to BKT-3.5 after the same poling condition. However, we could not apply enough electric field as a poling treatment to other compositions. This is strongly related to the resistivities of the samples. Anyway, only two compositions of BKT-0 and 3.5 showed good piezoelectric properties by poling treatment because of high resistivities. Then, the measured piezoelectric properties of BKT ceramic are very sensitivity to amount of K ions.

4. Conclusions

$(\text{Bi}_{1/2}\text{K}_{1+x/2})\text{TiO}_3$ ($\text{BKT-10000}_x$), ceramics were fabricated using KHCO$_3$ as a starting material instead of K$_2$CO$_3$ powder. BKT-10000$_x$ had high density ratios of about 97% when sintered over 1040°C. The remanent polarization $P_r$ of BKT-3.5 ceramic was 35 $\mu$C/cm$^2$. The electromechanical coupling factor of BKT-3.5 ceramics was 0.367. And piezoelectric constant $d_{33}$ of BKT-3.5 ceramics was 84.8 pC/N. The BKT-0 and BKT-3.5 ceramics had good electrical properties. However other compositions had deteriorated electrical properties. Therefore, electrical properties of BKT ceramics are very sensitive to the amount of K ions. So, it is very important to control the amount of K in BKT ceramics.

References

Fig. 10. Frequency dependences of impedance $|Z|$ and phase $\theta$ of BKT-3.5 ceramic.