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Dielectric Properties of Ba$_{1-x}$Ca$_x$Ti$_2$O$_5$ Prepared by Arc Melting

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**1. Introduction**

BaTiO$_3$ (BT) is a well-known ferroelectric material exhibiting distinctly high permittivity and a Curie temperature ($T_c$) of 400 K. In the BaO-TiO$_2$ system, several TiO$_2$-rich compounds such as BaTi$_4$O$_9$ and Ba$_2$Ti$_3$O$_{20}$ are promising dielectric materials in the microwave frequency range due to a significantly small dielectric loss. BaTi$_4$O$_9$ (BT$_2$), on the other hand, has not received much attention since it has been misunderstood to be a common paraelectric compound. BT$_2$ has been thought to be unstable above 1500 K, decomposing into BT and Ba$_6$Ti$_3$O$_{20}$. Recently, our research group and Akishige et al. have independently synthesized single crystalline BT$_2$ and detected ferroelectricity in the $b$-direction. As single crystalline BT$_2$ has a high permittivity (20500) with a high Curie temperature (750 K), comparable to widely used PZT (Lead zirconium titanate), it is promising as a new lead-free high temperature ferroelectric material. In practical applications, however, polycrystalline material is preferable to single crystalline material due to its ease of manufacturing and low cost. In a previous study, we prepared (020) oriented polycrystalline BT$_2$ by arc melting. Substitution of foreign element has been commonly applied to improve and modify the performance of ferroelectric compounds. We have studied the effects of several foreign element substitutions, e.g., Sr and Zr, on the dielectric properties of polycrystalline BT$_2$ prepared by arc melting.

It has long been known that the substitution of Ca in BT is effective to modify the dielectric properties. Mitsui et al. reported that the $T_c$ of BT increased from 403.8 to 409.2 K with increasing Ca substitution until $x = 0.08$ in Ba$_{1-x}$Ca$_x$Ti$_2$O$_5$ (BCT). Chen et al. reported that the permittivity of BCT decreased with increasing Ca substitution. Tikhonovsky et al. demonstrated that Ca substitution inhibited the grain growth of BT. Jayanthi et al. reported that the lattice parameters of BT decreased with increasing Ca substitution. Wang et al. found the highest content of the Ca substitution in BT to be $x = 0.21$. In the present study, $b$-axis oriented polycrystalline Ba$_{1-x}$Ca$_x$Ti$_2$O$_5$ (BCT$_2$) was prepared by arc melting and the effect of Ca substitution on the dielectric properties of polycrystalline BCT$_2$ was investigated.

**2. Experimental**

TiO$_2$, BaCO$_3$, and CaCO$_3$ (99.9% in purity) powders were mixed in compositions of Ba$_{1-x}$Ca$_x$Ti$_2$O$_5$ ($x = 0$–0.10). The mixed powders were pressed into pellets 20 mm in diameter at 10 MPa and calcined at 1223 K for 43 ks in air. The pellets were melted on a water-cooled copper plate by arc melting in Ar. The specimens were heat-treated at 1323 K for 43 ks in air. The crystal orientation was measured by X-ray diffraction (XRD). The lattice parameters were calculated based on a least squares analysis. The Ca content ($x$) in BCT$_2$ melted specimens was analyzed by electron probe micro-analyzer (EPMA). The microstructure was observed by scanning electron microscopy (SEM) and field-emission scanning electron microscopy (FESEM). Specimens, 3 $\times$ 3 $\times$ 1 mm$^3$ in size, for dielectric measurements were cut out parallel to the copper plate. Gold paste as an electrode was painted on both sides of the specimens, and was fired at 1123 K for 300 s. The polarization ($P$)–electric field ($E$) characteristics were evaluated by Radiant RT6000HVS at room temperature. The dielectric properties were measured using an AC impedance analyzer (Hewlett Packard 4194A) at frequencies ($f$) from $10^2$ to $10^7$ Hz and temperatures from 293 to 1073 K in air.

**3. Results and Discussion**

Figure 1 shows the XRD pattern of polycrystalline BCT$_2$ at $x = 0.04$ for a powdered specimen (a) and for an as-prepared bulk specimen (b). BCT$_2$ in a single phase was obtained (Fig. 1(a)) and showed a strong orientation of (020) (Fig. 1(b)). We have previously reported that the powder XRD pattern of Sr- or Zr-substituted polycrystalline BCT$_2$ contained second phases when the substitution content was more than 0.15 and 0.01 mass%, respectively. Bulk XRD patterns of Zr-substituted polycrystalline BCT$_2$ showed no $b$-axis orientation when the Zr content was more than 0.07 mass%. In the present study, however, XRD patterns of polycrystalline BCT$_2$ showed no second phase of BCT$_2$ until $x = 0.10$. XRD patterns of polycrystalline BCT$_2$ also showed a significant $b$-axis orientation less than $x = 0.10$. 
Figure 2 shows the effect of Ca substitution on the lattice parameters of BCT$_2$. The lattice parameters linearly decreased with increasing CaO content up to around \( x = 0.08 \), obeying Vegard’s law, and then became almost constant. The decrease of lattice parameters may have been caused by the ionic radius of Ca$^{2+}$ (0.13 nm) being smaller than that of Ba$^{2+}$ (0.16 nm). The solubility limit of Ca$^{2+}$ in BT$_2$ (\( x = 0.08 \)) could be smaller than that in BT (\( x = 0.21 \)). We have previously reported that the solubility limit of Sr$^{2+}$ in BT$_2$ (\( x = 0.12 \)) was also smaller than that in BT (\( x = 1.9^{17} \)). It is known that the perovskite structure accommodates a large number of foreign elements.\(^{18} \) However, BT$_2$ has a lower symmetry structure than BT, which consists of a combination of corner- and edge-shared TiO$_6$ octahedrons.\(^{19,20} \) This may cause the smaller range of solid solution in BT$_2$.

Figure 3 depicts the Cole-Cole plot (a) and \( M' \) and \( Z' \) as functions of frequency (b) of polycrystalline BCT$_2$ (\( x = 0.10 \)) at 976 K. The Cole-Cole plots of polycrystalline BCT$_2$ showed a slightly depressed semicircle. The capacitance values associated with the semicircle can be calculated from the relationship of \( \!/\! = \!/\! \) where \( \!/\! \) (\( \!/\! = 2\pi f \)) is the angular frequency and \( \!/\! \) (\( \!/\! = RC \), \( R \): resistivity and \( C \): capacitance) is the relaxation time. The associated capacitance value was \( 4.21 \times 10^{-11} \) F at \( x = 0.10,^{21,22} \) implying a bulk response. No grain boundary or second phase response was identified in the polycrystalline BCT$_2$. The single peaks of the \( Z' \) vs. frequency plots (Fig. 3(b)) also indicated a bulk response. The peak frequency at \( Z'' \) vs. frequency plot should have been theoretically the same (\( f = 1/2\pi RC \)) as that of \( M'' \) vs. frequency plot. However, a discrepancy is often observed due to a slightly distributed \( \!/\! \), mainly resulting from a defect structure; the greater the discrepancy, the greater the defect.\(^{23} \) In the present study, the discrepancy was minimal, suggesting a less defect structure, even with a significant amount of the Ca substitution, \( x = 0.10 \).

Figure 4 shows the temperature dependence of the permittivity of BCT$_2$. The measurement deviation of \( \varepsilon_r \) in the present study was 5 to 8% at \( T < T_c \) and less than 3% at \( T > T_c \). The peak value of permittivity (\( \varepsilon_{\text{max}} \)) at the \( T_c \) changed depending on \( x \) and showed the highest value of 4950 at \( x = 0.02 \). Many researchers have studied the temperature and composition dependences of the permittivity.
of BCT. Mitsui et al.\(^{11}\) reported that Ca substitution caused almost no change in the peak height at the \(T_c\), but broadened the width of the peak of permittivity vs. temperature plot.

This could have been resulted from the distribution of \(C_{28}\) in BCT. Figure 5 demonstrates the effect of \(x\) on the \(T_c\) and the \(\varepsilon_{\text{max}}\) at \(T_c\). The \(\varepsilon_{\text{max}}\) was 2780 at \(x = 0\) and increased with increasing \(x\), showing the highest value of 4950 at \(x = 0.02\). Comparing to the \(\varepsilon_{\text{max}}\) at \(x = 0\) in the previous study (1800),\(^{9}\) the \(\varepsilon_{\text{max}}\) value in the present study was increased by modifying the mixing time of powders and slightly elongating an arc-melting time to eliminate the secondary phases of BaTiO\(_3\) and Ba\(_6\)Ti\(_{17}\)O\(_{40}\) and to improve the \(b\)-axis orientation. The \(T_c\) of BCT decreased from 750 K at \(x = 0\) to 665 K with increasing \(x\) up to 0.10. The \(\varepsilon_{\text{max}}\) of polycrystalline BCT\(_2\) showed the highest value among those of the Sr, Zr and Ta substituted polycrystalline BT\(_2\).\(^{9,10,24}\)

Figure 6 shows the temperature dependence of the electrical conductivity (\(\sigma\)) of BCT\(_2\). The \(\sigma\) of BCT\(_2\) had a linear relationship with temperature in the Arrhenius format and showed a slight decrease with Ca substitution. The activation energy of BCT\(_2\) increased slightly from 1.41 eV (\(x = 0\)) to 1.70 eV (\(x = 0.08\)).

Figure 7 shows the polarization (\(P\)) vs. electric field (\(E\)) plots perpendicular to the (010) plane at room temperature. The \(P-E\) plots showed hysteresis loops, indicating ferroelectricity. The remnant polarization (\(P_r\)) and coercive electric field (\(E_c\)) of polycrystalline BCT\(_2\) at \(x = 0.08\) were 1.6 \(\times\) 10\(^{-2}\) Cm\(^{-2}\) and 4.0 \(\times\) 10\(^6\) Vm\(^{-1}\), respectively. The \(P_t\) of polycrystalline BCT\(_2\) was larger than that of polycrystalline BT\(_2\) (\(P_t = 0.9 \times 10^{-2}\) Cm\(^{-2}\) and the \(E_c\) of BCT\(_2\) was smaller than that of BT\(_2\) (\(E_c = 0.7 \times 10^6\) Vm\(^{-1}\)). Wang et al.\(^{16}\) have reported that the highest \(P_t\) (17 \(\times\) 10\(^{-2}\) Cm\(^{-2}\)) of BCT is at \(x = 0.23\) (near the solubility limit composition.
of \( x = 0.21 \), where the electrostrictive strain (0.22\% at \( 5 \times 10^6 \text{Vm}^{-1} \)) is 157\% higher than that in pure \( \text{BaTiO}_3 \) ceramic (0.14\% at \( 5 \times 10^6 \text{Vm}^{-1} \)). With a further increase of Ca content from \( x = 0.21 \) to 0.50, the remnant polarization and electrostrictive strain decreased. They suggested that the large electrostrictive strain may originate to form a non-\( 180^\circ \) domain rotation driven by an external electric field. In the present study, the highest \( P_r \) at the solubility limit composition of \( x = 0.08 \) may have been caused by the electrostrictive strain being as high as that in BCT.

4. Conclusions

\( b \)-axis-oriented polycrystalline CaO-substituted \( \text{BaTi}_2\text{O}_5 \), \( \text{Ba}_{1-x}\text{Ca}_x\text{Ti}_2\text{O}_5 \) (BCT), was prepared by arc melting. The lattice parameters of BCT decreased with increasing \( x \) up to 0.08. The remnant polarization of BCT (1.6 \( \times \) 10\(^{-2} \) Cm\(^{-2} \)) was greater than that of polycrystalline BT (0.9 \( \times \) 10\(^{-2} \) Cm\(^{-2} \)). The maximum permittivity (\( \varepsilon_{\text{max}} \)) increased from 2780 (BT) to 4950 at \( x = 0.02 \), and then decreased with increasing \( x \). The \( T_c \) of BCT decreased from 750 to 665 K with increasing \( x \) from 0 to 0.10.

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