Effect of CaO and ZrO₂ co-substitution on dielectric properties of BaTi₂O₅ prepared by arc melting

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CaO and ZrO₂ co-substituted polycrystalline BaTi₃O₇ (Ba₁₋ₓCaₓ)(Ti₀.95Zr₀.05)O₅ (BCT,Z) was prepared by arc melting and the dielectric properties were investigated by AC impedance spectroscopy. b-direction orientation was obtained at any composition. The lattice parameters of α-, b- and c-axes first increased until x = 0.003 and then slightly decreased with increasing CaO content up to x = 0.020. The maximum permittivity of polycrystalline BaTi₃O₇ showed the highest value of 6230 at x = 0.020. The Tₚ of polycrystalline BaTi₃O₇ slightly decreased from 750 to 716 K when CaO content was increased up to 0.020.

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Ba₆Ti₁₇O₄₀ (B₆T₁₇) at equilibrium. However, it was known from XRD results that only BT₂ phase was identified and no peaks of other phases appeared in the XRD pattern as shown in Fig. 2(b), might be due to the rapid cooling avoiding the decomposition.

Figure 3 shows the SEM photos of a polished surface perpendicular to the growth direction of BCT₂Z at x = 0.006 (Fig. 3(a)) and 0.015 (Fig. 3(b)). A small amount of secondary phases of BT in white color and B₆T₁₇ in black grey color located in BT₂ matrix were identified although the XRD patterns showed no secondary phases. The sensitivity of XRD would be insufficient to detect the small amount of second phases in BCT₂Z as that reported for polycrystalline BST₂ (Sr substituted BT₂). According to a recent equilibrium phase diagram of BaO–TiO₂, a melt with the composition of BT₂ would be first solidified to a mixture of BT and B₆T₁₇. However, the BT₂ phase was obtained due to the narrow temperature range of the BT + B₆T₁₇ mixture zone and the quench of the melt in arc melting process. Nevertheless, BT and B₆T₁₇ might be precipitated as secondary phases in a small amount. Several cracks were observed in the BCT₂Z specimens. It might have been caused by two reasons: one was a significant difference of thermal expansion (α) among the α-, β- and c- directions of BT₂ (αₐ = 5.14, αₜ = 0.86 and αₖ = 12.5 × 10⁻⁶ K⁻¹ at 900 K), the other reason of the crack formation could be the difference of thermal expansion between BT₂ matrix and second phases.

Figure 4 depicts the effect of CaO content on the lattice parameters of BCT₂Z. The lattice parameters of α-, β- and c-axes first increased from 1.6895, 0.3934 and 0.9411 nm to 1.6912, 0.3935 and 0.9418 nm with increasing x up to 0.003 and then slightly decreased to 1.6908, 0.3932 and 0.9410 nm with x up to 0.020. The volume of unit cell showed the same behavior as those of the length of α, β and c. The β angle slightly decreased from 103.11° to 103.01° with increasing x up to 0.020. Since the ionic radius of Zr⁴⁺ (0.072 nm) is larger than that of Ti⁴⁺ (0.0605 nm), Zr⁴⁺ substituted in Ti⁴⁺ site would enlarge the TiO₆ octahedra and result in the increase in lattice parameters. The ionic radius of Ca²⁺ (0.13 nm) is smaller than that of Ba²⁺ (0.16 nm), Ca²⁺ substituted in Ba²⁺ site would reduce the TiO₆ octahedra and result in the decrease in lattice parameters. When the CaO content was less than x = 0.003, the increase of the lattice parameters could be caused by the effect of the Zr⁴⁺ substitution predominantly. When the CaO content was more than x = 0.003, the decrease of the lattice parameters could be caused by the effect of the Ca²⁺ substitution predominantly.
Figure 5 depicts the Cole–Cole plots of polycrystalline BCT$_2$Z and the effect of frequency on the imaginary parts of complex impedance ($Z''$) and modulus ($M''$) of polycrystalline BCT$_2$Z at 970 K with $x = 0.020$. The Cole–Cole plot of polycrystalline BCT$_2$Z showed a single, almost ideal semicircle as shown in Fig. 5(a). The capacitance value associated to the semicircle could be calculated from the relationship of $\omega RC = 1$, where $\omega (= 2\pi f)$ is an angular frequency and $\tau ( = RC, R$ is resistance and $C$ is a capacitance) is a relaxation time. The associated capacitance value was $4.8 \times 10^{-11}$ F for the specimen. It could be contributed to the response of the bulk BCT$_2$Z. The $Z''$ and $M''$ vs. frequency plots also shared only one single peak, implying the bulk response. The peak frequencies for $Z''$ and $M''$ vs. frequency plots were almost consistent with each other as shown in Fig. 5 (b). These data of present study demonstrated conclusively that the electrical properties can be represented by a single, parallel $RC$ element.$^{2,10}$

Figure 6 shows the temperature dependence of electrical conductivity ($\sigma$) of BCT$_2$Z. The $\sigma$ of poly-crystalline BCT$_2$Z had a linear relationship with temperature in the Arrhenius format and slightly decreased with increasing $x$. The activation energy of polycrystalline BCT$_2$Z was 1.52 eV independent of compositions of specimens and higher than that of BT$_2$ (1.41 eV).

Figure 7 shows the frequency dependence of the permittivity...
\((\varepsilon_r)\) of BCT\(_2\)Z at \(f = 10^5\) Hz. The permittivity of the specimens showed a peak at \(T_c\). The peak permittivity at the \(T_c\) changed depending on \(x\). The maximum permittivity (\(\varepsilon_{\text{max}}\)) of polycrystalline BCT\(_2\)Z increased from 4200 (Ba\(\text{Ti}_2\)O\(_5\)) to 6230 at \(x = 0.020\). The \(T_c\) of polycrystalline BCT\(_2\)Z slightly decreased from 750 to 716 K with \(x\) up to 0.020. The polycrystalline BCT\(_2\)Z showed higher maximum permittivity than that of BT\(_2\)Z substituted only by CaO (BCT\(_2\), \(\varepsilon_{\text{max}} = 4950\) at \(x = 0.02\)) or ZrO\(_2\) (BT\(_2\)Z, \(\varepsilon_{\text{max}} = 3050\) at \(y = 0.005\)).

4. Conclusions

(010) oriented polycrystalline (Ba\(_{1-x}\)Ca\(_x\))(Ti\(_{0.995}\)Zr\(_{0.005}\))\(_2\)O\(_5\), (BCT\(_2\)Z), were prepared by arc melting. The lattice parameters of \(a\), \(b\) and \(c\) axes first increased from 1.6895, 0.3934 and 0.9411 nm to 1.6912, 0.3935 and 0.9418 nm with increasing \(x\) up to 0.003 and then slightly decreased to 1.6908, 0.3932 and 0.9410 nm with \(x\) up to 0.020. The activation energy of polycrystalline BCT\(_2\)Z was 1.52 eV, independent of compositions of specimens. The highest maximum permittivity of BCT\(_2\)T of 6230 was obtained at \(T_c = 716\) K and \(x = 0.020\). The \(T_c\) slightly decreased from 750 to 716 K with increasing \(x\) from 0 to 0.020.

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