

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 BaTi₂O₅, (Ba_{1-x}Ca_x)(Ti_{0.995}Zr_{0.005})₂O₅, (BCT₂Z), 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 *a*-, *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 BaTi₂O₅ showed the highest value of 6230 at *x* = 0.020. The *T_c* of polycrystalline BaTi₂O₅ slightly decreased from 750 to 716 K when CaO content was increased up to 0.020.

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1. Introduction

A large number of ferroelectrics with perovskite structure such as BaTiO₃ (BT) based solid solution have been extensively studied in order to find new environment-friendly materials. BT is a common lead-free ferroelectric material and has a sharp peak of permittivity at a Curie temperature (*T_c* = 400 K).^{1)–4)} Substitution of Ba and/or Ti site is usually characterized by a shift of the *T_c* and an enhancement of permittivity. Some works have been done on effect of A- and B-sites co-substitutions on BT and several reports could be available such as Sr modified BaZr_{0.05}Ti_{0.95}O₃ ceramics (BSZT) and Ca substituted BaZr_{0.05}Ti_{0.95}O₃ ceramics (BCZT).^{5)–6)} Sen et al. reported that BT with the co-substitution of Ca²⁺ ion at the Ba-site and Zr⁴⁺ at Ti-site (Ba_{1-x}Ca_x)(Zr_{0.05}Ti_{0.95})O₃ (BCZT) has a strong effect on the dielectric properties of BT. The transition temperature of BCZT decreased and the dielectric constant also decreased with the increase of the Ca concentration.⁷⁾ Lee et al. also demonstrated that the ceramic dielectric properties of 1 mol% MnO₂ doped (Ba,Ca)(Ti,Zr)O₃ were strongly effected with the different co-substitutions content.⁸⁾ However, the *T_c* of BT was difficult to be improved in any case. Recently, our research group first prepared BaTi₂O₅ (BT₂) single crystals by a floating-zone melting method and reported the high permittivity (20500) of its ferroelectricity along the *b*-axis and a high *T_c* (750 K).⁹⁾ We have successfully obtained *b*-axis oriented polycrystalline BT₂ by arc melting and have demonstrated the effect of substitution on the dielectric properties of BT₂, i.e., Sr²⁺ and Zr⁴⁺.^{10)–12)} The substitution of foreign elements would be effective to enhance the ϵ_r or modify the *T_c*, however, no study about the effect of co-substitutions on the dielectric properties of BT₂ has been reported. Because the permittivity of ZrO₂ substituted BT₂, Ba(Ti_{1-y}Zr_y)₂O₅, showed the highest maximum permittivity of 3050 at *y* = 0.005 and *T_c* = 725 K, in the present study, *b*-axis oriented polycrystalline (Ba_{1-x}Ca_x)(Ti_{0.995}Zr_{0.005})₂O₅ (BCT₂Z) were prepared by arc melting and the effect of CaO substitution on the dielectric properties of poly-

crystalline BCT₂Z was investigated.

2. Experimental procedure

TiO₂, BaCO₃, CaCO₃ and ZrO₂ (99.9% in purity) powders were mixed in a molar ratio of (Ba + Ca) / (Ti + Zr) = 1/2, and the molar fraction (*R* = Ca / (Ba + Ca)) was changed from 0 to 0.030. 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. Then the specimens were heat-treated at 1323 K for 43 ks in air. The Ca concentration (*x*) in BCT₂Z specimens was analyzed by electron probe microanalysis (EPMA). The specimens were obtained with a composition of (Ba_{1-x}Ca_x)(Ti_{0.995}Zr_{0.005})₂O₅ (*x* = 0–0.020).

The crystal orientation was measured by X-ray diffraction (XRD, Cu K α). The lattice parameters were calculated based on a least square analysis. The microstructure was observed by scanning electron microscopy (SEM). The 3 × 3 × 1 mm specimens for dielectric measurements were cut parallel to the copper plate. Gold paste was painted on both sides and then the specimens were fired at 1123 K for 5 min to make an electrode. The dielectric properties were measured using an AC impedance analyzer (Hewlett Parckard 4194A) at frequencies (*f*) from 10² to 10⁷ Hz and temperatures from 293 to 1073 K in air.

3. Results and discussion

Figure 1 shows the relationship between the Ca concentration (*x*) in BCT₂Z as-grown specimens analyzed by EPMA and the molar fraction in raw materials (*R* = Ca / (Ba + Ca)). The *x* linearly increased from 0.002 to 0.020 with increasing *R* from 0.002 to 0.030. The Ca concentration in the bulk specimen was slightly lower than that of nominal composition of raw materials.

Figure 2 shows the XRD patterns of the bulk specimen and the ground powder of polycrystalline BCT₂Z at *x* = 0.020. The BCT₂Z specimen showed orientation of (010) plane as shown in Fig. 2(a). The orientation of the specimen even could be macroscopically observed as a significant columnar cross section. BT₂ as a metastable phase usually could be decomposed into BT and

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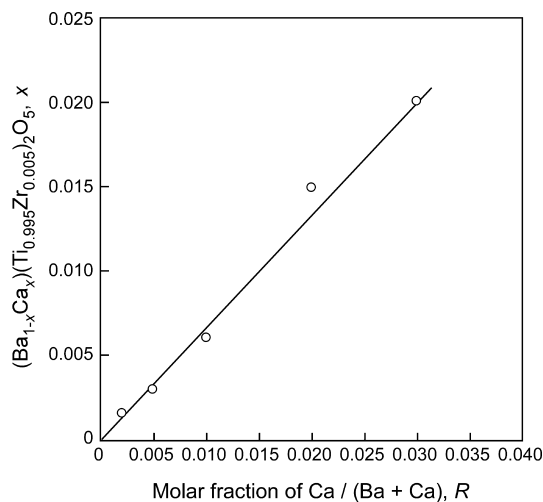


Fig. 1. Relationship between the Ca concentration (x) in BCT₂Z specimens and the molar fraction of raw materials ($R = \text{Ca} / (\text{Ba} + \text{Ca})$).

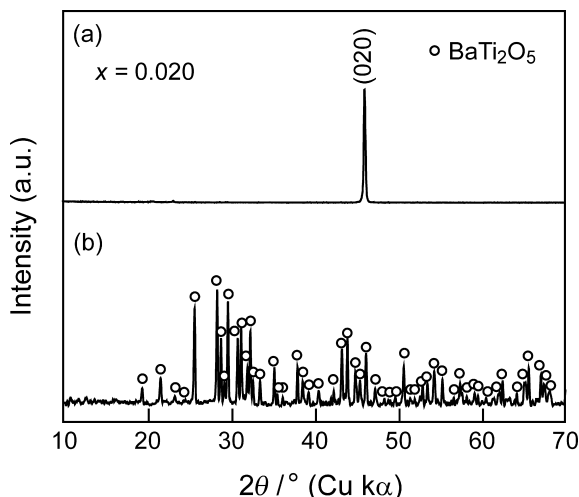


Fig. 2. XRD patterns of polycrystalline BCT₂Z at $x = 0.020$: the bulk specimen (a) and the ground powder (b).

Ba₆Ti₁₇O₄₀ (B₆T₁₇) at equilibrium.^{13,14} 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).¹¹ According to a recent equilibrium phase diagram of BaO–TiO₂,¹⁴ 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

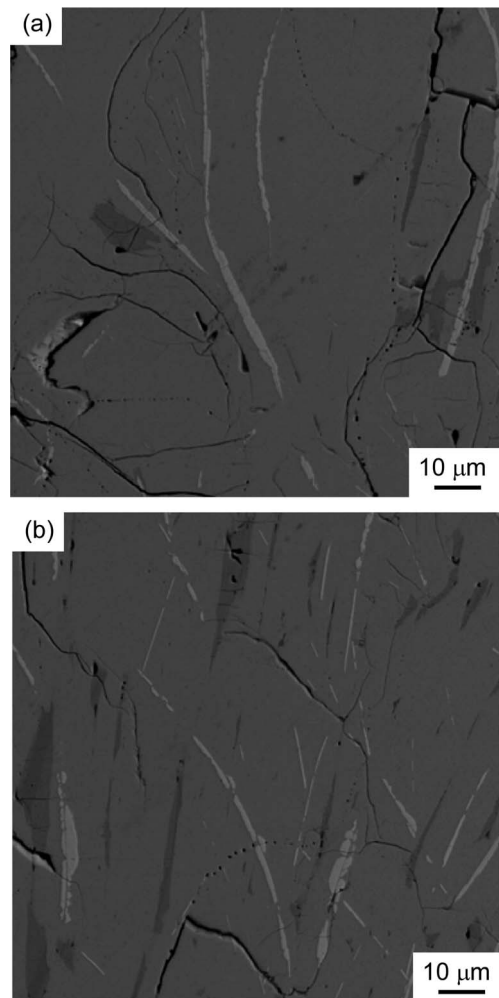


Fig. 3. Microstructure of BCT₂Z at $x = 0.006$ (a) and $x = 0.015$ (b).

specimens. It might have been caused by two reasons: one was a significant difference of thermal expansion (α) among the a -, b - and c - directions of BT₂ ($\alpha_a = 5.14$, $\alpha_b = 0.86$ and $\alpha_c = 12.5 \times 10^{-6} \text{ K}^{-1}$ at 900 K),¹⁵ the other reason of the crack formation could be the difference of thermal expansion between BT₂ matrix and second phases.¹⁶

Figure 4 depicts the effect of CaO content on the lattice parameters of BCT₂Z. 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 volume of unit cell showed the same behavior as those of the length of a , b 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),¹⁷ 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),¹⁸ 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.

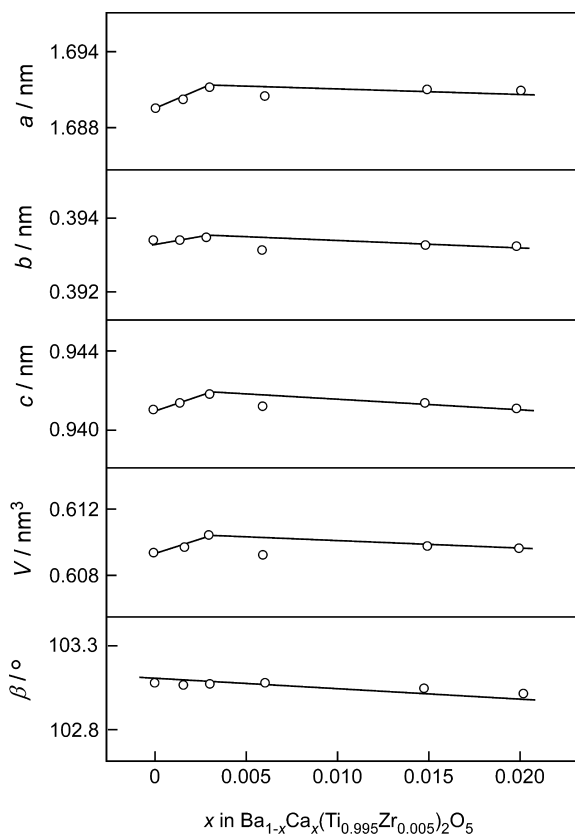


Fig. 4. Effect of CaO concentration on lattice parameters of BCT₂Z.

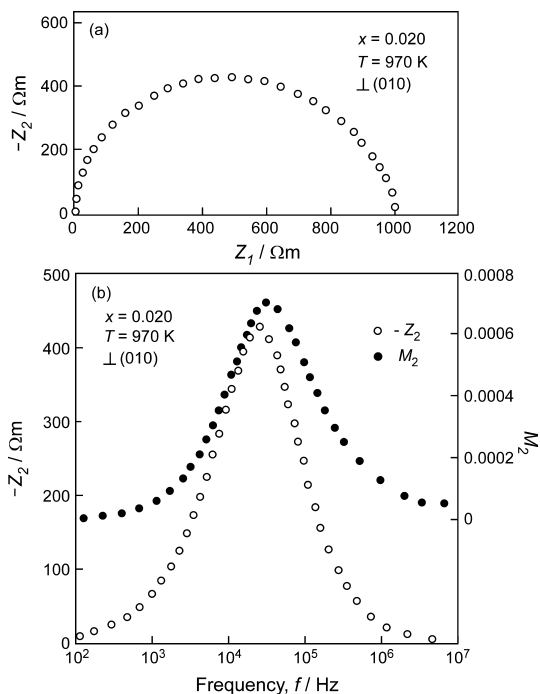


Fig. 5. Cole-Cole plots of BCT₂Z (a) and frequency dependence of $-Z''$ and M'' for BCT₂Z (b).

Figure 5 depicts the Cole-Cole plots of polycrystalline BCT₂Z and the effect of frequency on the imaginary parts of complex impedance (Z'') and modulus (M'') of polycrystalline BCT₂Z at 970 K with $x = 0.020$. The Cole-Cole plot of poly-

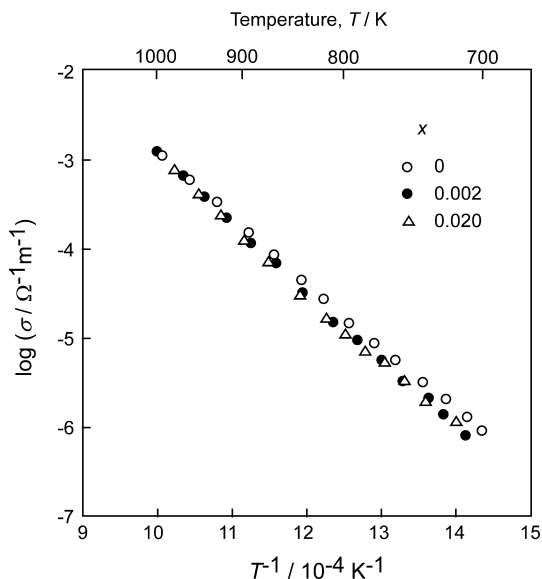


Fig. 6. Temperature dependence of σ for BCT₂Z.

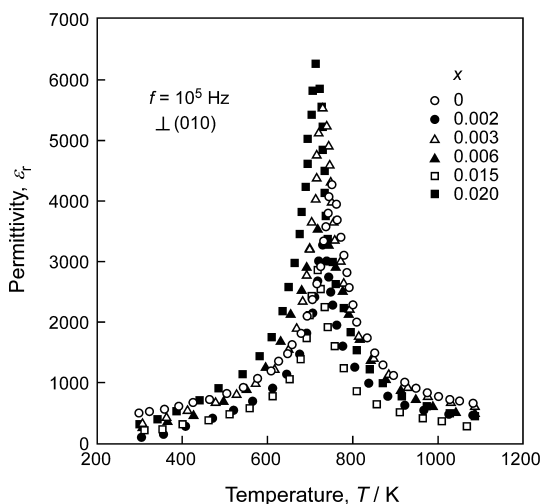


Fig. 7. Temperature dependence of ϵ_r for BCT₂Z at $f = 100$ kHz.

crystalline BCT₂Z 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 resistivity and C is a capacitance) is a relaxation time. The associated capacitance value was 4.8×10^{-11} F for the specimen. It could be contributed to the response of the bulk BCT₂Z. 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 (σ) of BCT₂Z. The σ of poly-crystalline BCT₂Z had a linear relationship with temperature in the Arrhenius format and slightly decreased with increasing x . The activation energy of polycrystalline BCT₂Z was 1.52 eV independent of compositions of specimens and higher than that of BT₂ (1.41 eV).

Figure 7 shows the frequency dependence of the permittivity

(ϵ_r) of BCT₂Z 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 (ϵ_{\max}) of polycrystalline BCT₂Z increased from 4200 (BaTi₂O₅) to 6230 at $x = 0.020$. The T_c of polycrystalline BCT₂Z slightly decreased from 750 to 716 K with x up to 0.020. The polycrystalline BCT₂Z showed higher maximum permittivity than that of BT₂ substituted only by CaO (BCT₂, $\epsilon_{\max} = 4950$ at $x = 0.02$) or ZrO₂ (BT₂Z, $\epsilon_{\max} = 3050$ at $y = 0.005$).¹²⁾

4. Conclusions

(010) oriented polycrystalline (Ba_{1-x}Ca_x)(Ti_{0.995}Zr_{0.005})₂O₅, (BCT₂Z), 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 BCT₂Z was 1.52 eV, independent of compositions of specimens. The highest maximum permittivity of BCT₂T 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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