Enhanced electrical resistivity and mechanical properties in BCTZ-based composite ceramic*

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Environmental and human health concerns about lead toxicity have prompted the development of lead-free piezoceramics. Among them, $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ (BCTZ) with excellent piezoelectric properties has the most potential and attracts extensive attention. However, lack of concern toward electrical resistivity and mechanical properties has greatly hindered its practical application. Here, we report the achievement of enhanced insulation characteristics (grain electrical resistivity increased by one order of magnitude) and superior mechanical properties (Vickers hardness value increased by 40%) in Al_2O_3 -added BCTZ composite ceramics. Such improvement can be attributed to specific composite microstructure, where the nonferroelectric second phase dispersed in the grain interior and grain boundary of BCTZ matrix results in blocking effect on the electric current paths as well as propagation of microcracks. These findings will pave a new way for the practical application of BCTZ ceramics.

Keywords: Lead-free; perovskite; composite ceramic; electrical resistivity; mechanical properties.

1. Introduction

Piezoelectric materials as a class of functional materials can respond to applied mechanical stress and vice-versa, and are widely used in actuator, sensor and energy harvesting devices.^{1–3} Due to the excellent piezoelectric properties, lead-based perovskite ferroelectrics are the most popularly used piezoelectric materials.⁴ However, they are currently facing global restrictions due to their Pb toxicity, thus, a lead-free alternative that can compete with lead-based ones is urgently needed to be designed and studied. Among the family of lead-free piezoelectric materials,⁵ BaTiO_3 -based perovskite has stood out since its solid solution $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (abbreviated as BCTZ) was reported to possess surprisingly high piezoelectric properties (e.g., $d_{33} \sim 620$ pC/N) due to the composition proximity of the morphotropic phase boundary (MPB) to the tricritical triple point, which leads to a nearly vanishing polarization anisotropy and thus facilitates polarization rotation.⁵ This discovery has stimulated intensive research on the lead-free piezoelectric ceramics, especially for $(\text{Ba,Ca})(\text{Ti,Zr})\text{O}_3$ systems. Keeble *et al.*⁶ constructed revised structural phase diagram of BCTZ system and confirmed the implication of the orthorhombic phase in reconciling the exceptional piezoelectric properties. Ehmke and Li *et al.*^{7,8} studied the effect of poling processing on the performance of the BCTZ ceramics. Tao *et al.*⁹ investigated the dielectric relaxation behavior and impedance

spectroscopic of BCTZ ceramics. Meanwhile, enhanced piezoelectric properties have also been achieved via some methods such as chemical doping or optimization of the experimental process (powder synthesis, sintering control and poling condition).^{10–13} But there are two important items which are generally neglected. One is the electrical resistivity as a ceramic needs to be fully polarized at high enough field, and the leakage current should be as low as possible for device operation.^{7,14} To the best of our knowledge, there are rare reports focused toward enhancing electrical resistivity of $(\text{Ba,Ca})(\text{Ti,Zr})\text{O}_3$ ceramics. In general, doping can greatly affect the electrical resistivity of materials.^{14,15} The donor impurities can induce A-site vacancies, contribute electrons to the conduction process and compensate O-site vacancy in the p-type electrical conduction compounds, such as PZTs, and increase their resistivity.¹⁶ Zhou *et al.*¹⁴ found that W^{6+} donor dopant decreased the conductivity in $\text{Bi}_3\text{TiNbO}_9$ piezoceramics by as much as two orders of magnitude. In addition, a composite design strategy that introduces high insulation second phase into matrix phase is also considered as an effective approach.^{17–19} Recently, Zhao and Wu investigated effects of secondary phases on the permittivity in TiO_2 ceramics, and found that the increased grain boundary resistance can be contributed to the optimized permittivity and low dielectric loss with appropriate contents of secondary phases.¹⁹ Zhou *et al.*¹⁸ found that the resistivity of $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$ piezoceramics increased about two orders of

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magnitude by adding highly insulating Al_2O_3 , leading to the higher electric field being applied during poling process.

Another aspect are the mechanical properties, which are essential for improving the working stability of devices, especially for piezoelectric vibration energy harvester,²⁰ where the piezoelectric materials experience large number of mechanical cycles and, in some situations, shock stresses. Currently, a few results toward enhancing mechanical properties of BCTZ ceramics were reported,^{21,22} and constructing composite ceramics reinforced with the second phase have been proved to be an effective means.²³ However, there is a lack of substantial discussions on the physical mechanism of mechanical performance improvement.

In this work, we are committed to improving the resistivity and mechanical properties of BCTZ ceramics. The classical $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ with superior piezoelectric properties was selected as starting composition, which was widely investigated for high-performance lead-free piezoelectric devices. However, as two major factors affecting performance in practical applications, its resistivity and mechanical properties have not been intensively studied. Here, we achieved both high electrical resistivity and good mechanical properties in BCTZ ceramics by introducing highly insulated Al_2O_3 into BCTZ ceramic matrix. As a major contributor, the formation sequence and ingredient of secondary phase were systematically studied.

2. Experimental

Lead-free BCTZ powders were synthesized by a conventional solid-state reaction technique. The calcining was performed

at 1200°C , and then the BCTZ powders were milled for 12 h. After drying, required amounts of Al_2O_3 ($x = 0\text{--}6\text{ vol.}\%$) were added to the calcined BCTZ powders and ball milled again for 12 h. Two-step sintering process was conducted to obtain dense ceramic, rate-controlled sintering was programmed at a heating rate of 300°C/h . After maintaining at 1500°C for 5 min, the temperature was rapidly decreased to 1350°C , then held for 4 h. The morphology and composition of polished samples were analyzed by field-emission scanning electron microscopy (SEM-BSE; FEI, Quanta 650, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS). Vickers indentation hardness of the materials was determined via a digital microhardness tester (HXD-1000TMC/LCD, Taiming Inc., Shanghai, China). AC impedance analysis were measured using a broadband impedance spectrometer (Novocontrol Technologies, Montabaur, Germany). Samples for piezoelectric measurements were poled in a silicone oil bath at 40°C under a DC field of 40 kV/cm for 30 min. Other detailed preparation process and measurement methods have been described elsewhere.²⁴

3. Results and Discussion

Figures 1(a)–1(c) show the AC impedance spectroscopic measured at every 20°C interval in a temperature range of $220\text{--}300^\circ\text{C}$ for Al_2O_3 added BCTZ ceramics. In the order of decreasing frequency, two arcs are corresponding to the responses of the grain and the grain boundaries, respectively.²⁵ To investigate the variation of the electrical properties of grain and grain boundary with increasing Al_2O_3 content,

Fig. 1. Complex impedance plots of BCTZ ceramics with different Al_2O_3 additions: (a) $x = 0$, (b) $x = 2$ and (c) $x = 6$.

an impedance spectroscopy fitting was applied, and the simulated results (red line) are also shown in Fig. 1. Two distinct RQ responses with smaller error can easily be observed in all temperature ranges for the pure BCTZ specimen. In contrast, arcs corresponding to the low frequency responses present a larger deviation for $x = 2$ and $x = 6$ specimens, which are attribute to more complex grain boundary structure due to the introduction of secondary phase. To further investigate effect of secondary phase on insulating properties and defect structure of grain and grain boundary, their conductivities σ_g, σ_{gb} were calculated, respectively by the following formula:²⁶

$$\sigma_g = \frac{t}{R_g \cdot A}, \quad (1)$$

$$\sigma_{gb} = \frac{t \cdot C_g}{R_{gb} \cdot A \cdot C_{gb}}, \quad (2)$$

where t is thickness of sample and A is area. R_g, C_g, R_{gb} and C_{gb} represents resistance and capacitance of grain and grain boundary, respectively. The temperature dependence of σ_g and σ_{gb} are presented in Fig. 2, the specific grain boundary conductivity was roughly four-orders of magnitude lower than the grain one. With the Al_2O_3 addition, grain conductivity shows a significant drop (about one order of magnitude), indicating existence of highly insulating phase in BCTZ ceramic matrix.¹⁴ Furthermore, we can detect the

activation energies (E_a) of the grain and grain boundary for electrical conductivity by using the Arrhenius equation:²⁷

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (3)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. Figure 2 shows the plot of $\ln \sigma_g, \ln \sigma_{gb}$ versus $1/T$, in which the solid line is fitted by Eq. (3). As can be seen, the activation energies for grain increases from 0.95 eV for $x = 0$ to 1.09 eV for $x = 2$, then to 1.10 eV for $x = 6$, which indicates reduced concentration of defect such as oxygen vacancies.⁹ As a comparison, the activation energy for grain boundary has no obvious variation with introduction of Al_2O_3 .

To uncover the origin of the evolution of conductivity as well as activation energy, microstructure analysis of specimens was conducted. Figure 3(a) gives XRD patterns of Al_2O_3 added BCTZ ceramics, and it is evident that all the samples are dominated by perovskite structure, whereas some additional peaks for Al_2O_3 added specimens appear by magnified patterns for 2θ regions around $28-29^\circ, 34-35^\circ$, as shown in Figs. 3(b) and 3(c), surprisingly, these peaks do not belong to Al_2O_3 phase. When $x = 1$, only single additional peak can be observed at 2θ near 28.8° , which can not correspond well with anyone of JCPDF. With further increase of Al_2O_3 content, peaks at 2θ near 28.3° and 34.4° emerge and gradually increase in intensity, which is consistent with diffraction lines of BaAl_2O_4 (JCPDF#17-0306). For further characterizing the phase evolution, the temperature-dependent dielectric constant and loss curves are presented in Fig. 3(d). When $x = 0$, three anomalies can be clearly observed, indicating three phase transition, which correspond to rhombohedral-orthorhombic ($R-O$) phase transition temperature T_{R-O} , orthorhombic-tetragonal ($O-T$) phase transition temperature T_{O-T} and tetragonal-cubic ($T-C$) phase transition temperature T_m , from low temperature to high temperature.⁶ With the addition of Al_2O_3 , these phase transitions become gradually diffuse, and Curie peaks present a drastically decreasing trend, which may be related to effect of nonferroelectric second phase.²⁸

To confirm the presence of BaAl_2O_4 and identify the ingredient of incipient secondary phase, backscattered electron SEM image of polished section for Al_2O_3 added ceramics and EDS analysis of different contrast regions is implemented and shown on Fig. 4. For pure BCTZ ceramic, EDS result confirm that the composition is initial BCTZ, as shown on Fig. 4(a). More importantly, some secondary phase (gray region) are dispersed in the grain boundary for $x = 1$ sample, shown on Fig. 4(b), EDS result indicates that incipient secondary phase is a compound consisted of Ba, Ca, Ti, Zr, Al and O, followed by formation of BaAl_2O_4 at matrix with $x = 2$, shown on Fig. 4(c), which could be attributed to the chemical reactions between BCTZ and Al_2O_3 occurring during high temperature sintering process.²² With further

Fig. 2. Arrhenius plots of the temperature-dependent (a) bulk and (b) grain boundary conductivities of the Al_2O_3 added BCTZ ceramic, and the fitted activation energy (E_a) values are obtained.

Fig. 3. (a) XRD patterns, enlargement of (b) $28^{\circ} \sim 29^{\circ}$, (c) $34^{\circ} \sim 35^{\circ}$ and (d) temperature dependent dielectric constant and loss curves for the Al_2O_3 added BCTZ ceramics.

increase x , content of second phase simultaneously increase and distributed in not only grain boundary triangle but also grain inside (see Fig. 4(d)). As a result, addition of Al_2O_3 result in formation of different secondary phase depend on amount of Al_2O_3 in BCTZ ceramic, small amount of Al_2O_3 can induce a new compound. However, higher amount of Al_2O_3 addition (>1 vol.%) resulted in nonferroelectric secondary phase BaAl_2O_4 . These highly insulating secondary phases locating at the grain boundaries and the smaller spherical grains being formed by Al_2O_3 addition, can reduce or even avoid pores at triangle, which can result in significant blocking effect on the electric current paths and hence enhanced electrical resistivity.¹⁸

Figure 5(a) shows the polarization–electric field (P – E) hysteresis loops of the Al_2O_3 added BCTZ composite ceramics. The pure BCTZ ceramic presents typical hysteresis loop with low coercive field E_c and a relatively high remnant

polarization (P_r). However, the P_r and maximum polarization ($P_{\max}$) decreased with increasing Al_2O_3 content, which can be attributed to the formation of nonferroelectric BaAl_2O_4 phase.^{22,28} Piezoelectric coefficient (d_{33}) and electromechanical coupling coefficient (k_p) of BCTZ composite ceramics are shown in Fig. 5(b). It is observed that the d_{33} and k_p values also gradually decrease with increasing Al_2O_3 content.²⁸

Generally, the microstructure of ceramics not only has an important influence on the electrical properties, but also will determine their mechanical properties. To evaluate the mechanical performance of Al_2O_3 added BCTZ ceramics, the indentation test was carried out. Figure 6(a) presents a representative SEM image of Vickers indentation for 1 vol.% Al_2O_3 added BCTZ ceramic. The Vickers indentation hardness H_v values were measured using a load of 1.96 N for 10 s,

Fig. 4. Backscattered electron SEM images and EDS analysis of matrix grain and the secondary phase of composite ceramics (dark color refer to the secondary phases) with different Al_2O_3 additions: (a) $x = 0$, (b) $x = 1$, (c) $x = 2$ and (d) $x = 6$.

and the corresponding fracture toughness K_{IC} was calculated using the following equation:²⁹

$$K_{\text{IC}} = \frac{0.0624P}{d^{3/2}},$$

where P is the load, d is the diagonal length of the indentation, l is the crack's vertical length measured from the tip of indentation, as marked in Fig. 6(a). Figure 6(b) gives the composition dependent H_v and K_{IC} values. For pure BCTZ sample, H_v and K_{IC} is about 4.35 GPa and 0.91 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. With the addition of Al_2O_3 , both K_{IC} and H_v value gradually increase, which are significantly higher than unadded counterpart. Classically, high H_v and K_{IC} values are considered to be related to the effect of increased grain boundaries, resulted from decreasing grain sizes (see Fig. S1, Supplementary Materials), which is consistent with the

(a)

(b)

Fig. 5. (a) Polarization–electric field (P – E) hysteresis loops and (b) d_{33} and k_p of the Al_2O_3 added BCTZ ceramics.

(a)

(b)

Fig. 6. (a) SEM image of Vickers indentation for the 1 vol.% Al_2O_3 added BCTZ ceramic and (b) the Vickers hardness and fracture toughness values of the samples with different Al_2O_3 content.

previous reports.^{30,31} In addition, secondary phase particles precipitated into BCTZ matrix, leading to undulating grain-boundary structure, which can provide additional obstacles for the movement of lattice dislocations and propagation of microcracks in the adjacent grains, may be partly contributing to the increasing K_{IC} .²¹ For sample with $x = 4$, H_v and K_{IC} reach about 6.26 GPa (increased by $\sim 40\%$ compared with initial value) and $1.06 \text{ MPa} \cdot \text{m}^{1/2}$, respectively. The H_v value achieved here is higher than that of most piezoelectric ceramics (usually below 5.00 GPa) and even comparable with fine-grained PZT-based ceramics,^{20,21,29,30} indicating that Al_2O_3 added BCTZ ceramics are potential in high quality piezoelectric application.

4. Conclusions

Enhanced electrical resistivity and superior mechanical properties were reported in BCTZ composite ceramics by the introduction of highly insulating Al_2O_3 . The results indicate that Al_2O_3 induced two kinds of secondary phase, including Al-rich BCTZ compounds and BaAl_2O_4 phases. These secondary phase distributed in not only grain boundary but also grain inside, leading to significant effect on mechanical properties and electrical properties of BCTZ ceramics. We believe that properly modified BCTZ composite ceramic with the comprehensive performance were promising candidates for lead-free piezoelectric applications.

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