Temperature-Dependent Ferroelectric and Piezoelectric Response of Yb^{3+} and Tm^{3+} co-Doped $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ Lead-Free Ceramic

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Abstract

The electrical properties of piezoelectric ceramics are temperature-dependent, which affects their potential for applications in environments with temperature variation. In this work, a Yb^{3+} and Tm^{3+} co-doped $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ (BCTZ-YT) dense lead-free ceramic was prepared using a modified polymeric precursor route. The structural characteristics were investigated by X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. The temperature-dependence of the ferroelectricity, piezoelectricity, and permittivity was studied in detail. On the basis of structural and electrical measurements at various temperatures, the mechanism of a lack of oxygen vacancies, small structural defects, and small defect dipoles was deduced. This study reveals that the ferroelectricity and piezoelectricity are temperature-dependent, whereas the capacitance is essentially unchanged with increasing temperature owing to the presence of a pure orthorhombic phase. The results of this study are expected to inform future research.

1. Introduction

Lead-free piezoelectric materials, i.e., materials based on $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$, BaTiO_3 , and BiFeO_3 , have been attracting interest because they are more environmentally friendly than lead zirconate titanate (PZT) materials [1, 2]. However, lead-free piezoelectric materials are less suitable for application in electronic devices than PZT-based materials owing to their poor piezoelectric response [3]. Thus, to improve the piezoelectricity, researchers have attempted to develop lead-free materials with specific polymorphic phase transitions or a suitable morphotropic phase boundary structure similar to that of PZT-based materials [4, 5]. Calcium and zirconium co-doped BaTiO_3 (BCTZ) is a promising candidate for use in lead-free materials; its outstanding piezoelectric constant (~ 700 pC/N) has attracted widespread attention for electronic device applications [6]. Doping the perovskite structure of BCTZ materials with rare earth elements or eutectic mixtures could reduce the internal stress and improve the electrical properties by reducing the number of defects [7, 8]. Additionally, BCTZ materials co-doped with rare earth elements have electrical properties similar to those of pristine BaTiO_3 materials, which feature phase transformations from the hexagonal, rhombohedral, or tetragonal phase to the cubic phase with increasing temperature [9, 10]. Although BCTZ materials co-doped with rare earth elements have shown excellent electrical properties, up-conversion luminescence, and thermal expansion behaviour [11–13], the temperature dependence and mechanism of the piezoelectric response have not been extensively studied, despite its importance for practical use of these materials in electronic components. Thus, in this work, the temperature-dependent electrical properties of Yb^{3+} and Tm^{3+} co-doped $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ lead-free ceramics are systematically studied. The results provide valuable insights into their application in environments with temperature variation.

2. Experimental Procedure

Stoichiometric $\text{Ba}_{0.95-x}\text{Ca}_{0.05}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3-0.7 \text{ mol\%Yb}-0.5 \text{ mol\%Tm}$ (BCTZ-YT; $x = 0.012$) lead-free ceramic nanoparticles were sintered using a modified polymeric precursor method reported in our previous work [14]. The nanoparticles were mixed with 2.5 wt.% polyvinyl alcohol and pressed by cold isostatic pressing at 200 MPa to obtain a disc-shaped green body. Then, the green body was sintered in air at 1240 °C to obtain the BCTZ-YT ceramic. Silver electrodes were coated on the ceramic to examine the electrical properties.

The phases of the sample were identified by X-ray diffraction (XRD; X'Pert-Pro, Holland) using Cu K α radiation at a 2θ scanning rate of 0.05°/s. The permittivity was measured using a dielectric measurement system (HDMS-1000V, Partulab, P.R. China). A Radiant precision workstation (RTI-Multiferroic II, USA) was used to detect the polarisation–electric field (P – E) hysteresis loops, leakage current, capacitance, and resistivity. The strain–electric field (S – E) loops were measured by an optical reflectance sensor (MTI-2100, USA).

3. Results And Discussion

Figure 1 shows the XRD pattern of the BCTZ-YT ceramic and the Rietveld-refined XRD pattern for the *Amm2* space group obtained using the Fullprof software. The sample was found to have a pure orthorhombic phase (JCPDS Card No. 81-2200) with perovskite (ABO_3) structure and no secondary phase, indicating that the ytterbium and thulium entered the ABO_3 crystal lattice successfully. The single orthorhombic phase of the BCTZ-YT ceramic was explored by Raman spectroscopy (Fig. S1), and the temperature dependence of the relative permittivity is shown in Fig. S3. The fitting parameters, $R_p = 0.037$, $R_{wp} = 0.060$, and $\chi^2 = 0.31$, indicated that the fitting procedure was highly accurate. The fitted lattice parameters were $a = 3.906 \text{ \AA}$, $b = 5.559 \text{ \AA}$, and $c = 5.577 \text{ \AA}$, and the axial angle was 90°.

A scanning electron microscopy image of the fracture surface (Fig. S2) shows that the BCTZ-YT ceramic underwent high densification (relative density, 96.37%; Table S1) and has a high fracture strength (71.43 MPa), with an average grain size of $\sim 0.92 \text{ \mu m}$. The Ba, Ca, Yb, Tm, Ti, Zr, and O in the ceramic were distributed uniformly in the structure (Fig. S2 and Table S2), and their contents were consistent with the chemical formula.

Figure S3 shows the dielectric properties of the BCTZ-YT ceramic at various frequencies. The small frequency dispersion of the permittivity indicates that the ceramic has good ferroelectricity [15]. Moreover, the low loss tangents suggested that the ceramic had high density, with small flaws (Table S2 and Fig. S2) and few oxygen vacancies (Fig. S4). The oxygen vacancy content and electron binding energy are also revealed by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S4). The mechanism of the small defect dipoles as lack of oxygen vacancies is given by Eq. 1.

The other fitted dielectric properties of the BCTZ-YT ceramic are shown in Figs. S4–S6 and Table S3. The BCTZ-YT ceramic possesses good ferroelectricity, as demonstrated by a weak diffuse phase transition (ΔT_m , 29.14 °C), where the diffuseness exponent was 1.595. To investigate the ferroelectricity and piezoelectricity of the ceramic, the polarisation–electric field (P – E) hysteresis loops (Fig. 2) and the strain–electric field (S – E) loops and piezoelectric coefficient at various temperatures (Fig. 3) were obtained. As shown in Fig. 2, the remanent polarisation (P_r) of the ceramic decreased from 6.1 to 2.4 $\mu\text{C}/\text{cm}^{-2}$ with increasing temperature (< 80 °C), and the coercive field (E_c) also decreased. The decrease in ferroelectricity (that is, the absence of typical saturated hysteresis) at high temperature was associated with the increased structural symmetry. Moreover, the continued appearance of the P – E loops at high temperature (higher than the Curie temperature, T_C) resulted from the formation of polar nanoregions in the structure [16]. The decrease in the coercive field at high temperature was attributed to easy dipole switching. Moreover, the low E_c value was attributed to the low internal stress resulting from small defects in the structure, which was consistent with the results in Figs. S3 and S4. As shown in Fig. 3, the piezoelectric response clearly decreased (from 562 to 241 pm/V) with increasing temperature. This variation was similar to that of the ferroelectricity and is attributed to the same mechanism [17].

To further investigate the structural defects in the BCTZ-YT ceramic at 20 °C, the piezoelectricity (Table S4) and thermal expansion behaviour (Fig. S7) were measured. The results were consistent with the presence of weak structural defects.

Figure 4 shows the leakage current, capacitance, and resistivity of the BCTZ-YT ceramic at various temperatures. The leakage current increased gradually with increasing temperature; this behaviour was attributed to faster charge transfer resulting from the easy dipole switching [18]. The faster charge transfer also caused the resistivity of the BCTZ-YT ceramic to decrease with increasing temperature. The leakage current and resistivity results were consistent with the analyses of Figs. 2 and 3. The capacitance of the BCTZ-YT ceramic was essentially constant at ~ 4.5 nF in a wide temperature range (-20 to 40 °C), whereas the other electrical properties temperature-dependent. The constant capacitance was attributed to the fact that only the orthorhombic phase was present in the tested temperature range, as shown in Figs. 1 and S1. Moreover, Fig. 4 shows that the capacitance increased owing to the phase transformation (Fig. S3) with increasing temperature.

4. Conclusions

A BCTZ-YT ceramic was prepared, and the temperature dependence of its electrical properties was investigated. A series of structural and electrical measurements demonstrated that the ceramic had small structural defects, few oxygen vacancies, and small defect dipoles. A formula explaining the lack of oxygen vacancies was presented. The ferroelectricity and piezoelectricity of the ceramic decreased with increasing temperature because the dipoles switched more easily at higher temperature. The leakage current of the ceramic increased with increasing temperature, whereas the resistivity showed the opposite

tendency. The capacitance was essentially constant because only a single orthorhombic phase was present, although at higher temperatures it increased with increasing temperature after a phase transformation. This work is expected to provide useful ideas for further research on the characteristics of BCTZ lead-free ceramics at various temperatures.

Declarations

Acknowledgements

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Figures

Figure 1

Detected and Rietveld-refined XRD patterns of the BCTZ-YT ceramic obtained using Fullprof software.

Figure 2

Polarisation–electric field (P–E) hysteresis loops of the BCTZ-YT ceramic. The inset show an enlarged view of a selected region (–4.9 to 0 °C) of the P–E loops.

Figure 3

Strain–electric field (S–E) loops and piezoelectric coefficient (d_{33}^* , inset) of the BCTZ-YT ceramic at various temperatures.

Figure 4

Leakage current, capacitance, and resistivity of the BCTZ-YT ceramic at various temperatures.

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