Effect of CeO2 Doping on the Properties of SrNa0.5Bi4.5Ti5O18 High-Temperature Lead-Free Piezoelectric Ceramics (Postprint)

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Abstract

SrNa0.5Bi4.5Ti5O18 + x wt% CeO2 (SNBTCx) bismuth layer-structured lead-free piezoelectric ceramics were prepared by solid-state synthesis, and the influence of CeO2 doping on the microstructure and electrical properties of SNBTCx ceramics was investigated. The results demonstrate that CeO2 doping did not alter the crystal structure of SNBTCx ceramics; all specimens exhibited a single-phase bismuth layer-structured structure. CeO2 doping did not induce significant changes in the Curie temperature of SNBTCx ceramics, with all values remaining above 560°C. As the CeO2 doping content increased, the dielectric constant of SNBTCx ceramic materials decreased, while the dielectric loss initially increased and subsequently decreased. The SNBTC0.03 ceramic with 0.3 wt% CeO2 doping content exhibited optimal electrical properties: Tc = 567°C, d33 = 29 pC/N, tanδ = 0.015. Moreover, after depolarization treatment at 500°C, its d33 remained above 22 pC/N, indicating that SNBTC0.03 ceramic is suitable for high-temperature applications.

Full Text

Preamble

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Effect of CeO_2 Doping on Properties of $SrNa_{0.5}Bi_{4.5}Ti_5O_{18}$-Based High-Temperature Lead-Free Piezoelectric Ceramics

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Abstract
Lead-free bismuth layer-structured piezoelectric ceramics of $SrNa_{0.5}Bi_{4.5}Ti_5O_{18}$

+ x wt.% CeO_2 (SNBTCx) were prepared by solid-state reaction, and the effect of CeO_2 doping on the microstructure and electrical properties of the ceramics was investigated. The results show that CeO_2 doping did not alter the crystallographic structure of the ceramics; all samples exhibited a single bismuth layer-structured phase. CeO_2 doping did not cause significant changes in the Curie temperature, which remained above 560°C for all samples. With increasing CeO_2 content, the dielectric constant decreased gradually, while the dielectric loss first increased and then decreased. The SNBTC0.03 ceramic (with 0.3 wt.% CeO_2 doping) exhibited optimal electrical properties: Tc = 567°C, d_{33} = 29 pC/N, tanδ = 0.015, and the d_{33} value remained above 22 pC/N after annealing at 500°C, demonstrating its suitability for high-temperature applications.

Keywords inorganic nonmetallic materials, high-temperature piezoelectric ceramics, bismuth layer-structured, piezoelectric properties, temperature stability

Introduction

Compared with lead-based and perovskite lead-free piezoelectric ceramics [1-3], bismuth layer-structured lead-free piezoelectric ceramics offer numerous advantages including high Curie temperature, low dielectric constant, small dielectric loss, high resistivity, excellent aging resistance, and superior high-temperature frequency stability, making them highly promising for high-temperature and high-frequency applications [4,5]. However, bismuth layer-structured lead-free piezoelectric ceramics suffer from low piezoelectric activity, high coercive field, and difficulty in poling. Consequently, researchers have conducted extensive studies on these materials [6-10].

Doping modification is a common approach to enhance piezoelectric properties. Cerium is a variable-valence element that can improve material resistivity, piezoelectric constants, and temperature stability, and is frequently used for doping modification in both perovskite and bismuth layer-structured piezoelectric ceramics [11-16]. Yan et al. [17] reported that (Li, Ce) and (K, Ce) co-substitution for A-site Ca in $CaBi_4Ti_4O_{15}$ increased the piezoelectric constant d_{33} from 7 pC/N to 20 pC/N. Ma et al. [18] also used (Li, Ce) co-doping in $NaBi_5Ti_5O_{18}$ ceramics, achieving a d_{33} value of 26.5 pC/N that remained at 19 pC/N after depolarization at 500°C. Among various bismuth layer-structured lead-free piezoelectric ceramics, $Sr_2Bi_4Ti_5O_{18}$ exhibits relatively low coercive field and higher piezoelectric activity, but its Curie temperature is only 296°C, limiting its high-temperature applications [9].

Based on these considerations, this work investigates CeO_2 doping in $SrNa_{0·5}Bi_{4·5}Ti_5O_{18}$ (SNBT) ceramics. Through external Ce doping combined with internal Na doping, we explore a new approach to enhance the Curie temperature, piezoelectric performance, and temperature stability of $Sr_2Bi_4Ti_5O_{18}$ ceramics.

1. Experimental Methods

Using Na_2CO_3 (99%), $SrCO_3$ (99%), Bi_2O_3 (99.64%), TiO_2 (99.5%), and CeO_2 (99.99%) as raw materials, $SrNa_{0.5}Bi_{4.5}Ti_5O_{18}$ + $xCeO_2$ (x = 0, 0.1, 0.2, 0.3, 0.4; weight fraction, %) ceramics were prepared by solid-state synthesis.

The raw materials were weighed and mixed by ball milling in anhydrous ethanol for 12 h using a planetary ball mill (XQM-1L, Nanjing Kexi Experimental Instrument Research Institute). The mixed powders were dried, calcined at 850°C for 2 h, then ball-milled again for 8 h using deionized water as the medium. After secondary ball milling and drying, the powders were ground thoroughly and granulated with 10 wt.% PVB solution to obtain free-flowing granules. These were dry-pressed at 230 MPa into green compacts with a diameter of 12 mm and thickness of 1 mm.

The green compacts were debindered at 800°C for 2 h, then sintered at 1140°C for 2 h to obtain dense ceramic samples. The sintered ceramics were ground, polished, and silver electrodes were applied. After firing the electrodes at 720°C for 20 min, the samples were poled in silicone oil at 180°C using an MS2671A withstand voltage tester at 30 kV/cm for 20 min.

The phase structure of SNBTCx ceramics was characterized by X-ray diffraction (D8 Advance). Microstructural morphology was observed using scanning electron microscopy (JSM-6380). Dielectric constant and dielectric loss were measured with an HP4294A precision impedance analyzer (Agilent Inc.). The piezoelectric constant d_{33} was measured using a YE2730A quasi-static d_{33} meter.

2. Results and Discussion

2.1 Phase Structure Analysis

Figure 1 [Figure 1: see original paper] shows the XRD patterns of SNBTCx ceramics in the 2 range of 20°–50°. The results indicate that external CeO_2 doping did not introduce secondary phases, and all samples exhibited a single orthorhombic bismuth layer structure with m = 5 [9]. This demonstrates that CeO_2 ions diffused into the SNBT lattice to form a homogeneous solid solution. As shown in Fig. 1 [Figure 1: see original paper]B, the main peak (1011) shifted to higher angles. This shift occurs because the doped Ce^{4+} radius (0.092 nm, coordination number 6) is smaller than the ionic radii of Sr^{2+}, Na^{+}, and Bi^{3+} (0.118, 0.102, and 0.103 nm, respectively, coordination number 6), leading to reduced unit cell volume [19]. This observation is consistent with the calculated lattice parameters. According to the Debye-Scherrer formula [20], the shift to higher angles indicates a grain growth trend with increasing CeO_2 doping content.

Figure 2 [Figure 2: see original paper] presents the variation of lattice parameters and unit cell volume with doping content x. The lattice parameter a first decreases then increases with increasing doping content, while parameter c

shows a decreasing trend. The unit cell volume V exhibits a similar decreasing behavior with increasing x. The reduction in unit cell volume results from Ce^{4+} diffusion into the lattice and substitution of partial A-site ions, causing moderate lattice distortion [21,22]. Under these conditions, domain motion becomes easier, facilitating ceramic poling and improving piezoelectric properties [23].

2.2 Microstructure

Figure 3 [Figure 3: see original paper] shows SEM micrographs of SNBTCx ceramic surfaces sintered at 1140°C for 2 h. All samples exhibit typical layered characteristics [24,25]. During sintering, the surface perpendicular to the c-axis has lower surface energy, causing grains to grow preferentially along low-energy planes. This results in faster growth rates along the a and b axes compared to the c-axis, ultimately producing a plate-like structure [26]. As shown in Fig. 3, grain size gradually increases with CeO_2 doping content, and the grains become more uniform. The grain boundaries become clearer and the surfaces denser with increasing CeO_2 content, indicating that CeO_2 doping not only promotes grain growth in SNBT ceramics but also enhances densification and suppresses defect formation, thereby optimizing the electrical properties of bismuth layer-structured lead-free piezoelectric ceramics [4,9].

2.3 Dielectric Properties

Figure 4 [Figure 4: see original paper] shows the temperature dependence of dielectric constant and dielectric loss for SNBTCx ceramics at 100 kHz. The ferroelectric-paraelectric transition temperature (Curie temperature Tc) is clearly observed. With increasing CeO_2 doping content, the Curie temperature first increases then decreases, but the variation is small (560–576°C, Fig. 5 [Figure 5: see original paper]). The change in Curie temperature of piezoelectric materials is primarily influenced by the ionic radius and electronegativity of dopant elements: Curie temperature increases with decreasing dopant ionic radius but decreases with decreasing dopant electronegativity [27]. In this study, Ce ions in the raw material CeO_2 have a +4 valence state, but Ce^{4+} may transform to Ce^{3+} during high-temperature sintering. The radii of Ce^{3+} and Ce^{4+} are 0.101 nm and 0.092 nm, respectively, which are smaller than those of Sr^{2+}, Na^{+}, and Bi^{3+} (0.118, 0.102, and 0.103 nm). Therefore, increasing CeO_2 doping should raise the Curie temperature. On the other hand, the electronegativity of Ce (1.12) is lower than the weighted average electronegativity of Sr, Na, and Bi (1.62), so increasing CeO_2 doping should lower the Curie temperature. As shown in Fig. 5, when $x < 0.1$, the effect of ionic radius dominates, causing the Curie temperature to increase with CeO_2 doping. When $x > 0.1$, the electronegativity effect becomes more significant, causing the Curie temperature to decrease with further doping.

Additionally, the dielectric constant of SNBTCx ceramics decreases with increasing CeO_2 doping content. According to Shannon's effective ionic radii [19], Ce^{3+} and Ce^{4+} radii (0.101 nm and 0.092 nm, coordination number 6) are close to

those of A-site ions. Therefore, Ce^{3+} and Ce^{4+} can substitute for Sr^{2+}, Na^{+}, and Bi^{3+} at A-sites, creating charge imbalance and A-site vacancies. Based on soft and hard doping theory, A-site vacancy generation is a soft doping effect that should increase piezoelectric constant and dielectric constant. However, excessive A-site vacancies cause excessive lattice distortion, leading to decreased dielectric constant [28]. Furthermore, the smaller ionic radii of Ce^{3+} and Ce^{4+} compared to Sr^{2+}, Na^{+}, and Bi^{3+} reduce ionic polarization [29], also decreasing the dielectric constant. As shown in Fig. 4b, the dielectric loss remains below approximately 5% from room temperature to 450°C, and for the x = 0.3 sample, the loss stays below 5% even at 500°C. This indicates excellent temperature stability of the material.

2.4 Piezoelectric Properties and Temperature Stability Analysis

Figure 6 [Figure 6: see original paper] shows the room-temperature piezoelectric constant d_{33} and its variation with annealing temperature for SNBTCx ceramics. The room-temperature d_{33} value first increases then decreases with increasing doping content, reaching a maximum of 29 pC/N at x = 0.3. This value is higher than those of other high-temperature bismuth layer-structured piezoelectric ceramics such as $SrBi_4Ti_4O_{15}$ [31], $CaBi_4Ti_4O_{15}$ [33], $SrCaBi_4Ti_5O_{18}$ [9], $SrBi_2Nb_2O_9$ [32], and $Bi_4Ti_3O_{12}$ [30]. This demonstrates that appropriate external CeO_2 doping can significantly enhance the piezoelectric activity of bismuth layer-structured ceramics by generating moderate vacancies and lattice distortion that facilitate domain wall rotation under external fields, enabling sufficient poling and improved piezoelectric performance [23,34,35].

Figure 6 also shows that the d_{33} values of SNBTCx ceramics remain stable with increasing annealing temperature, with performance degradation occurring only near 400°C for all samples. This results from increased ionic bond energy and higher binding energy between ions due to appropriate CeO_2 doping, requiring more energy to disrupt the structure and thus improving temperature stability. The most prominent temperature stability is observed for the x = 0.3 composition, which maintains d_{33} above 22 pC/N after annealing at 500°C for 30 min. This indicates that SNBTC0.3 ceramic possesses superior temperature stability and is suitable for fabricating piezoelectric devices for high-temperature applications.

3. Conclusion

SNBTCx bismuth layer-structured lead-free piezoelectric ceramics were successfully prepared by solid-state synthesis. All ceramics exhibited pure five-layer bismuth layer structure with plate-like grains that gradually increased in size and became more densely packed with increasing CeO_2 doping content. At the optimal CeO_2 doping content of 0.3 wt.%, the piezoelectric constant d_{33} reached 29 pC/N, which is higher than other high-temperature bismuth layer-structured piezoelectric ceramics. The SNBTCx ceramics exhibited high Curie temperature (Tc = 567°C) and low dielectric loss ($\tan\delta < 5\%$). The piezoelectric

constant d_{33} remained above 22 pC/N after annealing at 500°C, demonstrating that SNBTC0.3 lead-free ceramic possesses excellent temperature stability and is suitable for high-temperature, high-frequency piezoelectric device applications.

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