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ARTICLE

Microstructure and Electrical Properties of Cerium-Doped Bismuth-Layer $0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$ Piezoelectric Ceramics

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Abstract: The cerium doped $0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$ (BTO-KNN) piezoelectric ceramics were synthesized using conventional solid state processing. The effects of CeO_2 doping on the microstructure and the electrical properties of BTO-KNN ceramics were investigated. It is found that the ceramics possess a pure phase of bismuth oxide layer-type structure. The piezoelectric properties of BTO-KNN-based ceramics are significantly improved after cerium doping. The piezoelectric constant d_{33}, dielectric loss tan δ, mechanical quality factor Q_m and remanent polarization P_r for the BTO-KNN ceramics with 0.75 wt% CeO_2 dopant are found to be 28 pC/N, 0.29%, 2897, 11.83 μC/cm^2, respectively, and with high Curie temperature T_C (~615 °C) and stable piezoelectric properties, demonstrating that the cerium doped BTO-KNN piezoelectric ceramics are the promising candidates for high-temperature applications.

Key words: bismuth layer-structured; piezoelectric ceramics; microstructure; $Bi_4Ti_3O_{12}$

Since first reported by Aurivillius, bismuth layer-structured ferroelectrics (BLSFs) had been investigated extensively [1]. They are composed of pseudo-perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ blocks interleaved with bismuth oxide $(Bi_2O_2)^{2+}$ layers along the *c*-axis and have a general formula of $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A is a mono-, di-, or trivalent ion (or their combination), B is a combination of tetra-, penta-, and hexavalent ions, e.g., Fe^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, or W^{6+}, and m is the number of BO_6 octahedral (m = 1~5) [2-4].

Because of the high Curie temperature (T_C), the BLSFs can be used in high-temperature piezoelectric devices [5]. In addition, they possess low temperature coefficients of dielectric, piezoelectric properties and resonant frequency, low aging rate, and strong anisotropic electromechanical coupling factors, which make them suitable for pressure sensors and trapped energy filters, etc [6,7]. Therefore, the BLSFs, such as $Bi_4Ti_3O_{12}$, Bi_3NbTiO_9, $CaBi_2(Nb,Ta)_2O_9$, $CaBi_4Ti_4O_{15}$, $M_{0.5}Bi_{2.5}Nb_2O_9$ (M=Li, Na, K), $M_{0.5}Bi_{4.5}Ti_4O_{15}$ (M=Li, Na, K), and $SrBi_2Ta_2O_9$, have attracted much attention recently [2-23]. However, the piezoelectric activities in high T_C BLSFs were found to be very low. To improve the piezoelectric activities of bismuth layer-structured compounds, grain orientation techniques, such as hot-forging, templated grain growth, and spark plasma sintering have been proposed. Using the grain orientation technique, the piezoelectric coefficient d_{33} can be significantly improved. But it is desirable to obtain high d_{33} BLSF piezoelectric ceramics by the conventional sintering method from the viewpoint of commercial applications. It has been reported that A-site doping is more effective than B-site doping for enhancing the ferroelectric and piezoelectric properties of BLSFs, because B-site cations are similar in size and do not play a major structural role in

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the polarization process for BLSFs [13,24,25].

$Bi_4Ti_3O_{12}$ (BTO) is one of the most studied compounds among the bismuth-based layered ceramics. Its high Curie temperature (675 °C), excellent fatigue endurance and electrooptic switching behavior make it a potential candidate for application in electronic device [26]. Recently, a new bismuth titanate family compound of $0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$ (BTO-KNN) has been prepared, which exhibits relatively high piezoelectric coefficient (d_{33}= 11 pC/N) and high Curie temperature (T_C=619 °C) [27]. It is well known that cerium doping is an effective way to increase the resistivity and improve the piezoelectric property of the BLSF ceramics [2,13,16,24,28,29]. Based on above considerations, in the present paper, *A*-site cerium doped BTO-KNN ceramics were fabricated by a conventional solid state processing and their related properties were investigated.

1 Experiment

$0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$+$x$$CeO_2$($x$=0.00, 0.25, 0.50, 0.75, 1.00, 1.25, wt%) ceramics, were prepared via the traditional solid-state reaction method. High-purity oxides and carbonates, Na_2CO_3 (99.0%), K_2CO_3 (99.0%), Bi_2O_3 (99.0%), Nb_2O_5 (99.0%), TiO_2 (99.0%) and CeO_2 (99.0%) were used as the starting materials, which had been treated carefully by a drying process, particularly for Na_2CO_3 and K_2CO_3. The weighed chemicals were wet milled for 24 h in alcohol using zirconia-milling balls, and then calcined at 770 °C for 2 h. After calcination, the ball-milled powders were pressed into disk samples under a uniaxial pressure of 18 MPa. Finally, the samples were sintered at 1040 °C for 4 h. The crystalline phase of the crushed sample was identified by the X-ray methods (D8 Advanced, Bruker AXS GMBH, Karlsruhe, Germany). The microstructure evolution was observed using a scanning electron microscope (SEM, Model JSM-6700F, JEOL, Nippon Tekno Co. Ltd., Akishima, Tokyo, Japan). The temperature dependence of the dielectric constant was performed by an LCR meter in temperature range from room temperature to 700 °C (100 Hz~1 MHz). To measure the electrical properties, silver paste was painted on both sides of the samples to form electrodes, and subsequently fired at 850 °C for 15 min. After this, samples were poled in silicone oil at about 180 °C for 20~30 min under a dc electric field of 8~11 kV/mm. The d_{33} was conducted using a piezo-d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The mechanical quality factor (Q_m) and the planar electromechanical coupling coefficient (k_p) and the thickness electro- mechanical coupling coefficient (k_t) of the samples were determined by resonant (f_r) and anti-resonant frequencies (f_a) using an impedance analyzer (Agilent 4294A, Agilent Technology Inc., Santa Clara, CA). The *P*-*E* hysteresis loops were measured by a standard Sawyer-Tower circuit at 180 °C with a frequency of 1 Hz.

2 Results and Discussion

Fig.1a presents the X-ray diffraction patterns of pure and CeO_2-doped BTO-KNN piezoelectric ceramic powder. It can be seen that the highest intensity of the diffraction peak is (117) for all XRD patterns, which is consistent with the fact that the most intense reflection of BLSFs is all of the type of (112*m*+1). The ceramics have a single phase of the bismuth oxide layer-type structure with *m*=3, and no secondary phases are observed in the present range, suggesting that the Ce ions have diffused into the lattices to form solid solutions. Meanwhile, as can be seen from Fig.1b, the diffraction peaks firstly shift to higher angles slightly with increasing amount of CeO_2 and then move to lower angles with further increasing the CeO_2 content. It reveals that the interplanar spacing decreases firstly and then increases with increasing of CeO_2 content from 0 to 1.25.

Fig.2 shows the variations of the lattice parameters *a*, *b*, *c*, and unit cell volume *V* with *x*. As CeO_2 content increases, *c* and *V* firstly decrease and then increase, which is in good agreement with the diffraction peaks shift as shown in Fig.1b. From Fig.1 and Fig.2, it is found that the introduction of CeO_2 does not change the Aurivillius type orthorhombic structure. However, the doping induces the lattice distortion, which is beneficial for the piezoelectric properties.

Fig.3 shows SEM images for the surface of pure and CeO_2-doped BTO-KNN piezoelectric ceramic. It is clearly shown that the CeO_2-doped BTO-KNN ceramics exhibit the larger grain size compared to the pure BTO-KNN ceramics, indicating that the addition of CeO_2 enhances the grain growth of the ceramics. Due to high grain growth rate in the direction perpendicular to the *c*-axis of the BLSFs crystal, the

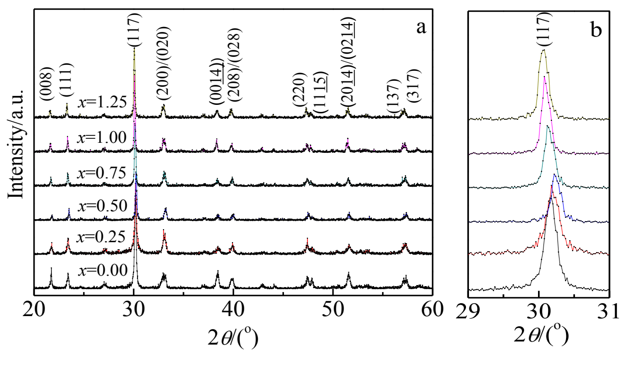

Fig.1 XRD patterns of the pure and CeO_2-doped BTO-KNN ceramics (a); enlarged XRD patterns in the range of 2θ from 29° to 31° (b)