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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 ℃) 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 ℃), 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 ℃)[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 ℃ 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 ℃ 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 ℃ (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 ℃ for 15 min. After this, samples were poled in silicone oil at about 180 ℃ 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 ℃ 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 (112m+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

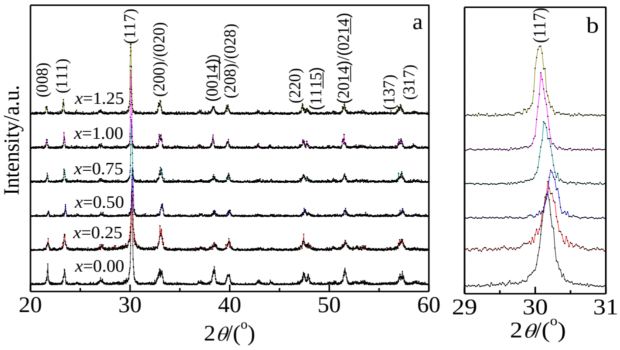

Fig.1 XRD patterns of the pure and CeO_2-doped BTO-KNN ceramics (a); enlarged XRD patterns in the range of 2θ from 29° to 31° (b)

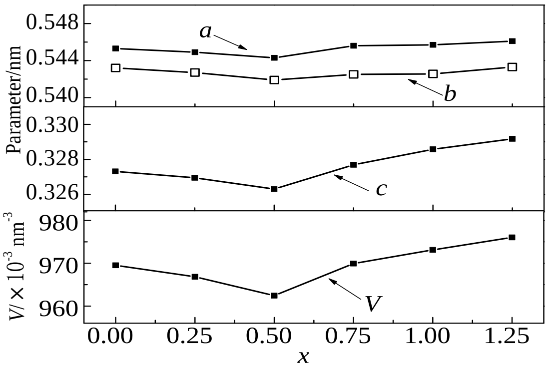

Fig.2 Lattice parameters as a function of CeO_2 content

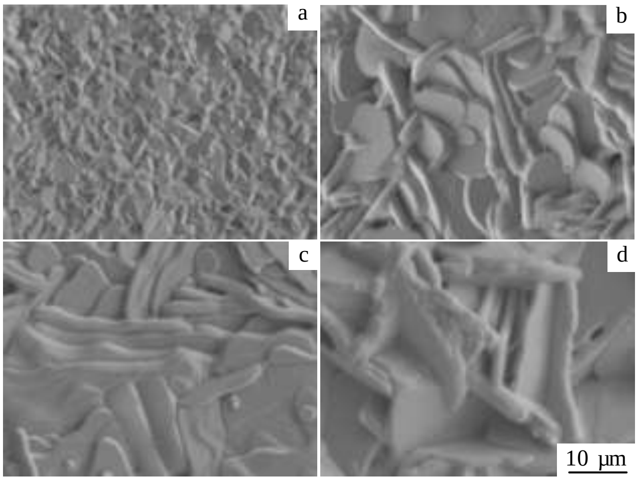

Fig.3 SEM images for the surfaces of the pure and CeO_2-doped BTO-KNN piezoelectric ceramics: (a) x=0.0, (b) x=0.50, (c) x=0.75, and (d) x=1.25

grain growth is highly anisotropic, namely, the length l of the plate-like grain is much bigger than the thickness t. Similar case had been reported for the CeO_2-doped bismuth-layer $Na_{0.5}La_{0.5}Bi_4Ti_4O_{15}$ and $K_{0.5}Bi_{4.5}Ti_4O_{15}$ ceramics [24,28].

Fig.4 shows the ferroelectric hysteresis loops of CeO_2-doped BTO-KNN ceramics under a maximum applied electrical field (E_m) of 80 kV/cm. It is found that pure BTO-KNN ceramics exhibit some conductive behavior. With increasing of CeO_2 content, the shapes of the hysteresis loop gradually become saturated. This implies that the leakage current for BTO-KNN ceramics can be depressed by the doping of CeO_2. On the other hand, with the increase of CeO_2 dopant, both the P_r (remanent polarization) and E_c (electrical field) of BTO-KNN-base ceramics monotonically increase. Compared to the pure BTO-KNN ceramic remnant polarization (P_r=8.11 μC/cm^2), the values of P_r for ceramics with x = 0.75, 1.25 are found to be 11.83 and 13.04 μC/cm^2, respectively. As a result, the introduction of CeO_2 can reduce the high leakage current and improve the ferroelectric properties, making the poling easier, therefore significantly enhancing the piezoelectric properties of BTO-KNN-base ceramics.

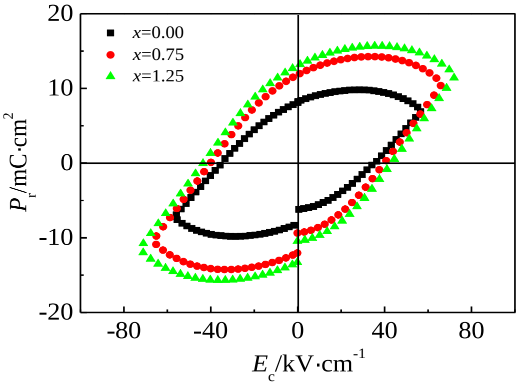

Fig.4 P-E hysteresis loops of the pure and CeO_2-doped BTO-KNN ceramics (x=0.00, 0.75, 1.25) measured at 180 ℃ and 1 Hz

The dielectric properties measured at 100 kHz as a function of temperature for BTO-KNN-base ceramics are shown in Fig.5. The inset of Fig.5 clearly shows that the Curie temperatures (T_C) of the CeO_2-doped BTO-KNN piezoelectric ceramics are found to be slightly lower than that of pure BTO-KNN ceramics, and T_C gradually decreases from 619 ℃ to 608 ℃ with increasing of CeO_2 content up to 1.25 wt%, showing that the cerium doping decreases the Curie temperature. Fig.5 also presents that the values of the dielectric loss tanδ are only about 7% when the temperature is below 500 ℃, with the temperature increasing, the dielectric loss increases slightly. The dielectric loss increases sharply when the temperature is higher than the Curie temperature.

The detailed room temperature dielectric, piezoelectric and electromechanical properties of pure and CeO_2-doped

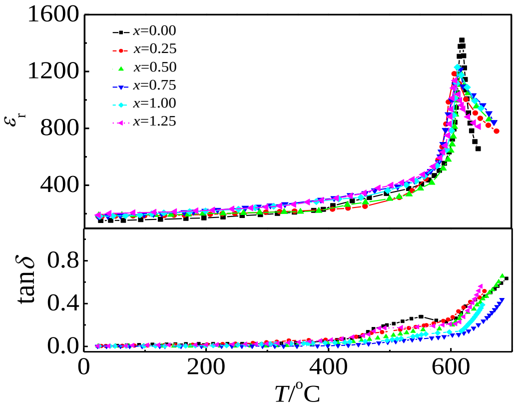

Fig.5 Temperature dependence of the ε_r and tanδ for pure and CeO_2-doped BTO-KNN piezoelectric ceramics at 100 kHz

BTO-KNN ceramics are listed in Table 1. The relative dielectric constant ε_r of the CeO_2-doped BTO-KNN materials are found to vary between 150 and 190. The dielectric loss tanδ of the doped BTO-KNN-based ceramics are found to be very low, less than 0.4%, and the ceramic (x=0.75) shows the minimum tanδ (~0.29%) with the highest d_{33} of 28 pC/N among the CeO_2-doped BTO-KNN piezoelectric ceramics, which is higher than those of other reported BLSF systems [6,11]. The increasing in the d_{33} can be attributed to the introduction of cerium. The replacement of K^+, Na^+, or Bi^{3+} by Ce^{3+}(or Ce^{4+}) creates the donors, resulting in increasing of the resistivity of the materials[30]. This is beneficial for the poling process, making the poling easier, so as to significantly improve the piezoelectric properties. The enhancement of d_{33} value in BTO-KNN-based ceramics is also due to the induced lattice distortion and decreases loss tanδ. As presented in Fig.2, the doping of CeO_2 can induce slight lattice distortion, which is also beneficial for the piezoelectric properties. So the piezoelectric properties of the CeO_2 doped BTO-KNN-based ceramics are obviously improved compared to pure BTO-KNN ceramics. However, with the cerium content further increasing, the excess cerium leads to excessive electrons, which decreases the resistivity of BTO-KNN-based ceramics, and then deteriorates the piezoelectric activities. Therefore, the d_{33} drops.

Table 1 also shows the electromechanical properties Q_m, k_p and k_t of all the BTO-KNN-based ceramics. It can be seen that the Q_m of the CeO_2-doped BTO-KNN ceramics is more than 2300, higher than that of pure BTO-KNN ceramics. This behavior is also observed in electro-mechanical coupling factors. Hence, the electrical properties of the BTO-KNN-based ceramics are greatly improved by CeO_2 doping.

The thermal annealing behavior for pure and CeO_2-doped BTO-KNN ceramics are shown in Fig.6, where d_{33} is plotted against the annealing temperature. The values of d_{33} of all the BTO-KNN-based piezoelectric ceramics show no obvious drop when the annealing temperature is lower than 400 ℃. This reveals that the BTO-KNN-based ceramics are very stable after thermal annealing. When the annealing temperature is higher than 500 ℃, d_{33} of all the BTO-KNN-based ceramics decrease sharply, and tends to zero above the Curie temperature.

Table 1 Room temperature electrical properties of pure and CeO_2-doped BTO-KNN ceramics

x	T_C/℃	ε_r	tanδ/%	d_{33}/pC·N^{-1}	Q_m	k_p/%	k_t/%
0.0	619	151	0.45	11	1216	4.52	10.13
0.25	618	179	0.39	16	2352	5.01	15.54
0.50	616	189	0.32	23	2519	5.72	18.62
0.75	615	180	0.29	28	2897	6.22	21.72
1.00	612	181	0.31	25	3187	6.05	20.07
1.25	608	190	0.33	21	3031	5.85	19.53

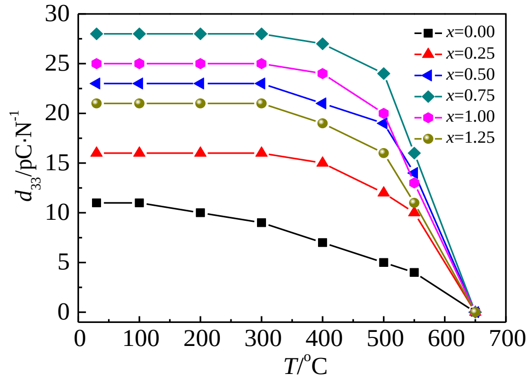

Fig.6 Effect of annealing temperature for 1 h on d_{33} of pure and CeO_2-modified BTO-KNN piezoelectric ceramics

3 Conclusions

1) The BTO-KNN piezoelectric ceramics with CeO_2-modification can be synthesized using conventional solid state processing.

2) The ceramics exhibit a single phase of bismuth layer-structured structure.

3) The piezoelectric properties of BTO-KNN-based ceramics are significantly enhanced and the dielectric loss decreased by cerium doping.

4) T_C shifts to low temperature slightly with increasing of cerium doping.

5) d_{33} and Q_m of the BTO-KNN ceramics with 0.75 wt% CeO_2 are found to be 28 pC/N and 2897, respectively, with high T_C (~615 ℃), demonstrating that the cerium doped BTO-KNN piezoelectric ceramics are the potential materials for high-temperature applications.

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Ce 掺杂 $0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$ 铋层状压电陶瓷结构与性能研究

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摘　要：采用传统固相法制备了CeO_2掺杂$0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$ (BTO-KNN) 铋层状陶瓷材料。系统研究了CeO_2掺杂对BTO-KNN基陶瓷物相结构、微观结构以及电性能的影响。结果表明：所有陶瓷样品均为单一的铋层状结构；BTO-KNN基陶瓷的压电性能随着CeO_2的掺杂而显著提高，损耗明显降低。当CeO_2掺量为0.75 % (质量分数) 时，样品具有最佳的电性能: d_{33}=28 pC/N，介电损耗tanδ=0.29%，机械品质因数Q_m=2897，剩余极化强度P_r=11.83 μC/cm^2，且居里温度 T_C 高达615 ℃；研究结果表明CeO_2掺杂$0.9Bi_4Ti_3O_{12}$-$0.1K_{0.5}Na_{0.5}NbO_3$铋层状陶瓷是一种潜在的高温陶瓷材料。

关键词：铋层状；压电陶瓷；微观结构；$Bi_4Ti_3O_{12}$

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