

Effect of an oxygen treatment on the structure and dielectric property of BiFeO₃-doped Na_{0.47}Bi_{0.47}Ba_{0.06}TiO₃ lead-free ceramics

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BiFeO₃-doped Na_{0.47}Bi_{0.47}Ba_{0.06}TiO₃ lead-free ceramics were prepared by a solid state reaction method. The ceramics obtained were annealed in a nitrogen atmosphere (N₂) and dipped in hydrogen peroxide ambient (H₂O₂). The different processes of the oxygen treatment had an obvious effect on the X-ray diffraction (XRD) peak positions of the ceramics. No obvious variation in the microstructure was found between the N₂-annealed and H₂O₂-dipped ceramics. The changes in the dielectric property of the ceramics with different processes of oxygen treatment are discussed according to the variation of the oxygen vacancy concentration.

Key words: Bismuth sodium titanate, Structure, Dielectric property, Oxygen treatment.

Introduction

Bismuth sodium titanate (Bi_{0.5}Na_{0.5}TiO₃, NBT), as one of the lead-free ferroelectrics, has attracted considerable attention in recent years owing to environmental protection concerns. Various NBT-based ceramics have been studied, such as NBT-BaTiO₃ [1], NBT-BaTiO₃-K_{0.5}Bi_{0.5}TiO₃ [2], NBT-BaTiO₃-(K_{0.5}Na_{0.5})NbO₃ [3], NBT-BaTiO₃-Nd₂O₃ [4], NBT-Bi_{0.5}K_{0.5}TiO₃-BiFeO₃ [5-6], NBT-BiFeO₃ [7-8], NBT-Bi_{0.5}K_{0.5}TiO₃-Nb [9], etc. Among them, (1-x)NBT-xBaTiO₃-based ceramics have a rhombohedral-tetragonal morphotropic phase boundary (MPB) near x = 0.06 [1-4]. The excellent electrical properties of the (1-x)NBT-xBaTiO₃-based ceramics are always attributed to (Bi_{0.5}Na_{0.5})²⁺ ions, especially Bi³⁺ ions, at the A-sites of the ABO₃ perovskite structure [10]. So, doping of BiFeO₃ into NBT-based ceramics can influence their electrical properties [5-8].

Oxygen vacancies are very important in determining the electrical properties of oxide ceramics. Jiang et al. [11] found that oxygen vacancies could restrain the transition of the ferroelectric phase to the antiferroelectric phase in Mn-doped (Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO₃ ceramics. Sintering (Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O₃ ceramics in a protective atmosphere could increase the dielectric constants [12]. Fisher et al. [13] reported that (K_{0.5}Na_{0.5})NbO₃ ceramics with a high oxygen vacancy concentration demonstrated an increased degree of diffuseness of the phase transitions between the orthorhombic-tetragonal and tetragonal-cubic phases.

Generally, the oxygen vacancy concentration in ceramics can be efficiently increased or decreased when processed in an oxygen deficient or oxygen sufficient ambient, respectively [12-14]. In this study, the BiFeO₃-doped Na_{0.47}Bi_{0.47}Ba_{0.06}TiO₃ lead-free ceramics were annealed in a nitrogen atmosphere and dipped in a hydrogen peroxide ambient. The effect of these different processes of oxygen treatment on the structure and dielectric property was studied.

Materials and Experimental Methods

The xBiFeO₃-(1-x)Na_{0.47}Bi_{0.47}Ba_{0.06}TiO₃ (x = 0.005 and 0.05, denoted as NBT/0.005BF and NBT/0.05BF, respectively) ceramics were prepared using a conventional solid state reaction method. Raw materials of BaCO₃, TiO₂, Na₂CO₃, Bi₂O₃, and Fe₂O₃ powders (purity > 99%) were weighed according to the chemical formula and then ball-milled for 5 h in a Fritsch Vario-Planetary ball milling system. The milled powders were calcined at 800 °C for 2 h. The calcined powders were pulverized with approximately 5 wt% polyvinyl alcohol. Pellets 11.5 mm in diameter and approximately 1.5 mm in thickness were pressed at a uniaxial pressure of 200 MPa. The binder in the pellets was burned out at 500 °C for 2 h, and sintered at 1170 °C for 2 h in air. Heating and cooling rates were 3 °C per minute. All pellets were embedded in powders with the same composition and placed in covered alumina crucibles during the sintering. The ceramics obtained were mechanically polished using fine-grained emery paper under cold-water circulation to reduce the thickness of pellets to about 0.8 mm. The pellets were then divided into two. One was annealed in a nitrogen atmosphere (N₂) at 600 °C for 72 h to reduce the oxygen content in

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the ceramic. The other was dipped in a hydrogen peroxide ambient (H_2O_2) for 72 h to diffuse oxygen into the ceramics and then baked at 100 °C for 10 minutes to get rid of the water.

X-ray diffraction (XRD) was carried out on a Rigaku D/Max 2550 with $\text{Cu K}\alpha$ radiation. Microstructural characterization was performed with a scanning electron microscope (SEM) (Quanta 200, FEI Co., Eindhoven, Netherlands). Silver electrodes were coated and fired at 500 °C for 30 minutes. Dielectric measurements were performed using an Agilent E4980A precision LCR.

Results and Discussion

Fig. 1(a) shows XRD patterns of the ceramics with different processes of oxygen treatment. All ceramics exhibit typical diffraction peaks of the ABO_3 perovskite phase. No second phase is observed. One distinguishable feature induced by the different processes of oxygen treatment is noted. The XRD peak positions shift due to the different processes of oxygen treatment. A magnified view of peaks corresponding to the maximum intensity is shown in Fig. 1(b). For a given x, one can find that the ceramic annealed in N_2 shifts the peak position towards a higher diffraction angle direction compared with a specimen dipped in H_2O_2 . For a given process of oxygen treatment, the ceramic shows a decreased peak position as x increases from 0.005 to 0.05.

The above phenomena are tentatively explained according to two converse effects on the crystal structure caused by the incorporation of Fe^{3+} ions and the different processes of oxygen treatment. According to Shannon's effective ionic radii with a coordination number of six, Fe^{3+} has a radius of 0.0645 nm, which is close to that of Ti^{4+} (0.0605 nm) [15]. Therefore, Fe^{3+} can enter into the sixfold coordinated B site of the perovskite structure to substitute for Ti^{4+} because of radius matching. The substitution of the relatively larger Fe^{3+} for the relatively smaller Ti^{4+} can lead to an

enlargement of the unit cell. On the other hand, oxygen vacancies are created to maintain the overall electrical neutrality as Fe^{3+} ions substitute for Ti^{4+} ions. From the viewpoint of crystal chemistry, the generation of oxygen vacancies results in a contraction of the unit cell. The oxygen vacancy concentration can be efficiently decreased when processed in an oxygen sufficient ambient while increased when processed in the oxygen deficient ambient [12-14]. So, it can be expected that the oxygen vacancy concentration in the ceramics annealed in N_2 should be higher than that in their counterparts dipped in H_2O_2 . This can be proved by the shift of the XRD peak positions of the NBT/0.005BF or NBT/0.05BF ceramics annealed in N_2 towards a higher diffraction angle direction compared with those dipped in H_2O_2 . The NBT/0.05 ceramic dipped in H_2O_2 shows a decreased peak position compared with the NBT/0.005 ceramic dipped in H_2O_2 . Both samples have been dipped in H_2O_2 , which should have reduced the oxygen vacancies. The amount of Fe^{3+} ions dissolved in the NBT/0.05 ceramic is higher than that in the NBT/0.005 ceramic. In this case, the radius effect is presumably responsible for the shift of the peak positions to lower diffraction angle directions. For the ceramics annealed in N_2 , both NBT/0.005BF and NBT/0.05 ceramics should have a higher oxygen vacancy concentration. The competing effect between the oxygen vacancy effect and radius effect could be assigned to the difference in the XRD peak positions between the NBT/0.005 and NBT/0.05 ceramics annealed in N_2 . From Fig. 1 one can suggest that the changes in XRD peak positions give an evidence for the dissolution of Fe^{3+} into the $\text{Na}_{0.47}\text{Bi}_{0.47}\text{Ba}_{0.06}\text{TiO}_3$ structure and a variation in the oxygen vacancy concentration.

Fig. 2 shows SEM images of surfaces of the ceramics with different processes of oxygen treatment. Almost no pores are found on surfaces and all ceramics are dense, corresponding to high relative densities (> 95%). Average grain sizes of the ceramics were determined by

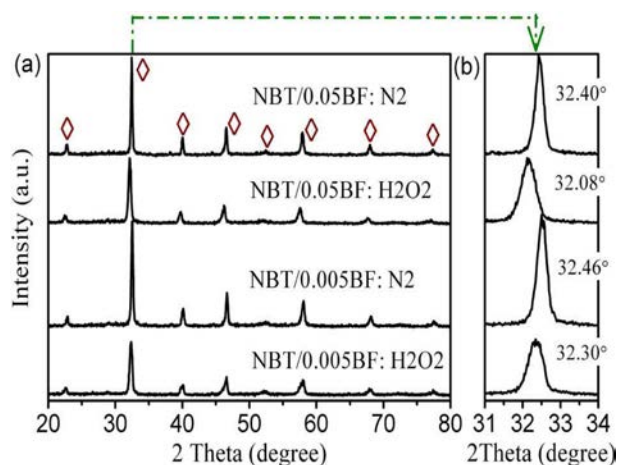


Fig. 1. XRD patterns of the ceramics with different processes of oxygen treatment (a), and patterns at 2θ between 31–34 °(b). The symbol (◊) in (a) demonstrates the perovskite structure.

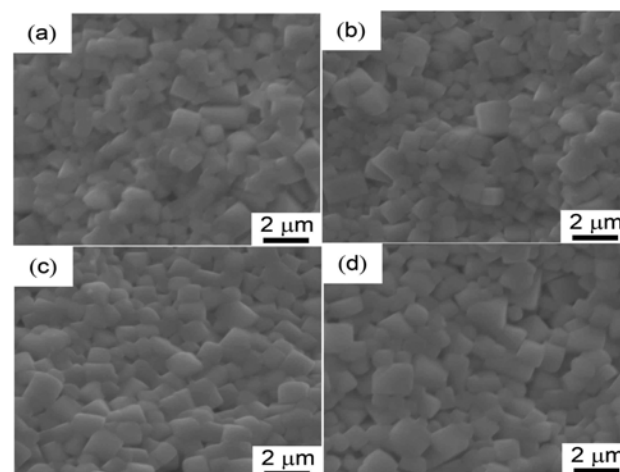


Fig. 2. SEM images of the surfaces of the NBT/0.005BF dipped in H_2O_2 (a) and annealed in N_2 (b); NBT/0.05BF dipped in H_2O_2 (c) and annealed in N_2 (d).

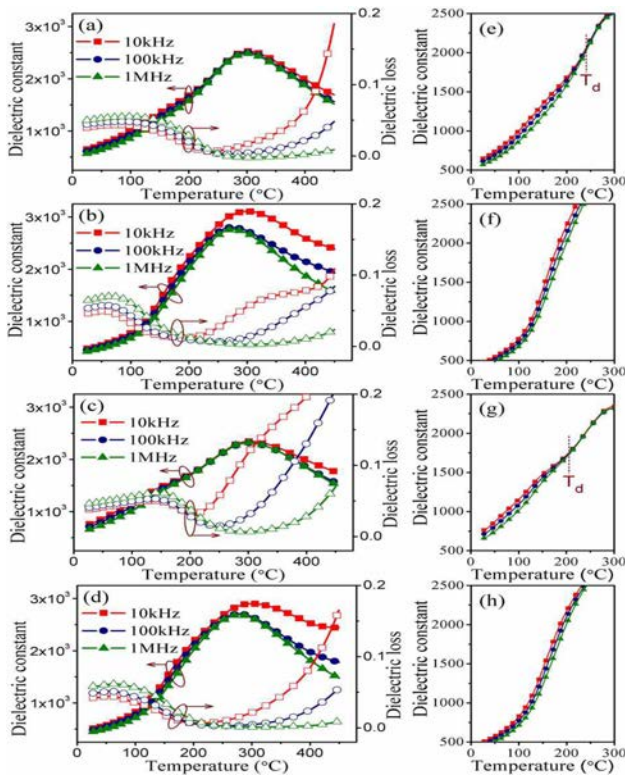


Fig. 3. Dielectric constant and dielectric loss vs. temperature at frequencies of 10 kHz, 100 kHz and 1 MHz for the NBT/0.005BF dipped in H₂O₂ (a) and annealed in N₂ (b); NBT/0.05BF dipped in H₂O₂ (c) and annealed in N₂ (d). The enlarged curves of dielectric constant between 0–300 °C are shown in (e, f, g, h) corresponding to (a, b, c, d), respectively.

the line intercept method. The NBT/0.005BF ceramics with different oxygen treatments have a similar grain size of about 1.1 μm. The NBT/0.05BF ceramics with different oxygen treatments also have a similar grain size of about 1.4 μm. So, the different processes of oxygen treatment show a negligible effect on the mean grain size of the ceramics with a given x.

Fig. 3(a–d) shows variations in the dielectric constant and the dielectric loss of the ceramics with different processes of oxygen treatment as a function of temperature. The enlarged curves of the dielectric constant between 0–300 °C are shown in Fig. 3(e–h) corresponding to (a–d), respectively. For the ceramics dipped in H₂O₂ (Fig. 3a, c), two dielectric anomalies are observed in the dielectric constant–temperature curves. The first dielectric anomaly appears around T_d , as shown in Fig. 3(e, g). At temperatures lower than T_d , the dielectric constant at a higher frequency is lower than that at a lower frequency. With an increase in the temperature above T_d , the dielectric constant at different frequencies merges together. Traditionally, T_d was reported to indicate a phase transition between a ferroelectric phase and an “anti-ferroelectric phase” [16]. But, this has not been proved by other experimental measurements if an anti-ferroelectric phase exists in NBT-based ceramics above T_d [17–18]. So, the so-called “anti-ferroelectric phase” may not be strictly

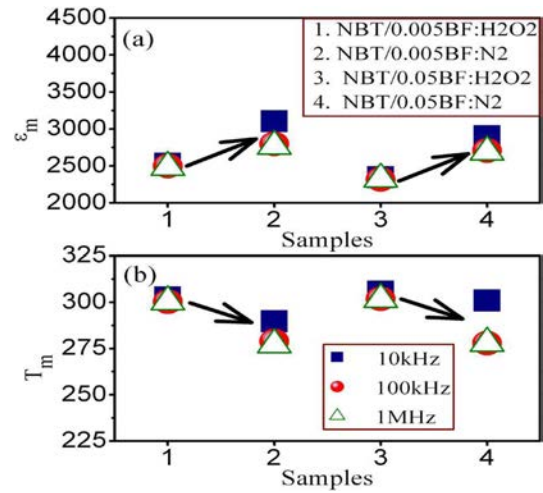


Fig. 4. Maximum values of the dielectric constant (ϵ_m) and corresponding temperatures (T_m) of the ceramics with different processes of oxygen treatment.

classified as a normal anti-ferroelectric state and the term “intermediate phase” is widely used [19–20]. The second dielectric anomaly corresponding to the maximum value of the dielectric constant is at the Curie temperature, which is associated with the transition of the so-called “intermediate phase” to a paraelectric phase. The dielectric loss–temperature curves are similar to those observed in other NBT-based ceramics [2, 4]. At low temperatures, the dielectric loss measured at lower frequencies is lower than that measured at higher frequencies. With a further increase in the temperature, the dielectric loss measured at lower frequencies is larger than that measured at higher frequencies.

By comparing the NBT/0.005BF or NBT/0.05BF ceramics annealed in N₂ with their counterparts dipped in H₂O₂, one distinguished difference in dielectric constant–temperature curves is noted. For the ceramics annealed in N₂, the first dielectric anomaly disappears (Fig. 3f, h). As has been stated in the foregoing, annealing in N₂ will increase the oxygen vacancy concentration of the ceramics. Oxygen vacancies can cause domain wall clamping, which will restrain the macro-micro domain switching and inhibit the transition between the ferroelectric phase and the “intermediate phase” [21]. So, the disappearance of the first dielectric anomaly for the ceramics annealed in N₂ can be attributed to an increased oxygen vacancy content. A similar phenomenon has also been observed in Mn-doped (Na_{0.8}K_{0.2})_{0.5}Bi_{0.5}TiO₃ ceramics [11].

Fig. 4 shows the maximum values of the dielectric constant (ϵ_m) and corresponding temperatures (T_m) measured at different frequencies. It is found that the processes of oxygen treatment have an important effect on both ϵ_m and T_m . For the ceramics with a given x, annealing in N₂ increases the ϵ_m values, while the T_m values of the N₂-annealed ceramics decreases at a given frequency.

The dielectric constant–temperature curves of the

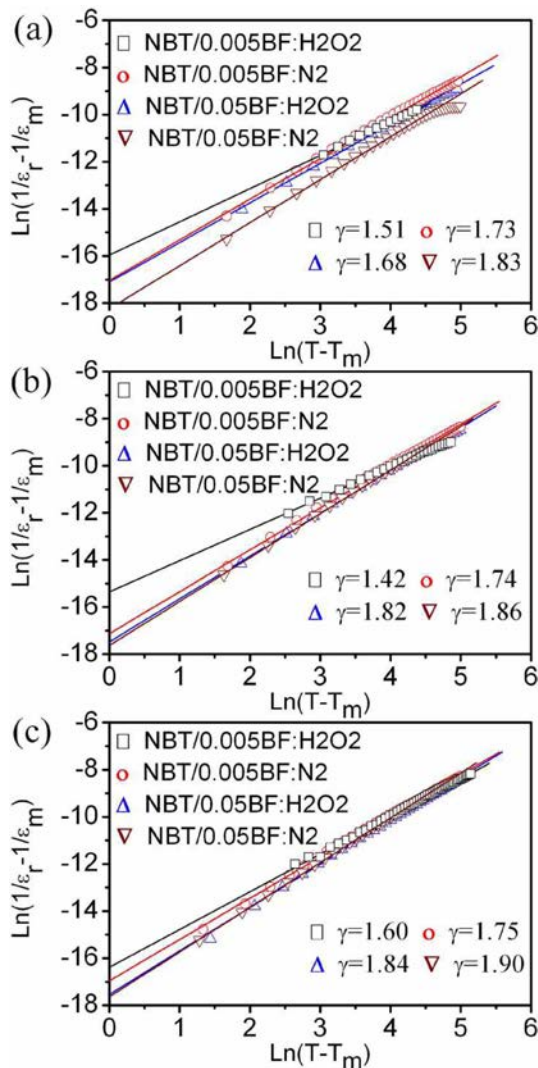


Fig. 5. Plots of $\ln(1/\epsilon_r - 1/\epsilon_m)$ vs. $\ln(T-T_m)$ for the ceramics with different processes of oxygen treatment at frequencies of 10 kHz (a), 100 kHz (b) and 1 MHz (c). The symbols denote experimental data, while the solid lines denote least-square fitting of the curves to the modified Curie-Weiss law.

ceramics exhibit broad dielectric peaks around T_m . In order to characterize the diffuseness of the phase transition, a modified Curie-Weiss law proposed by Uchino and Nomura [22] was employed: $1/\epsilon_r - 1/\epsilon_m = (T-T_m)^{\gamma}/C'$, where ϵ_m is the maximum value of the dielectric constant at the phase transition temperature T_m , C' is the Curie-like constant, and γ is the degree of diffuseness. γ usually ranges from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric. Plots of $\ln(1/\epsilon_r - 1/\epsilon_m)$ as a function of $\ln(T-T_m)$ for all samples at frequencies of 10 kHz, 100 kHz and 1 MHz are shown in Fig. 5. All ceramics exhibit a linear characteristic. By least-squared fitting the experimental data to the modified Curie-Weiss law, γ was determined. The diffuseness exponent γ of all samples is close to 2, implying a diffuse character. For the ceramics with a given x , annealing in N_2 increases the γ values at a given frequency. This is believed to be caused by the

formation of oxygen vacancies, which increase the local compositional heterogeneity and therefore lead to a more diffusive characteristic of the phase transition.

Conclusions

The XRD peak positions were influenced by the different processes of oxygen treatment. No substantial variation in microstructure was found between the N_2 -annealed and H_2O_2 -dipped ceramics. Compared with the H_2O_2 -dipped ceramics, the N_2 -annealed ceramics had decreased T_m values, increased ϵ_m and γ values. For the ceramics annealed in N_2 the first dielectric anomaly corresponding to the transition of the ferroelectric phase to the so-called “intermediate phase” disappeared.

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