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Structure and electrical properties of Nd_2O_3-doped $0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3$ ceramics

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Abstract

Nd_2O_3 doped $0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3$ (abbreviated to BNKT) binary lead-free piezoelectric ceramics were synthesized by the conventional mixed-oxide method. The results show that the BNKT ceramics with 0–0.15 wt.% Nd_2O_3 doping possesses a single perovskite phase with rhombohedral structure. The grain size of BNKT decreased with the addition of Nd_2O_3 dopant. The temperature dependence of the dielectric constant ε_r revealed that there were two-phase transitions from ferroelectric to anti-ferroelectric and anti-ferroelectric to paraelectric. A diffuse character was proved by linear fitting of the modified Curie–Weiss law. At room temperature, the specimens containing 0.0125 wt.% Nd_2O_3 with homogeneous microstructure presented excellent electrical properties: the piezoelectric constant d_{33} = 134 pC/N, the electromechanical coupling factor K_p = 0.27, and the dielectric constant ε_r = 925 (1 kHz).

Keywords: A. Powders solid state reaction; C. Dielectric properties; C. Piezoelectric properties; $Na_{0.5}Bi_{0.5}TiO_3$

1. Introduction

Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated to BNT), first discovered by Smolenshii et al. in 1960 [1], is an attractive lead-free A-site complex-perovskite due to its relatively large remanent polarization (P_r = 38 μC/cm^2) and high Curie temperature (T_c = 320 °C) [2–4]. However, high conductivity and high coercive field E_c can cause problems in the poling process, and thus limit its application.

$Bi_{0.5}K_{0.5}TiO_3$ (abbreviated to BKT) is a perovskite-type ferroelectric structure and belongs to the tetragonal crystal system at room temperature. It undergoes a phase transition at about 380 °C, which is the ferroelectric Curie point. BKT has a lower E_c and the obtained lattice parameters are: a = 3.913 Å and c = 3.993 Å [5]. On one hand, when BKT substitutes BNT, E_c can be reduced to 4 kV/mm [6]. The rhombohedral–tetragonal morphotropic phase boundary (MPB) of $(1 - x)$BNT–xBKT ceramics locates at x = 0.16–0.20, where the ceramics have relative high piezoelectric properties [6,7]. Our previous work has indicated that the ceramics presented optimum electrical properties with x = 0.18 [8]. On the other hand, the effects of some rare earth elements doping into BNT-based ceramics have already been investigated. Li et al. [9] found that CeO_2 doping could reduce the coercive field E_c and improve the piezoelectric properties of $Bi_{0.5}Na_{0.44}K_{0.06}TiO_3$ ceramics. Wu et al. [10] reported that at a low Er_2O_3 concentration, the Er doped BNT ceramics showed enhanced electrical properties with a low dielectric dissipation factor, a low coercive field and a high piezoelectric constant. Herabut demonstrated that dielectric, piezoelectric and electromechanical properties could be improved by doping appropriate amount of La in $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$ system [11]. These results show that those rare earth elements were effective additives in enhancing the electrical properties of the BNT-based system. Nd as a kind of rare earth element, is reported to lead to higher remanent polarization and improve the ferroelectric properties of $Bi_4Ti_3O_{12}$ ceramics [12]. Nevertheless, few studies are available on the effects of Nd_2O_3 on electrical properties of BNT-based system.

In this work, the effects of different content of Nd_2O_3 dopant on the phase structure, microstructure and electrical properties of $0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3$ were investigated,

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and the modification mechanism of doped Nd_2O_5 was also discussed.

2. Experimental

The ceramics were prepared by using the conventional mixed-oxide processing. The general formula of the materials was $0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3 + x$ wt.% Nd_2O_3 ($x = 0$, 0.005, 0.0125, 0.025, 0.05, 0.1, 0.15). Reagent grade oxide or carbonate powders of Bi_2O_3, Na_2CO_3, K_2CO_3, TiO_2 and Nd_2O_3 were used as raw materials. These were mixed in ethanol with zirconium balls by ball-milling for 12 h, then dried and calcined at 850 °C for 2 h in air. The calcined powders were pressed into disks with a diameter of 15 mm under 100 MPa pressure using a solution of polyvinyl alcohol as binder. After a 500 °C binder burnout, the samples were sintered at 1160 °C for 2 h in air. Silver paste was fired on both faces of the samples as electrodes. Samples for piezoelectric measurements were poled at 80 °C in a silicone oil bath by applying a DC electric field of 3–4 kV/mm for 15 min.

The crystalline phase of the sintered ceramics was identified by X-ray diffraction (XRD, Model DMX-2550/PC, Rigaku, Japan) technique using Cu Kα radiation. The surface microstructures of the obtained ceramics were observed by a scanning electron microscopy (SEM, Model Quanta 200, FEI Company). Temperature dependence of dielectric properties was measured with a LCR meter (TH2617, China) from room temperature to 400 °C at 0.1, 1, 10 and 100 kHz. The piezoelectric constant d_{33} was measured by using a quasi-static piezoelectric d_{33} meter (Model ZJ-3d, Institute of Acoustics Academic Sinica, China). The electromechanical coupling factor K_p was determined by the resonance and anti-resonance technique on the basis of IEEE standards using an impedance analyzer (HP 4294A).

3. Results and discussions

X-ray diffraction patterns shown in Fig. 1 indicate that a solid solution with perovskite phase has been formed for all samples, implying that Nd_2O_3 diffused into the BNKT lattice. Only one peak is observed at about 46° for all samples, which indicates that all the ceramics have rhombohedral symmetry structure. There is no significant difference among all the diffraction patterns. With increasing the amount of Nd_2O_3, the diffraction peaks shift to lower angle. Because the ionic radius of Nd^{3+} (0.983 Å) is smaller than that of Bi^{3+} (1.03 Å) and Na^+ (1.02 Å), when Nd^{3+} fills A site, lattice distortion will occur, which induces the lattice constant to change, and then the diffraction peaks may shift.

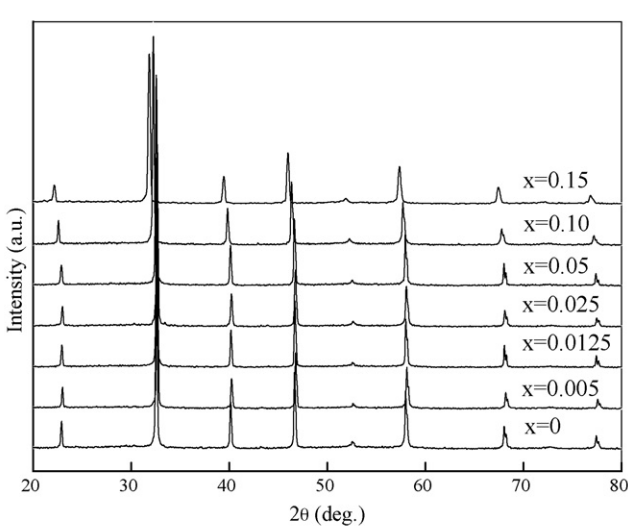

Fig. 1. XRD patterns of ceramics as a function of Nd_2O_3 content.

Fig. 2 shows the SEM micrographs of the BNKT ceramics sintered at 1160 °C and doped with different Nd_2O_3 contents. Grains with regular crystal shape and crystalline boundaries are clear in all samples. At the meantime, the grain size of the BNKT ceramics is restrained obviously by Nd_2O_3 doping. The grain size of undoped BNKT ceramics is about 2.0 μm and the ceramics are inhomogeneous. The grain size decreases obviously with the addition of Nd_2O_3 dopant at an amount lower than 0.0125 wt.%. It can be attributed to that segregation of some Nd^{3+} ions at grain boundaries, thus preventing grain boundary movement during sintering, and inhibiting grain growth. The effect of Nd_2O_3-doping on the grain size is consistent with the report of Li [9]. When the amount of Nd_2O_3 reaches 0.0125 wt.%, the grain size is about 1.5 μm, and the ceramics are homogeneous with fewer pores. By further increasing Nd_2O_3 content from 0.0125 wt.% to 0.1 wt.%, the grain size decreases slightly, but the porosity increases.

Fig. 3 shows the temperature dependence of the dielectric constant ε_r of Nd_2O_3 doped BNKT system and measured at different frequencies. Two abnormal dielectric peaks can be observed, signed as T_t (the temperature at which the phase transition from rhombohedral to tetragonal) and T_m (the temperature at which ε_r reaches the maximum). Both T_t and T_m exhibit a clear dependence on the frequency. ε_r shows a very strong dependence on frequency below T_t, this dependence becoming weaker between T_t and T_m. However, this kind of dependence becomes obvious again above T_m. The temperature dependence of ε_r shows the typical character of a ferroelectric relaxor. Besides, ε_r lowers with increasing Nd_2O_3 content and the temperature of dielectric peaks moves to a lower temperature region. According to the theory of dielectric response of relaxor ferroelectrics discovered by Thomas [13], when the coupling reaction between A-site cation and BO_6 octahedron decreases, the stability of ferroelectric domain decreases. In the view of the ionic radius, it is obvious that Nd^{3+} (0.983 Å) can occupy the A-site of Bi^{3+} (1.03 Å) or Na^+ (1.02 Å), but it cannot enter into the B-site because Ti^{4+} is in the radius of 0.605 Å. Nd^{3+}occupying A-site of Na^+ can lead to valence imbalance, which brings on vacancy of A-site. So the coupling reaction between A-site cation and BO_6 octahedron is weakened and the T_t moves to lower a temperature region.

The modified Curie–Weiss law is used to explain the dielectric behavior of complex ferroelectrics with diffuse phase transition: $\varepsilon_m/\varepsilon = 1 + ((T - T_m)^\gamma/(2\Delta^2))$ [14–16], where γ is a constant which is used to express the diffuseness exponent of the phase transition. ε_m is the peak value of the dielectric constant and T_m is the temperature at which ε_r reaches the

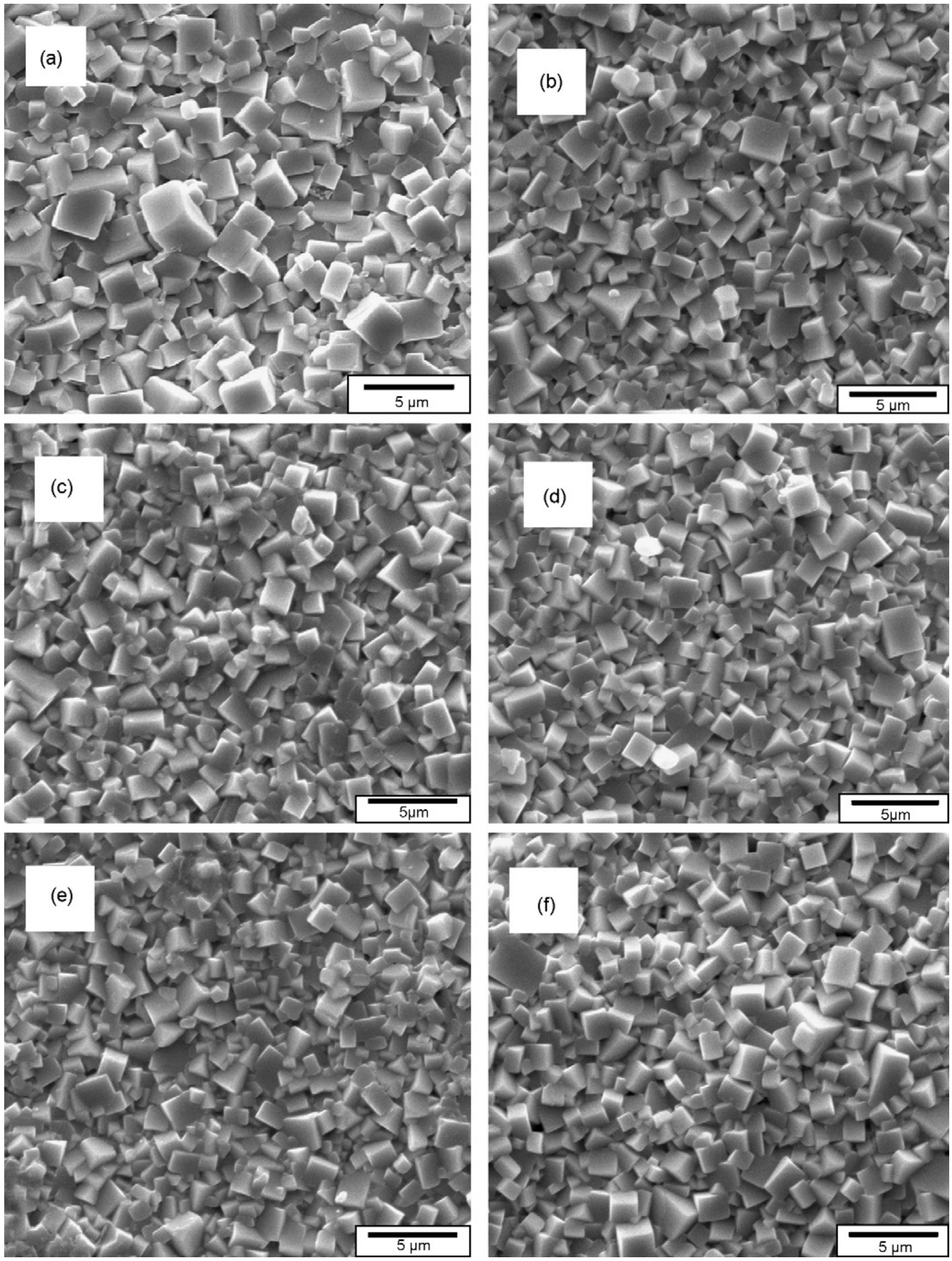

Fig. 2. SEM images of the ceramics as a function of Nd_2O_3 content: (a) $x = 0$ wt.%; (b) $x = 0.005$ wt.%; (c) $x = 0.0125$ wt.%; (d) $x = 0.025$ wt.%; (e) $x = 0.075$ wt.%; (f) $x = 0.1$ wt.%.

maximum. When $\gamma = 1$, the materials with this type of phase transition belongs to normal ferroelectrics; when $1 < \gamma < 2$, the materials belongs to relaxor ferroelectrics; when $\gamma = 2$, the materials belongs to ideal relaxor ferroelectric.

Fig. 4 shows $\ln[(\varepsilon_m - \varepsilon)/\varepsilon]$ as a function of $\ln(T - T_c)$ for ceramics at 1 kHz. A linear relationship is observed in all samples. It can be seen that γ of all ceramics is very close to 2, and the phase transition has a diffuse characteristic. This is in accordance with the results of Fig. 3.

Fig. 5 shows the piezoelectric constant d_{33} and electromechanical coupling factor K_p of the sintered ceramics as a function of Nd_2O_3 content. When the Nd_2O_3 content is 0 wt.%, d_{33} shows a value of 124 pC/N. With increasing x, d_{33} increases to the maximum value (134 pC/N) at $x = 0.0125$ wt.%. Further increasing x causes d_{33} to decrease to 93 pC/N at $x = 0.15$ wt.%. The variation tendency of K_p is similar to that of d_{33}. K_p is 0.21 at $x = 0$, and it increases with increasing x. K_p reaches the maximum (0.27) at $x = 0.0125$ wt.%, and then begins to decrease to 0.18 at $x = 0.15$ wt.%. As we have referred, considering the ionic radius, the Nd^{3+} can enter into A-site not B-site. During sintering, Bi^{3+} in BNKT may leave the ceramics and form some vacancies in the lattice because Bi^{3+} is volatile at

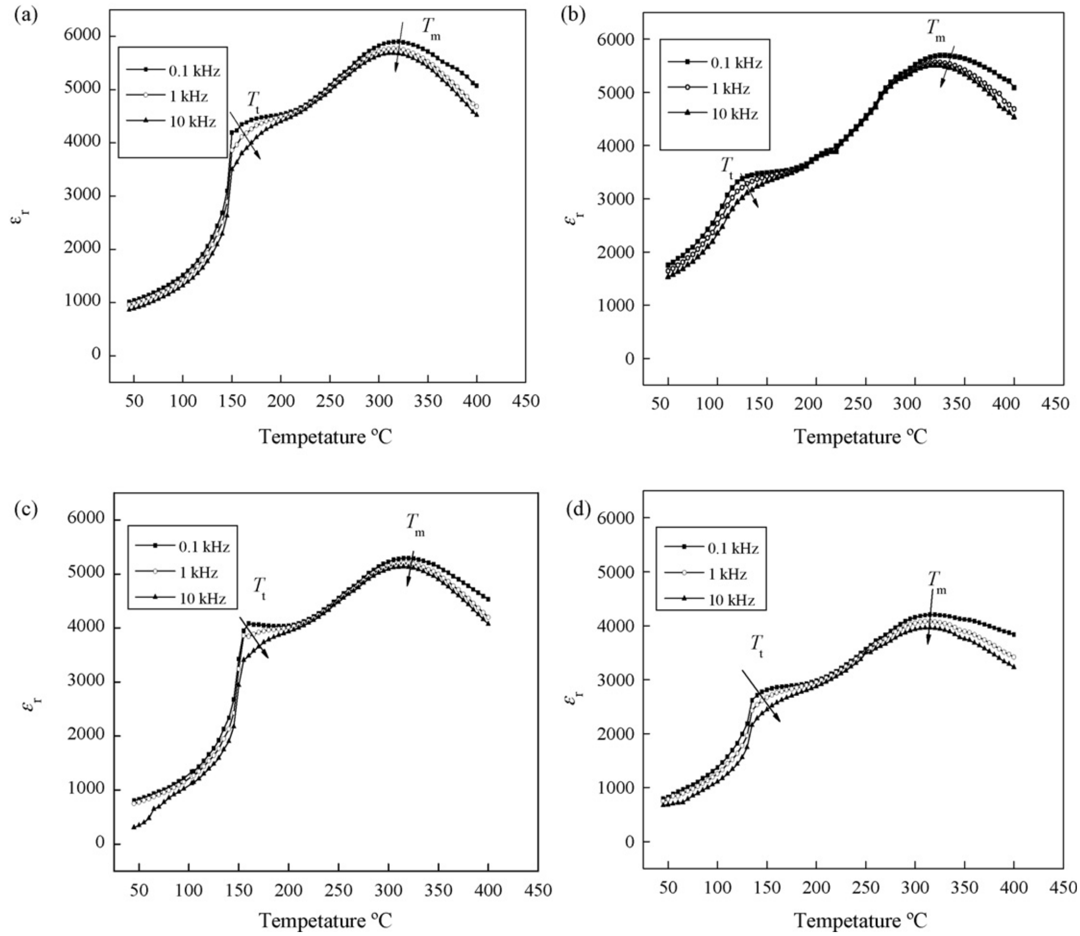

Fig. 3. the temperature dependence of ε_r for Nd_2O_3 doped BNT–BKT system: (a) 0 wt.%; (b) 0.0125 wt.%; (c) 0.025 wt.%; (d) 0.1 wt.%.

high temperature. It is possible for Nd^{3+} to fill in Bi^{3+} vacancies. As Nd^{3+} has a radius of 0.983 Å which is smaller than 1.03 Å of Bi^{3+}, when Nd^{3+} occupies Bi-site, the substitution of Bi^{3+} by Nd^{3+} may cause the slack of BNKT lattice. The lattice deformation can enhance the motion of domains which leads to the improvement of piezoelectric properties. Additionally, Nd^{3+} can also occupy the A-site of Na^+ (1.02 Å). In this case, Nd^{3+} acts as a donor leading to some vacancies of A-site in the lattice, which facilitates the movement of the domains and thus improving the piezoelectric properties significantly.

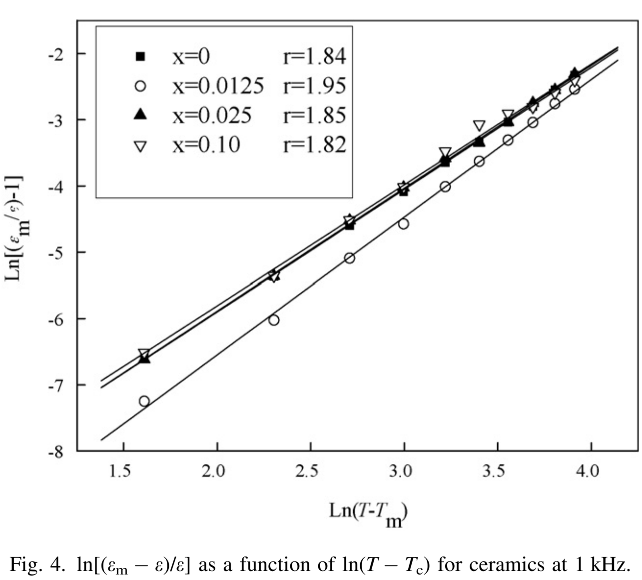

Fig. 4. $\ln[(\varepsilon_m - \varepsilon)/\varepsilon]$ as a function of $\ln(T - T_c)$ for ceramics at 1 kHz.

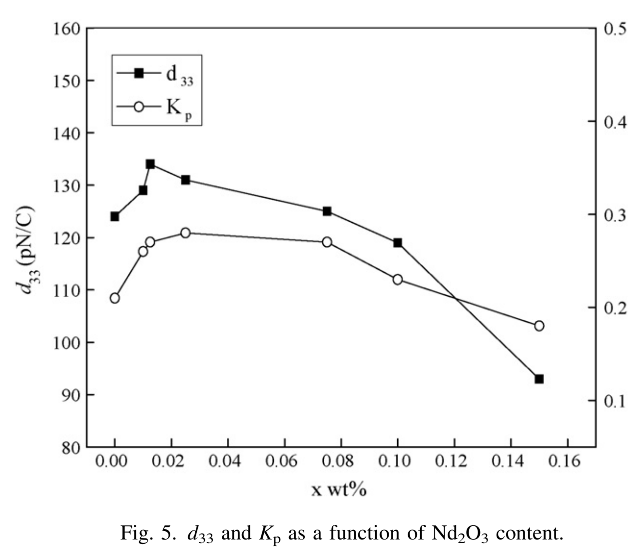

Fig. 5. d_{33} and K_p as a function of Nd_2O_3 content.

4. Conclusions

$0.82Bi_{0.5}Na_{0.5}TiO_3$–$0.18Bi_{0.5}K_{0.5}TiO_3$ ceramics with 0–0.1 wt.% Nd_2O_3 have been investigated. The XRD patterns show that the BNKT ceramics doped with 0–0.1 wt.% Nd_2O_3 can form a pure perovskite type solid solution with rhombohedral symmetry structure. The SEM images indicate that the growth of grain is restrained by Nd_2O_3 doping. All the ceramics, both doped and undoped, have two abnormal dielectric peaks, corresponding to the phase transition from ferroelectric to anti-ferroelectric and anti-ferroelectric to para-electric. ε_r becomes lower with increasing the Nd_2O_3 content and the temperature of dielectric peaks moves to a lower temperature region. The relaxor ferroelectric characteristics are proved by modified Curie–Weiss law. The piezoelectric properties are also promoted by Nd_2O_3 doping. Optimized piezoelectric properties are obtained at 0.0125 wt.% Nd_2O_3, i.e. d_{33} = 134 pC/N, K_p = 0.27, ε_r = 925 (1 kHz) and T_c = 335 °C.

Acknowledgments

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