Enhanced multiferroic property in Co_2O_3 -added BiFeO_3 - BaTiO_3 ceramics

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0.7BiFeO_3 - $0.3\text{BaTiO}_3 + 1 \text{ mol } \% \text{ MnO}_2 + x \text{ mol } \% \text{ Co}_2\text{O}_3$ multiferroic ceramics were fabricated by an ordinary sintering technique and the effects of Co doping on the microstructure, multiferroic and piezoelectric properties of the ceramics were studied. All the ceramics possess a pure perovskite structure with rhombohedral symmetry. The addition of a small amount of Co_2O_3 enhances the ferroelectricity, ferromagnetism, piezoelectricity and temperature stability of the ceramics. The ceramic with $x = 1.0$ possesses enhanced piezoelectricity ($d_{33} = 134 \text{ pC/N}$), good ferroelectricity ($P_r = 19.9 \mu\text{C/cm}^2$) and increased high depolarization temperature ($T_d = 475^\circ\text{C}$). The $1 \text{ mol } \% \text{ Co}_2\text{O}_3$ doping greatly improves the ferromagnetic property of the ceramics and the optimum remnant magnetization M_r of 0.191 emu/g of the ceramic is obtained at $x = 1.0$. These results show that the ceramic with $x = 1.0$ is a promising candidate for lead-free high-temperature piezoelectric and room-temperature multiferroic materials.

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1. Introduction

Perovskite lead-based ceramics represented by $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$ (PZT) and PZT-based system have been widely used in sensors, transducers and actuators owing to their superior piezoelectric property. However, the use of these ceramics has caused serious environmental and health problems because of the strong toxicity of lead oxide and its high vapor pressure during sintering process. Therefore, lead-free piezoelectric ceramics have attracted considerable attention in recent years. As most promising candidates for lead-free materials, BaTiO_3 (BT-),¹⁾ $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT-)²⁾ and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN)-based³⁾ ceramics show excellent piezoelectricity and thus have been intensively investigated. However, above-mentioned lead-free ceramics show poor temperature stability of electrical property due to the coexistence of tetragonal and orthorhombic phases near room temperature and low depolarization temperature and/or Curie temperature.¹⁾⁻³⁾ Therefore, it is necessary to develop lead-free piezoelectric materials with high Curie temperature.

BiFeO_3 (BFO) has a rhombohedral symmetry with perovskite structure at room temperature. As a single-phase multiferroic material, BFO has attracted much attention and gives potential applications in advanced devices due to the coexistence of ferroelectricity and ferromagnetism.^{4),5)} BFO may be a promising candidate for high-temperature lead-free piezoelectric and room-temperature multiferroic material because of its high ferroelectric Curie temperature ($T_C \sim 830^\circ\text{C}$) and Néel temperature ($T_N \sim 370^\circ\text{C}$).^{6),7)} However, pure BFO ceramic possesses low resistivity due to the reduction of Fe^{3+} to Fe^{2+} during sintering and the formation of oxygen vacancies for charge compensation.⁸⁾ This leads to high dielectric loss and poorly saturated ferroelectric hysteresis. Moreover, single-phase BFO with pure perovskite structure is difficult to synthesize due to the narrow temperature range of phase stabilization, and thus some impurity phases (e.g., $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_{40}$, etc.) are usually detected.^{9),10)} To enhance

electric insulation and inhibit the formation of impurity phases of BFO, a great deal of studies have been carried out, including the use of various synthesis techniques (chemical leaching, rapid liquid phase sintering, etc.).¹¹⁾⁻¹³⁾ The partial substitution of A-site ion Bi^{3+} by La^{3+} and Sm^{3+} ^{14),15)} or B-site ion Fe^{3+} by Nb^{5+} and Co^{3+} ^{16),17)} and the formation of solid solutions of BFO with other ABO_3 -type perovskites such as BT and $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT).^{18),19)} Among these BFO-based materials, BiFeO_3 - BaTiO_3 (BFO-BT) solid solution has been extensively studied. However, these investigations mostly focus on dielectric and magnetic properties and seldom give considerable ferroelectricity and piezoelectricity because of the poor electric insulation of the ceramics. Recently, Mn-modified BFO-BT with good piezoelectricity has been prepared, but its ferromagnetism is seldom reported.^{20),21)} In summary, BT as the typical ferroelectric is expected to enhance the ferroelectricity and can improve dielectric response and reduce dielectric loss of BF.²²⁾ Therefore, BT is a good additive, it can be added into BFO to improve electrical and magnetic properties. According to the literature, 0.7BFO - 0.3BT ceramics show optimum ferroelectric and piezoelectric properties.²³⁾⁻²⁶⁾ A small amount of MnO_2 (1 mol %) can strengthen the electric resistivity, ferroelectric and piezoelectric properties of the ceramics.³⁸⁾ On the other hand, Co_2O_3 is an effective additive and has been added widely to many perovskite piezoelectric ceramics to tailor the electrical and magnetic properties.^{27),28)} To our knowledge, there are few reports on the ferroelectric, piezoelectric and ferromagnetic properties of Co_2O_3 -modified BFO-BT. In the present work, a lead-free multiferroic solid solution of 0.7BFO - $0.3\text{BT} + 1 \text{ mol } \% \text{ MnO}_2 + x \text{ mol } \% \text{ Co}_2\text{O}_3$ (BFO-BT-Co- x , $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0) was synthesized by a conventional ceramic technique in air and the phase transition, ferroelectric, piezoelectric and ferromagnetic properties of the ceramics were studied. On the basis of reported work,^{20),21)} MnO_2 is added to improve the electric insulation of the ceramics. Our study shows that Co_2O_3 doping is an effective method to enhance the multiferroic property of BFO-BT materials.

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2. Experimental

The BFO–BT–Co– x ceramics were prepared by a conventional solid-state reaction method using metal oxides and carbonate powders: Bi₂O₃ (99%), Fe₂O₃ (99%), TiO₂ (99.88%), BaCO₃ (99%), Co₂O₃ (99%) and MnO₂ (99.9%). The raw materials in the stoichiometric ratio of 0.7BFO–0.3BT were first mixed thoroughly in ethanol using zirconia balls for 8 h, then dried and calcined at 800°C for 4 h. After the calcination, MnO₂ and Co₂O₃ were added, and the resulting mixture was re-milled for 8 h and then pressed into discs using polyvinylalcohol (PVA) as a binder. The samples were sintered at 960°C for 2 h in air atmosphere. Silver electrodes were fired on both surfaces of the sintered ceramics at 650°C for 30 min. The samples were poled at 100°C for 20 min and then cooled to room temperature in a silicone oil bath under a dc field of 5 kV/mm.

The crystalline structure of the sintered samples was determined using X-ray diffraction (XRD) analysis with Cu K α ($\lambda = 1.540598$ Å) radiation (SmartLab; Rigaku, Tokyo, Japan), 0.01° scan step and continuous scanning type in the 2θ range of 20–70°. The lattice parameters of the ceramics were refined by the Rietveld refinement using a general diffraction/reflectivity analysis program MAUD.²⁹⁾ The microstructures were observed by scanning electron microscopy (FEI-Quanta 250; FEI, Portland, OR). The relative density was measured by Archimedes' method. The average grain size D_A was obtained by multiplying the average linear intercept length of grains by 1.56.³⁰⁾ The relative permittivity ϵ_r at 1 MHz was measured as a function of temperature using a LCR meter (Agilent E4980A; Agilent Technologies Inc., Santa Clara, CA) and temperature-controlled probe stage (Linkam TS1500E; Linkam Scientific Instruments Ltd., Guildford, UK). The polarization hysteresis (P - E) loops were measured at 10 Hz at room temperature using a precision materials measuring system (Premier II; Radiant Technologies Inc., Northford, CT). Leakage current and resistivity R were measured at room temperature using a precision materials measuring system (Premier II; Radiant Technologies Inc., Northford, CT). The planar electromechanical coupling factor k_p was determined by the resonance method according to the IEEE Standards 176 using an impedance analyzer (Agilent 4294A; Agilent Technologies Inc.). The piezoelectric constant d_{33} was measured using a piezo- d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The magnetic hysteresis (M - H) loops were measured using magnetic measurement instrument (MPMS-XL-7, Quantum Design, San Diego, CA).

3. Result and discussion

The XRD patterns of the BFO–BT–Co– x ($x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$ and 3.0) ceramics are shown in Fig. 1. From Fig. 1(a), all the ceramics possess a pure perovskite structure without any impurity peaks detected, suggesting that Co can be absolutely diffused into BFO–BT structure due to the small difference atomic radius and the same valance between Fe³⁺ and Co³⁺. From Fig. 1(b), it can be found that as x increases, the splitting of two diffraction peaks gradually becomes weak and merges into a single peak, suggesting that the rhombohedral distortion of the ceramics become small with Co₂O₃ doping increasing.

Based on the XRD patterns of the ceramics shown in Fig. 1, the lattice parameters (a , c , and V) of the ceramics were refined by the Rietveld method refinement using a general diffraction/reflectivity analysis program MAUD and the refined lattice parameters a and c for the various compositions along with their respective R-factors are listed in Table 1. From Table 1, for all the

Fig. 1. Room temperature X-ray diffraction patterns of the 0.7BFO–0.3BT–Co– x ceramics.

Table 1. Cell parameters (a and c) and fitting parameters (R_{wp} and S) of the BFO–BT–Co– x ceramics

x	Lattice parameters			R factor (%)	
	a (Å)	c (Å)	Unit Cell volume (Å ³)	R_{wp}	S
0	5.6487(3)	13.8336(5)	382.2692(0)	11.61	1.46
0.5	5.6425(8)	13.8763(7)	382.6147(2)	10.59	1.35
1.0	5.6449(9)	13.8926(5)	383.3906(3)	10.98	1.43
1.5	5.6427(8)	13.8698(1)	382.4614(0)	11.35	1.46
2.0	5.6465(8)	13.8277(5)	381.8156(1)	11.00	1.32
2.5	5.6531(3)	13.8322(3)	382.8256(2)	9.90	1.26
3.0	5.6464(9)	13.8445(6)	382.2673(9)	8.72	1.09

Fig. 2. Lattice parameter a , b and c of the BFO–BT–Co– x ceramics sintered at 960°C for 2 h as a function of x .

refinement, the value of reliability R_{wp} fluctuates between 8.72 and 11.61%; the goodness-of-fit indicator S changes between 1.09 and 1.46%. It can be seen that R_{wp} and S are respective less than 15 and 2%, which suggests a good matching between observed and calculated patterns. All the diffraction peaks of the ceramics can be refined to the rhombohedral structure $R3c$ by the Rietveld method. Figure 2 shows the variations of the lattice parameters (a , b , c and V) of the BFO–BT–Co– x ceramics as a function of x . From Fig. 2, the observed lattice parameter a and b exhibit the fluctuations of 5.6426–5.6531 Å, c and V increase with x increasing from 0 to 1.0 and then decrease with x increasing to 2.0. The variation of lattice parameters should be attributed to the distortion of the orthorhombic structure caused by the substitution of smaller Co³⁺ for Fe³⁺/Ti⁴⁺.

Fig. 3. SEM graphs of the surface microstructure of the 0.7BFO-0.3BT-Co- x ceramics with $x = 0$ (a), 0.5 (b), 1 (c), 1.5 (d), 2 (e), 2.5 (f) and 3 (g).

Fig. 4. SEM graphs of the cross-section morphology of the BFO-BT-Co- x ceramics sintered at 960°C for 2 h: (a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 1.0$, (d) $x = 1.5$, (e) $x = 2.0$, (f) $x = 2.5$, (g) $x = 3.0$.

Figure 3 shows SEM graphs of the surface microstructure of the BFO-BT-Co- x ceramics with $x = 0, 0.5, 1, 1.5, 2, 2.5$ and 3 sintered at 960°C for 2 h. From Fig. 3, all the ceramics are dense with clear grain boundary. From Figs. 3(a) and 3(b), the ceramics with $x = 0$ and 1.0 exhibit similar average grain size, giving the values of 4.22 and $4.26\mu\text{m}$, respectively. As x increases, the average grain size gradually decreases from 4.26 to $0.79\mu\text{m}$, indicating that the addition of excess Co_2O_3 greatly inhibits the grain growth of the ceramics. In order to further confirm the density and grain size of all the ceramics, the cross-section morphology of all specimens has been taken, which is shown in **Fig. 4**. From Fig. 4, the grain size show the same variation trend compared with SEM graphs of the surface microstructure. Similar suppression phenomenon of the grain growth has been reported in many lead-free ceramics such as Sm_2O_3 and Co_2O_3 -modified BFO.³¹⁾ This inhibition of grain growth may be interpreted to grain boundary aliquidation.^{32),33)} In order to further confirm the chemical composition of these as-prepared ceramics, EDS has been taken at whole fracture section of the ceramics with $x = 0.5$,

Fig. 5. Composition analysis of the whole fracture section in the ceramics with $x = 0.5, 2.0$ and 3.0 .

Fig. 6. Composition dependence of ρ_r for the BFO-BT-Co- x ceramics.

2.0 and 3.0 , which is shown in **Fig. 5**. From Fig. 5, it can be seen that all the elements are observed. The ratio of Co element increases with x increasing from 0.5 to 3.0 , which is very close to the theoretical values, indicating that the chemical composition are very average in the ceramics.

Figure 6 shows the relative density ρ_r of the BFO-BT-Co- x ceramics as a function of x . From Fig. 6, all the BFO-BT-Co- x ceramics exhibit the high values of 91.9 – 96.7% . The observed relative density ρ_r first increases from 95 to 96.7% with x increasing from 0 to 0.5 and then decreases to 92.9% with x further increasing from 0.5 to 3.0 , suggesting that the addition of a small amount of Co_2O_3 can promote the sintering of the ceramics and the ceramics can be well sintered at the low temperature of 960°C for 2 h.

Figure 7(a) shows the leakage current density J of the BFO-BT-Co- x ceramics at room temperature as a function of the

Fig. 7. (a) Leakage current density J of the BFO-BT-Co- x ceramics at room temperature as a function of the electric field E ; (b) dependences of resistivity R of the BFO-BT-Co- x ceramics on the electric field E .

electric field E , while Fig. 7(b) provides the dependence of the resistivity R of the BFO-BT-Co- x ceramics on the electric field E . As a comparison, the J and R of the pure BFO were also given in Fig. 7. It can be seen that pure BFO exhibits very large leakage current density of 8.18×10^{-4} A/cm² and low resistivity of $2.62 \times 10^7 \Omega$ ·cm under the electric field of 3 kV/mm. As well known, the pure BFO ceramic gives poor electric insulation due to the valence transformation of Fe ions from Fe³⁺ to Fe²⁺ and the creation of oxygen vacancies.¹²⁾ However, all the ceramics of BFO-BT-Co- x exhibit the low J values of 10^{-5} – 10^{-4} A/cm² and high R values of 10^9 – $10^{10} \Omega$ ·cm under the electric field of 3 kV/mm. It can be seen that, the electric insulation of the BFO-BT-Co- x ceramics is much better than pure BFO. The good electric insulation of the present ceramics may be attributed to the partial substitutions of Mn⁴⁺ and Ti⁴⁺ for Fe³⁺ in the ceramics.³⁴⁾ As a result of the suppression of the formation of O²⁻ vacancies, the high resistivity is obtained in the present ceramics.

Figure 8(a) shows the P - E loops of the BFO-BT-Co- x ceramics measured under an electric field of 6.5 kV/mm at room temperature, while the composition dependences of the remanent polarization P_r and coercive field E_c of the ceramics are shown in Fig. 8(b). Obviously, all the ceramics give typical and saturated P - E loops because of the high resistivity [Fig. 8(a)]. From Fig. 8(b), for the BFO-BT-Co- x ceramics, the observed P_r slightly fluctuates from 21.4 to 20.0 μ C/cm² with x increasing from 0 to 0.5, then increases from 20.0 to 23.0 μ C/cm² with x increasing from 0.5 to 1.5, and finally decreases greatly to 15.8 μ C/cm² with x further increasing to 3.0, while the observed E_c exhibits weak dependence on x and gives the values of 2.8 to 4.0 kV/mm at $x = 0$ –3.0. The optimum ferroelectric property is obtained at $x = 1.50$, suggesting that after addition a certain amount of Co₂O₃, the ferroelectricity of the ceramics have been improved. This should be ascribed to the better crystallization, higher density, and lower leakage current of the ceramics.

Fig. 8. (a) P - E loops for the BFO-BT-Co- x ceramics with $x = 0, 0.5, 1, 1.5, 2, 2.5$ and 3.0 at room temperature; (b) variations in P_r and E_c of the BFO-BT-Co- x ceramics with x .

Fig. 9. Compositional dependence of piezoelectric constant d_{33} , planar electromechanical coupling factor k_p , relative dielectric constant ϵ_r and loss tangent $\tan \delta$ of the BFO-BT-Co- x ceramics sintered at 960°C for 2 h.

Figure 9 shows the variations in piezoelectric constant d_{33} , planar electromechanical coupling factor k_p , relative dielectric constant ϵ_r and loss tangent $\tan \delta$ with x measured at 1 MHz for the BFO-BT-Co- x ceramics sintered at 960°C for 2 h. From Fig. 9(a), the observed d_{33} maintains relatively large values of 133–134 pC/N at $x = 0$ –1.0 and then gradually decreases to 59 pC/N with x further increasing to 3.0, displaying a similar trend as the grain size does. Similarly, the k_p remains the slight increase of 29.1–31.7% at $x = 0$ –1.0 and decreases to 15.6% with x increasing to 3.0. The observed ϵ_r decreases monotonously from 556 to 493 with x increasing from 0 to 3.0, while the observed $\tan \delta$ increases from 4.07 to 9.90% with x increasing from 0 to 3.0. In summary, piezoelectric properties of the ceramics with $x = 0.5$ should be ascribed to the extrinsic contributions to the

Fig. 10. Thermal-depoling behavior of the BFO-BT-Co- x ceramics sintered at 960°C.

piezoelectric performance induced by grain size, which is consistent with the results of microstructure of BFO-BT-Co- x ceramics (as observed in Fig. 3).

Figure 10 shows the effect of thermal depoling on the piezoelectric property of the BFO-BT-Co- x ceramics. All the poled samples were annealed at selected temperature for 30 min then re-measured at room temperature. From Fig. 10, the observed d_{33} of the ceramic without Co₂O₃ doping (with $x = 0$) decreases as the temperature increases and decreases dramatically when the temperature exceeds 400°C (i. e. $T_d \sim 400^\circ\text{C}$). The observed d_{33} of the ceramics with $x = 0.5$ and 1.0 exhibit similar variation with the temperature. The observed d_{33} possesses relatively high value and decreases slightly from ~ 140 to ~ 120 pC/N as the temperature increases from 25 to 400°C and then decreases dramatically as temperature further increases above 475°C (i. e. $T_d \sim 475^\circ\text{C}$), indicating that the small amount of Co₂O₃ doping can improve the thermostability of the ceramics. In addition, for the ceramics with $x = 1.5$ –3.0, the observed d_{33} possesses relative low value and decreases monotonously with the temperature increasing, suggesting that the excess doping of the Co₂O₃ can degrade the thermostability of the ceramics. Compared with other lead-free ceramics [e.g., (Bi_{0.5}Na_{0.5})TiO₃ (BNT)³⁵ and Bi₄Ti₃O₁₂³⁶ ceramics], the BFO-BT ceramics with 0.5–1.0 mol % Co₂O₃ content exhibit much higher T_d of 475°C, which is even much higher than the T_d of most of the lead-based ceramics. These suggest that Co₂O₃-doped BFO-BT may be suitable for high-temperature applications.

Figure 11(a) shows the M - H hysteresis loops measured at room temperature of the BFO-BT-Co- x ceramics with $x = 0, 1.0, 2.0$ and 3.0, while Fig. 11(b) shows the composition dependence of M_r and H_c for the BFO-BT-Co- x ceramics. As shown in the inset of Fig. 11(a), the pure BFO ceramic gives a linear M - H curve, indicating that BFO is antiferromagnetic (AFM), which is consistent with the previous report.³⁷ However, with the addition of Co₂O₃, BT and MnO₂, it can be seen that all the ceramics exhibit a typical magnetization hysteresis loop, suggesting that magnetism and ferroelectricity are observed simultaneously for the BFO-BT-Co- x ceramics (Figs. 8 and 11). From Fig. 11(b), the observed remnant magnetization M_r and coercive field H_c of the ceramics with $x = 0$ are 0.065 emu/g and 3.51 kOe, respectively. After the addition of 1 mol % Co₂O₃, the ferromagnetism of ceramic is significantly enhanced and exhibits the M_r of 0.191 emu/g and H_c of 2.26 kOe. However, the ferromagnetism of the

Fig. 11. (a) M - H hysteresis loops of the BFO-BT-Co- x ceramics with $x = 0, 1.0, 2.0$ and 3.0 (the inset in (a) is the M - H loop of the pure BFO ceramics sintered at 775°C for 2 h); (b) composition dependence of M_r and H_c for the BFO-BT-Co- x ceramics.

ceramic degrades to $M_r = 0.088$ emu/g and $H_c = 0.15$ kOe with x further increasing to 3.0. Obviously, a small amount of Co₂O₃ doping can enhance the magnetism of the BFO-BT ceramics and the best ferromagnetic property are obtained after the addition of 1 mol % Co₂O₃. It has been known that the Fe³⁺ magnetic moments ordering forms a long-range cycloid in pure BFO, which causes zero magnetization.³⁸ It has been known that the doping of irons such as Nd³⁺, Eu³⁺, Co³⁺, Ho³⁺, Ni²⁺^{9,39}) can change the inherent structure of BFO to trigger the breaking of the local spin helix structure. For the present ceramics, a structural distortion occurs due to the ionic radius of Co³⁺ (0.61 Å) is different with those of Bi³⁺/Ba³⁺ (1.03 Å/1.35 Å) and Fe³⁺/Ti⁴⁺ (0.645 Å/0.605 Å). So, the local spin helix structure of BFO is broken when Co³⁺ enters into the lattice. The net magnetic moment of BFO changes due to the bond angles of Fe³⁺-O-Co³⁺ is different with that of Fe³⁺-O-Fe³⁺ and magnetic moments of Fe³⁺ and Co³⁺ are different. Therefore substantial enhancement in the magnetization of the ceramic reaches at $x = 1.0$. However, the excess Co may lead to the appearance of other AFM ordering in the pseudocubic structure and thus degrades the magnetization of the ceramics when $x \geq 3.0$. The similar phenomenon of decreased ferromagnetism has been reported in Sc-doped BFO-based ceramics.³⁹

4. Conclusions

BFO-BT-Co- x multiferroic ceramics has been synthesized using an ordinary solid-state reaction method. The ceramics exhibit pure perovskite structure with rhombohedral symmetry, indicating that Co₂O₃ have diffused into the BFO-BT lattice to form a solid solution. The grain sizes of the ceramics decrease with x increasing. After the addition of 1 mol % Co₂O₃, the multiferroic property of the ceramics is significantly enhanced. The ceramic with $x = 1.0$ shows strong piezoelectricity, improved multiferroic property and good temperature stability of piezo-

electric property, suggesting a promising candidate for high-temperature lead-free piezoelectric and room-temperature multi-ferroic materials.

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Reference

- 1) W. Liu and X. Ren, *Phys. Rev. Lett.*, **103**, 257602 (2009).
- 2) C. Xu, D. Lin and K. W. Kwok, *Solid State Sci.*, **10**, 934–940 (2008).
- 3) R. Zuo, J. Rodel, R. Chen and L. Li, *J. Am. Ceram. Soc.*, **89**, 2010–2015 (2006).
- 4) Q. Q. Wang, Z. Wang, X. Q. Liu and X. M. Chen, *J. Am. Ceram. Soc.*, **95**, 670–675 (2012).
- 5) H. B. Qin, H. L. Zhang, B. P. Zhang and L. H. Xu, *J. Am. Ceram. Soc.*, **94**, 3671–3674 (2011).
- 6) F. P. Gheorghiu, A. Ianculescu, P. Postolache, N. Lupu, M. Dobromir, D. Luca and L. Mitoseriu, *J. Alloys Compd.*, **506**, 862–867 (2010).
- 7) J. Silva, A. Reyes, H. Esparza, H. Camacho and L. Fuentes, *Integr. Ferroelectr.*, **126**, 47–59 (2011).
- 8) S. T. Zhang, M. H. Lu, D. Wu, Y. F. Chen and N. B. Ming, *Appl. Phys. Lett.*, **87**, 262907 (2005).
- 9) F. Azough, R. Freer, M. Thrall, R. Cernik, F. Tuna and D. Collison, *J. Eur. Ceram. Soc.*, **30**, 727–736 (2010).
- 10) S. K. Pradhan and B. K. Roul, *Physica B*, **406**, 3313–3317 (2011).
- 11) M. M. Kumar, V. R. Palkar, K. Srinivas and S. V. Suryanarayana, *Appl. Phys. Lett.*, **76**, 2764–2766 (2000).
- 12) A. K. Pradhan, K. Zhang, D. Hunter, J. B. Dadson and G. B. Loutts, *J. Appl. Phys.*, **97**, 093903 (2005).
- 13) Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu and Z. G. Liu, *Appl. Phys. Lett.*, **84**, 1731–1733 (2004).
- 14) G. LeBras, P. Bonville, D. Colson, A. Forget, N. Genand-Riondet and R. Tourbot, *Physica B*, **406**, 1492–1495 (2011).
- 15) X. M. Chen, J. L. Wang, G. L. Yuan, D. Wu, J. M. Liu, J. Yin and Z. G. Liu, *J. Alloys Compd.*, **541**, 173–176 (2012).
- 16) Y. K. Jun, W. T. Moon, C. M. Changa, H. S. Kima, H. S. Ryua, J. W. Kimb, K. H. Kimb and S. H. Hong, *Solid State Commun.*, **135**, 133–137 (2005).
- 17) L. Peng, H. M. Deng, J. J. Tian, Q. Ren, C. Peng, Z. P. Huang, P. X. Yang and J. H. Chu, *Appl. Surf. Sci.*, **268**, 146–150 (2013).
- 18) T. H. Wang, C. S. Tu, Y. Ding, T. C. Lin, C. S. Ku, W. C. Yang, H. H. Yu, K. T. Wu, Y. D. Yao and H. Y. Lee, *Curr. Appl. Phys.*, **11**, S240–S243 (2011).
- 19) H. Matsuo, Y. Noguchi, M. Miyayama, M. Suzuki and A. Watanabe, *J. Appl. Phys.*, **108**, 104103 (2010).
- 20) S. O. Leontsev and R. E. Eitel, *J. Am. Ceram. Soc.*, **92**, 2957–2961 (2009).
- 21) H. B. Yang, C. R. Zhou, X. Y. Liu, Q. Zhou, G. H. Chen, W. Z. Li and H. Wang, *J. Eur. Ceram. Soc.*, **33**, 1177–1183 (2013).
- 22) T. H. Wang, Y. Ding, C. S. Tu, Y. D. Yao, K. T. Wu, T. C. Lin, H. H. Yu, C. S. Ku and H. Y. Lee, *J. Appl. Phys.*, **109**, 07D907 (2011).
- 23) Y. X. Wei, X. T. Wang, J. T. Zhu, X. L. Wang and J. J. Jia, *J. Am. Ceram. Soc.*, **96**, 3163–3168 (2013).
- 24) A. Ianculescu, L. Mitoseriu, H. Chiriac, M. M. Carnasciali, A. Braileanu and R. Trusca, *J. Optoelectron. Adv. Mater.*, **10**, 1805–1809 (2008).
- 25) K. C. Verma and R. K. Kotnala, *Solid State Commun.*, **151**, 920–923 (2011).
- 26) H. B. Yang, Q. Q. Ke, H. Y. Si and J. S. Chen, *J. Appl. Phys.*, **111**, 024104 (2012).
- 27) G. L. Song, H. X. Zhang, T. X. Wang, H. G. Yang and F. G. Chang, *J. Magn. Magn. Mater.*, **324**, 2121–2126 (2012).
- 28) C. Indrani, P. Neeraj, T. Amit, B. Igor and A. L. Kholkin, *Thin Solid Films*, **520**, 6493–6498 (2012).
- 29) L. Lutterotti, MAUD, *Material Analysis Using Diffraction*, 2011. <http://www.ing.unitn.it/~maud/index.html>.
- 30) M. I. Mendelson, *J. Am. Ceram. Soc.*, **52**, 443–446 (1968).
- 31) G. L. Song, H. X. Zhang, T. X. Wang, H. G. Yang and F. G. Chang, *J. Magn. Magn. Mater.*, **324**, 2121–2126 (2012).
- 32) H. Yabuta, M. Shimada, T. Watanabe, J. Hayashi, M. Kubota, K. Miura, T. Fukui, I. Fujii and S. Wada, *Jpn. J. Appl. Phys.*, **51**, 09LD04 (2012).
- 33) J. Y. Yi, J. K. Lee and K. S. Hong, *Jpn. J. Appl. Phys.*, **43**, 6188–6192 (2004).
- 34) D. Lin, Q. J. Zheng, Y. Li, Y. Wan, Q. Li and W. Zhou, *J. Eur. Ceram. Soc.*, **33**, 3023–3026 (2013).
- 35) Y. Hiruma, H. Nagata and T. Takenaka, *J. Appl. Phys.*, **105**, 084112 (2009).
- 36) H. X. Yan, M. J. Reece, J. Liu, Z. J. Shen, Y. M. Kan and P. L. Wang, *J. Appl. Phys.*, **100**, 076103 (2006).
- 37) D. Lebeugle, D. Colson, A. Forget, M. Viret, A. M. Bataille and A. Gukasov, *Phys. Rev. Lett.*, **100**, 227602 (2008).
- 38) Y. Wan, Y. Li, Q. Li, W. Zhou, Q. J. Zheng, X. C. Wu, C. G. Xu, B. P. Zhu and D. M. Lin, *J. Am. Ceram. Soc.*, **97**, 1809–1818 (2014).
- 39) Y. J. Wu, X. K. Chen, J. Zhang and X. J. Chen, *J. Appl. Phys.*, **111**, 053927 (2012).