Piezoelectric and electro–optic properties of tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals by phenomenological theory*

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An eighth-order Landau–Devonshire theory is constructed to investigate the piezoelectric and electro–optic properties of tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals ($x=0.38$ and $x=0.4$). The dielectric stiffness coefficients of the Landau potential are obtained by fitting to the dielectric properties and the phase transition temperature between cubic phase and tetragonal phase. It is indicated that tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals have the first-order cubic-tetragonal phase transitions. The dielectric constants are in great agreement with the experimental results. The piezoelectric coefficients d_{33} and d_{31} at room temperature are about 145 pC/N and −62 pC/N respectively which are smaller than that of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals around the morphotropic phase boundary. Moreover, tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals have the linear electro–optic coefficients $r_c=33.7$ pm/V and $r_c=28.8$ pm/V for $x=0.38$ and $x=0.4$, respectively which are in accordance with the measurements.

Keywords: dielectric property, piezoelectric property, electrooptic effect

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1. Introduction

Recently, ferroelectric $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ and $(1-x)$Pb$(Zn_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals have attracted a great deal of attention due to their large piezoelectric properties, high electromechanical coupling factors, and field-induced strain response.[1–8] Moreover, the large piezoelectric coefficient is attractive for the photorefractive effect because the field-induced strain enhances the refractive index change via the photoelastic effect.[9] Therefore, ferroelectric single crystals with high electro–optic coefficients have practical applications in many optical devices, such as electro–optic modulators, switches, frequency shifters and light valves.

Experimentally, the photorefractive properties of tetragonal 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ single crystals have been investigated by the two-wave mixing experiment.[9] The effective electro–optic coefficient $r_{\rm eff}=70$ pm/V was observed at room temperature. On the other hand, the electro–optic measurements were performed by using the Senarmont compensator method at room temperature and the linear electro–optic coefficients of tetragonal 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ single crystals were 41–43 pm/V at the wavelength of 633 nm.[10–12] In addition, the electro–optic effects of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals with different structures were measured. Tetragonal 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ single crystals poled along the $\langle 001\rangle$ direction shown $r_{33}=70$ pm/V, and rhombohedral 0.67Pb$(Mg_{1/3}Nb_{2/3})O_3-0.33$PbTiO$_3$ single crystals poled along the $\langle 111\rangle$ direction had $r_{33}=107$ pm/V.[13] The larger electro–optic coefficient of rhombohedral 0.67Pb$(Mg_{1/3}Nb_{2/3})O_3-0.33$PbTiO$_3$ single crystals attributed to their high piezoelectric properties.

Many papers on the electro–optic effect were reported experimentally, however, there have hardly been any publications about theoretical researches of an electro–optic effect in $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals. This is due to the complexity of the phase transitions of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals that no theory can be applied to explain the physical properties very well. Therefore, we suggest an eighth-order Landau–Dovenshire phenomenological theory to investigate the electro–optic effect of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals because of its success in explaining the phase transition and electro–optic effect of BaTiO$_3$ and $(Ba_{1-x}Sr_x)TiO_3$.

Here, an eighth-order Landau–Dovenshire theory is constructed by fitting to the phase transition temperature and dielectric properties of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals; then the piezoelectric coefficients and electro–optic effect are investigated. Theoretical calculations indicate that the observations of piezoelectric and electro–optic coefficients can be explained by the eighth-order theory.

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2. Model and method

Ferroelectric $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals ($x = 0.38$ and $x = 0.4$) have the phase transition from cubic paraelectric phase to tetragonal phase.[14,15] Given the spontaneous polarization and the applied electric field are along the [001] direction, the eighth-order thermodynamical potential can be given as a polynomial of the polarization component P_3 under mechanical stress-free boundary condition[16]

$$G = \alpha_1 P_3^2 + \alpha_{11} P_3^4 + \alpha_{111} P_3^6 + \alpha_{1111} P_3^8 - E_3 P_3, \quad (1)$$

where α_1, α_{11}, α_{111}, and α_{1111} are dielectric stiffness coefficients. The temperature dependence of ferroelectricity is mainly governed by the dielectric stiffness coefficient α_1, and the other dielectric stiffness coefficients may be taken as temperature-independent parameters. $\alpha_1 = (T - T_0)/2\varepsilon_0 C$ obeys the Curie–Weiss law. Here, T_0 and C are the Curie–Weiss temperature and constant respectively, and ε_0 is the dielectric constant of free space. In order to investigate the thermodynamic properties, these dielectric stiffness coefficients should be obtained firstly. Therefore, α_1 is fitted to the dielectric constant of the C phase by using the Curie–Weiss law. α_{11}, α_{111}, and α_{1111} are fitted to the phase transition temperature from the cubic phase to the tetragonal phase, and to the dielectric constant of the tetragonal phase. The dielectric stiffness coefficients obtained in this work are listed in Ref. [17].

The polarization of the tetragonal phase is determined by the equilibrium condition $\partial G/\partial P_3 = 0$, which is

$$2\alpha_1 P_3 + 4\alpha_{11} P_3^3 + 6\alpha_{111} P_3^5 + 8\alpha_{1111} P_3^7 - E_3 = 0. \quad (2)$$

The dielectric constant ε_{33} can be given by differentiating the thermodynamic potential G

$$\varepsilon_{33} = \frac{1}{\varepsilon_0(2\alpha_1 + 12\alpha_{11} P_3^2 + 30\alpha_{111} P_3^4 + 56\alpha_{1111} P_3^6)}. \quad (3)$$

The piezoelectric coefficient d_{ln} can be derived by the relation $d_{ln} = \partial S_n/\partial E_l$, where S_n is the spontaneous strain.[18] Therefore, the piezoelectric coefficients $d_{33} = \partial S_3/\partial E_3$ and $d_{31} = \partial S_1/\partial E_3$ are calculated with the strain $S_3 = Q_{11} P_3^2$ and $S_1 = -Q_{12} P_3^2$,[15] where Q_{11} and Q_{12} are electrostrictive coefficients.

The optic property of crystal is generally described by the refractivity n_{mn}, which is along the spontaneous polarization. The relation between optic frequency permittivity and refractivity ascribed to the electro–optic effect is $n_{mn}^2 = \varepsilon_{mn}(\infty)/\varepsilon_0$. Defining $B_{mn} = 1/n_{mn}^2$, the shifting of refractivity is written as

$$\Delta B_{mn} = \frac{1}{n_{mn}^2} - \frac{1}{n_0^2}, \quad (4)$$

where n_0 is the refractive index of the single crystals without applying an electric field.

On the other hand, the refractivity is also described by the independent parameter P which is the sum of spontaneous polarization P_S and the field-induced polarization P_E. Therefore, the variety of refractivity can be given as a function of field-induced polarization P_E

$$\Delta B_{mn} = f P_p + g P_p P_q, \quad (5)$$

where P_p and P_q are the field-induced polarization, f is the linear polarization-optic coefficient, and g is the quadratic polarization-optic coefficient. The linear polarization-optic coefficient f and quadratic polarization-optic coefficient g, which are the functions of spontaneous polarization P_S, can be deduced from Eqs. (4) and (5).

The relation between linear electro–optic coefficient r_c and linear polarization-optic coefficient f can be found by[19]

$$r_c = f\varepsilon_0\varepsilon_{33}. \quad (6)$$

3. Results and discussion

The spontaneous polarizations P_s of tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals ($x = 0.38$ and $x = 0.4$) are presented in Fig. 1. As shown in the figure, the cubic-tetragonal phase transitions occur at 175 °C and 182 °C for 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3$−0.38PbTiO$_3$ and 0.6Pb$(Mg_{1/3}Nb_{2/3})O_3$−0.4PbTiO$_3$ single crystals respectively, which are in accordance with the measurements of 174 °C[14] and 190 ± 5 °C.[15] The polarizations increase as the temperature cools down to room temperature, and are discontinuous at the phase transition temperature, which indicates that the phase transitions from the cubic phase to the tetragonal phase are of the first-order. These results are in agreement with the experimental measurements.[15,20] Moreover, the polarization of 0.6Pb$(Mg_{1/3}Nb_{2/3})O_3$−0.4PbTiO$_3$ single crystals is larger than that of 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3$−0.38PbTiO$_3$ single crystals because of possessing more ferroelectric PbTiO$_3$ composition.

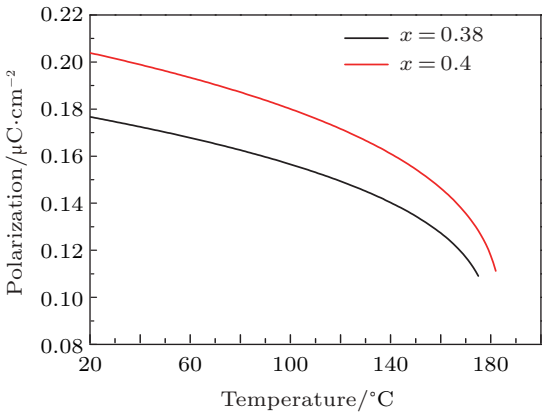


Fig. 1. (color online) The temperature dependence of spontaneous polarizations of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals.

Figure 2 shows the temperature dependence of dielectric constants ε_{33} in $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals. The scattered dots are experimental measurements resulted from Refs. [14] and [15] for $x = 0.38$ and $x = 0.4$ respectively. The solid lines are the theoretical results. The dielectric constants in the cubic phase are fitted by the Curie–Weiss law $\varepsilon = C/(T - T_0)$, and in the tetragonal phase are fitted using Eq. (3). Due to the relaxor behavior, the dielectric constants of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals with less PT composition have a strong deviation to the Curie–Weiss law above the Curie temperature. However, for $x > 0.35$, $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals show a weak relaxor behavior.[15] Therefore, the dielectric constants above the Curie temperature are fitted to the Curie–Weiss law for simplicity. The dielectric constants are discontinuous at the phase transition temperature, which show the first-order phase transitons. The room temperature dielectric constants of 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ and 0.6Pb$(Mg_{1/3}Nb_{2/3})O_3-0.4$PbTiO$_3$ single crystals are 834 and 713 respectively, which are in agreement with the observations of 734–828[3,9,14] and 420.[21] In a word, the calculations of dielectric constants for $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals are in accordance with the experimental results. Most importantly, the dielectric constants of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals are much larger than those of conventional ferroelectrics, such as BaTiO$_3$[16] and PbTiO$_3$.[22]

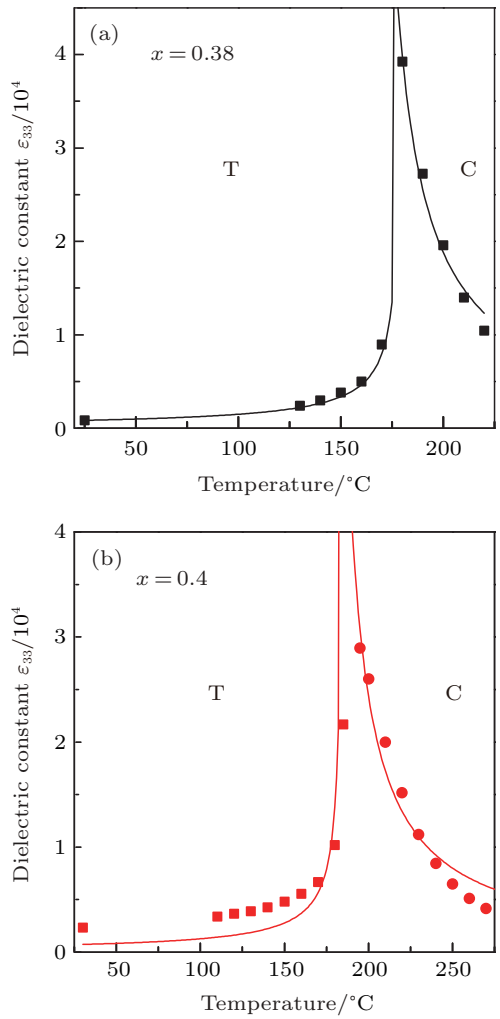


Fig. 2. (color online) Dielectric constants ε_{33} of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals. Solid lines are the theoretical results calculated by eighth-order Landau–Dovenshire theory. Scattered dots are experimental observations originated from Ref. [14] for $x = 0.38$ (a), and Ref. [15] for $x = 0.4$ (b).

The piezoelectric coefficients d_{33} and d_{31} as a function of temperature are plotted in Fig. 3 for $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals. The definition of piezoelectric coefficient d_{ln} shown in Section 2 is associated with the electrostrictive coefficients $Q_{i,j}$. Therefore, the electrostrictive coefficients $Q_{11} = 0.056$ m^4/C^2 and $Q_{12} = -0.024$ m^4/C^2 are taken into account in the calculations for $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals ($x = 0.38$ and $x = 0.4$).[23] It is worthwhile noting that another critical piezoelectric coefficient d_{15} is important to $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals and a high shear piezoelectric behavior was observed in tetragonal 0.58Pb$(Mg_{1/3}Nb_{2/3})O_3-0.42$PbTiO$_3$ single crystal.[24] However, piezoelectric coefficient d_{15} cannot be obtained by our eighth-order theory because of the electric field applied along the [001] direction. As seen from the figure, the piezoelectric coefficients d_{33} and d_{31} both increase with the temperature increasing. The piezoelectric coefficients d_{33} at room temperature are 145 pC/N and 143 pC/N for 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ and 0.6Pb$(Mg_{1/3}Nb_{2/3})O_3-0.4$PbTiO$_3$ single crystals respectively, which are comparable with the measurements of 210–400 pC/N[14,20,25,26] and 300 pC/N.[27] The piezoelectric coefficient d_{31} of 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ single crystals is -62 pC/N which is in great agreement with the experimental result of -60 pC/N.[11,13] Furthermore, the piezoelectric coefficients of 0.62Pb$(Mg_{1/3}Nb_{2/3})O_3-0.38$PbTiO$_3$ and 0.6Pb$(Mg_{1/3}Nb_{2/3})O_3-0.4$PbTiO$_3$ single crystals are about the same. Tetragonal $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals have large piezoelectric properties, however, they are smaller than those of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals, which are around the morphotropic phase boundary. Because they have the complicated crystal structure and the larger piezoelectric coefficients, they could be attributed to the relaxor ferroelectric state,[20] polydomain crystal structure,[25] or the polarization rotation induced by an electric field.[28]

By utilizing Eqs. (4)–(6), the linear electro–optic coefficients r_c of $(1-x)$Pb$(Mg_{1/3}Nb_{2/3})O_3$–xPbTiO$_3$ single crystals ($x = 0.38$ and $x = 0.4$) are obtained and shown in Fig. 4. The linear electro–optic coefficients increase as the temperature increases. However, the linear electro–optic coefficients are nearly invariant at the

low temperature, which are very similar to those of the measurement.[12] The linear electro–optic coefficient of $0.62Pb(Mg_{1/3}Nb_{2/3})O_3-0.38PbTiO_3$ single crystals is larger than that of $0.6Pb(Mg_{1/3}Nb_{2/3})O_3-0.4PbTiO_3$ single crystals. Moreover, the $0.62Pb(Mg_{1/3}Nb_{2/3})O_3-0.38PbTiO_3$ single crystals have a linear electro–optic coefficient of 33.7 pm/V, which is in agreement with the experimental results of 41–43.3 pm/V.[10–12]

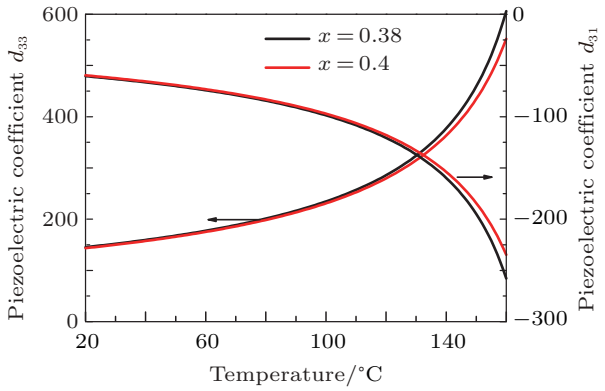


Fig. 3. (color online) Piezoelectric coefficients d_{33} and d_{31} of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ single crystals.

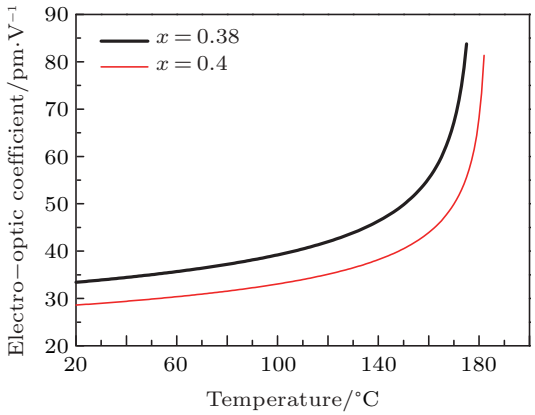


Fig. 4. (color online) The linear electro–optic coefficients of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ single crystals as a function of temperature.

4. Conclusion

In this paper, an eighth-order Landau–Devonshire theory is constructed to investigate the ferroelectric, dielectric, piezoelectric, and electro–optic properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ single crystals ($x = 0.38$ and $x = 0.4$). By fitting to the experimental measurements, the dielectric stiffness coefficients are obtained. Theoretical calculations indicate that the experimental observations of dielectric constants, piezoelectric coefficients, and linear electro–optic coefficients are explained very well by the eighth-order Landau–Devonshire theory. Therefore, these results could be useful for further experimental studies.

References

[1] Li X B and Luo H S 2010 *J. Am. Ceram. Soc.* **93** 2915
[2] Noheda B, Cox D E, Shirane G, Gao J and Ye Z G 2002 *Phys. Rev. B* **66** 054104
[3] Feng Z Y, Zhao X Y and Luo H S 2006 *J. Am. Ceram. Soc.* **89** 3437
[4] Fang S X, Tang D Y, Chen S M, Zhang H and Liu Y L 2015 *Chin. Phys. B* **24** 027802
[5] Li F, Zhang S J, Xu Z, Wei X Y, Luo J and Shrout T R 2010 *J. Appl. Phys.* **108** 034106
[6] He C J, Xu F, Wang J M, Du C L, Zhu K J and Liu Y W 2011 *J. Appl. Phys.* **110** 083513
[7] He C J, Fu X D, Xu F, Wang J W, Zhu K J, Du C L and Liu Y W 2012 *Chin. Phys. B* **21** 054207
[8] Park S E and Shrout T R 1997 *J. Appl. Phys.* **82** 1804
[9] He C J, Zhou Z X, Liu D J, Zhao X Y and Luo H S 2006 *Appl. Phys. Lett.* **89** 261111
[10] Wan X M, Xu H Q, He T H, Lin D and Luo H S 2003 *J. Appl. Phys.* **93** 4766
[11] He C J, Ge W W, Zhao X Y, Xu H Q, Luo H S and Zhou Z X 2006 *J. Appl. Phys.* **100** 113119
[12] Wan X M, Wang D Y, Zhao X Y, Luo H S, Chan H L W and Choy C L 2005 *Solid State Commun.* **134** 547
[13] Jeong D Y, Lu Y, Sharma V, Zhang Q M and Luo H S 2003 *Jpn. J. Appl. Phys.* **42** 4387
[14] Feng Z Y, Zhao X Y and Luo H S 2004 *J. Phys.: Condens. Matter* **16** 6771
[15] Noblanc O, Gaucher P and Calvarin G 1996 *J. Appl. Phys.* **79** 4291
[16] Li Y L, Cross L E and Chen L Q 2005 *J. Appl. Phys.* **98** 064101
[17] The list of the parameters of G (in SI units, the temperature T in °C) used in the calculations. For $x = 0.38$: $T_0 = 162.1$, $C = 7.13\times10^5$, $\alpha_{11} = -1.7\times10^8$, $\alpha_{111} = 6.9\times10^9$, and $\alpha_{1111} = 1.4\times10^{10}$. For $x = 0.4$: $T_0 = 175.6$, $C = 5.95\times10^5$, $\alpha_{11} = -1\times10^8$, $\alpha_{111} = 3.9\times10^9$, and $\alpha_{1111} = 1\times10^{10}$
[18] Emelyanov A Y, Pertsev N A and Kholkin A L 2002 *Phys. Rev. B* **66** 214108
[19] Di Domenico M and Wemple S H 1969 *J. Appl. Phys.* **40** 720
[20] Zhao X Y, Wang J, Chew K H, Chan H L W, Choy C L, Yin Z W and Luo H S 2004 *Mater. Lett.* **58** 2053
[21] Tang Y X, Wan X M, Zhao X Y, Pan X M, Lin D, Luo H S, Sun J L, Meng X J and Chu J H 2005 *J. Appl. Phys.* **98** 084104
[22] Huan M J, Furman E, Jang S J, Mckinstry H A and Cross L E 1987 *J. Appl. Phys.* **62** 3331
[23] Li F, Jin L, Xu Z, Wang D W and Zhang S J 2013 *Appl. Phys. Lett.* **102** 152910
[24] Li F, Zhang S J, Xu Z, Wei X Y and Shrout T R 2011 *Adv. Funct. Mater.* **21** 2118
[25] Feng Z Y, Zhao X Y and Luo H S 2006 *J. Appl. Phys.* **100** 024104
[26] Wan X M, Luo H S, Wang J, Chan H L W and Choy C L 2004 *Solid State Commun.* **129** 401
[27] Emelyanov A S, Raevskaya S I, Savenko F I, Topolov V Y, Raevski I P, Turik A V and Kholkin A L 2007 *Solid State Commun.* **143** 188
[28] Guo Y P, Luo H S, Ling D, Xu H Q, He T H and Yin Z W 2003 *J. Phys.: Condens. Matter* **15** L77