A polarized micro-Raman study of a $0.65PbMg_{1/3}Nb_{2/3}O_3$–$0.35PbTiO_3$ single crystal*

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(Received 21 June 2011; revised manuscript received 27 October 2011)

Polarized micro-Raman spectra of a $0.65PbMg_{1/3}Nb_{2/3}O_3$–$0.35PbTiO_3$ (0.65PMN–0.35PT) single crystal poled in the [001] direction are obtained in a wide frequency range (50–2000 cm^{-1}) at different temperatures. The best fit to the Raman spectrum at 77 K is achieved using 17 Lorenzians to convolute into it, and this is proved to be a reasonable fit. According to the group theory and selection rules of overtone and combinational modes, apart from the seven Raman modes that are from first-order Raman scattering, the remaining ones are attributed to being from second-order Raman scattering. A comparison between the experimental results and theoretical predictions shows that they are in satisfactory agreement with each other. Our results indicate that at 77 K the sample belongs to the rhombohedral symmetry with the $C_{3v}^5(R3m)$ space group ($Z = 1$). In our study, on heating, the 0.65PMN–0.35PT single crystal undergoes a rhombohedral → tetragonal → cubic phase transition sequence. The two phase transitions occur at 340 and 440 K, which correspond to the disappearance of the soft mode near 106 cm^{-1} recorded in VV polarization and the vanishing of the band around 780 cm^{-1} in VH polarization, respectively.

Keywords: 0.65PMN–0.35PT, polarized micro-Raman, second-order Raman scattering, phase transition

PACS: 78.30.–j, 77.80.B–, 77.80.Jk **DOI:** 10.1088/1674-1056/21/1/017803

1. Introduction

Ferroelectric relaxor solid solutions (1-x)Pb$(Mg_{1/3}Nb_{2/3})O_3$–$x$$PbTiO_3$ (PMN–xPT), each of which exhibit a drastic increase in piezoelectric property, have attracted much attention in the past few years because of their numerous potential applications and fundamental research interest. The solid solutions with compositions near the morphotropic phase boundary (MPB) ($0.32 \leq x \leq 0.35$)[1,2] have a large piezoelectric constant, $d > 2000$ pC/N, and an electromechanical coupling coefficient, $k_{33} > 90\%$, when they are poled along the [001] direction of cubic coordinates.[3–5] These results indicate that PMN–xPT are promising candidates for applications in medical ultrasonic imaging, sonar transducers and high strain actuators, but the solid solutions have unstable properties at MPB, where their structures are very complex, which is generally attributed to the coexistence of intermediate phases involving monoclinic (M) and/or orthorhombic (O) phases based on the polarization rotation mechanism.[6] For these reasons, much theoretical and experimental research work has been performed in order to fully ascertain the structural characteristics and the origin of this giant piezoelectricity of the PMN–xPT, especially for the compositions at MPB. However, the results and their interpretations, as well as the structural data presented by different authors, are not fully consistent. For example, the solid solutions of PMN–xPT near MPB have been well understood to be a tetragonal symmetry with the $C_{4v}^1(P4mm)$ space group above room temperature and a cubic symmetry with the $O_h^5(Pm3m)$ space group at high temperature. Various mechanisms have been proposed for their structural symmetry at low temperature, including low-temperature rhombohedral symmetry for the $C_{3v}^5(R3m)$ space group with $Z = 1$,[7,8] low-temperature rhombohedral symmetry for the $C_{3v}^5(R3m)$ space group with $Z = 2$[9,10] and low-temperature monoclinic symmetry for the $C_s^1(Pm)$ space group.[11,12] Therefore, despite intensive research, there has been no clear understanding of the structural symmetry of PMN–xPT at low temperature, and further systemic investigation is needed.

Raman spectroscopy (RS) is, owing to its intense sensitivity to local symmetry, an extremely useful tool for obtaining the structural information of materials, and has been proved to be an efficient method of studying PMN–xPT.[7–10,13–21] Although Raman

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10674171 and 10874236).

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scattering of PMN–xPT is extensively investigated, and most of the fundamental Raman-active modes are assigned,[7−10,13,19] no Raman spectra of PMN–xPT up to 2000 cm^{-1} have been reported so far.

In the present paper, we carry out a polarized micro-Raman study of a 0.65PMN–0.35PT single crystal poled in the [001] direction in a large frequency range (50–2000 cm^{-1}) at different temperatures to investigate the first and second Raman modes. According to the group theory and the selection rules of overtone and combinational modes, besides the seven Raman modes from the first-order scattering, the remaining ones are attributed to being from the second-order Raman scattering of the 0.65PMN–0.35PT single crystal. These results provide useful information for studying the relationship between the structural symmetry of 0.65PMN–0.35PT at low temperature and its vibrations.

2. Experimental details

The samples were transparent single crystals with a composition of 0.65PMN–0.35PT, and they were prepared at the Shanghai Institute of Ceramics at the Chinese Academy of Sciences.[22] The sample used in this experiment had a size of about 5 ×5 ×1 mm, and it was cut from crystal grown using a modified Bridgman technique. The samples were prepared in such a way that the large faces were perpendicular to the pseudocubic [100] direction with long edge orientations [100]/[010]. The samples were optically polished and annealed at 550 K for half an hour in air, in order to minimize residual stresses. Micro-Raman measurements were performed using an HR800 Jobin Yvon spectrometer equipped with an Olympus microscope and a cooled charge-coupled device to detect the scattered light. The spectra were excited with the 532 nm line of a solid state laser, and the 633 nm line of a He–Ne ion laser as an excitation source in order to identify whether the signal originated from Raman or from luminescence. The spectrometer slit was set to give a spectral resolution always better than 1 cm^{-1}. An Olympus 50× objective with a focal distance of 20 mm and a numeric aperture of 0.35 was used to focus the laser beam on the polished sample surface, and the spot size was about 1.5 μm. The polarization direction of the incident light was parallel to the y-direction (010). The spectra were recorded in the parallel $z(yy)\bar{z}$ (VV) and crossed $z(yx)\bar{z}$ (VH) polarization configurations, respectively, where x, y and z are the cubic axes. The sample was placed inside a cryostat cell and the temperature of the samples was monitored between liquid nitrogen temperature and 640 K at ± 0.1 K using a Linkman THMS 600 hot-stage.

3. Results and discussion

The polarized Raman spectra of 0.65PMN–0.35PT single crystals in a frequency range of 50–2000 cm^{-1} are presented in Fig. 1 in a temperature range from 77 to 640 K using 532 nm laser radiation, which are similar to the spectra obtained with an He–Ne laser, except for some increase in the intensities of the Raman bands. It is seen from Fig. 1 that the VV and VH polarized spectra at low temperature are very similar and differ only in their intensities. Meanwhile, the Raman spectra in Fig. 1 are similar to those presented by different authors.[9,13,16,20,21] They also consist of four broad bands around 780, 580, 260 and 60 cm^{-1}, even at 77 K. These modes correspond mainly to the Nb–O–Mg stretching mode, oxygen bending vibration, B-site ion against O stretching vibration inside the octahedral, and Pb against BO_6 octahedral translation vibration, respectively.[23] We can see that the peak intensities and the peak positions of the Raman modes shown in Fig. 1 vary with temperature. The sample cooled at 77 K has the strongest Raman scattering intensity and the narrowest linewidth at the temperatures investigated.

The structural symmetries of bulk PMN–xPT have been analysed by several authors based on the results from X-ray diffraction, polarization microscopy and dielectric measurements.[11−13,21,24,25] However, PMN–xPT is a typical material in structural-phase transition, and can exist in several polymorphs at different temperatures. For example, the unit cell of PMN–xPT with a rhombohedral symmetry $C_{3v}^5(R3m)$ space group at low temperature can consist of one formula unit ($Z = 1$) or two formula units ($Z = 2$) of ABO_3 due to the existence of a 1 : 1 order in the B-sublattice. Additionally, the existence of monoclinic symmetry for PMN–xPT at low temperature has also been reported.[11−13] According to group theory, there are seven Raman active modes which can be classified as $3A_1$ and $4E$ for C_{3v}^5 with $Z = 1$, 16 Raman active modes which can be classified as $7A_1$ and $9E$ for $C_{3v}^5$with $Z = 2$, and 12 Raman active modes which can be classified as $8A_1$ and $4A_2$ for C_s^1, respectively. The frequency, linewidth

and intensity of each Raman active mode shown in Fig. 1 are determined by Lorenzian curve fitting.

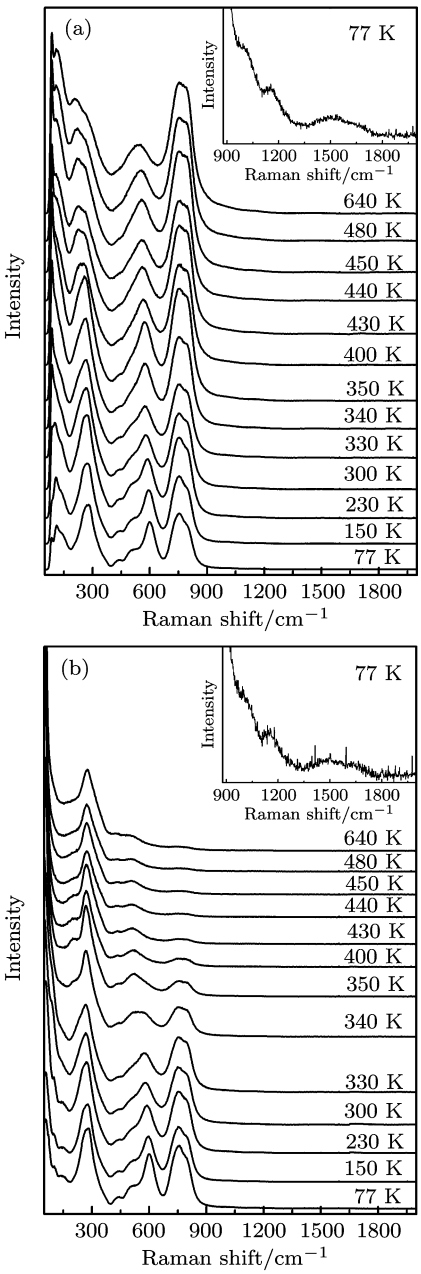


Fig. 1. Raman spectra of 0.65PMN–0.35PT single crystals from 77 to 640 K in (a) VV and (b) VH polarization geometry, respectively. The insets display the magnified high-order Raman modes of 0.65PMN–0.35PT single crystals at 77 K in both polarization geometries, respectively.

Figure 2 represents an example of fitting to the Raman spectrum of 0.65PMN–0.35PT single crystals at 77 K. The best fitting to the Raman spectrum over the frequency range 50–900 cm^{-1} was achieved by using 12 Lorenzians to convolute into the Raman spectrum. Additionally, the corresponding extra Raman modes over the range 900–2000 cm^{-1} are plotted in the inset with the magnified intensity scale. All 17 Raman modes are denoted as F_1–F_7 (fundamental Raman mode), H_1–H_9 (high-order Raman mode) and S (ferroelectric soft mode). Table 1 shows the frequencies, linewidths and intensities of all 17 Raman active modes at 77 K. Our fitting results in a frequency range of 50–900 cm^{-1} are similar to previous results by different authors,[7–9,13] and an extra five new weak modes over 900–2000 cm^{-1} are obviously observed, which has never been reported so far. These new Raman modes are advantageous in studying the structural properties of PMN–xPT and will be discussed later.

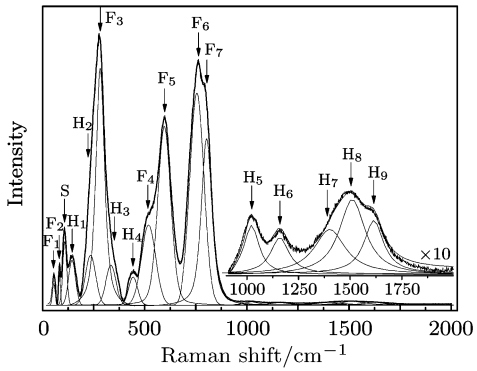


Fig. 2. The deconvolution of unpolarized Raman spectrum measured at 77 K. F_1–F_7 denote the seven fundamental Raman modes, H_1–H_9 the nine high-order Raman modes, and S the ferroelectric soft mode.

Regarding the nature of the Raman spectra of PMN–xPT, different interpretations are found in the published literature, and some of them are contradictory.[7,8,10,13] Idink and White[7] and Svitelskiy *et al.*,[8] respectively, reported on the broad Raman spectrum in the bulk PMN–xPT which consists of nine and 11 Raman modes obtained by Lorenzian curve fitting, and attributed them to the first-order Raman scattering from the space group C_{3v}^5 with $Z = 1$. However, the group theory analysis applied in keeping with their crystal structure refinement does not give good agreement. Recently, Slodczyk *et al.*[10,13] interpreted the correlation between 13 Raman modes observed in their Raman spectra and the symmetry of the space group C_{3v}^5 with $Z = 2$ of the PMN–xPT, in terms of the charge balanced random layer model. In this case, 16 active Raman modes are allowed for the space group C_{3v}^5 with $Z = 2$. They ascribed the 13 Raman modes distributed in the range 50–900 cm^{-1} to be first-order Raman spectra because of the decrease in intensity with temperature, as well as the lack of Raman bands above 900 cm^{-1}. Then they

Table 1. The frequencies, linewidths and intensities of the fundamental and higher order Raman modes obtained by deconvoluting the Raman spectrum of 0.65PMN–0.35PT single crystals at 77 K.

Mode	Frequency/cm^{-1}	Linewidth/cm^{-1}	Intensity	Fundamental mode	Higher order mode/cm^{-1}	Error/cm^{-1}
F_1	52	17.1	M	yes		
F_2	83	10.4	M	yes		
S	106	22.5	M			
H_1	142	39.7	M		52 + 83	+7
H_2	238	53.3	M, SH		514 − 280	−4
F_3	280	54.7	VS	yes		
H_3	334	56.9	W, SH		280+52	−2
H_4	434	51.6	M		514 − 83	−3
F_4	514	73.4	VS	yes		
F_5	597	74.3	VS	yes		
F_6	754	85.8	VS	yes		
F_7	807	61.6	VS	yes		
H_5	1025	86.8	VW		514+514	+3
H_6	1165	95.4	VW		597+597	+29
H_7	1402	176.2	VW		807+597	+2
H_8	1505	157.4	VW		754+754	+3
H_9	1618	135.1	VW		807+807	−4

Notes: For the intensity, VS, M, W, and VW represent the intensities as being very strong, medium, weak, and very weak, respectively; and SH represents the should peak.

ascribed 14 Raman modes distributed in the same frequency range to be the first-order Raman modes of the PMN–xPT with monoclinic symmetry because of the coexistence of different phases. In fact, comparison of the experimental results with theoretical predictions did not show a satisfactory agreement. In an attempt to explain their results, Slodczyk *et al.*[10] showed that the broadening of the Raman modes together with strong overlapping, which were caused by not being fully ordered and homogeneous at the low temperature, make it impossible to distinguish all of them. Unlike the other reports, the Raman spectrum in our sample consists of 12 modes over the range 50–900 cm^{-1} and five weak modes above 900 cm^{-1}. It is thus believed that the argument above cannot explain our experimental observation. It seems that the possibility of a second-order contribution is also involved.

A Raman or infrared spectrum of a crystal (molecule) may contain numerous combination and overtone bands arising from anharmonicity. The new weak modes at 1025, 1165, 1402, 1505 and 1618 cm^{-1} are clearly observable in Fig. 2. They are broad with a Lorentzian line shape and their linewidths are in the region 80–180 cm^{-1}. Meanwhile, their frequencies are too high to be related to the first-order silent modes. Consequently, they are likely to be second-order active Raman modes. These bands have well defined frequencies and widths, and are of the same order of magnitude as the fundamental bands. In these cases, predictions from selection rules based on the factor group are generally sufficient.[26,27] High-order Raman modes are usually very weak, e.g. the intensity of second-order Raman modes is about one or two orders of magnitude smaller than those of their fundamental modes. Figure 2 gives the intensity ratio $I_{754}/I_{1052} = 41$. The higher order Raman modes in the Raman spectrum at 77 K are listed in Table 1, which are in good agreement with the results from the quantum theory. The appearance of high-order modes in a Raman spectrum of 0.65PMN–0.35PT brings new possibilities for studying the structural symmetries of PMN–xPT because the selection rules of high-order modes are different from those of fundamental modes.

It can be seen from Fig. 1 that the mode intensity and mode position of the Raman spectrum varies with temperature. As the temperature increases, Raman lines broaden and some merge with each other. In the meantime, the relative intensities of Raman modes also change. Two significant changes can be observed as follows: firstly, the S mode around 106 cm^{-1} at 77 K, which appears only in VV polarization, decreases in intensity and shifts towards lower frequency with a temperature increase and eventually merges into a broad mode F_2 around 83 cm^{-1} when the temperature reaches 340 K. The mode F_2 at 83 cm^{-1} is almost stationary, but the S mode at 106 cm^{-1} shifts to 83 cm^{-1} from 77 to 340 K, with a redshift as large as 23 cm^{-1}. The S mode has been at-

tributed as characteristic of the rhombohedral ferroelectric phase in a 0.67PMN–0.33PT.[20,21] The disappearance of the S mode at 340 K manifests the appearance of a tetrahedral phase from a rhombohedral ferroelectric phase in our sample. Secondly, it can be seen from Fig. 1(b) that at 340 K the distinct broad modes around 780 cm^{-1} and the mode around 580 cm^{-1} decrease gradually with a temperature increase, while the modes around 200–400 cm^{-1} turn to intense gradually, compared with those of the spectra at $T < 340$ K. The Raman modes around 580 cm^{-1} disappear completely at 400 K, while those around 600–900 cm^{-1} can barely be observed at 440 K. In order to illustrate the evolution of the Raman selection rules (RSRs) as a function of temperature, we report on the evolution of the intensity ratio VH/VV ($I_{780}^{VH}/I_{780}^{VV}$) against temperature for the Raman mode around 780 cm^{-1} in Fig. 3. The ratio remains constant and equals unity when the temperature is below 340 K, and its value decreases abruptly on heating above this temperature. It is known that the bands around 780 and 550 cm^{-1} correspond to the Nb–O–Mg stretching mode and the Nb–O–Nb stretching mode, respectively.[23] It can be seen from Fig. 1(b) that the Raman spectrum starts to change due to the variation in the Nb–O bond as the temperature is above 340 K. This means that the Nb–O octahedral shows obvious distortion and even complete distortion. Actually, the variation of the intensity ratio corresponds to an increase in the absolute intensity of the mode in parallel polarizations and to a decrease in crossed polarization. This temperature of 340 K, which can be attributed to the appearance of the phase transition from a rhombohedral ferroelectric phase to a tetrahedral ferroelectric phase in 0.65PMN–0.35PT single crystals, coincides with the temperature where the S mode merges into the broad mode F_2 around 83 cm^{-1} for that described above. Figure 3 shows that the value of $I_{780}^{VH}/I_{780}^{VV}$ decreases monotonically with temperature increasing from 350 to 440 K, and is close to zero when the temperature reaches 440 K. Meanwhile, the number of Raman modes at high temperature are obviously less than those at low temperature, as shown in Fig. 1. This temperature of 440 K represents the phase transition from tetragonal to cubic, which also means the change between the ferroelectric and paraelectric phases. The Curie temperature (T_C) of the 0.65PMN–0.35PT single crystal is 440 K, which is in good agreement with the results from X-ray powder diffraction and micro-Brillouin scattering.[25,28]

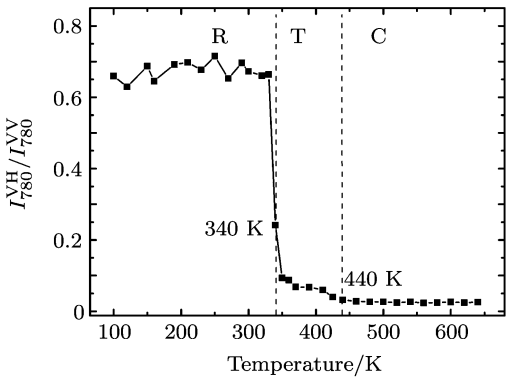


Fig. 3. The temperature dependence of the ratio between integral intensities of the band at 780 cm^{-1} in VH and VV polarization geometries.

4. Conclusion

Polarized micro-Raman scattering of a 0.65PMN–0.35PT single crystal poled in the [001] direction is performed in a frequency range of 50–2000 cm^{-1} at temperatures ranging from 77 to 640 K. The best fit to the Raman spectrum at 77 K was achieved by using 17 Lorenzians to convolute into it, and is proved to be a reasonable fit. According to the group theory and the selection rules of overtone and combinational modes, besides seven Raman modes from the first-order scattering, the remaining ones are attributed to being from the second-order Raman scattering of the 0.65PMN–0.35PT single crystal, which shows that they are in satisfactory agreement with theoretical predictions. These results show that the 0.65PMN–0.35PT single crystal poled in the [001] direction at 77 K belongs to the rhombohedral symmetry with the $C_{3v}^5(R3m)$ space group ($Z = 1$). The results of the Raman spectra show that the sample in our study undergoes the sequence of the phase transitions. The first phase transition, from the rhombohedral ($R3m$) to tetragonal phase ($P4mm$), occurs at $T_{R-T} = 340$ K, which corresponds to the disappearance of the soft mode S recorded in the parallel polarization. The second one, the tetragonal-cubic phase transition, appears at $T_{T-C} = 440$ K, which is verified by the vanishing mode of 780 cm^{-1} in crossed polarization and also marked by the variation of the mode of 262 cm^{-1} in crossed polarization.

References

[1] Ho J, Liu K and Lin I 1993 *J. Mater. Sci.* **28** 4497
[2] Kelly J, Leonard M, Tantigate C and Safari A 1997 *J. Am. Ceram. Soc.* **80** 957
[3] Park S E and Shrout T R 1997 *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **44** 1140

[4] Park S E E, Lopath P D, Shung K K and Shrout T R 1997 *Proc. SPIE* **3037** 140
[5] Zhang R, Jiang B and Cao W 2001 *J. Appl. Phys.* **90** 3471
[6] Fu H and Cohen R E 2000 *Nature* **403** 281
[7] Idink H and White W B 1994 *J. Appl. Phys.* **76** 1789
[8] Svitelskiy O, Toulouse J, Yong G and Ye Z G 2003 *Phys. Rev.* B **68** 104107
[9] Kamba S, Buixaderas E, Petzelt J, Fousek J, Nosek J and Bridenbaugh P 2003 *J. Appl. Phys.* **93** 933
[10] Slodczyk A, Kania A, Daniel P and Ratuszna A 2005 *J. Phys.* D: *Appl. Phys.* **38** 2910
[11] Noheda B, Cox D, Shirane G, Gao J and Ye Z G 2002 *Phys. Rev.* B **66** 054104
[12] Ye Z G, Noheda B, Dong M, Cox D and Shirane G 2001 *Phys. Rev.* B **64** 184114
[13] Slodczyk A, Daniel P and Kania A 2008 *Phys. Rev.* B **77** 184114
[14] Jiang F and Kojima S 1999 *Jpn. J. Appl. Phys.* **38** 5128
[15] Ohwa H, Iwata M, Orihara H, Yasuda N and Ishibashi Y 2001 *J. Phys. Soc. Jpn.* **70** 3149
[16] Slodczyk A, Colomban P and Pham-Thi M 2008 *J. Phys. Chem. Solids* **69** 2503
[17] Curecheriu L P, Mitoseriu L, Ianculescu A and Braileanu A 2009 *Appl. Phys.* A **97** 587
[18] Ching-Prado E, Cordero J, Katiyar R and Bhalla A 1996 *J. Vac. Sci. Technol.* A **14** 762
[19] Lima J A, Paraguassu W, Freire P T C, Souza Filho A G, Paschoal C W A, Filho J M, Zanin A L, Lente M H, Garcia D and Eiras J A 2009 *J. Raman. Spectrosc.* **40** 1144
[20] Sun J Y, Yang Y, K. Z, Liu Y L, Siu G and Xu Z 2008 *Chin. Phys. Lett.* **25** 290
[21] Shen M, Siu G G, Xu Z K and Cao W 2005 *Appl. Phys. Lett.* **86** 252903
[22] Luo H, Xu G, Xu H, Wang P and Yin Z 2000 *Jpn. J. Appl. Phys.* **39** 5581
[23] Husson E, Abello L and Morell A 1990 *Mater. Res. Bull.* **25** 539
[24] Han J and Cao W 2003 *Phys. Rev.* B **68** 134102
[25] Li F, Zhang S, Xu Z, Wei X, Luo J and Shrout T R 2010 *J. Appl. Phys.* **108** 034106
[26] Liu Y L, Jiang Y J, Liu J Q, Mo Y J, Xie S S, Zhang Z B and Quang S F 1994 *Phys. Rev.* B **49** 5058
[27] Poulet H and Mathieu J P 1976 *Vibration Spectra and Symmetry of Crystals* (New York: Gordon & Breach)
[28] Jiang F and Kojima S 2000 *Phys. Rev.* B **62** 8572