

High-pressure peculiarities in compositionally ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 7025

(<http://iopscience.iop.org/0953-8984/16/39/035>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:59

Please note that [terms and conditions apply](#).

High-pressure peculiarities in compositionally ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$

M Szafrński, A Hilczer and W Nawrociak

Institute of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

E-mail: masza@amu.edu.pl

Received 4 June 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/7025

doi:10.1088/0953-8984/16/39/035

Abstract

We report high-pressure dielectric spectroscopy measurements performed on the compositionally highly ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ ceramic ($S = 0.9$), in the pressure range up to 1 GPa. Two anomalies in the dielectric response of the ceramic have been observed: one related to the spontaneous ferroelectric phase transition in the ordered regions of the sample and the second one corresponding to the relaxor behaviour of the material. The p - T phase diagram indicates that pressure decreases linearly the temperatures of both anomalies, but with different slopes. The pressure-induced changes in the amplitude of the relaxor dielectric permittivity peak and activation energy of dipolar fluctuations suggest that different mechanisms leading to relaxor characteristics prevail in the disordered and ordered $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$. Two contributions arising essentially from the Pb displacements, (i) along $\langle 111 \rangle$ and (ii) in planes perpendicular to $\langle 111 \rangle$, have been proposed to explain the high-pressure effects and the coexistence of long- and short-range ferroelectric ordering in the system studied.

1. Introduction

Much experimental and theoretical effort has been devoted to study ferroelectric relaxors. They are prospective materials for multiple applications owing to their exceptional dielectric properties, extremely high piezoelectric responses and large electro-optic coefficients [1]. A prominent group among the relaxor compounds is that of lead-based complex perovskites $\text{Pb}(\text{B}'_x\text{B}''_{1-x})\text{O}_3$, where two kinds of cations with different valences, ionic radii and electronegativities occupy perovskite B sites [2]. Lead scandium niobate, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (abbreviated PSN), is a representative of the so-called 1:1 family. It attracts particular interest because the degree of chemical ordering of its B-site cations can be tuned by thermal treatment, and thus the properties of the material can be modified [3, 4]. Moreover, PSN belongs to those

relaxor compounds which transform spontaneously to the ferroelectric phase [4, 5]. The ordering of the Sc^{3+} and Nb^{5+} cations proceeds in the alternating planes perpendicular to the cubic [111] direction that leads to a doubling of the cubic lattice parameter and consequently to the superstructure reflections [3, 6, 7]. In highly ordered PSN the average size of the chemically ordered regions was reported by Malibert *et al* [6] to be about 20 nm, while Perrin *et al* [7] observed in their samples a long-range Sc–Nb order with a coherence length comparable to that of the coherent diffracting PSN crystalline grains. This indicates that the compositional microstructure of the samples strongly depends on the technology of preparation and even the samples characterized by the same degree of chemical order may exhibit different properties. The heterogeneity of this system is further complicated by the presence of polar nanodomains, as evidenced recently from neutron diffraction study [7], playing a key role in the relaxor behaviour. The other important factor is a possible existence of the Pb vacancies in the PSN structure, that can dramatically modify the dielectric response of the crystal [5, 6]. Therefore, the control of the chemical order of the B-site cations is insufficient to reach a controlled modification of the PSN relaxor properties. However, it should be stressed that all types of PSN compounds have a low-temperature structure with a long-range ferroelectric order [6]. The spontaneous transition from the average cubic phase, space group $Pm3m$, to the average rhombohedral phase, space group $R3m$, involves cooperative displacements of Pb and Sc/Nb atoms with respect to the oxygens [6, 7]. A review of the literature data indicates that this transition manifests very sharply in the dielectric response of the disordered PSN, while in the case of highly ordered samples the anomaly is barely detectable [8, 9] or invisible [6, 10]. The discrepancies between the results reported by different authors make it difficult to interpret the experimental data and understand the physics of this system. Therefore, in the present work we have undertaken a pressure study of the dielectric response of highly ordered PSN ceramic. The advantage of employing hydrostatic pressure to study relaxor systems was demonstrated and widely discussed by Samara [11, 12]. Moreover, the pressure studies have a practical meaning because the compressive stress effects can significantly modify the properties of relaxor films [13] engineered for electronic devices.

2. Experimental details

$\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ was prepared as described earlier [9] by the wolframite-type intermediate phase method. The PSN powder was pressed into pellets, sintered in a special closed capsule [3] at 1520 K for 4 h, then annealed at 1270 K for 42 h and finally slowly cooled to room temperature. The degree of order S of the sample was measured by x-ray diffraction using the method previously applied for PST [3, 14]. The ratio of the integrated intensities of the superstructure reflection $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ and fundamental reflection (100) compared to the theoretical value calculated for the fully ordered structure gave $S = 0.9$.

For dielectric studies the sample was prepared in the form of a 0.27 mm thick plate with golden electrodes sputtered on the surfaces to 5.3 mm^2 . The sample was mounted in a high-pressure beryllium–copper cell. Helium was used to transmit the pressure from a GCA-10 gas compressor (Unipress) to the cell. The pressure was calibrated using a manganin gauge and the temperature of the sample was controlled inside the cell by a copper–constantan thermocouple. The dielectric permittivity (ϵ') and tangent of dielectric losses ($\tan \delta$) were measured in the frequency range 100 Hz–1 MHz by a computer-controlled HP 4192A impedance analyser, on heating the sample at a rate of 1 K min^{-1} .

Calorimetric measurements were performed by differential thermal analysis (DTA) in the temperature range from 300 to 420 K. The sample was heated/cooled at a rate of 3 K min^{-1} .

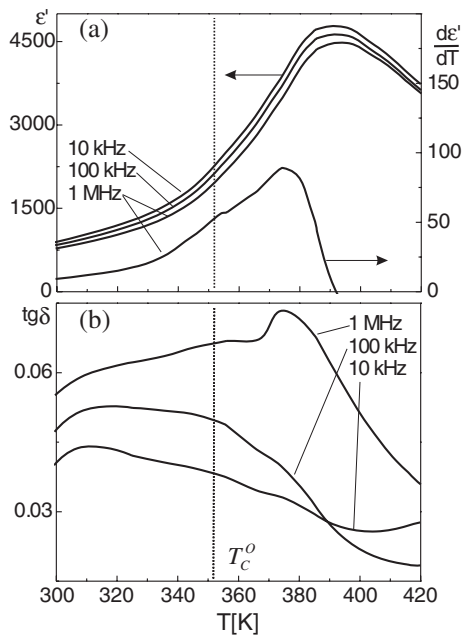


Figure 1. Temperature dependences of the real (a) and imaginary (b) parts of dielectric permittivity; the vertical dotted lines mark the transition temperature T_C^0 .

3. Results

The dielectric response of our highly ordered PSN ceramic, measured at ambient pressure, is shown in figures 1(a) and (b). The temperature dependence of the real part of dielectric permittivity reflects a typical relaxor ferroelectric behaviour, characterized by a diffuse peak and shift of the permittivity maxima ε'_m (at T_m) towards higher temperatures with increasing frequency of the measuring electric field. The maxima are situated around 390 K, which is close to T_m temperatures observed in disordered PSN. This relatively high temperature of T_m , when compared to the data published for ordered PSN [4–6, 9], indicates that the high degree of ordering in the sample cannot necessarily result in a shift of the dielectric peak to lower temperatures. It should also be pointed out that profound frequency dispersion in ε' is observed in the whole temperature range. A careful analysis of the $\varepsilon'(T)$ and $\varepsilon''(T)$ dependences indicates that apart from the main relaxor peak two singularities in the dielectric response of the sample can be distinguished. The first one is visible near $T_C^0 = 352$ K as a small variation in ε' , much more pronounced in the first derivative $d\varepsilon'(T)/dT$. This slight anomaly is a signature of the transition to the ferroelectric phase, taking place in the chemically ordered regions of the ceramic. The second singularity is visible in the $\varepsilon''(T)$ courses near 375 K (see figure 1(b)). This anomaly is most probably connected with the ferroelectric phase transition in the residual disordered regions. At elevated pressures, after the sample rejuvenation, it was hardly detectable; therefore, we were not able to study its pressure dependence.

The DTA measurements (figure 2), performed on the same sample as was used for dielectric studies, evidenced the occurrence of a broad thermal anomaly with the onset at 353 K. This temperature coincides with the dielectric anomaly observed at T_C^0 . The clearly diffuse character of the endothermic peak, stretching between 353 and 395 K, can be related to the local inhomogeneities of the sample.

The application of hydrostatic pressure causes a shift of the whole dielectric anomaly towards lower temperature as seen in figure 3. We employed the first derivative of $\varepsilon'(T)$, a

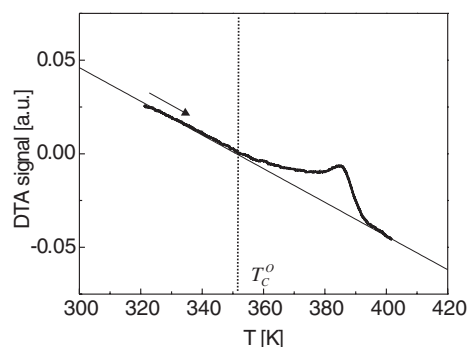


Figure 2. DTA run measured on heating the PSN ceramic. The thin solid line shows the baseline; the dotted line marks the transition temperature T_C^0 .

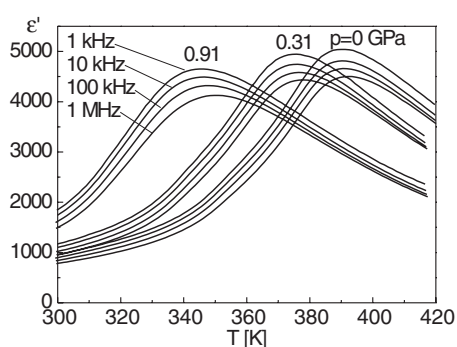


Figure 3. Temperature and frequency dependences of dielectric permittivity for PSN at different pressures.

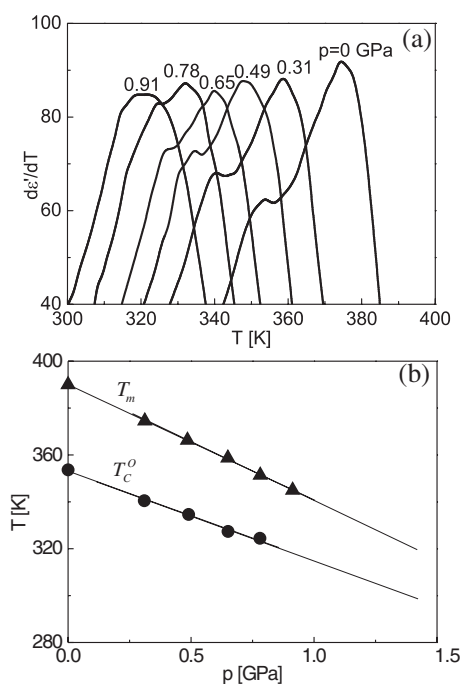


Figure 4. Pressure-induced changes in the first derivative of $\varepsilon'(T)$ (a) and p - T phase diagram of highly ordered PSN (b).

procedure adopted previously in [9], for monitoring the pressure effect on the ferroelectric transition in the ordered fraction of the material (see figure 4(a)). The pressure dependences of T_C^0 and T_m are plotted in figure 4(b). In the studied pressure range the temperatures T_m and T_C^0 decrease linearly with increasing pressure, but with different coefficients dT/dp : -49.2 K GPa^{-1} (at 1 MHz) and -38.0 K GPa^{-1} , respectively.

The other prominent effect of pressure, observed for many ferroelectric relaxors [12], is a pressure-induced decrease in the ε'_m amplitude. In contrast to most relaxor materials, in the highly ordered PSN this effect is relatively small, as clearly seen in figure 3. In figure 5 we plotted the normalized amplitudes of the dielectric anomalies as a function of pressure for PSN

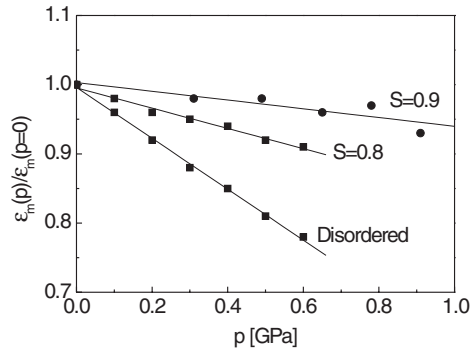


Figure 5. The influence of pressure on the relative amplitude of the dielectric anomaly $\epsilon'_m(p)/\epsilon'_m(p=0)$ for PSN with different degrees of order. For disordered and partly ordered ($S = 0.8$) PSN the data were taken from [10].

Table 1. The parameters calculated by fitting equation (1) to experimental data measured at different pressures for highly ordered PSN ($S = 0.9$, present work), and at ambient pressure for disordered PSN ($S = 0$, after Chu *et al* [5]).

PSN	p (GPa)	$\tau_0 \times 10^{10}$ (s)	E_a (K)	T_{VF} (K)
$S = 0.9$	0	56.0	11.9	388.8
	0.34	37.6	18.4	373.5
	0.48	2.47	47.0	363.4
	0.65	6.21	41.2	355.8
	0.78	0.76	73.2	347.2
	0.91	0.79	81.6	339.6
$S = 0$	0	0.36	162.4	376.0

with different degrees of order. From this comparison it is obvious that with increasing order the pressure influence on the amplitude ϵ'_m tends to diminution. Thus, a fundamental question arises of whether the mechanisms leading to relaxor behaviour in the ordered and disordered PSN have the same or different origins. To obtain some additional information corresponding to this problem we employed the Vogel–Fulcher relationship with our dielectric data. The characteristic relaxation times τ were determined from the frequencies f corresponding to T_m ($\tau = 1/\omega$, where $\omega = 2\pi f$). The $\tau(T)$ dependences at different pressures are described by the Vogel–Fulcher equation:

$$\tau = \tau_0 \exp[E_a/k(T - T_{VF})], \quad (1)$$

where E_a is the activation energy, T_{VF} is interpreted as a ‘static freezing’ temperature, and τ_0 is related to the cut-off frequency of the spectrum of dipolar entities. The exemplary fit of equation (1) to experimental data is shown in figure 6(a), and all parameters obtained from the fitting procedure are listed in table 1. For comparison we also included the parameters determined by Chu *et al*, for disordered PSN [5] at ambient pressure. It is evident that at ambient pressure the activation energy of dynamical dipolar fluctuations is extremely small in highly ordered PSN, and lower by about an order of magnitude than that observed in disordered material. This may suggest that in the former the sizes of polar regions, giving the main contribution to the dielectric response, are very small, though this conclusion is hardly reconcilable with the relatively high temperature T_{VF} (see table 1). The other explanation may be a complex nature of the dielectric response in highly ordered PSN. The dielectric measurements give only the effective parameters resulting from an averaging of different contributions. As suggested by the diffuse character of the thermal anomaly, shown in figure 2, the long- and short-range ferroelectric orders can both contribute to the dielectric response in the vicinity of T_m .

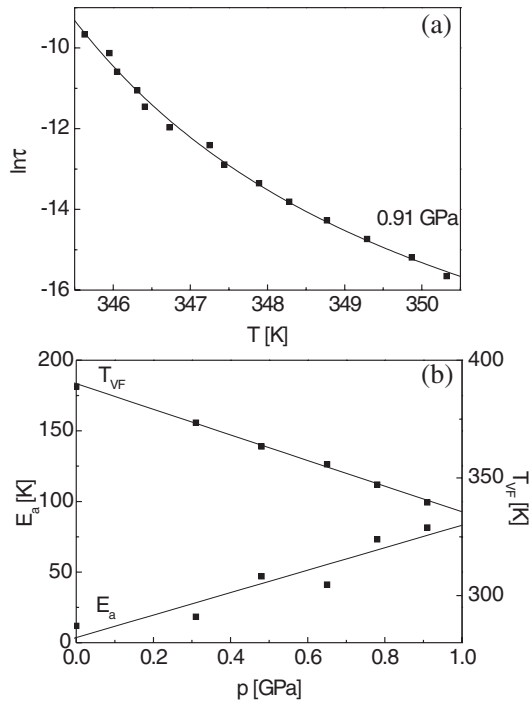


Figure 6. Vogel–Fulcher plot for the relaxation process in PSN under pressure of 0.9 GPa (a), and pressure dependences of the activation energy E_a and freezing temperature T_{VF} (b).

The other surprising result is the pressure effect on the activation energy E_a . While the freezing temperature T_{VF} exhibits typical pressure dependence, the activation energy increases with increasing pressure (see figure 6(b)), i.e. shows a behaviour in contrast to the other ferroelectric relaxors, for which a large decrease of this parameter with pressure was observed [11, 12].

It is well known that in the normal ferroelectrics the high-temperature side of the dielectric peak fulfils the Curie–Weiss law. Recently, an analogous universal formula has been proposed to describe the dielectric behaviour of relaxor ferroelectrics [15]. It was demonstrated that the $\varepsilon'(T)$ dependence can be well extrapolated in a wide temperature range above T_m , using the following phenomenological expression:

$$\frac{\varepsilon'_A}{\varepsilon'(T)} = 1 + \frac{(T - T_A)^2}{2\delta_A^2}, \quad (2)$$

where T_A , ε'_A and δ_A are parameters fitted to experimental data. The constants $T_A < T_m$ and $\varepsilon'_A > \varepsilon'_m$ define the temperature position and amplitude of the extrapolated peak. These parameters are interpreted as the temperature and magnitude of the relaxor static permittivity peak [16]. It was shown that δ_A is frequency independent and can be used for characterization of the diffuseness of the transition [15, 16]. Therefore, we applied this approach to our high-pressure data. The $\varepsilon'(T)$ dependences measured at different pressures were fitted to equation (2) in the temperature range starting from several degrees above T_m , as illustrated in figure 7. It is evident that pressure causes an increase in δ_A , although in the studied pressure range the effect is not very profound. Nevertheless, it can be concluded that pressure presumably leads to a broadening of the relaxation times spectrum of dipolar entities, strengthening the relaxor features of the material. A similar increase in the diffuseness of the transition with increasing pressure was observed for the disordered and ordered PST [17].

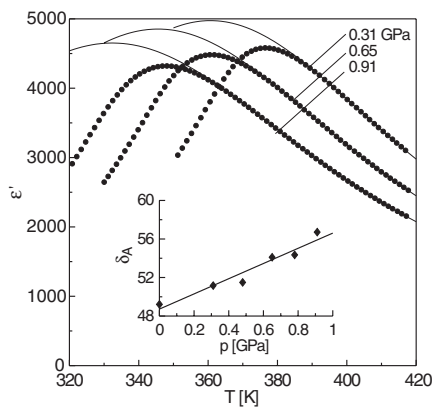


Figure 7. Exemplary fittings (solid curves) of the 10 kHz dielectric permittivity to equation (2). The inset shows the pressure dependence of the diffuseness parameter δ_A .

4. Discussion

The dielectric response of highly ordered PSN displays some outstanding features. The amplitude of the dielectric anomaly ϵ'_m is several times lower than in disordered material, and only weakly pressure dependent. The pressure effect on ϵ'_m is clearly different when compared to the disordered compound. While the decrease in ϵ'_m can be explained in terms of compositional order/disorder, the dielectric dispersion and typical relaxor dielectric peak—not vanishing in highly ordered samples—are rather puzzling. Moreover, the transition to the ferroelectric phase is associated with a very weakly pronounced dielectric anomaly and, most importantly, does not result in suppressing of the relaxor characteristics below T_C^O . The activation energy derived from the Vogel–Fulcher relationship is extremely small and shows untypical pressure dependence. These experimental facts give evidence that the mechanisms responsible for the properties of the disordered and ordered PSN are different.

It seems that the behaviour of PSN can be rationalized at the assumption of two contributions giving rise to its relaxor characteristics. In the disordered material the prevailing contribution is connected with the displacements of the Pb atoms along $\langle 111 \rangle$ cubic crystallographic directions. Chemical disorder on the B sites prevents the formation of macroscopic polar regions, resulting in a polar nanostructure. The transition to a long-range ferroelectric order switches off this relaxor contribution, hence the sharp drop in ϵ' observed in disordered PSN [4–6, 8, 9]. The second contribution can arise from the Pb displacements in planes perpendicular to $\langle 111 \rangle$. This supposition is based on the structural studies, where in all kinds of PSN samples, with different degrees of order, such a kind of Pb disorder was observed down to the lowest temperatures [6, 7] and also with recent NMR study of local structure in PSN [18]. This effect is superimposed onto the ferroelectric shift along [111] and, in our opinion, plays a prominent role in highly ordered PSN, where the compositionally induced contribution is significantly suppressed. Because the long-range and short-range ferroelectric orders have different origins, the ferroelectric transition is weakly visible in the dielectric response of the ordered PSN, and the transition does not suppress the relaxor behaviour of the material. The coexistence of these two contributions can be reconciled on the macroscopic level: in a macroscopic ferroelectric domain \mathbf{P}_s can be considered as composed of components that are slightly inclined to [111] due to small contributions perpendicular to this direction. Thus, it can be expected that the ferroelectric domains have a substructure built of small nanodomains or clusters. A similar effect was observed in the electron- and neutron-diffraction experiments on $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ perovskite compounds [19, 20]. The conception of

two coexisting contributions to the short/long-range ferroelectric orders seems to correspond to the theoretical model of mixed ferro-glass [21] proposed for 1:1 ferroelectric relaxors.

Acknowledgments

The authors are grateful to Professor C Caranoni, University of Aix-Marseille III, for kindly providing the PSN samples which made this work possible. The authors also wish to thank Professor A Pietraszko, Institute of Low Temperatures and Structural Research, Polish Academy of Sciences, for his help in determination of the degree of order in the PSN ceramic.

References

- [1] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectric and Related Materials* (Oxford: Clarendon)
- [2] Cross L E 1994 *Ferroelectrics* **151** 305
- [3] Stenger C G F and Burggraaf A J 1980 *Phys. Status Solidi a* **61** 275
- [4] Stenger C G F and Burggraaf A J 1980 *Phys. Status Solidi a* **61** 653
- [5] Chu F, Reaney I M and Setter N 1995 *J. Appl. Phys.* **77** 1671
- [6] Malibert C, Dkhil B, Kiat J M, Durand D, Bézar J F and Spasojevic-de Biré A 1997 *J. Phys.: Condens. Matter* **9** 7485
- [7] Perrin C, Menguy N, Suard E, Muller Ch, Caranoni C and Stepanov A 2000 *J. Phys.: Condens. Matter* **12** 7523
- [8] Bidault O, Perrin C, Caranoni C and Menguy N 2001 *J. Appl. Phys.* **90** 4115
- [9] Perrin C, Menguy N, Bidault O, Zahra C Y, Zahra A-M, Caranoni C, Hilczler B and Stepanov A 2001 *J. Phys.: Condens. Matter* **13** 10231
- [10] Yasuda N and Fujita K 1989 *Phys. Lett. A* **140** 455
- [11] Samara G A 1996 *Phys. Rev. Lett.* **77** 314
- [12] Samara G A 2001 *Solid State Phys.* **56** 239
- [13] Nagarajan V A *et al* 2000 *Appl. Phys. Lett.* **27** 438
- [14] Lampin P, Manguy N and Caranoni C 1995 *Phil. Mag. Lett.* **72** 215
- [15] Bokov A A and Ye Z-G 2000 *Solid State Commun.* **116** 105
- [16] Bokov A A, Bing Y-H, Chen W, Ye Z-G, Bogatina S A, Raevski I P, Raevskaya S I and Sahkar E V 2003 *Phys. Rev. B* **68** 052102
- [17] Setter N and Cross L E 1980 *Phys. Status Solidi a* **61** K71
- [18] Laguta V V, Glinchuk M D, Bykov I P, Blinc R and Zalar B 2004 *Phys. Rev. B* **69** 054103
- [19] Ricote J, Corker D L, Whatmore R W, Impey S A, Glazer A M, Dec J and Roleder K 1998 *J. Phys.: Condens. Matter* **10** 1767
- [20] Corker D L, Glazer A M, Whatmore R W, Stallard A and Fauth F 1998 *J. Phys.: Condens. Matter* **10** 6251
- [21] Glinchuk M D, Stephanovich V A, Hilczler B, Wolak J and Caranoni C 1999 *J. Phys.: Condens. Matter* **11** 6263