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2003 J. Phys.: Condens. Matter 15 4331

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Specific heat and heat conductivity of BaTiO₃ polycrystalline films in the thickness range 20–1100 nm

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Received 22 October 2002, in final form 23 April 2003

Published 13 June 2003

Online at stacks.iop.org/JPhysCM/15/4331

Abstract

Thermal properties—specific heat and heat conductivity coefficient—of polycrystalline BaTiO₃ films on massive substrates were studied as a function of the temperature and the film thickness by the ac-hot probe method. The anomalies of specific heat with the film thickness decreasing from 1100 to 20 nm revealed the reduction of T_c and excess entropy of the ferroelectric phase transition which becomes diffused. The critical thickness of the film at which $T_c = 0$ has been estimated as 2.5 nm.

1. Introduction

The physical properties of ferroelectric thin films are of growing interest because of their promising applications in microelectronics. As their spatial dimensions are reduced to nanometre scale, a considerable change to the properties of ferroelectric films and fine particles results, in comparison with bulk objects. Finite-size effects have been under consideration in the literature for a long time but only during the last decade have improved technology and deposition techniques provided a real possibility of obtaining films and particles with controlled and reproducible parameters. It seems to be proved experimentally that the ferroelectric properties of fine PbTiO₃ and BaTiO₃ nanometre powder disappear at 300 K for the ‘critical size’ of the particles, that is, about 10 nm for PbTiO₃ and 40 nm for BaTiO₃ [1–5]. Phenomenological analysis based on the Landau–Ginzburg theory of the structural phase transitions where the gradient and surface terms are taken into account was successively applied for the analysis of the phenomenon [6–8].

This theoretical approach is based on the milestone work [9] where the finite-size effects were considered for the magnetics in a similar way.

As to the size effects in thin and ultrathin ferroelectric films, understanding of the associated effects is still far from complete. The problem of reliable prognosis on the properties of thin ferroelectric films is much more intricate in comparison with the case of fine particles. It is extremely hard to deal with thin films alone in experiment. It means that the supporting substrate has always to be taken into account. However, the experimental data are in contradiction with results obtained through application of the above mentioned theory on thin films [7, 8, 10, 11].

It is widely accepted today that the real situation in epitaxial and polycrystalline thin films can be considered only in connection with the interaction between the film and substrate which is believed to be of mechanical origin and results from the two-dimensional misfit stresses in the film–substrate interface [12–15]. These misfit strains may crucially affect the ferroelectric phase transition. The ‘misfit strain–transition temperature’ phase diagram has been obtained for BaTiO₃ and PbTiO₃ epitaxial films [13] and predicted the possible changes of the sequence and order of the phase transitions as compared to the bulk crystals. In addition, the shift of the ferroelectric phase transition should be determined taking into account both surface effects and the misfit strains [14].

The experimental data seem to be quite contradictory. The real systems which are used in the experiment for the measurement of dielectric properties and the polarization switch are in fact a complex heterostructure consisting of a substrate, electrode (metal or some conducting substance), ferroelectric film and another electrode. The partial relaxation of the misfit strains is possible due to the formation of domain and edge dislocation patterns in the films [15–17]; also dead layers that are formed near the film–electrode plane can substantially change the domain structure and effective dielectric constant of the film [18]. As examples of the unsolved discrepancies we could point out the references [19–21] where quite different results were obtained for the thickness dependence of the spontaneous polarization and the transition temperature for epitaxial BaTiO₃ films grown on SrTiO₃ substrates.

The system might be significantly simplified if measurements of the nonelectrical parameters concerning the characterization of phase transitions in thin ferroelectric films were carried out without electrodes, which is our principal concern during this study. We used the thermal properties of the films (specific heat and heat conductivity coefficient) as fundamental material parameters closely related to the phase transitions.

We can indirectly estimate spontaneous polarization values through the specific heat temperature dependence as well as the Curie temperature itself. However, it should be noted that the thermal properties of thin ferroelectric films were not investigated practically despite the evident information value. This is because of the complexity of measuring these properties for the micron and submicron films deposited on a massive substrate. For example, traditional methods of ac-calorimetry are the best for measuring the specific heat of samples with a thickness exceeding 100 μm within the limited frequency range 0.1–1 Hz [22]. Since the thin film is supposed to be deposited on a substrate of such a thickness only the total thermal parameters of the film–substrate structure can be obtained [23, 24]. In [24] the specific heat of BaTiO₃ epitaxial films with thickness of 6 and 200 nm was measured with SrTiO₃ as substrate. No clear anomalies at the phase transitions were observed; we shall return to these results later.

2. Experimental details

Recently we have shown that ac-hot probe method can be successfully applied for the thermal characterization of thin dielectric films deposited on a massive substrate [25, 26]. The basic idea of the heater-probe method is that a metal strip or wire made of a metal with high thermal coefficient of resistivity serves as a source of heat and a temperature sensor simultaneously.

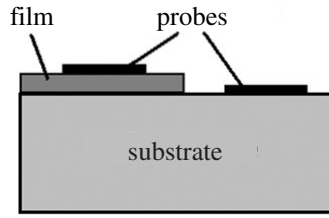


Figure 1. Sample arrangement: substrate, film and hot-probe positions.

The probe is heated by a periodic sinusoidal current with a given frequency ω (as a rule, this gives $f = \omega/2\pi$ in the Hz–kHz range). The probe temperature oscillations depend on the thermal properties of the surrounding media. These oscillations can be measured using the temperature dependence of the probe resistance. The temperature and resistivity oscillations occur at a frequency 2ω , and the voltage across the probe has a frequency component 3ω . By measuring the amplitude and phase of the voltage at the frequency 3ω one can determine the specific heat c and the thermal conductivity λ of the layer with thickness equal to the thermal wave penetration depth. It was found that for the condition

$$h_f \ll d_p \ll h_s$$

(h_f —thickness of the film, $d_p = (\lambda_s/2c_s\omega)^{1/2}$ —thermal wave penetration depth, λ_s , c_s —heat conductivity coefficient and specific heat of the substrate, h_s —thickness of the substrate), an important asymptotic relationship can be obtained for the ratio of the complex temperature oscillations of the probes deposited on the film and on the substrate (figure 1). This ratio has a form [25]

$$\delta T_f/\delta T_s \approx 1 + (1+i)(X_{fs} - 1/X_{fs})(2\omega c_f/\lambda_f)^{1/2}h_f \quad (1)$$

where $X_{fs} = (\lambda_s c_s/\lambda_f c_f)^{1/2}$ is the thermal contrast factor (here λ_f , c_f are the heat conductivity coefficient and specific heat of the film). The use of relation (1) requires the fulfilment of an additional condition. It is seen that, if $1/X_{fs} \gg X_{fs}$, equation (1) has the following asymptotic form:

$$\delta T_f/\delta T_s \approx 1 + (1+i)(\lambda_s c_s)^{-1/2}h_f \omega^{1/2} c_f. \quad (2)$$

If the value of X_{fs} cannot be neglected, compared with $1/X_{fs}$, it should be taken into account as a correction. To this end, we should have an approximate value of the thermal conductivity λ_f of the film. As a result this procedure gives a contribution to the systematic error of the specific heat determination.

In similar way, if $X_{fs} \gg 1/X_{fs}$ relation (1) becomes

$$\delta T_f/\delta T_s \approx 1 - (1+i)(\lambda_s c_s)^{1/2}h_f \omega^{1/2}/\lambda_f \quad (3)$$

and may be used to measure the thermal conductivity of a film. If the value of $1/X_{fs}$ cannot be neglected as compared with X_{fs} , an approximate value of specific heat of the film should be taken into account for a correction.

Therefore we have found that the role of the thermal contrast factor is very important: it is the X_{fs} value that defines which parameter of a film can be determined from the analysis of the probe temperature oscillation. As follows from equations (2) and (3) it is possible to determine the whole set of thermal parameters of a film by measuring the amplitudes of temperature oscillation of two probes on two different substrates which satisfy the conditions $X_{fs}^2 \gg 1$ (measurements of the heat conductivity coefficient) or $X_{fs}^2 \ll 1$ (measurements of the specific heat).

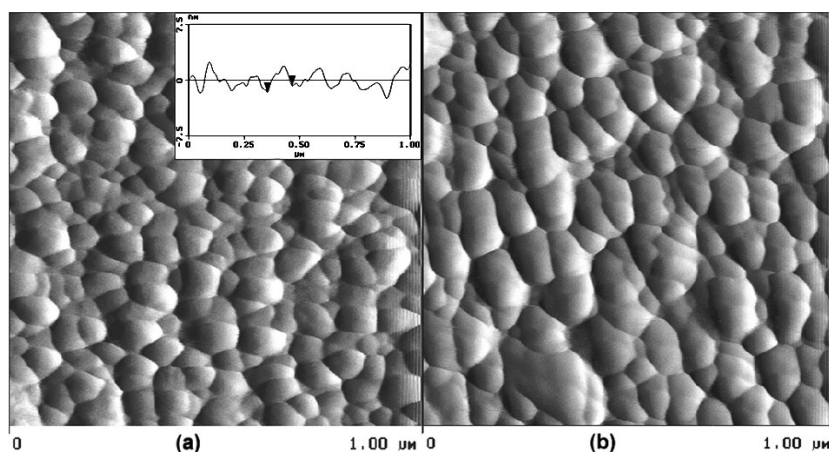


Figure 2. AFM image of the 100 nm BaTiO₃ film deposited on fused SiO₂ (a) and Al₂O₃ (b). Inset: roughness of the film shown in (a).

In our experiment we investigate the thermal properties of BaTiO₃ thin films ($c_f \approx 2.8 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$, $\lambda_f \approx 5 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K) on crystalline sapphire ($c_s \approx 3.2 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ [26], $\lambda_s \approx 47 \text{ W m}^{-1} \text{ K}^{-1}$ [26]) and fused quartz ($c_s \approx 1.7 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ [27], $\lambda_s \approx 1 \text{ W m}^{-1} \text{ K}^{-1}$ [28]) substrates. So we have $X_{fs}^2 \approx 11$ for the sapphire substrate and $X_{fs}^2 \approx 0.12$ for the fused quartz substrate. As follows from the above description, we can determine the thermal conductivity of BaTiO₃ film on sapphire and the specific heat on fused quartz using relations (2), (3) and taking into account the appropriate thermal parameter. This gives us additional contribution to the systematic error of about 1%.

Our experimental setup was described in [26] in full detail. The experimental errors of measurements of c_f and λ_f at the temperature range of 300–400 K was estimated as 3–5% and 2–3% for lower temperatures; the film thickness variation was 20–1100 nm.

3. Sample preparation

BaTiO₃ films were deposited on fused SiO₂ and monocrystalline sapphire substrates Al₂O₃ (typical size 4.0 mm × 5.0 mm × 0.5 mm) by rf magnetron sputtering ($f = 13.5 \text{ MHz}$) with the substrate position ‘off axis’ at 750 °C substrate temperature. X-ray diffraction for the BaTiO₃ films on both Al₂O₃ and SiO₂ substrates revealed ⟨111⟩ textured polycrystalline films with a tetragonal symmetry. The half-width of the {110} rocking curve was 5′–7′. A mixture of Ar: O₂ gas in a ratio 0.8 : 0.2 was introduced and the total pressure was held at 4×10^{-2} Torr. Deposition rate was estimated by the control of sputtering time as 5 nm min⁻¹. It is important that the BaTiO₃ films were deposited on the prepared and etched surface of substrate to have the necessary intimate film–substrate contact.

The surfaces of all the prepared films were inspected by the atomic force microscope. Figure 2 shows the typical in-plane micrographs of the 100 nm film surface on quartz and sapphire substrates. The average sizes of the monocrystalline grains determined by the linear intercept method and a roughness of the surface for the different films are presented in table 1. It follows from table 1, that the grain size is practically the same until the thickness of the film is at least 70 nm for the fused quartz as substrate. This probably means that the film has a columnar structure distorted only for the most thin (<50 nm) films.

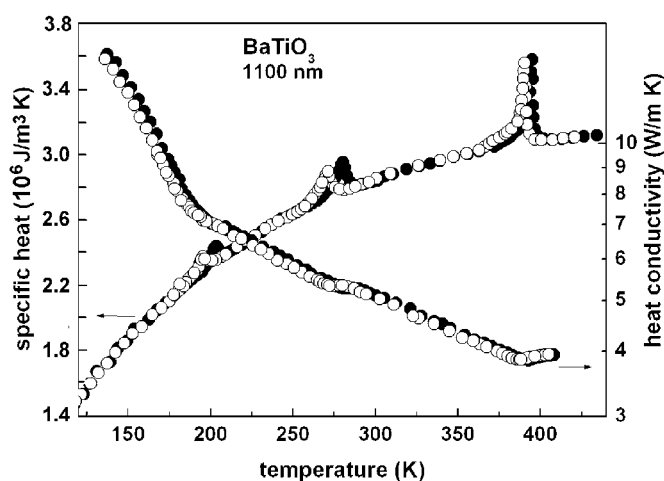


Figure 3. Temperature dependences of the specific heat and heat conductivity coefficient for the BaTiO₃ 1100 nm film on heating (●) and on cooling (○).

Table 1. Thickness dependence of the surface roughness Δh and of the average size D of BaTiO₃ crystallites for different substrates.

Substrate	Film thickness (nm)	Δh (nm)	D (nm)
Sapphire Al ₂ O ₃	1400	24	176
	1100	21	168
	400	22	140
	300	15	104
	40	15	93
Fused quartz SiO ₂	20	10	25
	1100	38	165
	400	13	170
	300	15	105
	100	13	125
	70	3	143
	40	4	90
20	8	42	

4. Experimental results and discussion

The set of basic thermal parameters of BaTiO₃ films on SiO₂ and Al₂O₃ substrates was determined in a wide temperature range of 80–420 K both in cooling and heating. A more detailed study has been conducted in the temperature range where the ferroelectric phase transition occurs in the bulk crystal (360–410 K).

The temperature dependence of c_f and λ_f for 1100 nm film is shown in figure 3. All three phase transitions typical for bulk BaTiO₃ are represented clearly: $m3m \rightarrow 4mm \rightarrow mm2 \rightarrow 3m$ for temperatures 395, 280, 204 K (in heating) respectively. Temperature hysteresis for all transitions was detected for $c(T)$ dependence revealing the main feature of the first order phase transition. It should be noted that the excess energy ΔQ of the ferroelectric phase transition was found to be 150 J mol^{-1} , that is, somewhat lower than the value obtained earlier for the bulk ceramic (190 J mol^{-1} in [29]). The temperature dependence of the heat conductivity

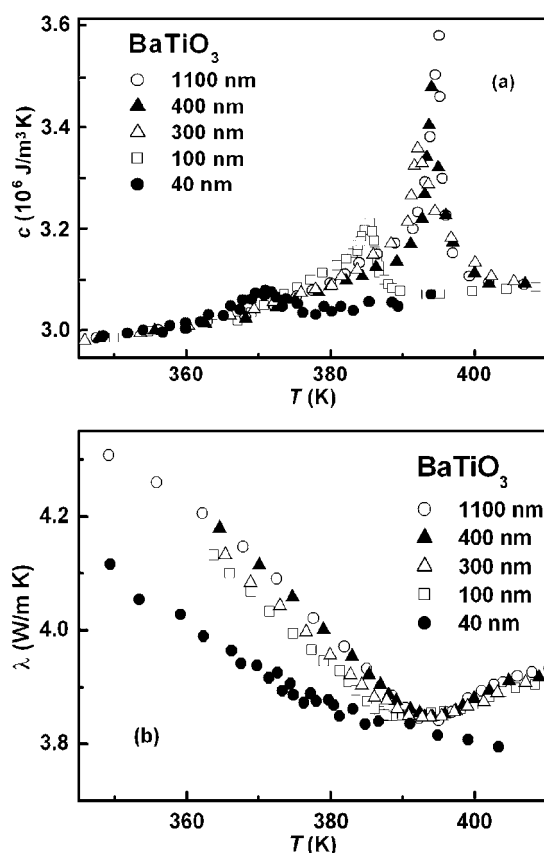


Figure 4. Temperature dependences of the specific heat (a) and the heat conductivity coefficient (b) in the area of ferroelectric phase transition in BaTiO₃ films with different thicknesses.

coefficient for this 1100 nm film is shown in figure 3 and seems to be similar to one for a bulk crystal [30]. Therefore such films can be considered as ‘thick’ from this point of view.

The same measurements were performed for thinner films. Previously we have presented the data for films with thickness greater than 0.1 μm [31]. Now this range is expanded down to 20 nm. The results are presented in figures 4(a) and (b). It should be noted that no anomalies were detected for 20 nm film and these data are not shown here. It is clear that when the thickness of the film reduces, the phase transition temperature decreases while diffusion of the anomalies increases. The temperature hysteresis of T_c of about 5 K revealed for films of 100 nm and thicker was the first order transition. No hysteresis was observed at 40 nm film, which is probably because of the large diffusion of the transition. In fact the anomaly of λ is very weak for this film as well; it is possible that this effect is connected with the increase in the film roughness for the submicron films [32].

The anomalies of the specific heat that we observed for the films under consideration can be used to determine transition temperature and the excess entropy change; besides, the temperature dependence of spontaneous polarization can be calculated with the use of simple thermodynamic relationships [33].

Figure 5 illustrates the dependence of the temperature and excess entropy of the ferroelectric transition in BaTiO₃ films on thickness (transition temperature was determined

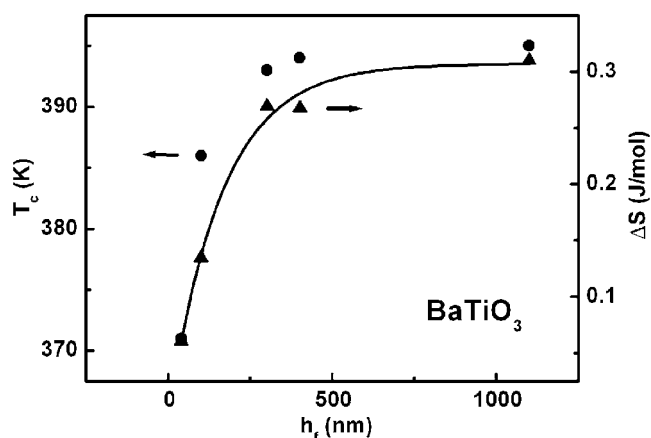


Figure 5. Temperature and excess entropy of the ferroelectric phase transition in BaTiO₃ films as a function of thickness. The curve is plotted as a guide to the eye.

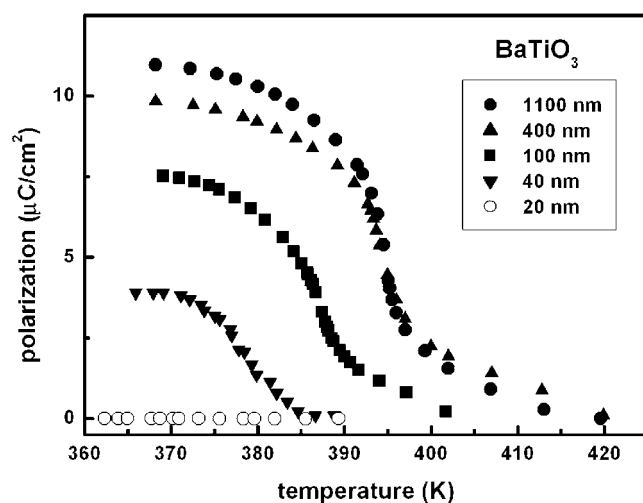


Figure 6. Temperature dependences of the spontaneous polarization in BaTiO₃ films restored from the specific heat data.

as the temperature of the maximum value of the specific heat). It is seen that both parameters have a clear tendency to decrease as film thickness decreases. The values obtained are shown in table 2. As pointed out earlier, no anomalies were observed for the film with $h_f = 20$ nm. The temperature dependences of spontaneous polarization that were restored from the specific heat data are presented in figure 6. It is evident from figure 6 that the spontaneous polarization of the films is progressively suppressed as their thickness is reduced.

Considering all the data one has to take into account that there are two size parameters in a polycrystalline film: the thickness of the film and the average in-plane size of crystalline grains. It follows from the table 1 that the average size of crystallites is practically the same for film thicknesses not lower than 70 nm. This means, first of all, that the polycrystalline system under consideration has a columnar structure, so we can suppose that only the film thickness will be the determining parameter.

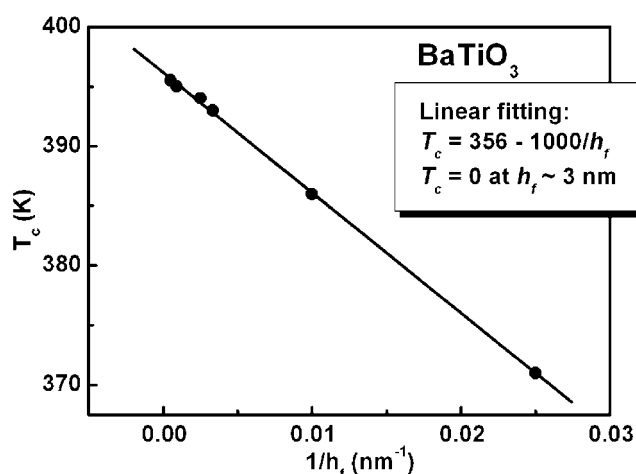


Figure 7. Dependence of the ferroelectric phase transition temperature on the reciprocal thickness for the BaTiO₃ films on SiO₂ substrates.

Table 2. Thickness dependence of the transition temperature T_c , excess entropy and spontaneous polarization P_s for BaTiO₃ films.

Film thickness (nm)	T_c (K)	ΔS (J mol ⁻¹ K ⁻¹)	P_s ($\mu\text{C cm}^{-2}$)
1100	395	0.31	11
400	394	0.26	10
300	393	0.27	10
100	387	0.14	7.5
40	371	0.06	4

As we discussed in the introduction, it is important to consider two-dimensional stresses, which are caused by the differences in lattice parameters and thermal expansion coefficients of BaTiO₃ films and substrates. These stresses can be partially or fully relieved by domain structure formation below phase transition temperature and by misfit dislocations above a certain critical film thickness. As a result, remanent stresses will depend on film thickness [34, 35]. We do not know exactly this dependence in our case and additional experiments will be needed in order to reveal it.

Evidently we have no knowledge of the influence of the size and stress effects pointed out above on the phase transition in sufficiently thick films (with thickness above 1000 nm). Nevertheless it is clear that the main features of the thickness evolution of T_c are very close to those predicted for free films or fine particles. It is interesting to note that the dependence of the transition temperature on the reciprocal thickness of the film is close to linear (figure 7). Such behaviour was predicted earlier for fine particles [6]; in addition, it was shown in [15] that a similar dependence can be obtained for films of proper ferroelastic–ferroelectrics where the relaxation of the surface stresses is connected with the domain formation. The extrapolation of the above dependence $T_c = T_c^{bulk} - 1000/h_f$ with $T_c^{bulk} = 396$ K to $T_c = 0$ gives $h_f = 2.5$ nm as the ‘critical thickness’ at which the phase transition in BaTiO₃ polycrystalline films is completely suppressed. It is worth noting that about the same value of the ‘critical thickness’ (2 nm) was obtained in [36] for BaTiO₃ by the atomic-level simulation approach.

Returning to reference [24], we should note that the thin epitaxial films of BaTiO₃ on SrTiO₃ substrate showed no specific heat anomaly even for $h_f = 200$ nm. It seems that in this case the two-dimensional clamping of the film by the substrate almost completely suppresses the phase transition.

5. Conclusions

In conclusion, we have presented data which give the full characterization of the thermal properties of polycrystalline BaTiO₃ films deposited on the massive SiO₂ glass and Al₂O₃ crystal substrates. The progressive evolution of the specific heat and heat conductivity coefficient anomalies provided us with unique information about the finite-size effects in these films. The critical thickness of the films can be estimated from the data. We suppose that the study of ferroelectric thin films by means of specific heat measurements gives an additional tool for the analysis of their properties and phase transitions.

Acknowledgments

Authors wish to express their gratitude to the Russian Foundation for Basic Research and Program 'Universities of Russia' for the financial support.

References

- [1] Uchino K, Sadanaga E and Hurose T 1989 *J. Am. Ceram. Soc.* **72** 1555
- [2] Zhong W L, Jiang B, Zhang P L, Ma J M, Cheng H M, Yang Z H and Lu L X 1993 *J. Phys.: Condens. Matter* **5** 2619
- [3] Chattopadhyay S, Ayyub P, Palkar V R and Multani M 1995 *Phys. Rev. B* **52** 13177
- [4] Wang C L and Smith S R P 1995 *J. Phys.: Condens. Matter* **7** 7163
- [5] Ishikawa K and Uemori T 1999 *Phys. Rev. B* **60** 11841
- [6] Zhong W L, Wang Y G, Zhang P L and Qu B D 1994 *Phys. Rev. B* **50** 689
- [7] Li S, Eastman J A, Vetrone J M, Foster C M, Newnham R E and Cross L E 1997 *Japan. J. Appl. Phys.* **36** 5169
- [8] Ishibashi Y, Orihara H and Tilley D R 1998 *J. Phys. Soc. Japan* **67** 3292
- [9] Kaganov M I and Omelyanchouk A N 1976 *Sov. Phys.-JETP* **34** 895
- [10] Wang Y G, Zhong W L and Zhang P L 1996 *Phys. Rev. B* **53** 11439
- [11] Zhang J, Yin Z, Zhang M C and Scott J F 2001 *Solid State Commun.* **118** 241
- [12] Speck J S and Pompe W 1994 *J. Appl. Phys.* **76** 466
- [13] Pertsev N A, Zembilgotov A G and Tagantsev A K 1998 *Phys. Rev. Lett.* **80** 1988
- [14] Zembilgotov A G, Pertsev N A, Kohlstedt H and Waser R 2002 *J. Appl. Phys.* **91** 2247
- [15] Bratkovsky A M and Levanyuk A P 2001 *Phys. Rev. Lett.* **86** 3642
- [16] Speck J S, Seifert A, Pompe W and Ramesh R 1994 *J. Appl. Phys.* **76** 477
- [17] Alpay S P and Roytburd A L 1998 *J. Appl. Phys.* **83** 4714
- [18] Bratkovsky A M and Levanyuk A P 2000 *Phys. Rev. Lett.* **84** 3177
- [19] Terauchi H, Watanabe Y, Kasatani H, Kamigaki K, Yano Y, Terashima T and Bando Y 1992 *J. Phys. Soc. Japan* **61** 2194
- [20] Yoneda Y, Okabe T, Sakaue K and Terauchi H 1998 *J. Appl. Phys.* **83** 2458
- [21] Yanase N, Abe K, Fukushima N and Kawakubo T 1999 *Japan. J. Appl. Phys.* **38** 5305
- [22] Sullivan P F and Siedel G 1968 *Phys. Rev.* **173** 679
- [23] Fominaya F, Fournier T, Gandit P and Chaussy 1997 *Rev. Sci. Instrum.* **68** 4191
- [24] Onodera A, Kawamura Y, Okabe T and Terauchi H 1999 *J. Eur. Ceram. Soc.* **19** 1477
- [25] Kravchun S N, Davitadze S T, Mizina N S and Strukov B A 1997 *Phys. Status Solidi* **39** 675
- [26] Davitadze S T, Kravchun S N, Mizina N S, Strukov B A, Goltzman B M, Lemanov V V and Shulman S G 1998 *Ferroelectrics* **208/209** 279
- [27] Grigorev I S and Meilikhov E Z 1991 *Handbook of Physics* (Moscow: Energoatomizdat) (in Russian)
- [28] Sergeev O A, Shashkov A G and Umansky A S 1972 *Inzh.-Phys. J.* **43** 960 (in Russian)
- [29] Volger J 1952 *Phil. Res. Rep.* **7** 21

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- [30] Mantle A J H and Volger J 1967 *Phys. Lett.* **24A** 137
- [31] Davitadze S T, Kravchun S N, Strukov B A, Goltzman B M, Lemanov V V and Shulman S G 2002 *Appl. Phys. Lett.* **80** 1631
- [32] Lu H and Chu J 2001 *Phys. Status Solidi* **222** 35
- [33] Strukov B A and Levanyuk A P 1998 *Ferroelectric Phenomena in Crystals* (Heidelberg: Springer) p 303
- [34] Kwak B S, Erbil A, Wilkens B J, Budai J D, Chisholm M F and Boatner L A 1992 *Phys. Rev. Lett.* **68** 3733
- [35] Yano Y, Lijima K, Daytoh I, Terashima T, Bando I, Watanabe Y, Kasatani H and Terauchi H 1994 *J. Appl. Phys.* **76** 7833
- [36] Tinte S and Stachotti M G 2001 *Phys. Rev. B* **64** 235403