

LATTICE DYNAMICS
AND PHASE TRANSITIONS

Calculations of the Lattice Dynamics and Spontaneous Polarization
for Thin Ferroelectric Films of Disordered Solid Solutions
 $\text{Pb}B'_{1/2}B''_{1/2}\text{O}_3$ ($B' = \text{Sc, Ga, In, Lu}$; $B'' = \text{Nb, Ta}$)

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Abstract—The lattice dynamics and spontaneous polarization in thin ferroelectric films of disordered solid solutions $\text{Pb}B'_{1/2}B''_{1/2}\text{O}_3$ ($B' = \text{Sc, Ga, In, Lu}$; $B'' = \text{Nb, Ta}$) are calculated in terms of the generalized Gordon–Kim model. It is found that all the compounds under investigation contain an unstable polar mode, the frequencies of this mode for all the compounds are close in magnitude, and the eigenvectors of the soft polar mode are different in character for different types of surfaces (PbO and $\langle B \rangle\text{O}_2$, where $\langle B \rangle$ is the average ion in the virtual crystal approximation). The frequency of the soft polar mode, the dynamic Born charges, and the rf permittivity are calculated as functions of the film thickness. It is demonstrated that, as the film thickness increases, all the above quantities tend to corresponding values for the bulk compound. The spontaneous polarization of the monoclinic phase distorted along the eigenvector of the soft mode is calculated as a function of the film thickness and in individual layers of the film for different types of surfaces.

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1. INTRODUCTION

In recent years, thin ferroelectric films based on oxides with a perovskite structure have attracted an increasing interest from the points of view of both basic science and practical application. By now, there are many theoretical and experimental papers investigating properties of thin films [1–5]. Unceasing interest in the films is due to their sometimes unusual novel properties that differ from properties of the bulk material, and to prospects of their utilization in all kinds of modern devices. In turn, ferroelectric solid solutions based on perovskite oxides are subjects of many studies in last decades [6–9]. Practical interest is caused by lead-based solid solutions, among them $\text{Pb}B'_{1/2}B''_{1/2}\text{O}_3$ ($B' = \text{Sc, Ga, In, Lu}$; $B'' = \text{Nb, Ta}$). With a decrease in temperature, these compounds undergo various sequential phase transitions, including ferroelectric and anti-ferroelectric ones; in this case, the symmetry of low-temperature phases and the sequence and types of phase transitions depend on chemical composition and degree of ordering of B' and B'' cations. Lattice dynamics and ferroelectric properties of disordered $\text{Pb}B'_{1/2}B''_{1/2}\text{O}_3$ solid solutions have been studied in [10]. In the present paper we report results of lattice

dynamics and spontaneous polarization calculations for thin ferroelectric films of disordered $\text{Pb}B'_{1/2}B''_{1/2}\text{O}_3$ ($B' = \text{Sc, Ga, In, Lu}$; $B'' = \text{Nb, Ta}$) solid solutions, which are compared with the results obtained for bulk compounds.

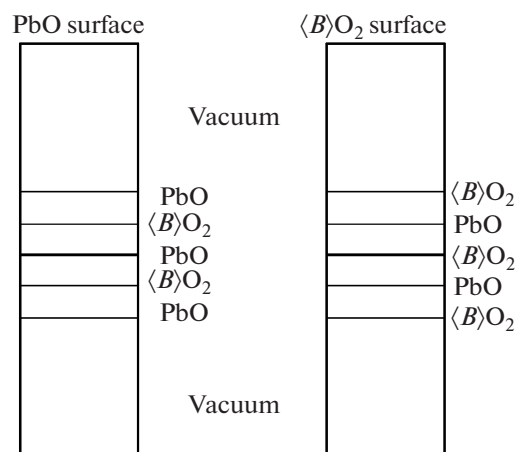


Fig. 1. Diagram of the periodic slab geometry with vacuum layer.

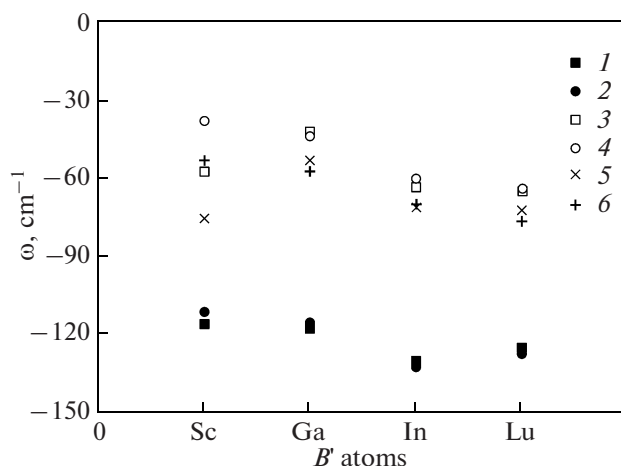


Fig. 2. Frequency of the soft polaron mode for films with (1, 2) PbO and (3, 4) $\langle B \rangle O_2$ surfaces of the compounds with $B' = (1, 3)$ Nb and (2, 4) Ta. (5, 6) Frequencies of the soft polaron mode for bulk niobium and tantalum compounds, respectively. Imaginary modes are represented by negative values. Different B' atoms that enter into the general formula $PbB'_{1/2}B''_{1/2}O_3$ of solid solutions shown in the figure are indicate on the horizontal axis.

2. RESULTS AND DISCUSSION

The calculations are performed in the periodic slab geometry, where, in order to generate periodic boundary conditions in the direction normal to the film surface, an N -monolayer thick film is surrounded by vacuum layers two lattice parameters thick and thus three-dimensional quasi-cell to be used in calculations is created. Two kinds of film surface are possible depending on which atoms are located on the surface: AO or $\langle B \rangle O_2$ kinds (where $\langle B \rangle$ is the average ion within the virtual crystal approximation). The geometry of the calculations is shown in Fig. 1.

The calculations are performed using the ab initio model that takes into account dipole and quadrupole polarization of ions. To simulate disordered solid solution we use the “virtual crystal” approximation [11]. The same lattice parameters as for bulk compounds [10] are employed.

The frequencies obtained as the result of simulations of solid solution films are shown in Table 1. In order to save space the table shows frequency values for 3-, 5-, and 7-layer $PbIn_{1/2}Nb_{1/2}O_3$ films for two surface types. Other compounds demonstrate quite similar pattern and corresponding frequencies, including unstable polar modes, are rather close to each other. For example, Fig. 2 shows frequency of the soft polar mode as a function of the compound for two surface types and film thickness of 5 monolayers (≈ 8 Å). Clearly, frequencies of soft polar modes for all compounds with the same surface type are quite similar to each other. As an example, it is shown in Table 1 for all thicknesses of the compounds in question that

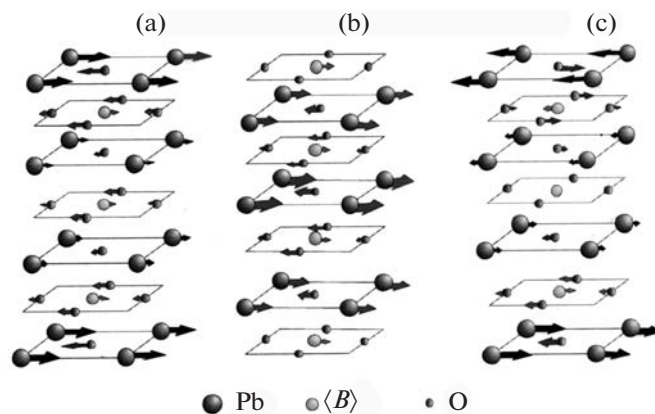


Fig. 3. Atomic displacements along eigenvectors: (a) the soft polar mode in the case of the PbO surface, (b) the soft polar mode in the case of the $\langle B \rangle O_2$ surface, and (c) the mode with antiparallel atomic displacements on opposite surfaces.

there is an unstable polar mode in the center of the Brillouin zone (it is indicated by asterisks in the table). The calculations show that, for all compounds, the instability is related only to atomic displacements within the film surface and polar mode with atomic displacements in the direction perpendicular to the surface is stable for all compounds and all thicknesses under consideration. Instability of the polar mode does not go away even for the minimum thickness of the film of 3 monolayers except for scandium compounds, in which the mode is stable for 3-monolayer

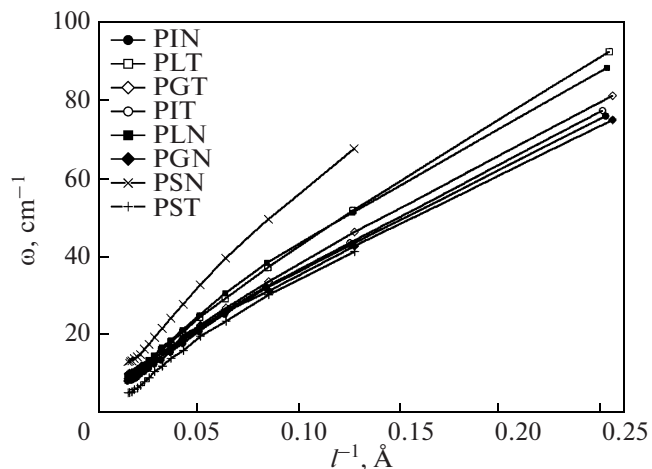


Fig. 4. Square root of the difference between the squares of the frequencies of the unstable polar mode in the bulk compound and in the film ($\omega = \sqrt{\omega_{\text{vol}}^2 - \omega_{\text{film}}^2}$) as a function of the inverse thickness of the film l^{-1} for the $\langle B \rangle O_2$ surface type.

Table 1. Calculated values of the lattice vibration frequencies (cm^{-1}) at the center of the Brillouin zone ($q = 0$) of $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ for film thicknesses of 3, 5, and 7 monolayers

PbO surface			$\langle B \rangle \text{O}_2$ surface		
3 layers (4.1 Å)	5 layers (8.2 Å)	7 layers (12.3 Å)	3 layers (4.1 Å)	5 layers (8.2 Å)	7 layers (12.3 Å)
146.1 <i>i</i> (2)*	135.0 <i>i</i> (2)*	132.8 <i>i</i> (2)*	46.7 <i>i</i> (2)*	61.2 <i>i</i> (2)*	68.2 <i>i</i> (2)*
110.9 <i>i</i> (2)	129.1 <i>i</i> (2)	131.7 <i>i</i> (2)	85.1(2)	36.9 <i>i</i> (2)	45.4 <i>i</i> (2)
73.3	55.4 <i>i</i> (2)	68.8 <i>i</i> (2)	92.9	57.8(2)	39.6 <i>i</i> (2)
106.5	51.5(2)	46.4 <i>i</i> (2)	123.8	68.5	39.5(2)
115.0(2)	58.12	35.8(2)	189.9	89.7	51.5
158.6(2)	81.9	46.5	203.2(2)	93.4(2)	76.6(2)
216.7	96.8	72.3	206.8	107.6	80.2
249.8(2)	134.9	76.5(2)	242.9(2)	142.8	89.0
337.9	137.2(2)	85.3	243.0(2)	194.2	96.9(2)
415.7	147.7(2)	91.5	356.1(2)	198.6	101.5
422.9(2)	211.8	119.5	360.4(2)	207.3(2)	125.8
423.5	212.3(2)	141.8(2)	376.1	207.8(2)	149.2
	222.6	144.4(2)	424.5	221.4	196.7
	247.5(2)	145.2	513.8	239.7(2)	206.6(2)
	249.5(2)	209.7		243.7(2)	208.5(2)
	343.2	210.1(2)		248.9(2)	211.2(2)
	363.8	213.6(2)		354.2	215.1
	405.8	217.3		358.5(2)	224.5
	419.8(2)	224.9		358.6(2)	241.5(2)
	422.8(2)	246.5(2)		409.8	241.6(2)
	438.8	248.0(2)		410.3	247.8(2)
	507.2	249.5(2)		419.3(2)	248.9(2)
		343.5		500.3	344.9
		354.3		522.9	358.6(2)
		376.8			358.7(2)
		415.3			383.5
		418.1(2)			403.5
		421.2(2)			416.4
		422.7(2)			417.8(2)
		434.9			420.9(2)
		501.4			491.7
		516.0			518.4
					522.9

Note: Soft modes are shown as imaginary values. Parenthetic numbers correspond to the degeneracy of the modes. Asterisks indicate unstable polar modes.

film and the instability appears in 5-layer film. Atomic displacements along eigenvector of the unstable polar mode for two surface types are shown in Figs. 3a and 3b. The eigenvector of the mode in the film differs from the eigenvector of ferroelectric mode in the bulk solid solution. In both cases, as for bulk compounds [10], the largest displacements occur for Pb and O_\perp atoms, but eigenvectors of the soft polar modes differ

for different types of surfaces. In the case of PbO surface, the amplitude of atomic displacements is maximum at the film surface and decreases toward film center, where they are very small (Fig. 3a). At the same time, the opposite situations takes place in the case of $\langle B \rangle \text{O}_2$ surface: the amplitude of atomic displacements increases from surface to center of the film. Atomic displacements along the mode eigenvector are shown

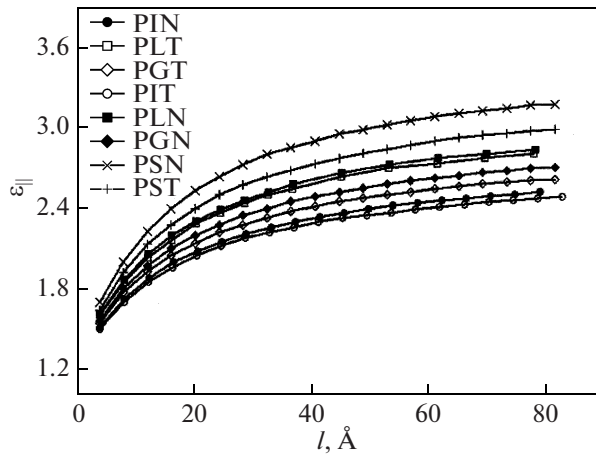


Fig. 5. Parallel component of the high-frequency permittivity tensor as a function of the film thickness.

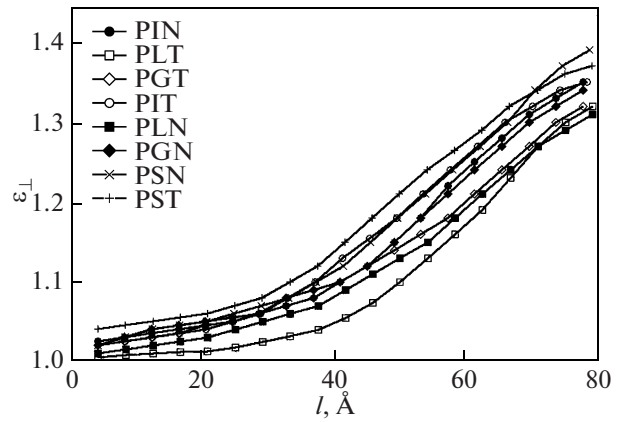


Fig. 6. Perpendicular component of the high-frequency permittivity tensor as a function of the film thickness.

in Fig. 3b. In the case of films with PbO surface, the frequency of the unstable polar mode is almost constant with thickness, but in the case of $\langle B \rangle O_2$ surface, there is a clear dependence of the soft mode frequency on film thickness. Figure 4 shows calculated dependence of the square root of the difference between squares of frequencies of the unstable polar mode in

the film and in the bulk crystal ($\omega = \sqrt{|\omega_{\text{vol}}^2 - \omega_{\text{film}}^2|}$) as a function of the inverse thickness of the film for compound with $\langle B \rangle O_2$ surface. Figure 4 demonstrates that the obtained dependence is almost linear and that, with increase in thickness, the frequency of the soft polar mode approaches the value of ferroelectric mode frequency in the bulk crystal (which is shown in Fig. 2). The obtained dependence can be described with reasonable accuracy by the equation $\omega = k/l$, where k is a proportionality factor and l is the film thickness. It should also be noted that, besides the soft polar mode, frequency spectra for both surface types contain unstable modes for which amplitudes of atomic displacements are maximum at surfaces, decrease toward center of the slab, and are equal to zero for the central layer. Displacements on the opposite surfaces are antiparallel to each other. Atomic displacements along the eigenvector of one of such modes are shown in Fig. 3c.

Apart from the dependence of unstable frequencies of lattice vibrations on film thickness, we calculate similar dependences for dynamic charges, high-frequency permittivity, and spontaneous polarization. It is well-known that large values of the dynamic charges in perovskite oxides act as a source of strong dipole-dipole interactions, which, in turn, are responsible for the ferroelectric state in the perovskites. It was demonstrated in [12] that dynamic charges on the surface and near it should differ from the values for bulk compounds, and this can affect ferroelectric instability in films. Calculated values of dynamic charges for the

solid solution films discussed in the present paper are shown in Tables 2 and 3. For all thicknesses, the components of the dynamic Born charge tensor in the plane of the film (Z_{\parallel}^*) are almost the same as the values obtained for the bulk crystal (Table 2). The components of dynamic charge tensor that are perpendicular to the film surface (Z_{\perp}^*) grow with increase in thickness, as it is demonstrated by Table 3, and approach the values for the bulk crystal [10]. As was found in [10], the dynamic charges of ions $\langle B \rangle$ and O_{\perp} decrease with an increase in the atomic number of the ion B' . It should be noted that values of dynamic charges for surface atoms are observed to be different, and they are 15–20% larger than corresponding values for atoms in the bulk of the film.

Figures 5 and 6 show the calculated dependences of parallel and perpendicular components of permittivity tensor on film thickness. Both components of the high-frequency permittivity grow with increase in the film thickness. But although at large film thickness,

Table 2. Dynamic Born charges Z_{\parallel}^* for disordered solid solution films with a thickness of 15 monolayers

Atom	PSN	PGN	PIN	PLN	PST	PGT	PIT	PLT
Pb	2.7	2.7	2.8	2.8	2.7	2.7	2.8	2.7
$\langle B \rangle$	5.1	4.5	4.6	4.2	4.3	4.0	4.1	3.6
O(Pb)	-1.8	-2.0	-2.5	-2.5	-2.0	-2.1	-2.6	-2.5
$O_1(\langle B \rangle)$	-4.1	-3.2	-3.0	-2.3	-2.8	-2.3	-2.2	-1.6
$O_2(\langle B \rangle)$	-1.8	-2.0	-2.2	-2.2	-2.0	-2.1	-2.3	-2.3

Note: PSN is PbScNbO₃, PGN is PbGaNbO₃, PIN is PbInNbO₃, PLN is PbLuNbO₃, PST is PbScTaO₃, PGT is PbGaTaO₃, PIT is PbInTaO₃, and PLT is PbLuTaO₃. O(Pb) is the oxygen ion in the PbO plane, and $O_1(\langle B \rangle)$ and $O_2(\langle B \rangle)$ are oxygen ions in the $\langle B \rangle O_2$ plane.

Table 3. Dynamic Born charges Z_{\perp}^* for disordered solid solution films at different thicknesses

Number of layers	Atom	PSN	PGN	PIN	PLN	PST	PGT	PIT	PLT
5	Pb	0.8	1.1	1.4	1.4	1.1	1.2	1.4	1.4
	$\langle B \rangle$	2.0	2.1	2.1	2.0	1.8	1.9	1.9	1.8
	O(Pb)	-1.6	-1.5	-1.4	-1.4	-1.4	-1.3	-1.2	-1.2
	O($\langle B \rangle$)	-0.7	-0.9	-1.0	-1.1	-0.9	-1.0	-1.0	-1.1
15	Pb	1.6	1.6	1.9	1.9	1.5	1.6	1.9	1.9
	$\langle B \rangle$	2.8	2.8	2.7	2.6	2.5	2.5	2.5	2.4
	O(Pb)	-2.3	-2.0	-1.9	-1.8	-1.9	-1.7	-1.6	-1.5
	O($\langle B \rangle$)	-1.0	-1.2	-1.3	-1.4	-1.1	-1.3	-1.4	-1.5
25	Pb	1.1	2.1	2.2	2.1	1.7	1.9	2.1	2.1
	$\langle B \rangle$	3.3	3.2	3.2	3.0	2.9	2.8	2.8	2.6
	O(Pb)	-2.7	-2.3	-2.2	-2.0	-2.1	-2.0	-1.9	-1.7
	O($\langle B \rangle$)	-1.2	-1.4	-1.6	-1.6	-1.4	-1.5	-1.6	-1.7
35	Pb	1.9	2.0	2.3	2.3	1.9	2.0	2.3	2.3
	$\langle B \rangle$	3.7	3.5	3.4	3.2	3.1	3.0	3.1	2.8
	O(Pb)	-2.9	-2.5	-2.4	-2.2	-2.4	-2.1	-2.0	-1.9
	O($\langle B \rangle$)	-1.3	-1.5	-1.6	-1.7	-1.4	-1.6	-1.7	-1.9

the magnitude of the parallel component almost reaches the permittivity of the bulk crystal for all compounds, the magnitude of perpendicular component significantly differs from the corresponding value for the bulk compound [10].

Using the obtained eigenvector of the unstable polar mode and magnitudes of dynamic charges, spontaneous polarization in ferroelectric phase is calculated for two surface types using the equation

$$P = \frac{1}{\Omega} \sum_{i, \alpha} u_{\alpha} Z_i^* \xi_{i\alpha},$$

where i is the number of atom, $\xi_{i\alpha}$ is eigenvector of the mode, u_{α} ($\alpha = x, y$) are components of displacement amplitude for ions, and Ω is the unit cell volume. Maximum amplitude is determined using dependence of the total energy of the film E on displacement of ions along eigenvector of the polar mode. The calculations show that the deepest energy minimum corresponds to displacement of ions along [110] direction. The calculated dependences of the energies $E - E_0$ (where E_0 is the total energy of undistorted phase) on amplitude in this direction for all compounds and both surface types are shown in Figs. 7a and 7b for the 11-layer film. It is found that, for PbO and $\langle B \rangle O_2$ surface types, the depth of the energy minimum grows with increase in atomic number of ion B' , but for PbO surface in the paraelectric phase, the amplitude of ion displacements from the equilibrium that corresponds to the energy minimum is the same, independently of thicknesses for each compound, and for $\langle B \rangle O_2$ surface,

it increases with increase in film thickness (this is demonstrated in Fig. 7c on the example of $PbIn_{1/2}Nb_{1/2}O_3$).

Figures 8 and 9 show calculated dependences of polarization of solid solution thin films ($P = \sqrt{P_x^2 + P_y^2}$) on the slab thickness for PbO and $\langle B \rangle O_2$ surface types. The graphs demonstrate that, for PbO surface, the magnitude of the spontaneous polarization achieves maximum value (which is higher than polarization of bulk compounds calculated in [10]) at a film thickness of 3 monolayers ($\sim 4 \text{ \AA}$). It decreases with increase in film thickness, and the polarization of sufficiently thick films ($\sim 50 \text{ \AA}$) is significantly lower than that of bulk compounds. It should be noted that similar dependence of spontaneous polarization magnitude on thickness was obtained in [13] for thin $PbTiO_3$ film. In the case of $\langle B \rangle O_2$ surface, behavior of the polarization as a function of the thickness is different, as it is shown in Fig. 9; namely, the magnitude of the polarization remains approximately equal to the corresponding value for the bulk crystal for entire range of film thicknesses under discussion. Figure 10 shows changes in spontaneous polarization with layer number, starting from surface, in $PbIn_{1/2}Nb_{1/2}O_3$ for two surface types being discussed here. The figures demonstrate that, in the first case, mainly surface layers of the film are polarized and the "bulk" of the film remains weakly polarized, and in the second case, on the contrary, internal layers turn out to be the most polarized ones.

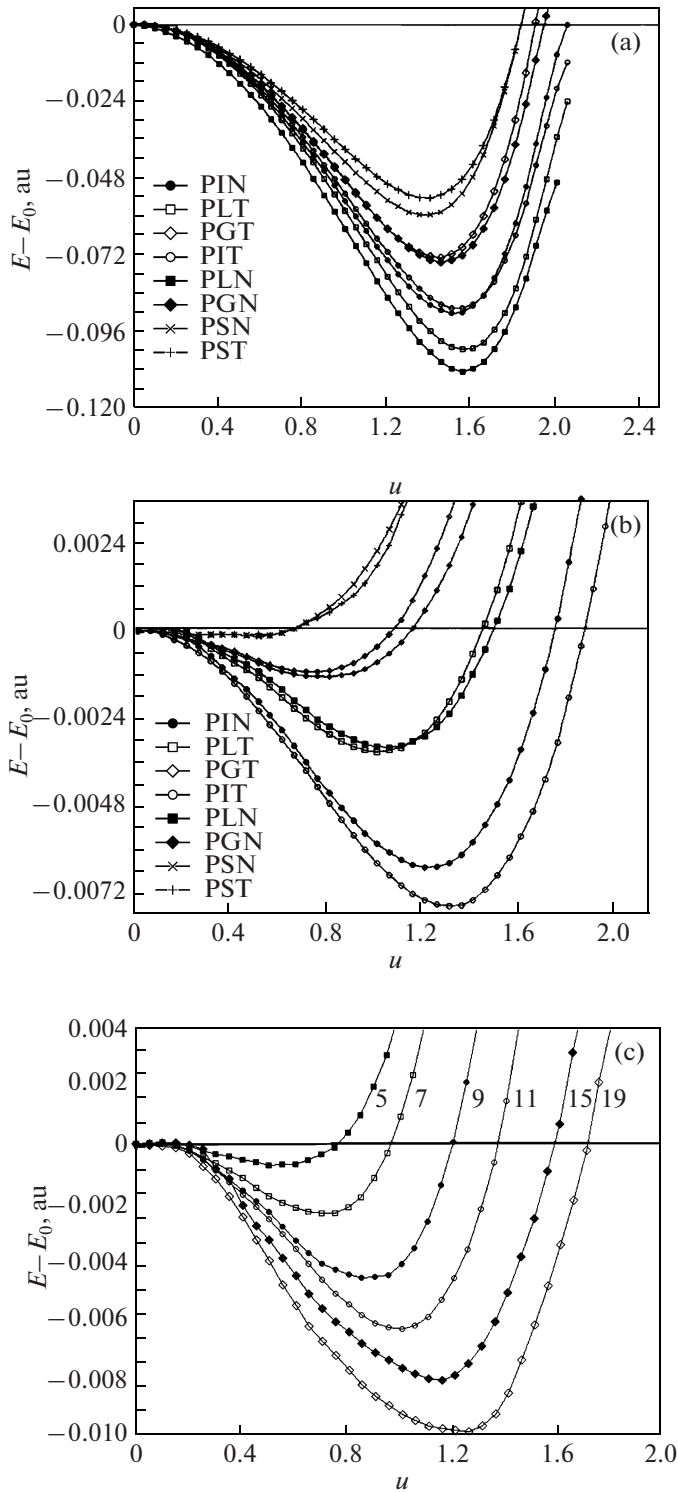


Fig. 7. Total energy of 11-layer thin films of $\text{Pb} B_{1/2}'' B_{1/2}' \text{O}_3$ solid solutions as a function of the amplitudes of ion displacements along the eigenvector of the soft polar mode in the $[110]$ direction for (a) PbO and (b) $\langle B \rangle \text{O}_2$ surfaces. (c) Total energy of thin films of the $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solution as a function of the amplitudes of ion displacements along the eigenvector of the soft polar mode in the $[110]$ direction and the thickness. The number of layers is indicated near the curves.

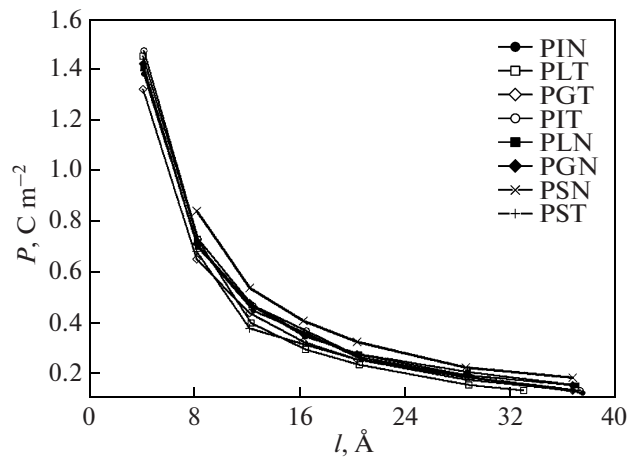


Fig. 8. Polarization in the plane of the slab as a function of the film thickness for the PbO surface.

3. CONCLUSIONS

The main results are as follows:

(1) It has been found that the phonon spectra of the films under study with all thicknesses contain an unstable polar mode with atomic displacements in the plane of the film, but the eigenvector of this mode is different for films with different types of surfaces. In the case of the PbO surface, the largest displacement is observed for the atoms lying on the surface and the atomic displacement amplitude decreases away from the surface of the film. In the case of the $\langle B \rangle \text{O}_2$ surface, by contrast, the atoms located at the center of the slab undergo the maximum displacement, whereas the surface atoms experience the minimum displacement.

(2) The calculation of the square root of the difference between squared frequencies of the soft polaron mode in the bulk crystal and in the film as a function of the inverse thickness of the film has demonstrated

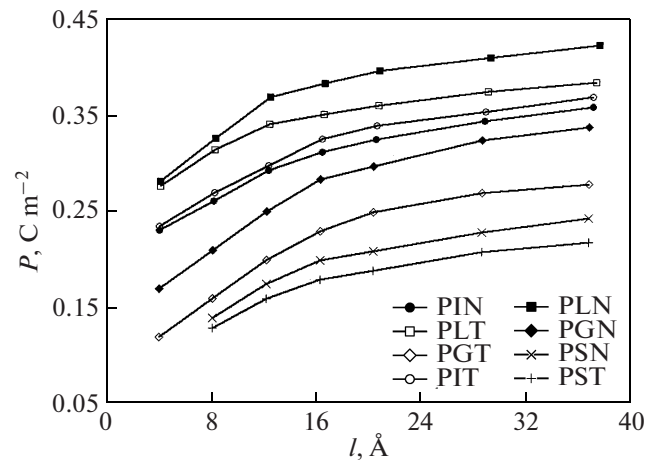


Fig. 9. The same as in Fig. 8 for the $\langle B \rangle \text{O}_2$ surface.

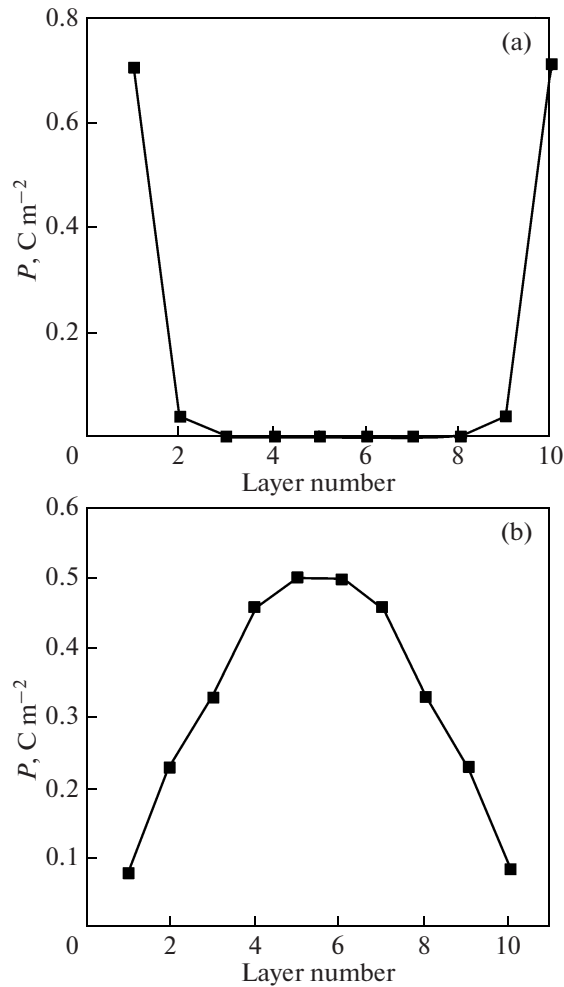


Fig. 10. Changes in the polarization P as a function of the layer number in the $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ film for two surface types: (a) PbO and (b) $\langle B \rangle \text{O}_2$. The variation in P is reckoned from the film surface.

that the dependence is approximately described by straight line. With increase in film thickness, the frequency of the soft polaron mode in the film approaches its value for the bulk crystal.

(3) Dependence of spontaneous polarization within the film plane in $[110]$ direction on its thickness is found for two surface types. In the case of PbO surface, the magnitude of spontaneous polarization of thin films turns out to be significantly larger than that for bulk compounds and it decreases with increase in film thickness in contrast to the case of $\langle B \rangle \text{O}_2$ surface,

where magnitude of the polarization remains almost constant with film thickness and it is approximately equal to the value for bulk compounds. Also, polarization of individual layers in $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ film is calculated. It is found that in the case of PbO surface mainly surface layers are polarized, and in the case of $\langle B \rangle \text{O}_2$ surface, on the contrary, the “bulk” of the film is polarized more strongly than surface, as it is demonstrated by the example of the film consisting of 11 layers.

4. ACKNOWLEDGMENTS

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REFERENCES

1. M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* **77**, 1083 (2005).
2. L. Pálková, P. Chandra, and K. M. Rabe, *Phys. Rev. B: Condens. Matter* **76**, 014112 (2007).
3. P. Ghoses and K. M. Rabe, *Appl. Phys. Lett.* **76**, 2767 (2000).
4. D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thomson, *Science (Washington)* **304**, 1650 (2004).
5. S. Tinte and M. G. Stachiotti, *Phys. Rev. B: Condens. Matter* **64**, 235404 (2001).
6. V. A. Isupov, *Ferroelectrics* **289**, 131 (2003).
7. K. Nomura, T. Shingai, N. Yasuda, H. Ohwa, and H. Tezuchi, *Ferroelectrics* **218**, 69 (1998).
8. V. A. Shuvaeva, Y. Azuma, I. P. Raevski, K. Yagi, S. Sakaue, and H. Tezuchi, *Ferroelectrics* **299**, 103 (2004).
9. P. Groves, *Phase Transform.* **6**, 115 (1986).
10. V. S. Zhandun, N. G. Zamkova, and V. I. Zinenko, *Zh. Éksp. Teor. Fiz.* **133** (6), 1266 (2008) [*JETP* **106** (6), 1109 (2008)].
11. V. I. Zinenko and S. N. Sofronova, *Fiz. Tverd. Tela (St. Petersburg)* **46** (7), 1252 (2004) [*Phys. Solid State* **46** (7), 1291 (2004)].
12. A. Ruini, R. Resta, and S. Baroni, *Phys. Rev. B: Condens. Matter* **57**, 5742 (1998).
13. M. Sempilarsky, M. G. Stachiotti, and R. L. Migoni, *Phys. Rev. B: Condens. Matter* **72**, 014110 (2005).

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