

Study of Ferroelectric Phase Transitions in Disordered $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ Solid Solutions

N. G. Zamkova, S. N. Sofronova, and V. I. Zinenko

Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia

e-mail: ssn@iph.krasn.ru

Abstract—Ferroelectric phase transitions and thermodynamic properties of disordered $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solutions have been investigated by the Monte Carlo method. The parameters of the effective Hamiltonian were calculated within the generalized Gordon–Kim model. The obtained values of the phase-transition temperatures and spontaneous polarization are in satisfactory agreement with the experimental data.

DOI: 10.3103/S1062873807020189

Solid solutions of $AB'_xB''_{1-x}\text{O}_3$ oxides with perovskite structure have been attracting the attention of researchers for many decades. These materials are of interest for both applications and fundamental study due to their unusual electromechanical properties [1]. Among numerous $AB'_xB''_{1-x}\text{O}_3$ solid solutions, heterovalent alloys (i.e., solutions with elements B' and B'' belonging to different columns of the periodic table) form an important class. The observed physical properties of $AB'_xB''_{1-x}\text{O}_3$ solid solutions (in particular, the ferroelectric phase transition and related anomalies in electromechanical properties) depend strongly on the degree of B -cation ordering [1, 2].

In this study, we investigated the ferroelectric phase transitions in completely disordered $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solutions. These compounds have perovskite and rhombohedral structures at high and low temperatures, respectively [3]. Previously, we investigated their lattice dynamics in the cubic phase [4]. The calculated lattice parameters, permittivities, and effective Born charges of these compounds are listed in Table 1.

To determine the ferroelectric-phase-transition temperatures and describe the thermodynamic properties of

disordered $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solutions near phase transitions, we used the effective Hamiltonian proposed in [5, 6]. Ferroelectric displacive phase transitions are related to the motion of ions along the eigenvector of the soft ferroelectric mode of lattice vibrations; therefore, to satisfactorily describe the phase transition, it is sufficient to use one local mode, determined by these displacements:

$$S^\alpha = u \sum_i \xi_{i\alpha}, \quad (1)$$

where $\alpha = x, y, \text{ or } z$; u is the local mode amplitude; and $\xi_{i\alpha}$ is the eigenvector of the lattice vibration mode (Table 2).

To study the ferroelectric phase transition, a three-component local mode (1) is placed at each site of a simple cubic cell. In this case, the effective Hamiltonian is written as [5]

$$E^{tot} = E^{anhar}(\{S_i\}) + E^{short}(\{S_i\}, \{S_j\}) + E^{dip}(\{S_i\}, \{S_j\}). \quad (2)$$

Table 1. Lattice parameters (au), permittivities, and effective Born charges of the $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) crystals

Compound	A_0	ϵ_∞	$Z_{\text{eff, Pb}}$	$Z_{\text{eff, (B)}}$	$Z_{\text{eff, O1}}$	$Z_{\text{eff, O3}}$
PSN	7.45	3.49	2.72	5.15	−4.10	−1.89
PST	7.62	3.31	2.65	3.94	−2.31	−2.14

Table 2. Eigenvectors of the ferroelectric vibration mode and its effective charge (au)

Compound	ξ_{Pb}	$\xi_{\langle\text{B}\rangle}$	ξ_{O1}	ξ_{O3}	Z^*
PSN	0.77	0.21	−0.15	−0.41	5.35
PST	0.79	0.07	0.01	−0.44	4.20

The first term in the effective Hamiltonian (2) is the energy of isolated local modes:

$$E^{anhar}(\{S_i\}) = \sum_i (AS_i^2 + BS_i^4 + C(S_i^{x2}S_i^{y2} + S_i^{x2}S_i^{z2} + S_i^{y2}S_i^{z2})), \quad (3)$$

A , B , and C are the single-site interaction constants.

The second term is the interaction energy between local modes:

$$E^{short}(\{S_i\}, \{S_j\}) = \frac{1}{2} \sum_{i \neq j} \sum_{\alpha\beta} J_{ij, \alpha\beta} S_i^\alpha S_j^\beta, \quad (4)$$

$J_{ij, \alpha\beta}$ are the intersite interaction constants. Since the crystal symmetry is cubic in this case and interactions with the first, second, and third neighbors are taken into account, there are only seven independent constants [5, 6]: j_1 and j_2 , j_3 – j_5 , and j_6 and j_7 describe interactions with the first, second, and third neighbors, respectively.

The last term in the effective Hamiltonian (2) represents the long-range dipole–dipole interaction between local modes:

$$E^{dip}(\{S_i\}, \{S_j\}) = \frac{3(Z^*)^2}{\epsilon_\infty + 2} \sum_{ij, \alpha\beta} Q_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta, \quad (5)$$

where $Z^* = \sum_{\alpha k} Z_{\text{eff}}^{\alpha k} \xi_{k\alpha}$ is the mode charge (Table 2);

Z_{eff}^k is the tensor of the effective Born charge of the k th ion; ϵ_∞ is the permittivity (Table 1); and $Q_{ij}^{\alpha\beta}$ are the structure constants, which depend on the lattice geometry and are calculated by the Ewald method. Note that we apply an expression for the long-range dipole–dipole interaction energy different from that used in [5, 6]. As was shown in [7], the expression for the dipole energy used in [5, 6] leads to a significant under-

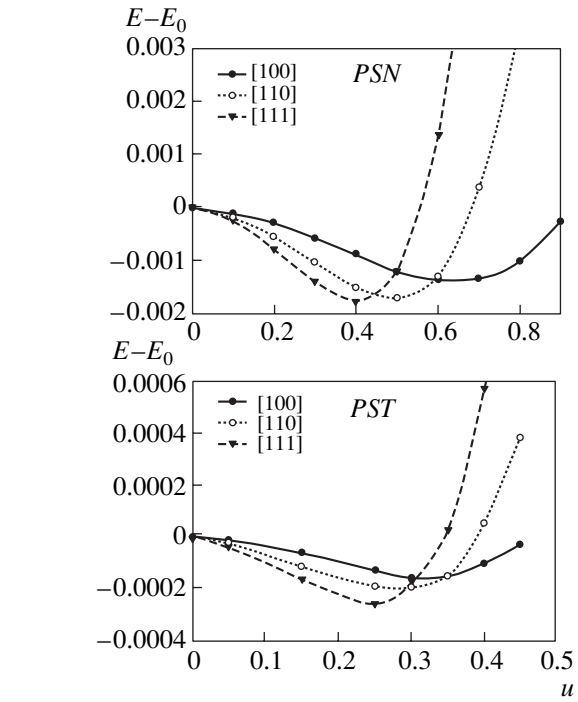


Fig. 1. Dependences of the energies (au) on the local mode amplitude in different directions; E_0 is the cubic structure energy.

estimation (by a factor of $(\epsilon_\infty + 2)/3\epsilon_\infty$) of the dipole–dipole contribution.

Parameters of the effective Hamiltonian are determined by calculating the energies of different distorted structures within the generalized Gordon–Kim model for an ionic crystal taking into account the deformability and dipole and quadrupole distortions of the ion electron density [8]. The energies were calculated within the virtual-crystal approximation [4] using the experimental lattice parameter approximately the same for both solid solutions and equal to 7.70 au [3]. The

Table 3. Energies expressed in terms of the interaction constants $\{J\}$ and the calculated energies (au) of the dipole–dipole and short-range interactions

No.	Interaction constants	PbSc _{1/2} Nb _{1/2} O ₃		PbSc _{1/2} Ta _{1/2} O ₃	
		E^{short}	E^{dip}	E^{short}	E^{dip}
1	$2j_1 + j_2 + 4j_3 + 2j_4 + 4j_6$	−0.0031406	−0.027210	−0.000303	−0.004195
2	$2j_1 - j_2 - 4j_3 + 2j_4 - 4j_6$	0.0188037	0.062928	0.003996	0.009702
3	$j_2 - 2j_4 - 4j_6$	0.0001699	−0.031464	0.000713	−0.004851
4	$-j_2 - 2j_4 + 4j_6$	0.0095878	0.017388	0.002930	0.002680
5	$-2j_1 + j_2 - 4j_3 + 2j_4 + 4j_6$	0.0003145	−0.034776	0.000465	−0.005361
6	$-2j_1 - j_2 + 4j_3 + 2j_4 - 4j_6$	0.0074552	0.0	0.002248	0.0
7	$j_1 - 2j_5 - 4j_7$	0.0075199	0.019047	0.001654	0.000380
8	$-j_1 - 2j_5 + 4j_7$	0.0009676	−0.003021	0.000614	−0.000465

Table 4. Parameters of the effective Hamiltonian for the $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solution

$\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$		$\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$	
without selection of DD interactions	with selection of DD interactions	without selection of DD interactions	with selection of DD interactions
Single-site interaction constants (au)			
$A = 0.01491$	$A = 0.02436$	$A = 0.01902$	$A = 0.02484$
$B = 0.01376$	$B = 0.01376$	$B = 0.01811$	$B = 0.01811$
$C = 0.01819$	$C = 0.01819$	$C = 0.01210$	$C = 0.01210$
Intersite interaction constants (au)			
$J_1 = 0.00274$	$J_1 = -0.02171$	$J_1 = 0.00136$	$J_1 = -0.01373$
$J_2 = -0.01664$	$J_2 = 0.06069$	$J_2 = -0.01460$	$J_2 = 0.03306$
$J_3 = -0.00257$	$J_3 = 0.00704$	$J_3 = -0.00175$	$J_3 = 0.00418$
$J_4 = 0.00068$	$J_4 = -0.00437$	$J_4 = -0.00061$	$J_4 = -0.00373$
$J_5 = -0.00217$	$J_5 = 0.00976$	$J_5 = -0.00154$	$J_5 = 0.00677$
$J_6 = -0.00089$	$J_6 = 0.00147$	$J_6 = -0.00057$	$J_6 = 0.00088$
$J_7 = -0.00159$	$J_7 = 0.00073$	$J_7 = -0.00110$	$J_7 = -0.00001$

single-site constants A , B , and C were calculated by the least-squares method from the dependences of the total crystal energy on the amplitude u of the three-component vector S (Fig. 1).

In both solid solutions, the most favorable structure is that with ions displaced in the $[111]$ direction. Such

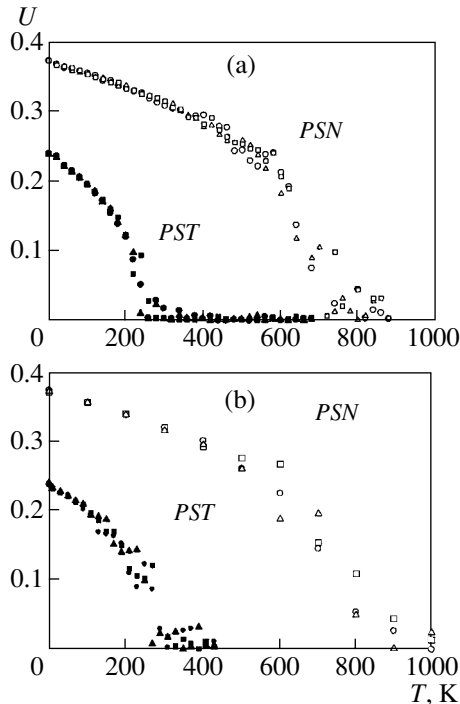


Fig. 2. Temperature dependences of the order parameter for the $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (white symbols) and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (black symbols) solid solutions calculated (a) without and (b) with selection of dipole–dipole interactions. Different symbols correspond to the three components of the local mode vector S .

displacements lead to a rhombohedral lattice distortion, which is in agreement with the experimental data [3].

To determine the intersite interaction constants $\{J_i\}$, we used the energies of seven different ordered structures reported in [5]. To separate the constants j_5 and j_7 , we added another structure, which was obtained by doubling the unit cell of structure 7 in [5]. Table 3 contains the expressions for the short-range part of the energy of ordered structures (column 2) and their numerical values, as well as the dipole energies.

To determine the effect of long-range dipole–dipole interactions on the ferroelectric-phase-transition temperatures, we calculated two sets of interaction constants: without and with explicit selection of long-range dipole–dipole interactions. Both sets of constants are listed in Table 4.

The temperature behavior of the system and the ferroelectric-phase-transition temperatures were determined by the Monte Carlo method. We used the standard Metropolis algorithm [9] for a simple $10 \times 10 \times 10$ cubic lattice with periodic boundary conditions.

The first 80000 steps for each temperature were rejected and not involved in averaging. The average values of the energy, order parameters, and specific heat were calculated in two stages. After each 50 steps, group means were calculated, and then averaging over 200 groups was performed. The phase transition temperature was determined from the temperature dependences of the energy and order parameter. High (1000 K) and low (50 K) temperatures were taken as initial. With a decrease in temperature, all three local mode components become disordered. Figure 2 shows the temperature dependences of the order parameter. The calculated ferroelectric-phase-transition temperatures for disordered $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid

Table 5. Ferroelectric-phase-transition temperatures of the $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ solid solutions

Crystal	Phase transition temperature, K			Spontaneous polarization, K m^{-2}	
	with selection of dipole–dipole interactions	without selection of dipole–dipole interactions	experiment	calculation	experiment
$\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$	670	620	350–370 [3]	0.27	0.25 [10]
$\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$	250	220	250–280 [3]	0.13	

solutions are listed in Table 5. It can be seen in Table 5 and Fig. 2 that the ferroelectric-phase-transition temperatures calculated with and without selection of long-range dipole–dipole interactions almost coincide with each other and are in qualitative agreement with the experimental data [3].

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 06-02-16091, and the President of the Russian Federation, grant MK-4140.2006.2.

REFERENCES

1. Cross, L.E., *Ferroelectrics*, 1987, vol. 76, p. 241.
2. Srenger, C.G.F. and Burggraaf, A.J., *Phys. Status Solidi A*, 1980, vol. 61, p. 275.
3. Malibert, C., et al., *J. Phys. Condens. Matter*, 1997, vol. 9, p. 7485.
4. Zinenko, V.I. and Sofronova, S.N., *Phys. Status. Solidi C*, 2004, vol. 1, no. 11, p. 3047.
5. Zhong, W., Vanderbilt, D., and Rabe, K.M., *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1995, vol. 52, no. 9, p. 6301.
6. Waghmare, U.V. and Rabe, K.M., *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, vol. 55, no. 10, p. 6161.
7. Kvyatkovskii, O.E., *Kristallografiya*, 2004, vol. 49, no. 1, p. 8 [*Crystallogr. Rep. (Engl. Transl.)*, vol. 49, no. 1, p. 4].
8. Zamkova, N.G., Zinenko, V.I., Ivanov, O.V., et al., *Ferroelectrics*, 2003, vol. 283, p. 49.
9. Metropolis, N. et al., *Chem. Phys.*, 1953, vol. 21, no. 60, p. 1087.
10. Chu, F., Reaney, I.M., and Setter, N., *J. Appl. Phys.*, 1995, vol. 77, p. 1671.