

The nonempirical calculation of the cation ordering and lattice dynamics in the solid solutions of $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ and $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$

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An effective Hamiltonian for the study of Sc–Nb(Ta) cation ordering in $\text{PbSc}_{1/2}\text{Nb}(\text{Ta})_{1/2}\text{O}_3$ solid solutions is written out. To determine the parameters of the effective Hamiltonian, a nonempirical calculation is performed within an ionic-crystal model taking into account the deformation, dipole and quadrupole polarizabilities of ions. The phase transition temperatures are calculated by mean field, cluster approximations and Monte-Carlo method. Within the same ionic-crystal model, we calculated the high-frequency permittivity, Born dynamic charges, and the phonon spectrum for a completely disordered and ordered phases.

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1 Introduction

The perovskite solid solution $\text{A}(\text{B}'\text{B}'')\text{O}_3$ have attracted much attention for several tens years from the theoretical, experimental and application points of view. From chemical point of view, two classes of these compounds can be distinguished: homo- and heterovalent alloys. In heterovalent alloys, the two B atoms belong to the different column of the Periodic Table. The solid solutions $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) are typical examples of heterovalent alloys. This compounds have been extensively studied by theoretical and experimental methods [1–4].

In this study we investigate order-disorder phase transitions and calculate phonon dispersions, Born effective charge and dielectric constant for ordered and disordered phases, using a nonparametric generalized Gordon-Kim model in which the deformability, dipole and quadrupole polarizabilities of ions are taken into account.

2 Statistical mechanics of B-cation ordering

To investigate the B-cation ordering for $\text{A}(\text{B}'\text{B}'')\text{O}_3$ solid solution, we use the model Hamiltonian method, which takes into account the positional disordering of the Sc and Nb(Ta) atoms. In this case the Hamiltonian can be written as [5]:

$$H = \sum_{i \neq j} J_{ij} \sigma_i^z \sigma_j^z \quad (1)$$

where $\sigma_i^z = \pm 1$ and J_{ij} are the interaction effective constants.

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The interaction effective constants are calculated by the nonparametric generalized Gordon-Kim model [6, 7]. In the model Hamiltonian, we restrict ourselves to the interactions within the first three coordination spheres.

Table 1 Energies of different ordered structures.

The configuration motif $\{\sigma_1 \sigma_2 \sigma_3 \sigma_4\}\{\sigma_5 \sigma_6 \sigma_7 \sigma_8\}$	Lattice parameters	The calculated energies E_1 (eV)		The expression for the energies by effective constants J_i
		PSN ($a_0=3.95 \text{ \AA}$)	PST ($a_0=4.01 \text{ \AA}$)	
$\{-1 \ 1 \ -1 \ 1\} \{1 \ -1 \ 1 \ -1\}$	$a=b=c=2a_0$	-0.399357	-0.448150	$-6J_1+12J_2-8J_3$
$\{-1 \ 1 \ -1 \ -1\} \{1 \ 1 \ 1 \ -1\}$	$a=b=c=2a_0$	-0.193832	-0.292024	$-8J_3$
$\{1 \ 1 \ 1 \ 1\} \{-1 \ -1 \ -1 \ -1\}$	$a=b=a_0$ $c=2a_0$	-0.125324	-0.239982	$2J_1-4J_2-8J_3$
$\{1 \ -1 \ 1 \ -1\} \{1 \ -1 \ 1 \ -1\}$	$a=b=c=\sqrt{2}a_0; c=a_0$	-0.349156	-0.378210	$-2J_1-4J_2+8J_3$
$\{-1 \ -1 \ -1 \ 1\} \{1 \ 1 \ 1 \ -1\}$	$a=b=c=2a_0$	-0.305748	-0.361138	$-2J_1$
$\{1 \ -1 \ -1 \ -1\} \{1 \ 1 \ 1 \ -1\}$	$a=b=c=2a_0$	-0.237239	-0.309096	$-4J_2$
$\{1 \ 1 \ 1 \ 1\} \{1 \ 1 \ 1 \ 1\} +$ $\{-1 \ -1 \ -1 \ -1\} \{-1 \ -1 \ -1 \ -1\}$	$a=b= a_0; c=4a_0$	0.848736	1.031372	$4J_1+4J_2$

To calculate the effective constants, we find the energies of several structures with different ordering of the Sc ions. Table 1 lists the configuration motif, the lattice parameters of the ordered structures, the energies E_1 per ABO_3 and expressions of the energy in terms of the effective constants.

$$E_1 = E_{full} - E_{self} - E_0 \quad (2)$$

where E_{full} is the total energy of the ordered structure, E_{self} is the ion self-energy. E_0 is a constant energy, which is independent of the positions of B' and B" ions. $E_0 = -161.455721$ eV for PSN and $E_0 = -157.692151$ eV for PST.

Since only the degrees of freedom related to the positional disorder of B' and B" atoms are taken into account in the model Hamiltonian, the effective interaction constants are calculated using the energies of unrelaxed structures. The calculated effective interaction constants are listed in Table 2.

As one can see from Table 2 the effective constants are antiferromagnetic in the first, second and third coordination spheres. Thus we have a competition of antiferromagnetic interactions. The phase transition temperature in mean field approximation is:

$$T_c^{mf} = (6J_1 - 12J_2 + 8J_3) / k_B \quad (3)$$

As one can see from Table 3 the calculated T_c^{mf} exceeds the experimentally observed temperature three times. The reason of the disagreement between the calculated and experimental temperatures is the strong short-range correlations, which are important in a system with a competitive interaction. The short-range correlations are not taken into account in the mean field approximation. These effects are well described by the cluster approximations, in particular, by the cluster field approximation [8, 9]. We use the 8-7-6-5 cluster approximations. In this case expression for the free energy is:

$$\beta F = \frac{11}{4} \ln Z_8 - \frac{5}{2} \ln Z_{7a} - \frac{5}{2} \ln Z_{7b} - 3 \ln Z_6 + 3 \ln Z_{5a} + 3 \ln Z_{5b} \quad (4)$$

where $\beta = 1/k_B T$, $Z_i = Sp\{\exp(-\beta H_i)\}$ are the i -th cluster partition functions and H_i are cluster Hamiltonians.

In this approximation we have six unknown cluster fields ϕ_i and ψ_i , which can be found from the variational conditions:

$$\partial F / \partial \phi_i = \partial F / \partial \psi_i = 0 \quad (5)$$

Table 2 The effective interaction constants.

Crystal	The effective interaction constants (eV)		
	J_1	J_2	J_3
PSN	0.152874	0.0593099	0.024229
PST	0.180569	0.077274	0.036503

Table 3 The calculated and experimental temperatures of the cation ordering.

(mf-mean field approximation, cl-cluster approximation, mc-Monte-Carlo simulation, exp-experimental data[1])

Crystal	$T_c(\text{mf})$	$T_c(\text{cl})$	$T_c(\text{mc})$	$T_c(\text{exp})$
PSN	4630 K	2250 K	1810 K	1480 K
PST	5200 K	2400 K	1920 K	1770 K

The phase transition temperature is defined from the equation (5), using the expansion (5) in linear terms of ϕ_i and ψ_i . The determinant, consisting of coefficients attached to the cluster fields ϕ_i and ψ_i , is taken equal to zero. From Table 3 we notice that the calculated T_c^{cl} is essentially less than T_c^{mf} .

We use Monte-Carlo method to take into account for the short- and long-range correlations, to describe B-cation phase transition. We studied the lattices $18 \times 18 \times 18$, $24 \times 24 \times 24$ and $30 \times 30 \times 30$ sizes with periodic boundary conditions. The temperature dependences of the heat capacity and long-range order parameters are shown in Fig. 1. Note, that the size of the lattice has no influence on the value of the phase transition temperature and the temperature dependences of the long-range order parameters. With increase of the lattice size the peak of heat capacity becomes sharper. The calculated phase transition temperatures (as one seen in Table 3) are in good agreement with the experimental data.

3 Lattice dynamics of the disordered and ordered phases

The frequency vibration spectrum, high-frequency permittivity, Born effective charges and elastic moduli of the ordered phases of PSN and PST solid solutions are calculated within the same model. The corresponding formulas for the calculations can be found in [7]. In the case of the disordered solid solutions, we calculated the dynamic properties using the virtual crystal approximation; in the dynamic matrix, all contributions are calculated by expanding the interaction energy between virtual $\langle B \rangle$ ion and the other ions into a Taylor series in small displacements. The results of calculation are shown in Tables 4–6.

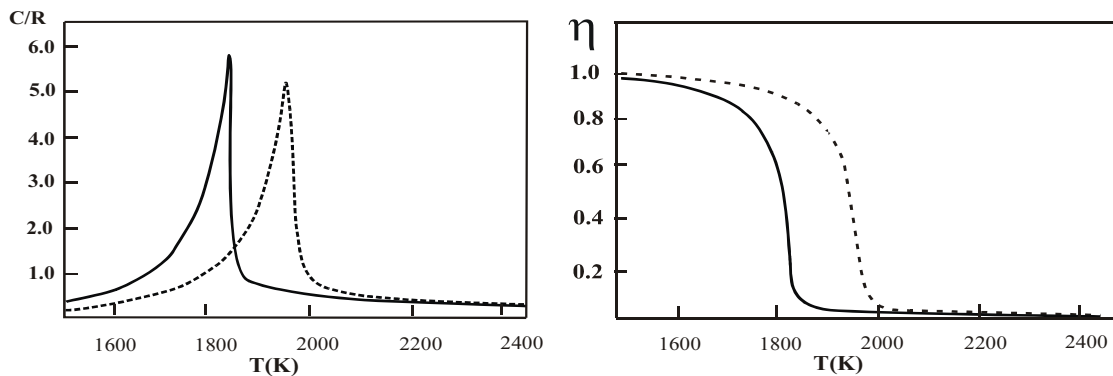
**Fig. 1** The temperature dependences of the heat capacity and long-range order parameter (solid lines - PSN, dashed lines - PST).

Table 4 Lattice parameter $a_0(\text{\AA})$, permittivity ϵ_∞ , Born effective charge Z and elastic moduli C_{ij} (10^2 GPa).

The ordered solid solution (elpasolite structure)										
	a_0	ϵ_∞	Z_{Pb}	Z_{Sc}	$Z_{\text{B}''}$	$Z_{\text{O} }$	$Z_{\text{O}\perp}$	C_{11}	C_{12}	C_{44}
PSN	7.93	5.70	2.74	3.39	8.77	-4.96	-1.92	1,96	0,88	0,90
PST	8.07 8.14[2]	4.54	2.65	3.30	5.64	-2.79	-2.16	1,96	0,77	0,80
The disordered solid solution (the virtual crystal approximation)										
	a_0	ϵ_∞	Z_{Pb}	$Z_{\langle\text{B}\rangle}$	$Z_{\text{O}1}$	$Z_{\text{O}3}$	C_{11}	C_{12}	C_{44}	
PSN	3.95 4.08[3]	5.85	2.83	6.02	-5.21	-1.83	2.27	0.89	0.87	
PST	4.01 4.07[1]	4.62	2.71	4.24	-2.67	-2.14	2.32	0.78	0.75	

Table 5 Vibration frequencies (cm^{-1}) calculated for disordered perovskite structure.

$q=(0,0,0)$							
	TO_1	LO_1	T_{2u}	TO_2	LO_2	TO_3	LO_3
PSN	23.1i	104.3	207.2	290.6	322.4	466.6	598.2
PST	51.6i	106.2	203.5	267.2	341.2	581.1	615.1
$q=R$							
	R_{15}	R_{25}	R_{15}	$\text{R}_{12'}$	$\text{R}_{25'}$	$\text{R}_{2'}$	
PSN	73.9i	35.7	216.7	345.8	484.6	589.3	
PST	68.6i	80.4i	236.8	282.6	552.8	580.1	

Table 6 Vibration frequencies (cm^{-1}) at $q=0$ for ordered elpasolite structures.

PSN		PST		
this calculation		this calculation		*exp [10]
200.6i(2) (T_{1u})	254.5(3) (T_{2g})	133.0i (3) (T_{1g})	279.9 (T_{1u})	50 (T_{2g})
181.4i(3) (T_{1g})	302.3(2) (T_{1u})	65.3i (2) (T_{1u})	341.4(2) (T_{1u})	370 (T_{2g})
51.7i(3) (T_{2g})	315.7 (T_{1u})	51.0i (3) (T_{2g})	356.8 (T_{1u})	
25.5 (T_{1u})	460.9(2) (E_g)	95.3 (T_{1u})	489.1(2) (E_g)	500 (E_g)
14.2(2) (T_{1u})	633.6(2) (T_{1u})	176.3(3) (T_{2u})	589.9(2) (T_{1u})	
122.5(3) (T_{2u})	677.2 (A_{1g})	201.6(2) (T_{1u})	609.4 (A_{1g})	740 (A_{1g})
239.3 (T_{1u})	695.7 (T_{1u})	270.7(3) (T_{2g})	631.2 (T_{1u})	

4 Conclusion

The first aim of the paper was to investigate the B-cation ordering in the solid solution PSN and PST using the nonempirical structure energy calculations plus CFA statistical mechanics and Monte-Carlo simulation. Our results show that such approach is quite promising for modeling the cation ordering in complex ionic systems. The agreement between the calculated phase transition temperatures and experimental data is reasonable.

The second aim of the work was to study the lattice dynamics of PSN and PST. As a result, (i) we have obtained the values of the dielectric constant ϵ_∞ , Born effective charges Z_i , phonon frequencies, elastic moduli C_{ij} and (ii) we have indicated unstable ferroelectric and ferrodistorstic modes in both disordered (perovskite structure) and ordered (elpasolite structure) phases PSN and PST.

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