Journal of Physics: Conference Series

OPEN ACCESS

Lattice dynamics and ferroelectric phase transitions in solid solutions $PbSc_{1/2}Nb_{1/2}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$

To cite this article: N G Zamkova and V I Zinenko 2007 *J. Phys.: Conf. Ser.* **92** 012162

View the article online for updates and enhancements.

Related content

- Ferroelectric Phase Transition in $PbZr_xTi_{1-x}O_3$ under High Pressure
Mitsuhiko Hayashi, Michihide Machida, Kanemitsu Hasegawa et al.
- Effect of Hydrostatic Pressure on the Ferroelectric Phase Transitions in CsH_2PO_4 and CsD_2PO_4
Kazuo Gesi and Kunio Ozawa
- Effect of Hydrostatic Pressure on the Ferroelectric Phase Transition in $Ca_2Sr(CH_3CH_2COO)_6$
Kazuo Gesi and Kunio Ozawa

This content was downloaded from IP address 84.237.90.20 on 05/04/2021 at 10:25

Journal of Physics: Conference Series **92** (2007) 012162 doi:10.1088/1742-6596/92/1/012162

Lattice dynamics and ferroelectric phase transitions in solid solutions $PbSc_{1/2}Nb_{1/2}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$

N G Zamkova and V I Zinenko

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

E-mail: zam@iph.krasn.ru

Abstract. The calculation of the lattice dynamics and ferroelectric phase transitions for disordered and ordered solid solution $PbSc_{1/2}Nb_{1/2}O_3$ and $PbSc_{1/2}Ta_{1/2}O_3$ in the framework of the Gordon-Kim model are performed. The unstable ferroelectric modes were found in all cases. The model Hamiltonian for the study finite temperature behavior during for the ferroelectric phase transition is used. The transition temperatures, phase sequences and spontaneous polarizations are calculated by Monte-Carlo method.

1. Introduction

The $PbSc_{0.5}Nb_{0.5}O_3$ (PSN) and $PbSc_{0.5}Ta_{0.5}O_3$ (PST) belong to large class of heterovalent solid solutions based on the perovskite structure $PbB'_{0.5}B''_{0.5}O_3$. The cations B' and B'' may be ordered, disordered or partly ordered in the sublattice of the oxygen octahedra. The degree of cation ordering has a tremendous influence on the properties of these compounds. The disordered PSN and PST exhibit a diffuse phase transition and relaxor properties at certain degree of ordering, whereas fully ordered one should be a conventional ferroelectrics [1]. The different physical properties of PSN and PST were studied in numerous experimental works [2, 3]. Theoretical works [4] are related mainly to the solid solution PSN.

In this work the calculation of lattice dynamics and ferroelectric phase transition in fully ordered and fully disordered PSN and PST was made.

2. Lattice dynamics

Lattice dynamics of these solid solutions are calculated in the framework of nonempirical generalized Gordon-Kim model, which takes into account dipole and quadrupole polarizabilities of ions [5]. The structures of high temperature phase in the ordered and disordered compounds are different. Fully disordered solid solutions $PbSc_{0.5}Nb_{0.5}O_3$ and $PbSc_{0.5}Ta_{0.5}O_3$ have a perovskite structure (Pm3m), whereas for ordered one (Pb_2ScNbO_6 and Pb_2ScTaO_6) the structure turns up elpasolite (double perovskite) structure with space group Fm3m.

The frequency vibration spectrum, high-frequency permittivity and Born effective charges of the ordered and disordered PSN and PST solid solutions are calculated. The corresponding formulas for the calculations can be found in [5]. The calculations were made for experimental value of lattice parameter: $a_0 = 7.7$ a.e. for disordered and $a_0 = 15.4$ a.e. for ordered solid solutions. Some results of calculations are shown in table 1.

© 2007 IOP Publishing Ltd

Table 1. Permittivity ε_∞, Born effective charge Z_{din} (in unit *e*), frequencies of soft ferroelectric modes ω_s (cm^{-1}) (negative values correspond to imaginary frequencies) and eigenvectors ξ of these modes for disordered and ordered solid solutions PSN and PST.

	ω_s	ε_∞		Pb	Nb(Ta)	Sc	$O_\perp$	$O_\parallel$
$PbSc_{1/2}Nb_{1/2}O_3$	–80.2	3.55	ξ	0.76	0.21		–0.42	–0.14
			Z_{din}	2.69	5.16		–1.89	–4.19
$PbSc_{1/2}Ta_{1/2}O_3$	–59.6	3.32	ξ	0.77	0.11		–0.44	–0.01
			Z_{din}	2.64	4.28		2.02	2.88
Pb_2ScNbO_6	–83.0	3.58	ξ	0.53	0.07	0.27	–0.29	–0.11
			Z_{din}	2.71	5.93	4.19	–1.80	–4.17
Pb_2ScTaO_6	–69.3	3.32	ξ	0.54	0.07	0.12	–0.31	–0.00
			Z_{din}	2.67	4.20	3.89	2.04	2.64

By now the most recognized mechanism of a ferroelectric instability of perovskite-like oxides is the dipole mechanism, namely the long-range dipole-dipole interactions favor the ferroelectric state [6]. As it is known these interactions are characterized by large magnitude of Born effective charges. Our calculated Born effective charges (table 1) for PSN are similarly to those for other ferroelectric perovskite, but for PST these values are noticeably lower. Some reasons of such difference were considered in detail in work [7]. In spite of this dissimilarities in dynamical charges, calculated phonon spectra of both solid solutions are exhibiting the unstable ferroelectric mode. The vibration frequencies and eigenvectors of soft ferroelectric modes of PSN and PST are given in table 1. As shown, the lead ions suffer largest displacements, in good agreement with experiments [2,3]. The distortion of crystal lattice according to three components of this eigenvectors results in a ferroelectric phase with rhombohedral structure.

3. Ferroelectric phase transition

Both disordered and ordered solid solution PSN and PST undergo ferroelectric phase transition [1,2]. To investigate these phase transitions the model Hamiltonian in local mode approximation is used [8]. The model Hamiltonian includes three parts: on-site anharmonic contributions, long-range dipole-dipole interactions and short-range interactions between local mode up to third neighbours for disordered PSN and PST and up to second neighbours for ordered compounds. Parameters of this model Hamiltonian are determined using the energies of distorted structures, which are calculated within the same model. For disordered solutions we use distorted structures from [8], and for ordered PSN and PST we used those proposed in [9]. Thus determined parameters of model Hamiltonian may be found elsewhere [9]. Then the finite-temperature behavior is simulated by Monte-Carlo method [8,10] for all compounds under consideration.

In figures 1 and 2, calculated temperature dependences of the local mode components and energies for all compounds are shown, and calculated phase transition temperatures, spontaneous polarizations and ion displacements are presented in table 2. For PSN solid solutions the Monte-Carlo simulation reveals that phase transition from cubic to ferroelectric rhombohedral phase takes place through the intermediate phase (orthorhombic or monoclinic) with two nonzero components of local mode. The PST solid solutions undergo phase transition from paraelectric cubic directly to ferroelectric rhombohedral phase. According to results of simulations the transition temperatures for both PSN and PST ordered solutions are higher than those for disordered ones, whereas experimentally in PSN reverse situation is observed. The calculated values of spontaneous polarizations and displacements of ions satisfactorily agree with experimental data.

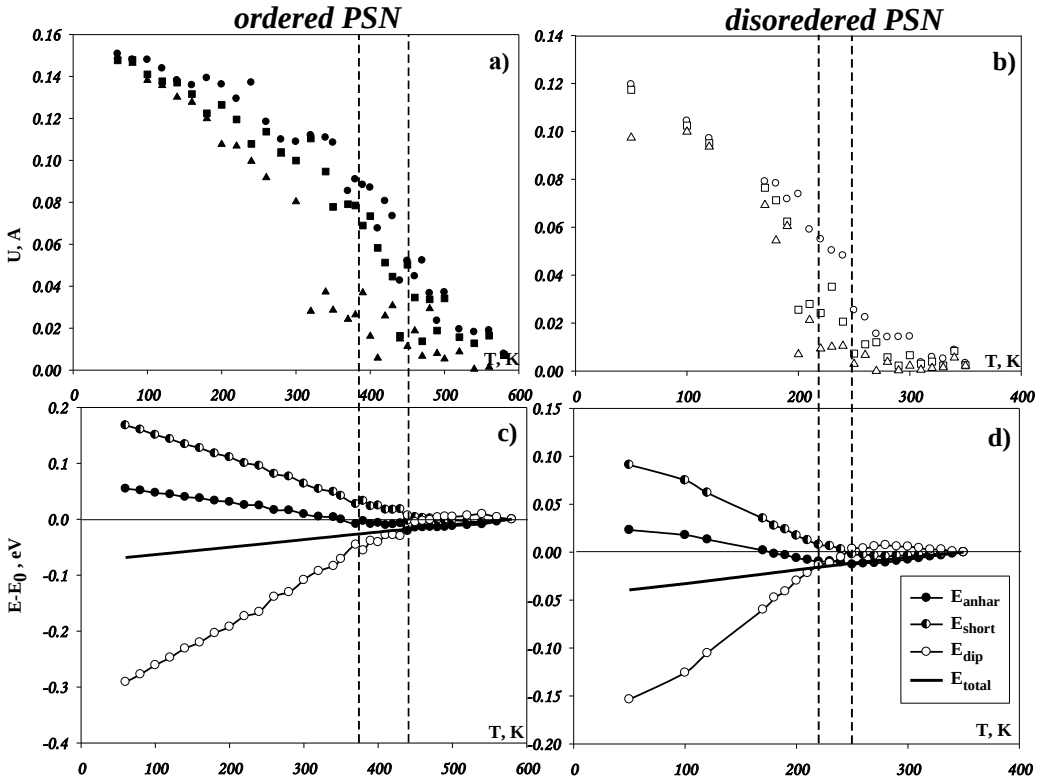

Figure 1. The temperature dependences of the components of local mode amplitude a), b) and energies c), d) for ordered and disordered PSN, obtained from Monte-Carlo simulation.

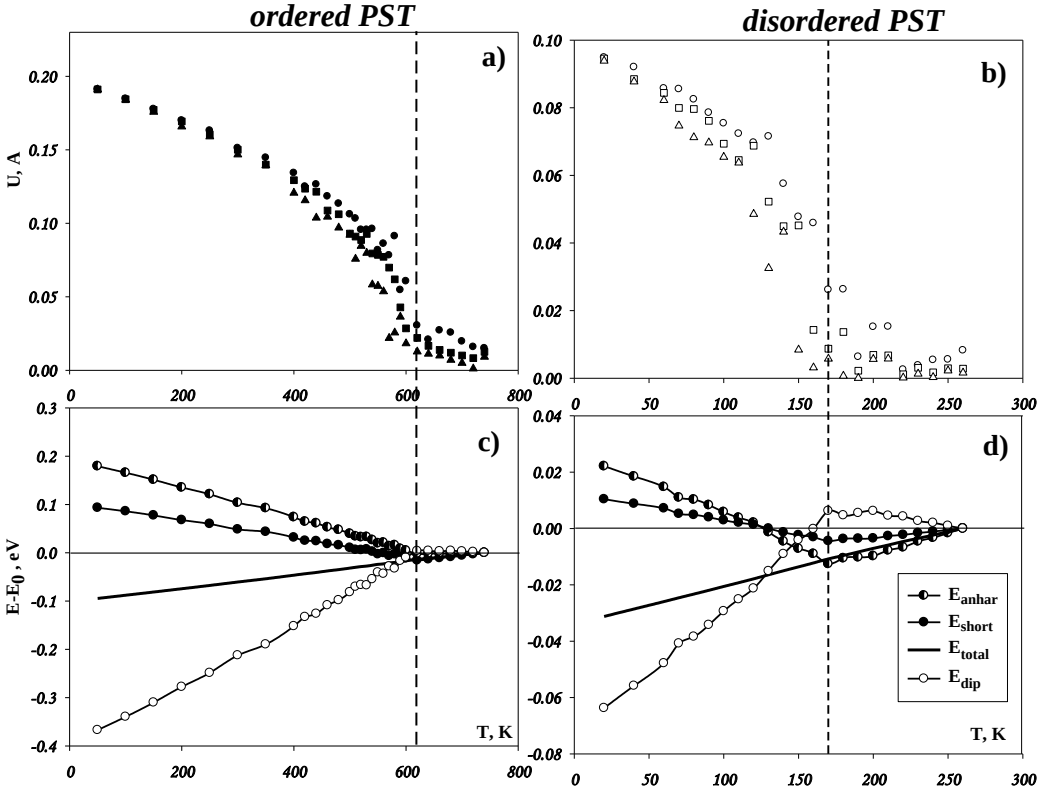

Figure 2. The same as in figure1 for PST solid solution..

Table 2. The temperatures of phase transitions, spontaneous polarization and displacements of ions along the [111] direction. In the last two columns are shown relative displacements of some ions.

		T_c, K	$P_s, C/m^2$	*displacements, Å*					
				Pb	**Nb(Ta)**	**Sc**	**O**	δ_{Pb-O}	δ_{Sc-O}
$PbSc_{1/2}Nb_{1/2}O_3$	calc.	220 250	0.26	0.17	0.05		–0.09	0.26	0.14
	exp.[3]	– 380						0.39	0.16
$PbSc_{1/2}Ta_{1/2}O_3$	calc.	170	0.17	0.14	0.02		–0.06	0.20	0.08
	exp.[3]	275	0.33						
Pb_2ScNbO_6	calc.	380 450	0.24	0.14	0.02	0.07	–0.09	0.23	0.16
	exp.[3]	– 350	0.26					0.36	0.14
Pb_2ScTaO_6	calc.	610	0.24	0.17	0.02	0.04	–0.08	0.25	0.12
	exp.[3]	300			0.0	0.0			

4. Conclusion

The first aim of the work was to study the lattice dynamics of disordered and ordered PSN and PST. As results, (i) we have obtained the values of the dielectric constant ε_∞, Born effective charges Z_{din}, phonon frequencies and (ii) we have obtained unstable ferroelectric modes in both disordered (perovskite structure) and ordered (elpasolite structure) phases PSN and PST.

The second aim of the work was to investigate the ferroelectric phase transition in PSN and PST solid solutions using the nonempirical structure energy calculations and Monte-Carlo simulation. Results obtained show that both ordered and disordered PSN and PST undergo ferroelectric phase transitions into rhombohedral phase, with intermediate phase for PSN. Experimental search of this phase would be highly desirable.

Acknowledgements

This study was supported by the Russian Foundation for Basic Research (project no. 06-02-16091).

References

[1] Isupov V A 2003 *Ferroelectrics* **289** 131 and references therein
[2] Siny I G, Lushnikov S G and Katiyar R S 1999 *Ferroelectrics* **231** 115 ; Dwoski W, Akbas M K, Davies P K and Egami T 2000 *J Phys. and Chem.Solids* **61** 229 ; Woodward P M and Baba-Kishi K Z 2002 *J.Appl.Cryst.* **35** 233
[3] Malibert C, Dkhil B, Kiat J M, Durand D, Berar J F and Spasojevic-de Bire A 1997 *J.Phys.: Condens.Matter* **9** 7485
[4] Iniguez J and Bellaiche L 2001 *Phys.Rev.Lett.* **87** 095503-1; Tinte S, Burton B P and Waghmare U V 2006 *Phys.Rev.Lett.* **97** 137601 ; Waghmare U V, Cockayne E J and Burton B P 2003 *Ferroelectrics* **291** 187
[5] Zamkova N G, Zinenko V I, Ivanov O V, Maksimov E G and Sofronova S N 2003 *Ferroelectrics* **283** 49
[6] Kvyatkovskii O E 1994 *Ferroelectrics* **153** 201
[7] Zinenko V I, Zamkova N G, Maksimov E G and Sofronova S N 2007 *JTEF* (in preparation)
[8] Zhong W and Vanderbilt D 1995 *Phys.Rev.* **B52** 6301
[9] Zinenko V I and Zamkova N G (to be published)
[10] Metropolis N, Rosenbluth A W, Rosenbluth M N, Teller A H and Teller E 1953 *J.Chem.Phys.* **21** 1087