Effect of Ca^{2+} Ion Substitution by the Trivalent Ions (Sc^{3+}, In^{3+}, La^{3+}, Bi^{3+}) on the Ferroelectric Instability in Orthorhombic $CaTiO_3$

N. G. Zamkova , V. I. Zinenko & A. S. Shinkorenko

Published online: 15 May 2012.

Submit your article to this journal

Article views: 79

View related articles

Citing articles: 1 View citing articles

Taylor & Francis
Taylor & Francis Group

Effect of Ca^{2+} Ion Substitution by the Trivalent Ions $(Sc^{3+}, In^{3+}, La^{3+}, Bi^{3+})$ on the Ferroelectric Instability in Orthorhombic $CaTiO_3$

N. G. ZAMKOVA,* V. I. ZINENKO, AND A. S. SHINKORENKO

L.V. Kirensky Institute of Physics, Siberian Branch, Russian Academy of Science, Krasnoyarsk, Russia

Vibration frequencies of instable ferroelectric modes, as well as dependencies of crystal energy on ion's displacement amplitudes of these modes in doped compounds $Ca_{1-x}A_xTi_{1-x/4}\square_{x/4}O_3$ (space group Pbmn) with $A–Sc^{3+}, In^{3+}, La^{3+}, Bi^{3+}$ ($\square$–vacancy) have been calculated in the framework of generalized nonparametric Gordon–Kim model. To compensate excessive positive charge the vacancies were considered to be at Ti^{4+} sites. Calculations were carried out in the «average» crystal approximation for the impurity concentration x = 0.25. For this purpose 40 atoms' supercell sets with the different ordering of the heterovalent ions Ca^{2+} and impurity A^{3+} have been considered. Every type of impurity has been found to induce ferroelectric instability in doped compounds.

Keywords Ferroelectric; polarization; lattice dynamics

1. Introduction

Heterovalently doped perovskite-like oxides open up broad opportunities to produce new functional materials; such compounds have been the focus of numberous of experimental and theoretical works. Heterovalent impurities embedding into crystals with perovskite structure substantially affect both phase diagram and physical properties of doped compounds. For example, this changes magnetic properties in manganites [1, 2] or electrical properties perovskite-like ferroelectrics [3, 4].

$CaTiO_3$ crystal for T > 1980 K has ideal perovskite structure. As temperature decreases, $CaTiO_3$ undergoes a sequence of phase transitions and below T ≈ 1380 K has low-temperature primitive orthorhombic phase. It has four $CaTiO_3$ formula units in an orthorhombic cell with $a \approx b \approx \sqrt{a_0}$ and $c \approx 2a_0$, where a_0 is the lattice parameter of high-temperature cubic phase. Ferroelectric state is not observed in $CaTiO_3$ until sufficiently low temperature, but dielectric constant increases as temperature decreases [5].

Thus, the effect of substitution of calcium ion by trivalent impurities on the lattice dynamic and ferroelectric properties of crystal is always of interest. The aim of this work is to calculate nonempirically vibration frequencies, dielectric permittivity, effective Born's charges and spontaneous polarization of doped compounds $Ca_{1-x}A_xTi_{1-x/4}\square_{x/4}O_3$, where A - $Sc^{+3}, In^{+3}, La^{+3}, Bi^{+3}$; $\square$-vacancy.

---

2. Method of Calculation

All calculations have been made in the framework of nonempirical model of ionic crystal taking into account dipole and quadropole polarizability of ions [6]. To calculate properties of CaTiO$_3$ crystal doping with trivalent ions, where impurity ions are considered to be at the Ca^{+2} site. The ionic mechanism of charge compensation is realized with formation of vacancy on the Ti^{+4} site.

In supercell with 40 atoms and impurity concentration $x = 0.25$ the heterovalent ions may be ordered in 28 various ordering configurations. However, some of them have equal energies. Figure 1 shows the configuration types with different energies and weight factors. The dynamical matrix, frequencies of vibrations and eigenvectors of soft ferroelectric modes were calculated for each type of structure. Then, for each configuration type the dependence of doping crystal's full energy on the ferroelectric mode amplitude was calculated and the energy was supercell set averaging. The same procedure was carried out also for getting of spontaneous polarization vector $\vec{P}$: for each type of structure the components of spontaneous polarization vector were calculated

$$P_n^\alpha = U \sum_{k=1}^{N_{atom}} \sum_{\beta=1}^{3} Z_n^{\alpha\beta}(k) \xi_n^\beta(k).$$

After that they were averaged for all structures. Here, n is the number of ordering structure, $Z_n^{\alpha\beta}(k)$ are the matrix components of Born effective charges of k-th ion, $\xi_n^\beta(k)$ are the polar mode eigenvector, U is ion's displacement amplitude of this mode.

There is a further point to be made here. In cubic CaTiO$_3$, as it will be show below, there are lattice instable antiferrodistorsive modes at the boundary points R and M of Brillouin zone. The low-temperature structures of CaTiO$_3$ can largely be described as a TiO$_6$ octahedra tilting structure ($\varphi\varphi\psi$ in notation [7]) or $a^-a^-c^+$ in notation [8]. In present investigation the trivalent impurity ions are considered to be Ca^{2+} site of the Pbmn (Z = 4) structure.

All calculations were made on experimental lattice parameter of cubic CaTiO$_3$ perovskite ($a = 3.84$ Å).
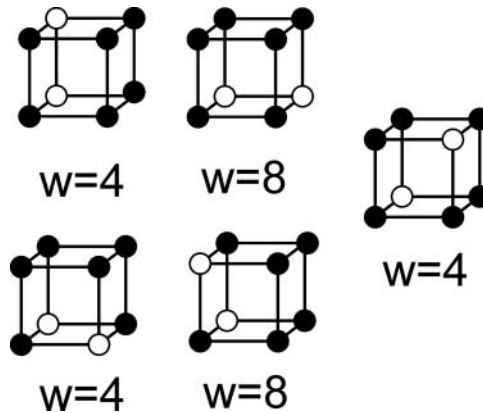
Figure 1. The ordering structures with different energies for concentration x = 1/4. Weight factors for each structure shown under them. The filled circles are calcium ions, white circles are trivalent impurity ions.
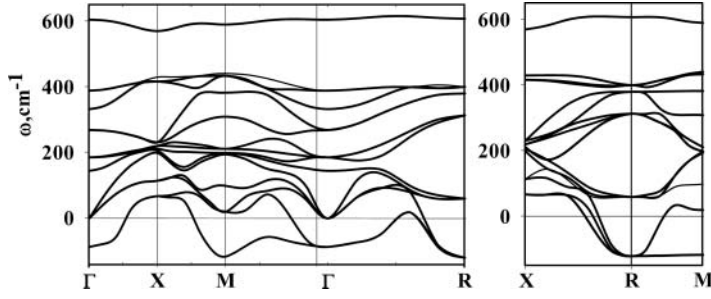
Figure 2. Phonon-dispersion curves calculated in cubic $CaTiO_3$. Imaginary frequencies are indicated by negative values.

3. Results and Discussions

Phonon spectra of cubic $CaTiO_3$ is shown in Fig. 2. The most instable modes are at the boundary points R ($\omega_R = 120i$ cm^{-1}) and M ($\omega_M = 116i$ cm^{-1}) of Brillouin zone, and eigenvectors of these modes are associated with "rotation" of TiO_6 octahedra. Polar mode in cubic $CaTiO_3$ is instable too ($\omega_S = 86i$cm^{-1}).

Full energy $CaTiO_3$ in supercell with 40 atoms is minimized with different combinations of eigenvector components of R and M modes. The orthorhombic phase with space group Pbmn (Z = 4) has a lowest energy. Next, we can allow ionic positions to relax under used model. The relaxation was done to a convergence of better than 10^{-3}eV/Å. Table 1 presents ionic coordinates, rotation angles, electronic dielectric tensor and elastic modules for relaxed Pbmn (Z = 4) structure. All lattice modes are stable in this structure.

Table 1

Structural parameters (x, y, z), rotation angles (φ, ψ), electronic dielectric tensor (ε_{ii}) and elastic modules C_{ij} (GPa) for relaxed orthorhombic structure $CaTiO_3$

	calc.	exp.					calc.	exp.
			C_{11}	2,22				
Ca (4c)			C_{22}	2,35			$\varphi \approx 6{,}0°$	$\approx 9{,}0°$
x	−0,0015	−0,0065	C_{12}	2,04			$\psi \approx 5{,}8°$	$\approx 9{,}5°$
y	0,0053	0,0349	C_{13}	0,89				
z	0,2500	0,2500	C_{23}	0,88				
Ti (4b)			C_{33}	0,63				
x	0,500	0,500	C_{44}	0,57				
y	0,000	0,000	C_{55}	0,82				
z	0,000	0,000	C_{66}	0,83				
O (4c)								
x	0,0515	0.0707	ε_∞	calc.	exp.			
y	0,4919	0,4842	ε_{xx}	5,99				
z	0,2500	0,2500	ε_{yy}	6,01				
O (8d)			ε_{zz}	6,02				
x	0,7238	0,7111	$(\varepsilon_{xx} + \varepsilon_{yy}$	6,00	5,81			
y	0,2756	0,2884	$+ \varepsilon_{zz})/3$					
z	0,0265	0,0372						

Table 2

Soft and low-energy polar modes frequencies for ordered structures (imaginary frequencies are indicated by negative values)

Conf.	Bi^{+3}		In^{+3}		La^{+3}		Sc^{+3}	
1	53i	36	63i	20	51i	30	162i	138i
2	45i	32	63i	37i	43i	16i	159i	154i
3	59i	50i	88i	66i	51i	32i	181i	181i
4	73i	4i	90i	38i	61i	15	189i	155i
5	61i	43i	67i	47i	56i	33i	172i	162i

In first column of Table 3 calculated diagonal components of Born effective charges tensor are given for orthorhombic CaTiO₃. Off-diagonal components are 10 times smaller than diagonal ones and not given to save space.

At substitution of calcium ions by trivalent impurities there are unstable ferroelectric modes. In the Table 2 frequencies of soft and low-frequencies polar modes for each ordered structures (Fig. 1) are given. In Table 3 diagonal components of Born effective charges tensor Z_i^{aa} are shown for 'average' crystals $Ca_{0.75}A_{0.25}Ti_{0.9375}O_3$ (A - Sc^{+3}, In^{+3}, La^{+3}, Bi^{+3}) in orthorhombic phase Pbmn. As expected, the introduction of trivalent impurity in the position of Ca^{2+} perovskite structure increases dynamic ionic charge in this positions. The dynamic ionic charge in position Ti^{4+} is decreased by a vacancy in this position.

As evident from Table 2, there are unstable polar modes for each type of ordered by impurities structures. For each structures dependence of full energy on the polar modes amplitude was calculated, as it is shown in Fig. 3 for example $Ca_{0.75}In_{0.25}Ti_{0.9375}O_3$. Maximal ion displacements in the ferroelectric phase are found from the full energy minimum for the "average" crystal in the ferroelectric phase. The results for compounds under consideration are shown in Fig. 4. As it is seen for all considered compounds the monoclinic polar

Table 3

The effective Born's charges (in electronic charge units) and high-frequency dielectric permittivities for CaTiO₃ and different ordered by impurity structures.

Ion	Z	CaTiO₃	Bi^{+3}	In^{+3}	La^{+3}	Sc^{+3}
Ca (4c)	Z_{xx}	3,01	3,35	3,23	3,43	3,41
	Z_{yy}	2,62	2,96	2,88	3,00	2,98
	Z_{zz}	2,79	3,13	3,04	3,19	3,18
Ti (4b)	Z_{xx}	6,37	5,78	5,72	5,75	5,71
	Z_{yy}	6,38	5,81	5,73	5,77	5,72
	Z_{zz}	6,38	5,79	5,73	5,76	5,72
O (4c)	Z_{xx}	−1,75	−1,88	−1,87	−1,92	−2,00
	Z_{yy}	−1,75	−1,89	−1,88	−1,94	−2,03
	Z_{zz}	−5,67	−5,17	−5,02	−5,10	−4,88
O (8d)	Z_{xx}	−1,75	−1,88	−1,88	−1,93	−2,01
	Z_{yy}	−5,68	−5,18	−5,02	−5,11	−4,89
	Z_{zz}	−1,75	−1,88	−1,87	−1,93	−2,01
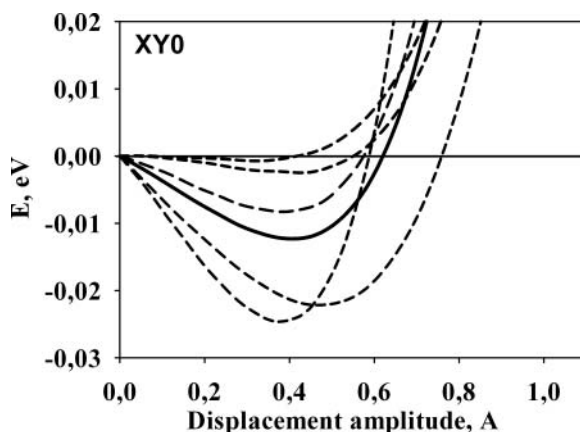
Figure 3. Dependences of full energy on the polar modes amplitude in different ordered structures (dashed lines) for $Ca_{0.75}In_{0.25}Ti_{0.9375}O_3$. Dependence of averaged full energy is shown by solid line.

phase with the polarization vector in the plane XY has the lowest energy. Orthorhombic polar phase with polarization direction along the axis Z can be realized only in compound $Ca_{0.75}Sc_{0.25}Ti_{0.9375}O_3$. The energy of this phase is close to the energy of the monoclinic phase in this compounds. The values of spontaneous polarization in the different polar phases for the compounds under consideration are shown in Table 4.
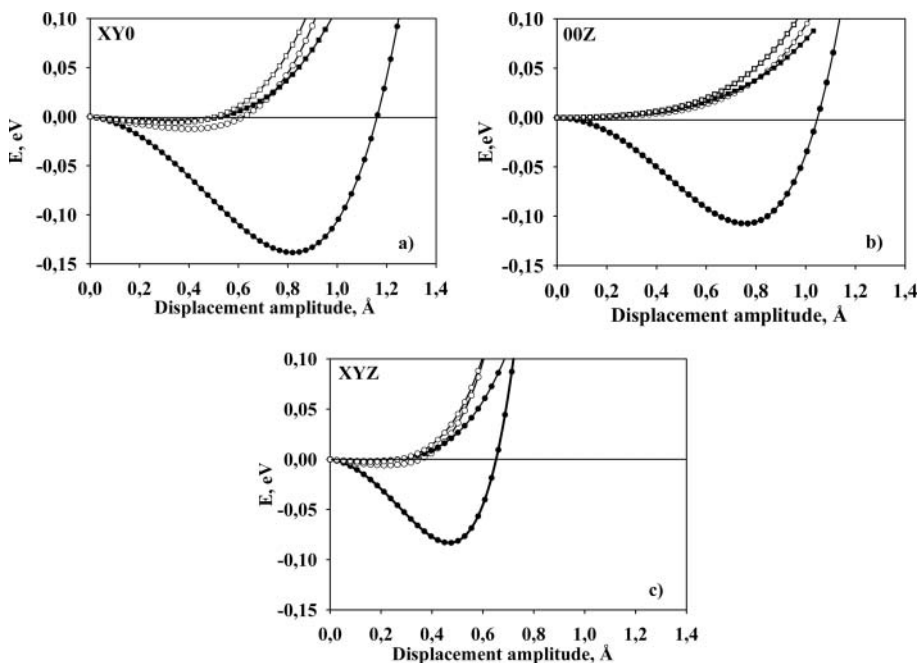
Figure 4. Dependences of doped "average" crystal total energy (E) on ions displacement amplitudes of polar mode for different directions in a crystal: a) [XY0] direction, b) [00Z] direction, c) [XYZ] direction. $Ca_{0.75}Sc_{0.25}Ti_{0.9375}O_3$—solid circles, $Ca_{0.75}In_{0.25}Ti_{0.9375}O_3$—open circles, $Ca_{0.75}La_{0.25}Ti_{0.9375}O_3$—solid squares, $Ca_{0.75}Bi_{0.25}Ti_{0.9375}O_3$—open squares.

Table 4

The values of polarization ($\mu C/cm^2$).

	Bi^{+3}				In^{+3}				La^{+3}				Sc^{+3}			
	P_x	P_y	P_z	|P|	P_x	P_y	P_z	|P|	P_x	P_y	P_z	|P|	P_x	P_y	P_z	|P|
XY0	3,4	0,3	0,0	3,4	3,8	0,7	0,0	3,9	2,8	0,3	0,0	2,8	0,8	17,6	0,0	19,3
00Z	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	30,5	30,5
XYZ	1,8	0,5	1,1	2,2	1,4	0,5	6,6	6,8	1,4	0,5	6,3	6,4	6,3	9,5	18,8	21,9

4. Summary

In the framework of generalized model of ionic crystal the lattice dynamics and ferroelectric instability in doped compounds $Ca_{1-x}A_xTi_{1-x/4}\square_{x/4}O_3$, where A - Sc^{3+}, In^{3+}, La^{3+}, Bi^{3+} and $\square$ - vacancy have been calculated. In this work for the ferroelectric instability calculation we used 'average' crystal approximation [9]. In our calculation we obtained advantage of ferroelectric phase for all compounds under consideration. The energy minima depth in the ferroelectric phase depends on type of impurity ion. The energy minima are deeper at the $CaTiO_3$ doping by light scandium ions.

It would be very desirable to check these results by experiment.

Acknowledgment

References

1. E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance. The Physical of Manganites and Related Compaunds Series: Springer Series in Solid State Science. (2003) p. 136.
2. T. Chatterji, *Colossal Magnetoresisitive Manganites*, Kluwer Academic Publisher. 2004.
3. A. Kerfah, K. Taibi, A. Guehrai-Laidoudi, A. Simon, and J. Ravez, *Solid State Science* **8**, 613 (2006).
4. F. D. Morrison, D. C. Sinclair, and A. R. West, *Int. J. Inorg. Mater.* **3**, 1205 (2001).
5. A. R. Chakhmouradian and R. H. Mitchell, *J. Solid State Chem.* **138**, 272 (1998).
6. E. G. Maksimov, V. I. Zinenko, and N. G. Zamkova, *Phys. Usp.* **47**, 1075 (2004).
7. K. S. Alexandrov, A. T. Anistratov, A. F. Beznosikov, and N. V. Fedoseeva, *Phase Transitions in Crystals of Halide Compounds ABX₃*. Novosibirsk: Ed. Nauka; 1981.
8. A. M. Glazer, *Acta Cryst.* **28**, 3384–3399 (1972).
9. N. G. Zamkova, V. S. Zhandun, and V. I. Zinenko, *Fizika Tverdogo Tela.* **53**, 2175 (2011).