

Simulation of the local electric field in tetragonal phase of $BaTiO_3$

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The region of possible combinations of electronic dipole polarizability and effective charges of ions in $BaTiO_3$ structure at T = 293 K is established. It is shown that electronic polarizability of apical O^{2-} ion is anisotropic. The results obtained can be used for the computer simulations of $BaTiO_3$ structure peculiarities.

Установлена область возможных комбинаций электронной дипольной поляризуемости и эффективных зарядов ионов в кристаллах $BaTiO_3$ при T = 293 К. Показано, что электронная поляризуемость апикальных ионов O^{2-} анизотропна. Полученные данные можно использовать для моделирования особенностей структуры $BaTiO_3$.

Barium titanate ($BaTiO_3$) is among ferroelectric materials of the most technologic importance and being studied intensively. Both these crystals and the barium titanate based ceramics are the objects of many theoretical and experimental investigations. At high temperatures (T > 415 K), $BaTiO_3$ is a paraelectric with the cubic structure. On cooling through the transition temperature, this material becomes ferroelectric. It is believed before that the "cubic → tetragonal" phase transition has the strongly first-order character and is associated with a remarkable optical anisotropy [1] and a large spontaneous polarization (P_s = 0.250 to 0.260 C/m^2) [2]. Nevertheless, there are some evidences for the coexistence of order-disorder and displacement components of these phase transition in $BaTiO_3$ [3]. So the phase transition at 407 to 415 K in $BaTiO_3$ is an object of good prospects for the investigation by the computer simulation method.

Computer simulation of ionic or partially ionic systems is widely used now in solid state physics [4]. There are two approaches of its realization, namely, using either one of non-empirical (*ab initio*) methods or the classical electrostatic approach [5]. If the correct information about the effective charges of ions, their electronic polarizability (EP) and short-range interaction parameters is available, this method is very effective. Nevertheless, the known information on this subject is inconsistent. So the main aim of this work is to determine the possible combinations of electric parameters of ions in $BaTiO_3$ at room temperature.

It is known that the mixed ionic-covalent type of interionic bonds results in an anisotropy of the O^{2-} ion EP, and an appreciable EP anisotropy of O^{2-} ions has been found before for $KTaO_3$ [6], $LiNbO_3$ [7] and rutile (TiO_2) [8] crystals. The lattice constants of tetragonal $BaTiO_3$ phase (space group P4*mm*) are a = 3.9945 Å, c = 4.0335 Å [9]. Let us denote the two O^{2-} ions localized near the center of facets as O_I. The O^{2-} ion localized at the 4-th order symmetry axis (apical oxygen ion) be denoted as O_{II}. For the O_{II}, the shortest Ti–O distance is equal to 1.9172 Å, so this bond is an ionic-covalent one. So the EP of O_{II} ion must be described by the 2-nd rank tensor with the main principal axis "3" being coincident with the 4-th order symmetry axis.

Some sets of ion EPs in tetragonal $BaTiO_3$ established before are listed in Table 1. It is of a principal importance that, except for α_{Ba} value, there are significant differences in the EP values of ions in the data cited. Moreover, these data are in contradic-

Table 1. Sets of EP of ions (in 10^{-24} cm^3) in tetragonal phase of $BaTiO_3$

α_{Ba}	α_{Ti}	α_{OI}	$(\alpha_{OII})_{11}$	$(\alpha_{OII})_{33}$	Reference
1.940	0.186	2.390	2.390	2.390	[10]
1.946	0.1858	2.3928	2.3321	2.0466	[11]
1.850	0.2715	3.966	1.677	1.677	[12]

tion to the ionic-covalent binding of Ti^{4+} and O_{II} ion. So, an additional independent recalculation of EP values of ions in $BaTiO_3$ is necessary to use those, e.g., in calculations of local electric field. To that end, the EP calculation method making use of modified Lorenz-Lorentz equation [7] was employed. This equation can be written as

$$\frac{n_k^2 - 1}{n_k^2 + 2} = \frac{1}{3\varepsilon_o} \sum_{i=1}^{S} N_i (\alpha_{eff})_{ik}, \qquad (1)$$

where n_k is the crystal refractive index for the electric component of light wave coincident with the k direction ($\mathbf{k} = \mathbf{x}, \mathbf{y}, \mathbf{z}$); S, the number of structurally non-equivalent ions in the crystal; N_i, volume concentration of the i-th ion kind; $(\alpha_{eff})_{ik}$, the so-called effective EP of i-th type of ion [7] influenced by the nearest (10 nm) dipole surrounding of these ions.

To calculate correctly the EP using Eq. 1, it is necessary to use the values of the crystal refractive indices in far IR band. For this purpose, we approximate the experimental dependence of ordinary (n_o) and extraordinary (n_e) indices on wavelength [13] by Sellmeier equation:

$$n_{o,e}^2 = 1 + \frac{A_{o,e}}{1 + \lambda_{o,e}^2/\lambda^2}, \qquad (2)$$

where λ is the wavelength; $\lambda_{o,e}$ and $A_{o,e}$, the fitting parameters. The following values were obtained and used in the further calculations: $(n_o)_{IR} = 2.278$ and $(n_e)_{IR} = 2.244$. The EPs of ions in $BaTiO_3$ were analyzed using so-named bond polarizability approximation (BPA) [7]. The calculations were provided under variation of α_{Ba} and α_{Ti} within reasonable ranges of their values. Some results of calculations are presented in Fig. 1.

Because there is a great number of possible combinations of the ion EPs, the additional analysis of all these data is necessary. To verify those, two criteria were used: (1) calculation of spontaneous polarization P_s of the crystal and (2) equivalence of calculated and experimentally obtained values of electric field gradient (EFG) V_{zz} at ^{137}Ba nuclei. According to the ^{137}Ba NMR investigation, V_{zz} value at Ba ion must be

Table 2. Calculated parameters of local electric field at Ba^{2+} ion according some sets of q_{eff} and EPs of ions in $BaTiO_3$ at T = 293 K

parameter	[10]	[11]	[12]	[9]	a	b
q_{Ba}, |e|	–	1.480	2.000	2.000	1.700	1.800
q_{Ti}, |e|	–	2.720	2.890	2.35	2.600	2.200
q_{OI}, |e|	–	−1.400	−1.630	−1.45	−1.408	−1.303 q_{OII}, |e|
α_{Ba}, 10^{-24} cm^3	1.940	1.946	1.850	–	2.10	1.850
α_{Ti}, 10^{-24} cm^3	0.186	0.1858	0.2715	–	0.150	0.200
α_O, 10^{-24} cm^3	2.390	2.3928	3.966	–	2.300	2.400
α_{11}, 10^{-24} cm^3	2.390	2.3321	1.677	–	1.794	1.524
α_{33}, 10^{-24} cm^3	2.390	2.0466	1.677	–	2.270	2.478
E_z(Ba), 10^{10} V/m	– –	– −0.704*	−0.174 −0.611*	–	−0.594	−0.708
V_{zz}(Ba), 10^{20} V/m^2 (exp. value ±0.061)	–	−0.214	−0.209	–	−0.057	−0.050
P_s, C/m^2 (exp. value 0.255)	0.260	0.241 0.235*	0.261 0.255*	–	0.249	0.263

* recalculated data

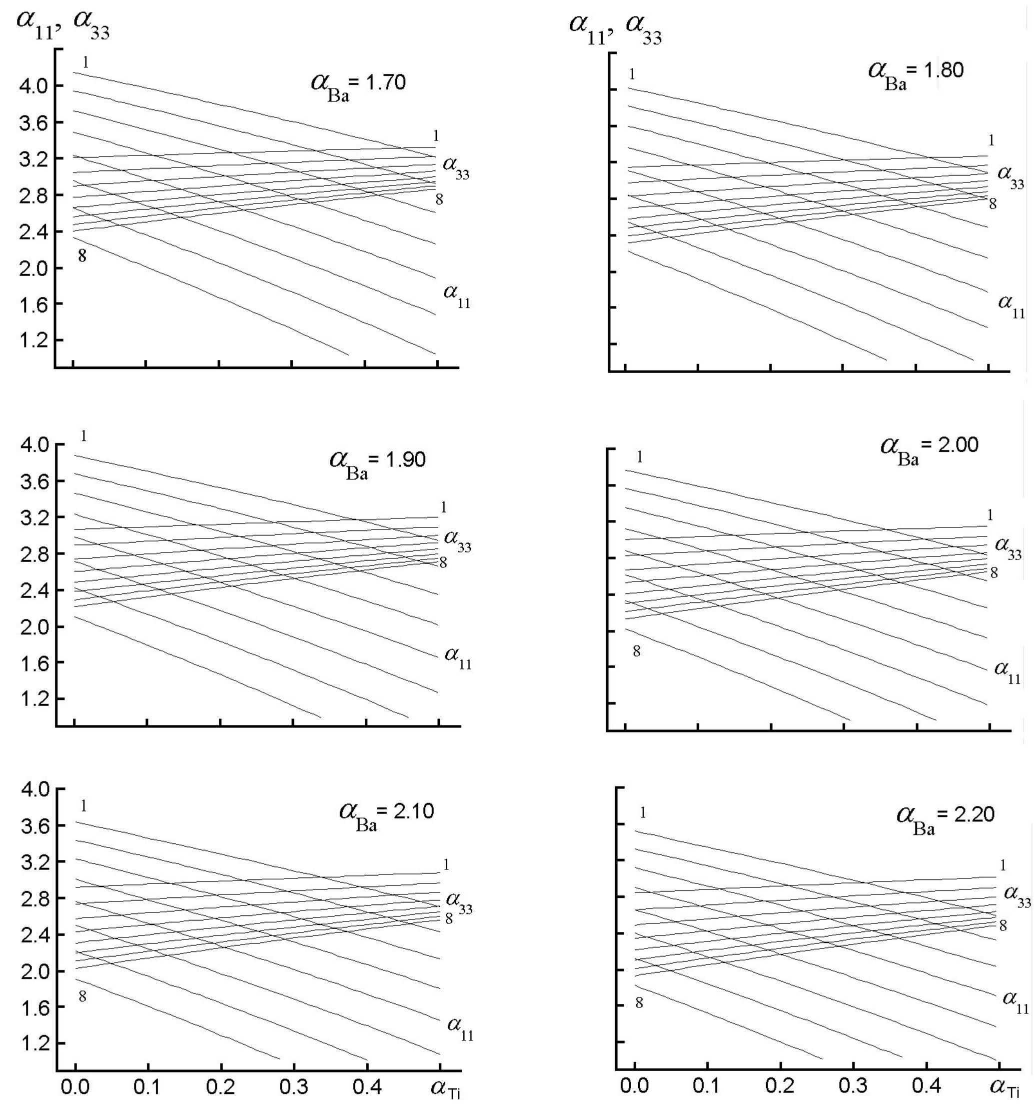

Fig. 1. Dependences of main components of a EP tensor for O_{II} ions α_{11}, α_{33} for some sets of α_{Ba} and α_{Ti} values. All data in 10^{-24} cm^3 units. EP of O_I ion varies from $1.6 \cdot 10^{-24}$ cm^3 (1) to $2.4 \cdot 10^{-24}$ cm^3 (8) with the increment $0.1 \cdot 10^{-24}$ cm^3.

± 0.061 V/m^2 [14]. For these calculations, the additional information on the effective charges of ions in $BaTiO_3$ is to be used. Some sets of the known effective charges (q_{eff}) of ions in tetragonal $BaTiO_3$ are presented in Table 2.

The local electric field at the ions in the $BaTiO_3$ structure were calculated for these purposes according to the modified classical point multipole method [15]. In such way, the known sets of electrical parameters of ions in $BaTiO_3$ were analysed as well as new data on EPs under variation of effective charges of ions (q_{Ba}, q_{Ti}, q_{OI}, q_{OII}) within reasonable limits. Original sets of electric parameters of ions (a) and (b) contain EPs of ions according to Fig. 1 and two possible different sets of q_{eff}. Results of the calculation of P_s, z component of $\mathbf{E}_{loc}$ at Ba^{2+} ion (E_z) and V_{zz} at ^{137}Ba nuclei are listed at Table 2, too. It is established that the criterion of the equivalence of calculated and experimental V_{zz} values is more strict one, in contrast to P_s analysis. Moreover, the identity of the experimental and calculated V_{zz}(Ba) values occur only if the relation $|q_{OII}| > |q_{OI}|$ is met. The dependences of V_{zz}(Ba) and P_s as functions of $\Delta q = |q_{OII} - q_{OI}|$ are presented in Fig. 2. Because V_{zz}(Ba) is small, it is possible that electric quadrupole moments of O^{2-} ions [16] must be additionally taken into consideration.

It is clear from comparison of (a) and (b) sets of electric parameters of ions in $BaTiO_3$

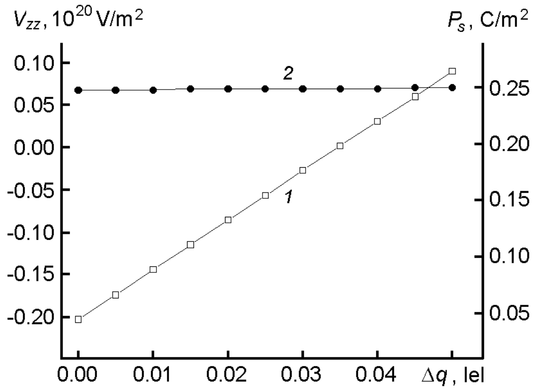

Fig. 2. Calculated V_{zz} value at ^{137}Ba nuclei (*1*) and P_s (*2*) as a function of $\Delta q = q_{OI} - q_{OII}$.

at $T = 293$ K that the additional verification of these data is necessary. A probable way to solve this problem is to analyze the balance between the long range Coulomb forces and interionic repulsive forces acting at Ba^{2+} and Ti^{4+} ions. After additional testing, these sets (or other ones estimated by us to be suitable sets of electrical parameters of ions) can be used for the computer simulations of $BaTiO_3$ physical properties. In any case, the both sets (a) and (b) are in a good agreement with the peculiarities of $BaTiO_3$ structure.

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Моделювання локального електричного поля у тетрагональній фазі кристала $BaTiO_3$

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Встановлено область ймовірних комбінацій значень електронної дипольної поляризовністі та ефективних зарядів іонів у кристалі $BaTiO_3$ за $T = 293$ К. Показано, що дипольна електронна поляризовність апікальних іонів O^{2-} суттєво анізотропна. Отримані дані можна використовувати для моделювання особливостей структури $BaTiO_3$.