

MAGNETISM
AND FERROELECTRICITY

Effect of Cation Substitution on the Lattice Dynamics and Ferroelectric Instability of Cubic BaTiO₃ and BaZrO₃ Doped with Bi and La Ions¹

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Abstract—The spectra of lattice vibration frequencies of solid solutions Ba_{1-x}Bi_{2x/3}□_{x/3}Ti(Zr)O₃ and Ba_{1-x}La_xTi(Zr)_{1-x/4}□_{x/4}O₃ are calculated in terms of a generalized Gordon–Kim model with inclusion of the dipole and quadrupole polarizabilities. Over the entire concentration range, the calculated phonon spectra contain a ferroelectric soft mode. The effect of various interactions on the ferroelectric instability of these solid solutions is studied. It is shown that the character of ferroelectric instability is largely determined by the mechanism of charge compensation.

PACS numbers: 63.20.-e, 63.20.D-

DOI: 10.1134/S1063783409050151

1. INTRODUCTION

Ferroelectrics with the perovskite structure ABO₃ and solid solutions based on them are promising multifunctional materials used widely in various devices. Moreover, owing to their simple structure, they are good model systems, on which the causes and origin of ferroelectricity have been studied for a long time.

A typical representative of this family is the classical ferroelectric BaTiO₃. Pure BaTiO₃ undergoes a sequence of three ferroelectric phase transitions [1]. Addition of Bi³⁺, La³⁺, and Zr⁴⁺ impurities to BaTiO₃ brings out an unusual change in the phase diagram and physical properties. Beginning from fairly low concentrations of both Bi and La impurities ($x \approx 5\text{--}10\%$), BaTiO₃-based solid solutions exhibit a relaxor behavior. However, the influence of an impurity on the phase-transition temperatures depends substantially on the type of the impurity (Ba³⁺ or La³⁺) [2–5]. The effect of an impurity on the physical properties of a solid solution depends on many factors and, in particular, on the position of impurity atoms and the mechanism of charge compensation. When BaTiO₃ is doped with trivalent Bi³⁺ and La³⁺ ions, these ions preferably occupy the Ba²⁺ sites [4, 5]; in this case, the mechanism of charge compensation is still not completely understood. As shown in [2, 4–6], when BaTiO₃ is doped with trivalent bismuth or lanthanum, the ion mechanism of charge compensation is most likely to operate

with vacancy formation on the Ba²⁺ sites (for Bi³⁺ dopant) or Ti⁴⁺ sites (for La³⁺ dopant).

In this work, simulation of the lattice dynamics of the Ba(Bi, La)TiO₃ and Ba(Bi, La)ZrO₃ compounds is carried out. To conserve the electrical neutrality of the crystal unit cell, we introduced vacancies on the Ba²⁺ sites when Bi³⁺ was added (Ba_{1-x}Bi_{2x/3}□_{x/3}Ti(Zr)O₃) and on sites occupied with Ti⁴⁺ when La³⁺ was doped (Ba_{1-x}La_xTi(Zr)_{1-x/4}□_{x/4}O₃). The calculation was performed in the virtual-crystal approximation [7] in terms of a generalized Gordon–Kim model with inclusion of multipole polarizabilities of ions [8].

In Section 2, we present the results of simulating the lattice dynamics of solid solutions Ba_{1-x}Bi_{2x/3}□_{x/3}TiO₃ (BBT), Ba_{1-x}La_xTi_{1-x/4}□_{x/4}O₃ (BLT), Ba_{1-x}Bi_{2x/3}□_{x/3}ZrO₃ (BBZ), and Ba_{1-x}La_xZr_{1-x/4}□_{x/4}O₃ (BLZ), where □ is a vacancy. In Section 3, the causes of the ferroelectric instability in these compounds are discussed. In Section 4, we briefly state the main results.

2. LATTICE DYNAMICS

The lattice dynamics of solid solutions BBT, BLT, BBZ, and BLZ were simulated, at all concentrations x , for the cubic perovskite structure using the experimental unit-cell parameter value 4.00 Å for the BaTiO₃-based solid solutions and 4.18 Å for the BaZrO₃-based solid solutions. (The calculated unit cell parameters are 3.85 and 4.01 Å, respectively.) The experimental data show that the doping of a BaTiO₃ crystal with Bi³⁺ and La³⁺ ions changes the unit cell parameter only slightly

¹ Report submitted to the XVIII All-Russia Conference on Physics of Ferroelectrics, St. Petersburg, June, 2008.

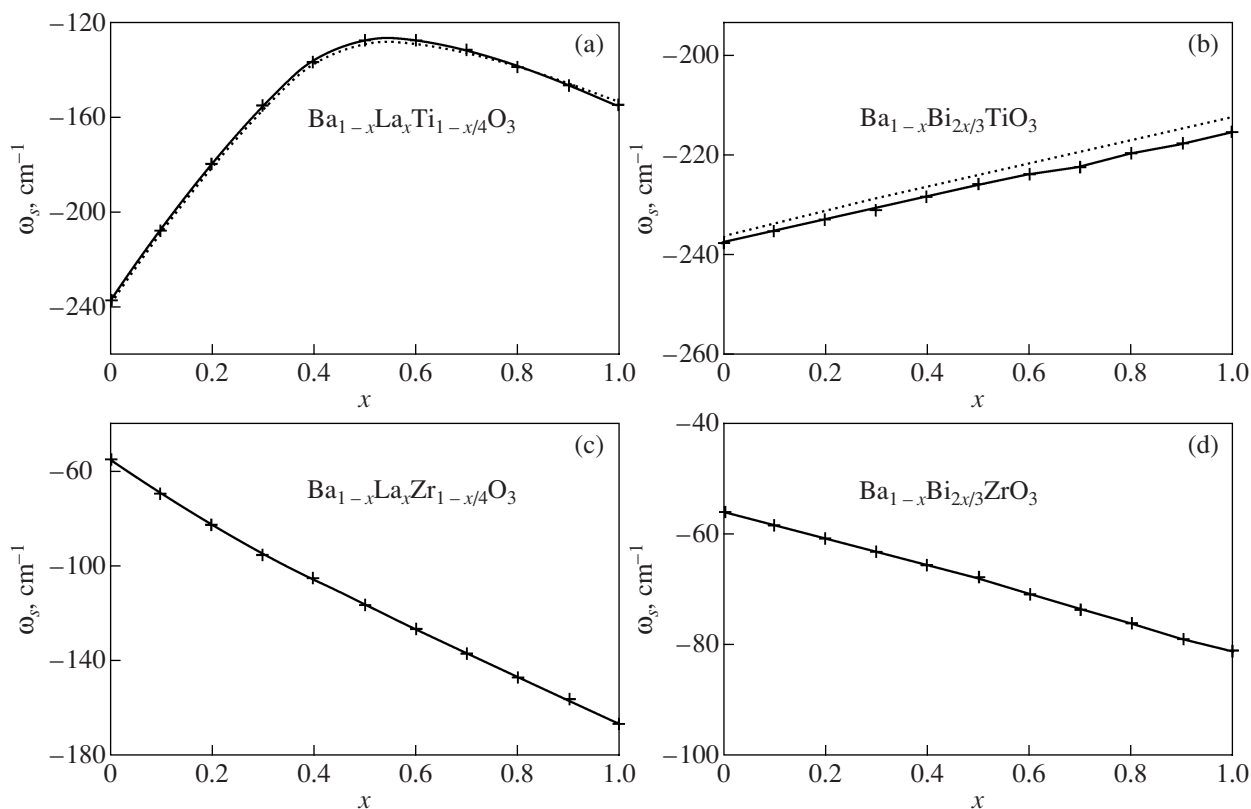


Fig. 1. Dependence of the frequency of the unstable ferroelectric mode on (a, c) the La^{3+} and (b, d) Bi^{3+} concentrations. The dotted lines show the dependences of the frequency for (a) $\text{Ba}_{1-x}\text{Bi}_x\text{Ti}_{1-x/4}\square_{x/4}\text{O}_3$ and (b) $\text{Ba}_{1-x}\text{La}_{2x/3}\square_{x/3}\text{TiO}_3$. The negative values correspond to imaginary frequencies.

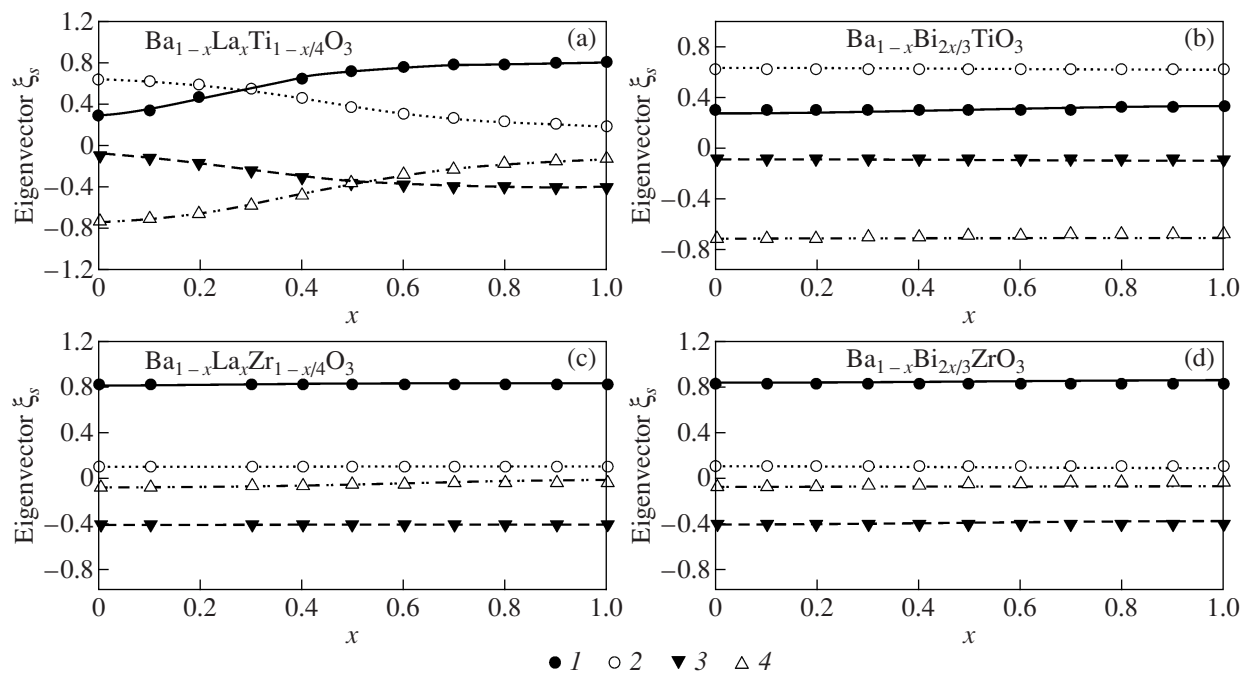


Fig. 2. Dependences of the ion displacements involved in the eigenvector (normalized to unity) of the unstable ferroelectric mode ξ_s on the La^{3+} (Bi^{3+}) concentration: (1) displacements of the virtual ion $\langle \text{BaLa} \rangle$ ($\langle \text{BaBi} \rangle$), (2) displacements of Ti^{4+} (Zr^{4+}), (3) displacements of O_\perp , and (4) displacements of O_\parallel .

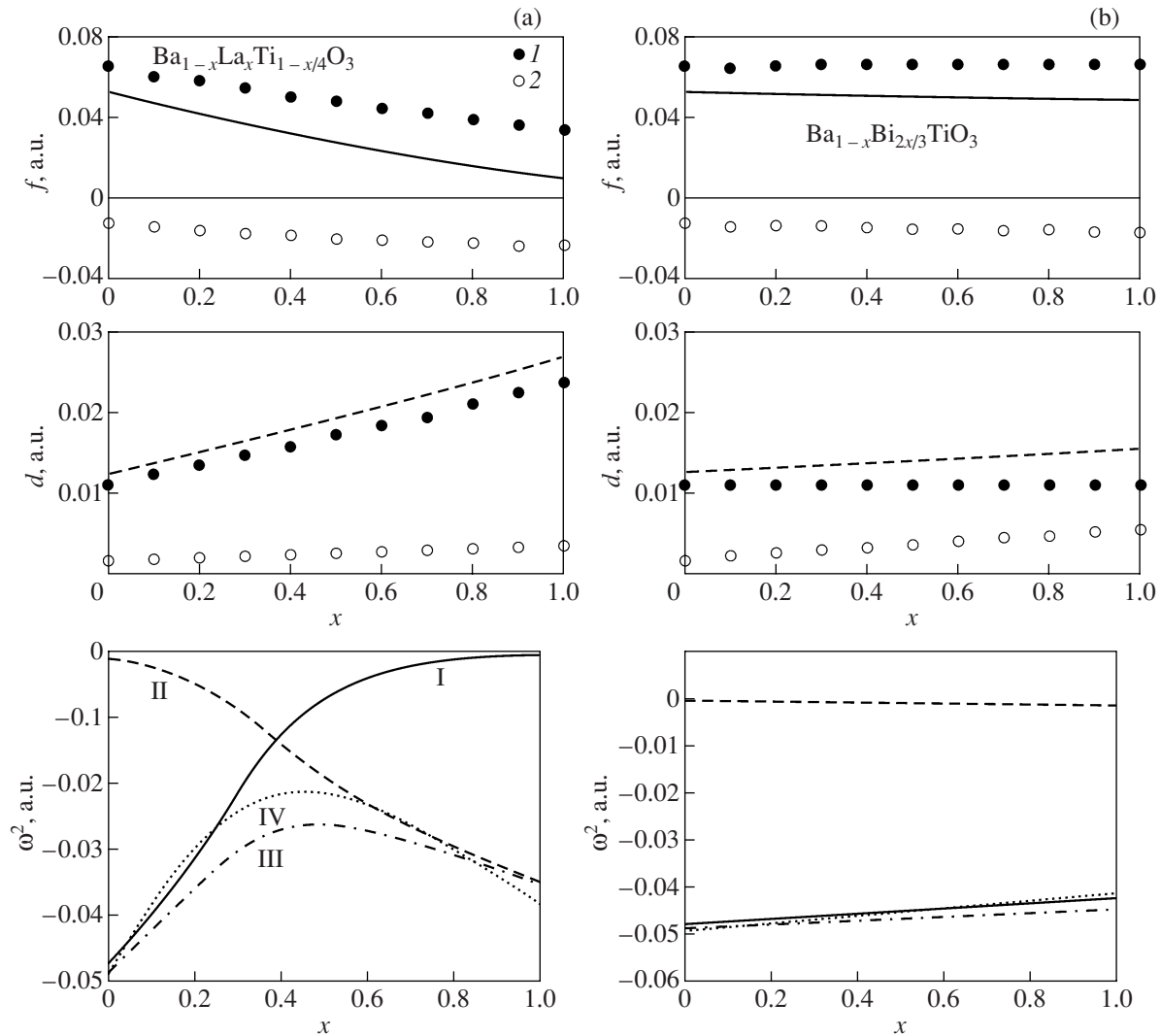


Fig. 3. Concentration dependences of the force constants f (solid line) and d (dashed line) and the separate contributions to them ((1) long-range contribution, (2) short-range contribution) and of the frequency squared of the unstable ferroelectric mode ((I) ω_{fs}^2 , (II) ω_{ds}^2 , (III) summed contribution $\omega_{fs}^2 + \omega_{ds}^2$, (IV) total frequency squared ω_s^2).

[5]. At the same time, using a constant parameter, one can determine the character of the dependences of the physical properties on the dopant concentration.

For all the compounds and over the entire concentration range, the calculated phonon spectra show the existence of an unstable ferroelectric vibrational mode at the center of the Brillouin zone. The concentration dependence of the frequency of this mode is shown in Fig. 1. Figure 2 shows the concentration dependence of the eigenvectors of this mode. As is seen from these figures, the ferroelectric instability in the BaTiO_3 -based solid solutions at impurity concentrations up to $x \approx 0.4$ is mainly due to the displacements of the Ti^{4+} ions and oxygen O_{\parallel} along the Ti–O bond. In the BLT solid solution (Fig. 2a), a further increase in the La^{3+} concentra-

tion brings out a substantial rearrangement of the eigenvector of the unstable ferroelectric mode. At La^{3+} concentrations higher than 60 at %, the displacements of a virtual ion $\langle \text{Ba}_{1-x}\text{La}_x \rangle$ and oxygen O_{\perp} perpendicular to the Ti–O bond become predominant. In the BBT solid solution (Fig. 2b), the eigenvector depends on the Bi^{3+} concentration only slightly and, for all concentrations, the displacements of Ti^{4+} and O_{\parallel} are decisive. It should be noted that such a concentration dependence of the eigenvector is determined by the mechanism of charge balancing rather than by the impurity type. The strong reconstruction of the eigenvector occurs when vacancies are formed on the sites occupied by titanium regardless of the type of impurity (lanthanum or bismuth), while the vacancy formation on the barium sites

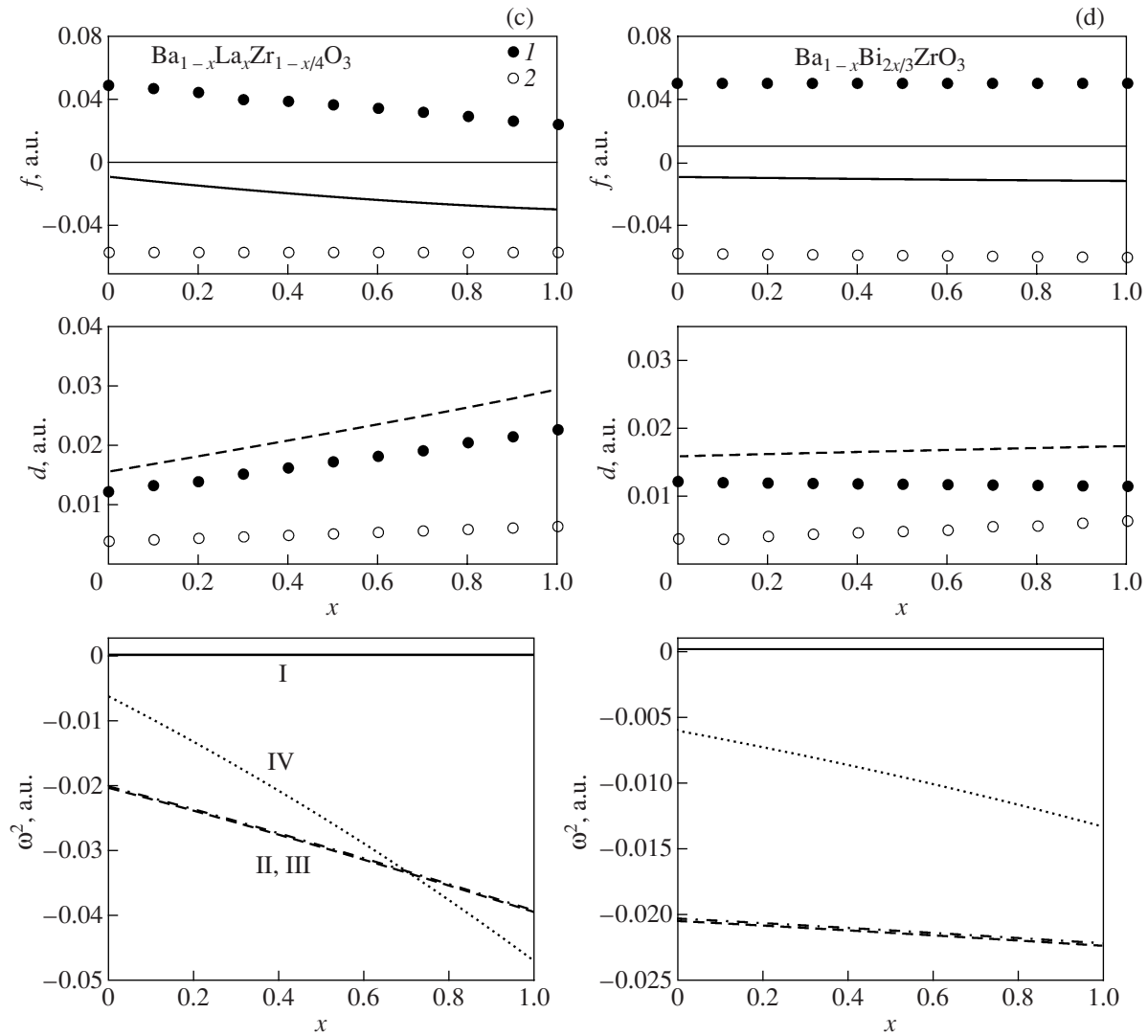


Fig. 3. (Contd.)

does not have a noticeable effect on the eigenvector of the unstable ferroelectric mode.

Another character of ferroelectric instability is observed in the BaZrO₃-based solid solutions. The dom-

inant components of the eigenvectors of the unstable ferroelectric phase in these compounds (Figs. 2c, 2d) are the displacements of virtual ions $\langle \text{Ba}_{1-x}\text{La}_x \rangle$ (or $\langle \text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3} \rangle$) and oxygen O_\perp irrespective of both

Dynamic Born charges (in units of e) and the high-frequency permittivity ϵ_∞ at the limiting concentrations x

x	Z_A	Z_B	Z_{O_\parallel}	Z_{O_\perp}	ϵ_∞	Z_A	Z_B	Z_{O_\parallel}	Z_{O_\perp}	ϵ_∞
$\text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3}\text{TiO}_3$						$\text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3}\text{ZrO}_3$				
0	2.74	5.37	-4.89	-1.61	3.80	2.66	5.01	-3.99	-1.85	3.32
0.5	2.60	5.34	-4.82	-1.56	3.61	2.58	4.98	-3.95	-1.80	3.19
1.0	2.49	5.31	-4.75	-1.53	3.44	2.50	4.95	-3.91	-1.77	3.09
$\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\square_{x/4}\text{O}_3$						$\text{Ba}_{1-x}\text{La}_x\text{Zr}_{1-x/4}\square_{x/4}\text{O}_3$				
0	2.74	5.37	-4.89	-1.61	3.80	2.66	5.01	-3.99	-1.85	3.32
0.5	3.39	4.52	-4.08	-1.92	3.57	3.30	4.17	-3.34	-2.06	3.12
1.0	4.00	3.74	-3.34	-2.20	3.37	3.89	3.41	-2.77	-2.26	2.94

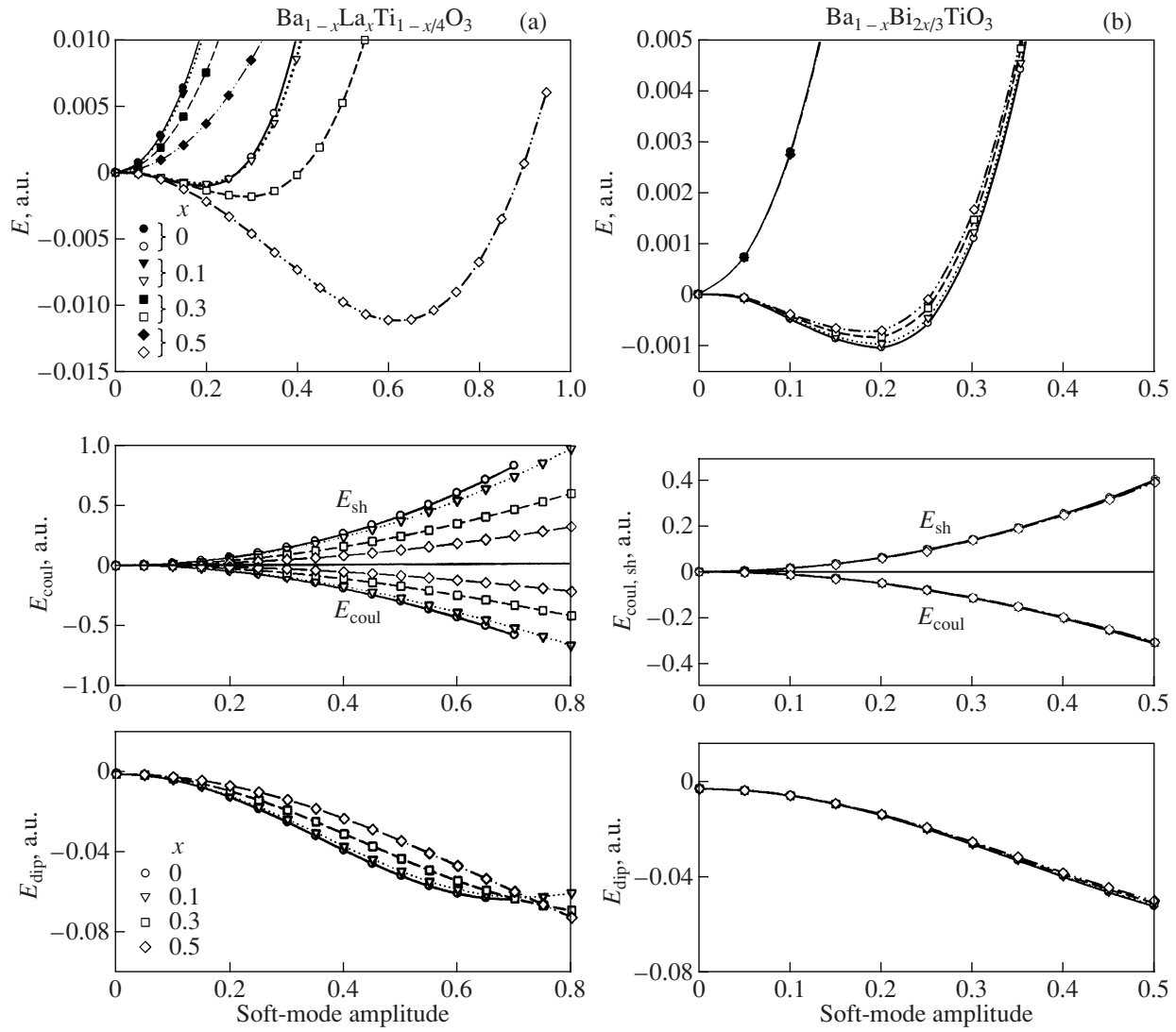


Fig. 4. Dependences of the total energy and the Coulomb, short-range, and dipole contributions to the total energy on the ion displacement amplitude. Dark symbols correspond to the model of nonpolarizable ion.

the impurity concentration and the site occupied by a vacancy.

As noted in [9, 10], the frequency of the unstable ferroelectric mode is determined by a fairly fine balance of practically all interactions in the crystal. In ferroelectrics in which this instability is mainly due to the displacements of the B ion (Ti^{4+} or Zr^{4+} in the compounds under consideration) in the center of the oxygen octahedron and oxygen O_{\parallel} along the Ti-O bond, the competition between the long-range dipole-dipole and short-range interactions between these ions plays the most substantial role [9, 10]. In the ferroelectrics in which the ferroelectric instability is due to the displacements of another ion pair, namely, ion A ($\langle \text{Ba}_{1-x}\text{La}_x \rangle$ or $\langle \text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3} \rangle$) and oxygen O_{\perp} , perpendicular to the

Ti-O bond, the weaker $A\text{-O}_{\perp}$ interactions became noticeable.

The force constants corresponding to these two interactions

$$f = D_{B\text{-O}_{\parallel}}^{xx}, \quad d = D_{A\text{-O}_{\perp}}^{xx}, \quad (1)$$

where $D_{ij}^{\alpha\beta}(q=0)$ is the force matrix calculated with the turned-off macroscopic field at $q=0$, can be represented as the sum of the long-range dipole-dipole part [10]

$$f_{\text{dd}} = -\frac{4\pi e^2 Z_B Z_{\text{O}_{\parallel}}}{\Omega \epsilon_{\infty} + 2}, \quad d_{\text{dd}} = -\frac{4\pi e^2 Z_A Z_{\text{O}_{\perp}}}{\Omega \epsilon_{\infty} + 2}, \quad (2)$$

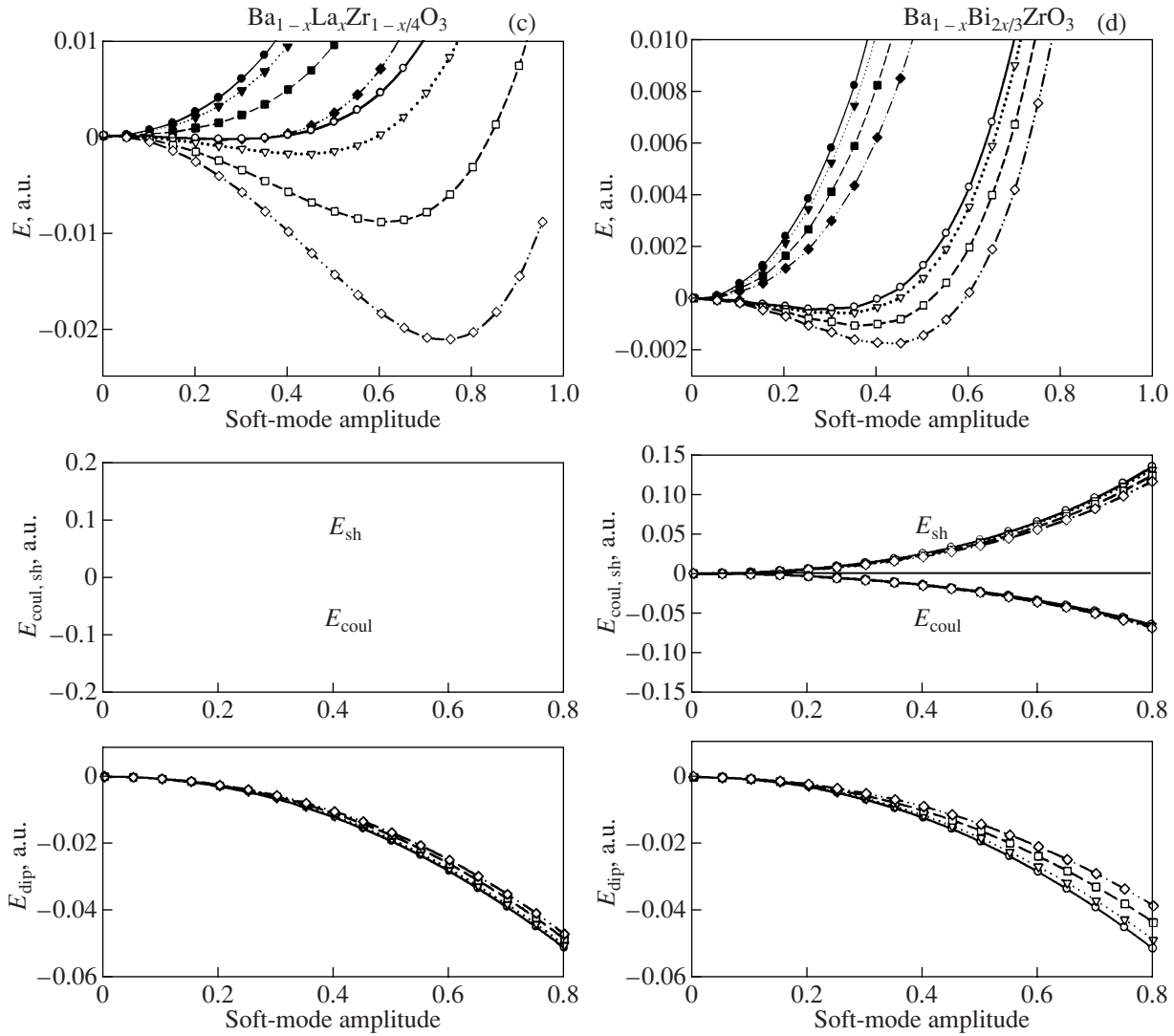


Fig. 4. (Contd.)

and the short-range part

$$f_{\text{sh}} = f - f_{\text{dd}}, \quad d_{\text{sh}} = d - d_{\text{dd}}. \quad (3)$$

Here, Z_A , Z_B , $Z_{O_{\parallel}}$, and $Z_{O_{\perp}}$ are the Born dynamic charges of the corresponding ions, ϵ_{∞} is the high-frequency permittivity, and Ω is the unit cell volume.

According to our calculations, the Born dynamic charges and the permittivity ϵ_{∞} are approximately linear functions of the impurity concentration. The table lists these quantities for the limiting ($x = 0$ and $x = 1$) and middle ($x = 0.5$) concentrations. Figure 3 shows the concentration dependences of the force constants f and d and also of the long-range and short-range contributions to them for the solid solutions under consideration.

The force constants of solid solutions BLT and BLZ are most strongly dependent on the concentra-

tion (Figs. 3a, 3c). In these compounds, the substitution of trivalent lanthanum for divalent barium increases the nominal charge of the virtual ion occupying the Ba^{2+} site.

At the same time, the vacancy formation on the titanium (zirconium) site decreases its nominal charge. Such a change in the nominal charges brings about variations in the dynamic charges [9] (see table), which, in turn, decreases the long-range contribution f_{dd} to the force constant f and increases the corresponding contribution d_{dd} to the force constant d . The short-range contributions f_{sh} and d_{sh} vary only slightly.

This redistribution of the long-range contributions also substantially influences the value of the unstable ferroelectric mode frequency squared $\omega_s^2 = \xi_s^{\dagger} \hat{\mathbf{D}} \xi_s$, where ξ_s is the mode eigenvector (ξ_s^{\dagger} is the Hermitian

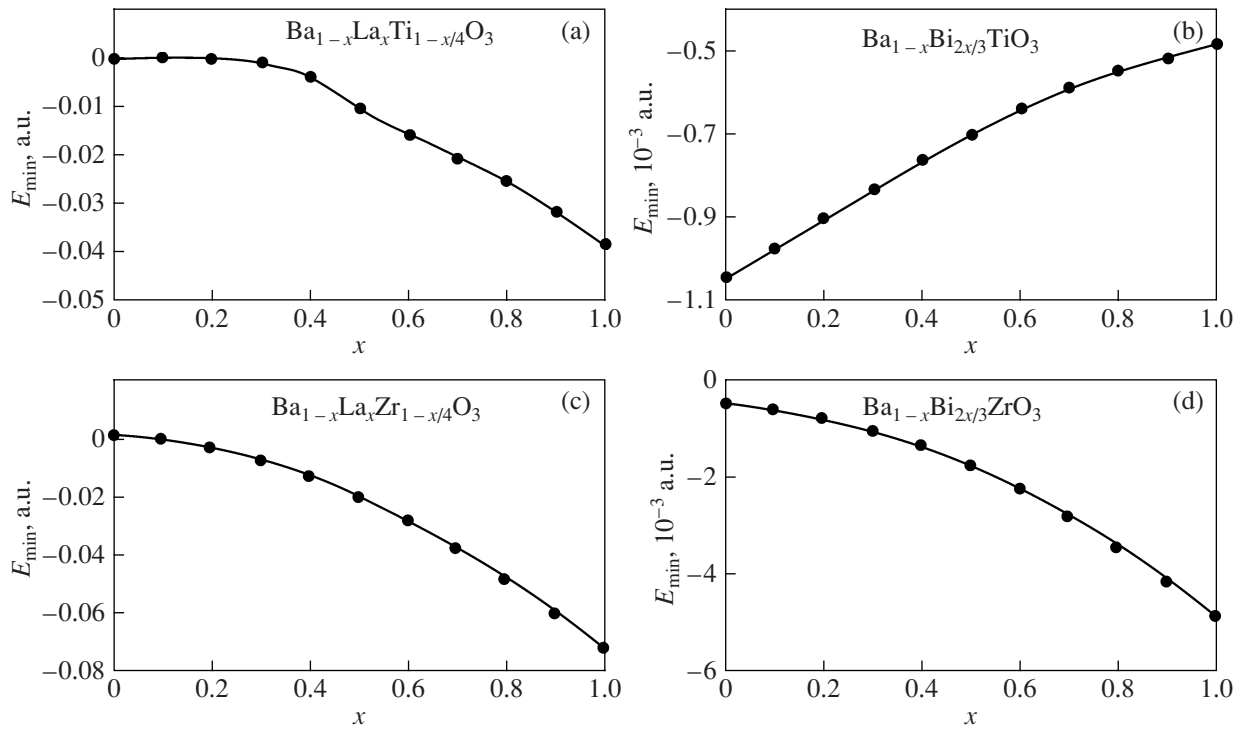


Fig. 5. Concentration dependence of the depth of the energy minimum.

conjugate vector) (Fig. 2) and $\hat{\mathbf{D}}$ is the force matrix. Figure 3 shows the concentration dependences of the contributions to the soft-mode frequency squared from the displacements of the Ti^{4+} and O_{\parallel} ions ($\omega_{fs}^2 = 2\xi_{\text{Ti}}f\xi_{\text{O}_{\parallel}}$) and virtual ion $\langle A \rangle$ ($\langle \text{Ba}_{1-x}\text{La}_x \rangle$ or $\langle \text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3} \rangle$) and oxygen O_{\perp} ($\omega_{ds}^2 = 4\xi_{\langle A \rangle}d\xi_{\text{O}_{\perp}}$), their summed contribution $\omega_{fs}^2 + \omega_{ds}^2$, and the total frequency squared ω_s^2 . As seen from the figures, at low concentrations (up to $x \sim 0.4$), the frequency of the unstable ferroelectric mode in solid solution BLT is almost completely determined by the long-range dipole–dipole Ti–O interaction; a decrease in the dipole–dipole interaction f_{dd} stabilizes the ferroelectric mode. At high concentrations ($x > 0.6$), the mode is destabilized because of the increase in the dipole–dipole $\langle \text{Ba}_{1-x}\text{La}_x \rangle$ –O interaction d_{dd} and the simultaneous increase in the corresponding components of the soft-mode eigenvector (Fig. 2a).

In solid solution BLZ, the destabilization of the ferroelectric mode is mainly due to an increase in the dipole–dipole $\langle \text{Ba}_{1-x}\text{La}_x \rangle$ –O interaction d_{dd} (Fig. 3c), whereas the Zr–O interaction plays a stabilizing role. The contribution from this interaction to the frequency of the unstable mode is practically zero because the eigenvector components ξ_{Zr} and $\xi_{\text{O}_{\parallel}}$ are small (Fig. 2c). As seen from Fig. 3c, the $\langle \text{Ba}_{1-x}\text{La}_x \rangle$ –O interaction

determines the frequency of the ferroelectric mode in BLZ only partly, since other interactions make equal contributions.

In solid solutions BBT and BBZ, in which vacancies form on the barium ion sites, the force constants f and d depend on the impurity concentration more slightly (Figs. 3b, 3d). In the eigenvector of solid solution BBT, the displacements of Ti^{4+} and O_{\parallel} ions are dominant (Fig. 2b), and the frequency of the unstable ferroelectric mode is mainly determined by the interaction of this ion pair and is almost independent of the concentration with a slight variation of f (Fig. 3b). In solid solution BBZ, the virtual ion $\langle \text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3} \rangle$ and O_{\perp} undergo the largest displacements; however, as in the case of BLZ, the force constant d determines the frequency of the unstable mode only partly.

The concentration dependences of the force constants and the frequency of the unstable mode in the solid solutions under study are determined only by the mechanism of charge balancing and are independent of the impurity type. As shown in Figs. 1a and 1b, the concentration dependence of the frequency of the unstable ferroelectric mode is determined by the vacancy position only. However, as mentioned above, the vacancy position in real solid solutions is determined by the impurity type.

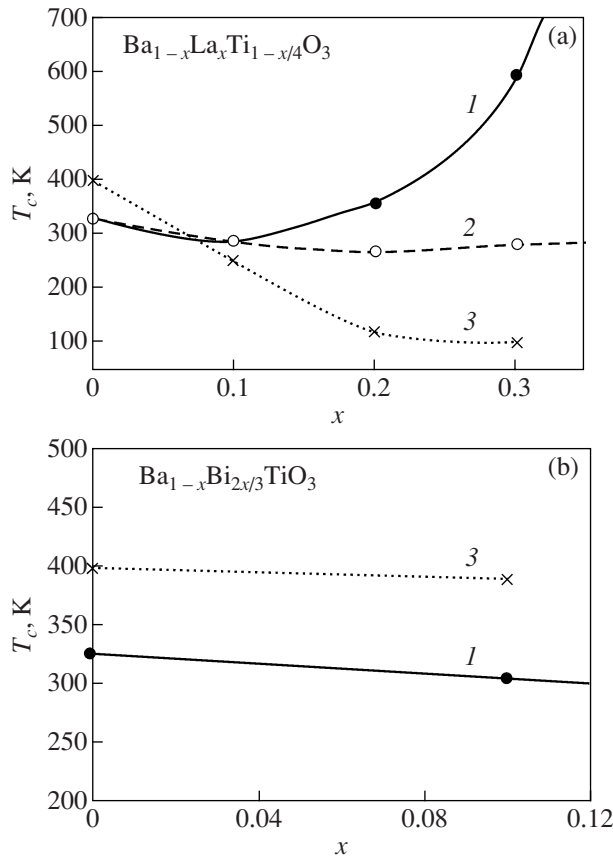


Fig. 6. (1, 2) Calculated (see text) and (3) experimental [3, 4] concentration dependences of the ferroelectric transition temperature.

3. FERROELECTRIC INSTABILITY

As the calculated eigenvectors show (Fig. 2), at all impurity concentrations, the ferroelectric instability of BaZrO_3 -based solid solutions BLZ and BBZ is due to the virtual ions occupying the Ba^{2+} sites and oxygen O_\perp that are displaced perpendicular to the Ti–O bond. In solid solution BBT, the ferroelectric instability exhibits a different character related to the displacement of the Ti^{4+} ions and oxygen O_\parallel along the Ti–O bond; this character of instability remains at all concentrations. Finally, the character of the ferroelectric instability in solid solution BLT is dependent on the impurity concentration; at low concentrations ($x < 0.4$), the displacements of Ti^{4+} ions and oxygen O_\parallel dominate in the mode eigenvector, while, as the concentration increases, the eigenvector is transformed and the displacements of ions in the Ba^{2+} sites and oxygen O_\perp sites become dominant. When distortions of the crystal correspond to the eigenvector of the soft ferroelectric mode, the structure with the displacements of the ions along a body diagonal of the cubic unit cell corresponding to the rhombohedral symmetry C_{3v}^1 is most energetically preferable

in all the solid solutions studied at all impurity concentrations.

Figure 4 shows the dependence of the total energy of the solid solutions on the amplitude of ion displacements according to the eigenvector of the unstable ferroelectric mode in the [111] direction. The energy is measured from that of the undistorted cubic crystal ($E_x - E_{x0}$). Figure 4 also shows the dependences of the Coulomb, short-range, and dipole–dipole contributions to the total energy of the crystal on the displacement amplitude. In solid solutions BLT and BLZ, wherein vacancies are formed on the Ti^{4+} or Zr^{4+} sites, the depth of the energy minimum decreases slightly with increasing impurity concentration to $x \sim 0.1$; then, as the concentration increases further, it increases sharply and shifts to larger amplitudes (Figs. 4a, 4c). The reasons for such an increase of the depth of the energy minimum in the solid solutions with Ti^{4+} and Zr^{4+} are different. In solid solution BLT, as the amplitude increases, the positive short-range contribution to the energy increases at high concentrations more slowly than at low concentrations. At the same time, the increase in the Coulomb contribution with the amplitude is approximately the same at all concentrations. Because of this, as the concentration increases, the dependence of the energy on the mode amplitude becomes smoother even in the nonpolarizable-ion model (filled symbols in Fig. 4), and the addition of the dipole energy, which increases with amplitude, shifts the energy minimum to larger amplitudes.

In solid solution BLZ (Fig. 4c), the change in the short-range energy with amplitude is similar at all concentrations, whereas the Coulomb contribution increases with amplitude more rapidly at high concentrations; so, even in the nonpolarizable-ion model, a ferroelectric distortion becomes energetically favorable at concentrations $x < 0.4$. As the dipole energy increases further, the energy minima in solid solution BLZ become deeper than those in BLT (at the same concentration). The concentration dependences of the depth of the energy minimum for solid solutions BLT and BLZ are shown in Figs. 5a and 5c.

The concentration dependences of the total energy for solid solutions BBT and BBZ are shown in Figs. 4b and 4d. Here, as in BLT and BLZ, the amplitude dependences of different contributions to the total energy are changed when Zr^{4+} is substituted for Ti^{4+} . In BBT (Fig. 4b), the amplitude dependences of the short-range and Coulomb contributions remain unchanged as the concentration is varied. The energetic preference of ferroelectric distortions is due to the dipole energy. The increase of the dipole energy with amplitude decreases somewhat as the concentration increases, which leads, in BBT, to an insignificant decrease in the depth of the energy minimum. When Zr^{4+} is substituted for Ti^{4+} (solid solution BBZ), the variation in the Coulomb contribution with displacement amplitude is also only slightly dependent on concentration, and the short-

range contribution increases more slowly with amplitude as the concentration increases. The contribution from the dipole energy decreases as the concentration increases. As a result of these two effects, the energy minimum becomes deeper with increasing concentration and shifts slightly in amplitude. The concentration dependences of the energy minimum depth for solid solutions BBT and BBZ are shown in Figs. 5b and 5d.

Thus, the dependence of the energy on the ion displacement amplitude is largely determined by the mechanism of charge balancing and the type of an ion occupying the position in the center of the oxygen octahedron. According to our calculations, when bismuth is substituted for lanthanum in solid solution BLT (or lanthanum is substituted for bismuth in BBT), the dependences of the energy on both the concentration and displacement amplitude are not substantially changed.

The ferroelectric phase transition temperature T_c can be estimated from the energy minimum depth assuming that T_c is approximately equal to the depth of the energy minimum. Figure 6 shows the concentration dependences of the estimated temperature of the ferroelectric phase transition $O_h^1 \rightarrow C_{3v}^1$ in solid solutions BLT and BBT together with the experimental data from [3, 4].

As seen from Fig. 6b, for solid solution BBT, the calculated dependence of T_c on the Bi^{3+} concentration qualitatively agrees with the experimental data from [4]. On the other hand, in solid solution BLT, when vacancies are formed only on the Ti^{4+} sites, the phase transition temperature T_c decreases slightly with increasing concentration to $x \sim 0.1$ (curve 1 in Fig. 6a) and then, as the concentration increases further, T_c sharply increases, unlike the experimental situation [3]. However, if we assume that, as the lanthanum concentration increases, vacancies are formed on both the Ti^{4+} and Ba^{2+} sites, then the estimated and experimental concentration dependences of the phase transition temperature qualitatively agree. For example, curve 2 in Fig. 6a corresponds to the concentration dependence of the transition temperature estimated assuming that, at La^{3+} concentrations exceeding 0.1, vacancies are formed to equal degree on both the Ti^{4+} and Ba^{2+} sites. The question as to where vacancies are formed at La^{3+} concentrations exceeding 0.1 is discussed in the literature [3, 5], and there are experimental data [6] showing that vacancies can be formed on the barium sites as the La^{3+} concentration increases.

4. CONCLUSIONS

The lattice vibration frequency spectra of solid solutions $\text{Ba}_{1-x}\text{Bi}_{2x/3}\square_{x/3}\text{Ti}(\text{Zr})\text{O}_3$ and $\text{Ba}_{1-x}\text{La}_x\text{Ti}(\text{Zr})_{1-x/4}\square_{x/4}\text{O}_3$ have been calculated in terms of a generalized Gordon–Kim model with inclusion of the dipole and quadrupole polarizabilities of ions. Over the entire concentration range, the calculated

phonon spectra contain unstable ferroelectric vibrational modes at the center of the Brillouin zone. Distortions corresponding to the eigenvectors of these modes lead to the energetically favorable ferroelectric rhombohedral phase. The character of the ferroelectric instability is mostly determined by the position of the vacancy formation and the type of an ion in the center of the oxygen octahedron rather than by the type of impurity. In solid solutions with the heavy zirconium ion, the ferroelectricity is mainly due to the ions occupying the barium sites and oxygen that are displaced perpendicular to the Ti–O bond. In solid solutions with the lighter titanium, the ferroelectricity is due to the displacements of another ion pair, namely, titanium and oxygen, along the Ti–O bond. The most unusual behavior of the ferroelectric instability is observed when BaTiO_3 is doped with lanthanum and vacancies are formed on the Ti^{4+} sites ($\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\square_{x/4}\text{O}_3$). In this case, the character of the ferroelectric instability is dependent on the impurity concentration. As the concentration increases, the soft-mode eigenvector is substantially transformed: the motion of the ion pair Ti^{4+} and O_\parallel is changed to the motion of another pair, namely, an ion on the Ba site and O_\perp .

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 07-02-00069.

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Translated by Yu. Ryzhkov