Combined first-principles and EXAFS study of structural instability in BaZrO₃

A. I. Lebedev* and I. A. Sluchinskaya
 Physics Department, Moscow State University
 Leninskie Gory, Moscow 119991, Russia
 *swan@scon155.phys.msu.ru

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Phonon spectrum of cubic barium zirconate is calculated from first principles using the density functional theory. Unstable phonon mode with the R_{25} symmetry in the phonon spectrum indicates an instability of the cubic structure with respect to rotations of the oxygen octahedra. It is shown that the ground-state structure of the crystal is $I4/mcm$. In order to find the manifestations of the predicted instability, EXAFS measurements at the Ba L_{III} -edge are used to study the local structure of BaZrO₃ at 300 K. An enhanced value of the Debye–Waller factor for the Ba–O atomic pair ($\sigma_1^2 \sim 0.015 \text{ \AA}^2$) revealed in the experiment is associated with the predicted structural instability. The average amplitude of the thermal rotations estimated from the measured σ_1^2 value is $\sim 4^\circ$ at 300 K. The closeness of the calculated energies of different distorted phases resulting from the condensation of the R_{25} mode suggests a possible formation of a quenched rotational disorder in BaZrO₃ at low temperature, which can explain the discrepancy between the calculations and experiment.

Keywords: First-principles calculations; EXAFS studies; phase transitions; quenched rotational disorder.

1. Introduction

Crystals with a general formula ABO_3 and the perovskite structure form a large family whose characteristic feature is a tendency to various (ferroelectric, ferroelastic, magnetic, superconducting) phase transitions. Barium zirconate (BaZrO₃), one of the members of this family, is a crystal with a high melting point ($\sim 2600^\circ\text{C}$), moderate dielectric constant (~ 40), low dielectric losses, and low thermal expansion coefficient. It is widely used as a material for microwave ceramic capacitors and for inert crucibles used for growth of single crystals of high-temperature superconductors. In recent years, the interest on BaZrO₃ has revived again because it was found that BaZrO₃ doped with acceptor impurities, in particular yttrium, is a high-temperature ionic conductor with high proton conductivity, which can be used in solid-oxide fuel cells.^{1–4} Its solid solutions with BaTiO₃ are relaxors with a very high electric-field tuning of the dielectric constant^{5–7}; this property can be used in tunable filters, oscillators, phase shifters, etc. It should be noted that up to now, the properties of BaZrO₃ have been studied mainly at room and higher temperatures. Only a few experiments^{8–12} (in addition to the first-principles calculations^{10,13–17}) were undertaken to study the properties of BaZrO₃ (the ground-state structure, the behavior of the dielectric constant, etc.) at low temperatures at which most perovskite oxides exhibit interesting properties.

Recent X-ray and neutron diffraction studies¹⁰ did not find any phase transitions in BaZrO₃ at $T < 300 \text{ K}$, so that BaZrO₃ retains the cubic $Pm\bar{3}m$ structure down to very low temperatures (2 K). These structural data, however, disagree

with the results of the first-principles phonon spectra calculations for BaZrO₃,^{10,13,14,16,17} in which the appearance of the unstable R_{25} mode indicates an instability of the cubic structure with respect to the rotation of the oxygen octahedra. In Ref. 14, the equilibrium low-symmetry $P\bar{1}$ structure was found, which results from the doubling of the unit cell parameters in all directions and the rotation of the ZrO₆ octahedra according to Glazer tilt system $a^-b^-c^-$. Taking into account of these rotations was shown to improve the agreement between the calculated values of the low-temperature dielectric constant and experiment.¹⁴ An indirect indication of the possible phase transformation in BaZrO₃ crystals can be its very low thermal expansion coefficient at $T < 300 \text{ K}$.¹⁰ At 300 K, the pressure-induced phase transition to the tetragonal phase was recently observed at 17.2 GPa.¹⁸ In order to explain the disagreement between the theory and experiment, it was suggested that, for some reason, the long-range order in the octahedral rotations in BaZrO₃ cannot be established at ambient pressure even at low temperatures. In particular, it was supposed that it may be caused by zero-point lattice vibrations.^{10,13,15}

The aim of this work is to calculate the phonon spectrum and the ground-state structure for BaZrO₃ from first principles and to find experimental evidence for the structural instability in this material. We started from the assumption that, even if the long-range order in BaZrO₃ is absent for some reason, the structural instability (if it exists) should be manifested in the change of the *local structure*. To search for these changes, the extended X-ray absorption fine structure

(EXAFS) studies are used. EXAFS is one of the modern powerful experimental techniques that enables to get detailed information on the local structure of crystals.¹⁹ We expected to find an evidence for the structural instability in BaZrO₃ from anomalous behavior of the Debye–Waller factors which characterize the magnitude of the local displacements and the amplitude of thermal vibrations.

2. Calculation and Experimental Techniques

In this work, the calculations were performed from first principles using the density functional theory implemented in the ABINIT code. The pseudopotentials for Ba, Zr, and O atoms used in the calculation were borrowed from Refs. 20 and 21. The cut-off energy of plane waves was 30 Ha (816 eV). The integration over the Brillouin zone was performed on the $8 \times 8 \times 8$ Monkhorst–Pack mesh. The lattice parameters and the equilibrium atomic positions were determined from the condition of decreasing of the residual forces acting on the atoms below $5 \cdot 10^{-6}$ Ha/Bohr (0.25 meV/Å) while the accuracy of the total energy calculation was better than 10^{-10} Ha. The density functional perturbation theory and the interpolation technique^{22,23} were used to calculate the phonon spectra. The calculated lattice parameter for cubic BaZrO₃ was $a_0 = 4.1659$ Å and agreed well with the experimental value obtained at 10 K (4.191 Å¹⁰). The slight difference of these values results from a systematic underestimation of the lattice parameter in the local density approximation (LDA) used in this work.

The sample of BaZrO₃ was prepared by the solid phase reaction method. The initial components were BaCO₃ and microcrystalline ZrO₂ obtained by the thermal decomposition of ZrOCl₂ · 8H₂O at 300°C. The components were dried at 600°C, weighed in proper proportions, ground in acetone, and calcined in air at 1100°C for 6 h. The resulting powder was ground again and annealed at 1500°C for 3 h. The single-phase character of the sample was confirmed by X-ray diffraction.

Four EXAFS spectra were recorded using the simultaneous registration of the transmission signal and X-ray fluorescence on the KMC-2 station of the BESSY synchrotron radiation source (the beam energy of 1.7 GeV, the beam current up to 300 mA) at the Ba *L*_{III}-edge (5.247 keV) at 300 K. The intensity of the incident radiation was measured by an ionization chamber, the intensity of radiation transmitted through the sample mounted at 45° to the X-ray beam was measured with a silicon photodiode, and the intensity of the X-ray fluorescence excited in the sample was measured using the RÖNTEC silicon energy-dispersive detector. The spectra were recorded in the 5.15–5.62 keV energy range limited by the proximity of the Ba *L*_{II}-edge (5.624 keV).

The Ba *L*_{III}-edge was chosen for measurements because the expected structural instability, which is accompanied by the rotation of the oxygen octahedra (Fig. 1), should manifest

Fig. 1. (Color online) Crystal structure of BaZrO₃ showing the octahedral rotations which result in $Pm\bar{3}m \rightarrow I4/mcm$ phase transition. The rotations change the lengths of 8 of 12 bonds between the Ba atom (shown in green) and nearest oxygen atoms. The lengths of the Zr–O bonds remain unchanged.

most strongly in the change of the Ba–O interatomic distances, and not in the Zr–O interatomic distances. This is because the Zr–O distances change very little when the octahedra are rotated. In principle, the rotation of the octahedra could be also observed at the Zr *K*-edge as the changes in the multiple scattering contributions to the EXAFS spectra as proposed in Ref. 24.

The EXAFS spectra were processed in the traditional way,²⁵ by fitting them to the theoretical EXAFS spectra calculated using the FEFF software.²⁶ According to FEFF simulations, the half-path lengths of all multiple scattering paths exceed the distance to the third shell, so only back-scattering paths to three nearest shells were taken into account in our data analysis. The obtained spectra were independently proceeded, and the results were then averaged. Since, according to our theoretical predictions, the temperature of the expected phase transition is below 300 K, the structure of BaZrO₃ at room temperature is cubic, and so the structural instability should be manifested as an enhanced Debye–Waller factor in the first shell.

3. Results of Calculations

The calculated phonon spectrum of BaZrO₃ with the cubic perovskite structure (space group $Pm\bar{3}m$) is shown in Fig. 2(a). It is seen that an unstable phonon with R_{25} symmetry (imaginary phonon energies are represented in the figure as negative values) appears in this spectrum. The eigenvector of the unstable phonon indicates that the cubic structure is unstable with respect to the octahedral rotations. The results of our calculations are consistent with the results of previous calculations,^{10,13,14,16,17} but it should be noted that an additional instability at the *M* point observed in Ref. 16 was not found in our phonon spectrum.

To determine the structure of the ground state, the energies of different distorted phases resulting from the condensation of triply degenerate unstable R_{25} mode were calculated. We

Fig. 2. Phonon spectrum of BaZrO₃ in the cubic $Pm\bar{3}m$ phase (a) and the ground-state $I4/mcm$ phase (b).

write a Landau-type expansion of the total energy of a crystal in a power series of the amplitudes of the distortions,

$$E_{\text{tot}} = E_{\text{tot}}(0) + a(\phi_x^2 + \phi_y^2 + \phi_z^2) + b(\phi_x^2 + \phi_y^2 + \phi_z^2)^2 + c(\phi_x^4 + \phi_y^4 + \phi_z^4) + d(\phi_x^2 + \phi_y^2 + \phi_z^2)^3 + e\phi_x^2\phi_y^2\phi_z^2 + \dots, \quad (1)$$

where $E_{\text{tot}}(0)$ is the total energy of the parent cubic phase, and ϕ_x , ϕ_y , and ϕ_z are the angles of rotation around three fourfold axes of the cubic structure. From this expansion it can be shown that to find the ground-state structure, it is sufficient to calculate the energies of phases described by the order parameters $(\phi, 0, 0)$, $(\phi, \phi, 0)$, and (ϕ, ϕ, ϕ) , which correspond to the minimums of E_{tot} for different combinations of signs of the coefficients c and e . The specified order parameters correspond to the Glazer tilt systems $a^0a^0c^-$, $a^0b^-b^-$, and $a^-a^-a^-$, and lead to the $I4/mcm$, $Imma$, and $R\bar{3}c$ space groups, respectively. As follows from Table 1, the $I4/mcm$ phase has the lowest energy among these phases. This phase can be obtained from the cubic $Pm\bar{3}m$ structure by the out-of-phase rotation of the oxygen octahedra around one of the fourfold axes. The energy of this phase is ~ 10 meV lower than the energy of the cubic phase; this gives an estimated phase transition temperature of ~ 120 K. The calculations of the phonon spectrum (Fig. 2(b)) and elastic properties for the $I4/mcm$ phase prove that this phase is the ground-state structure.

Table 1. The energies of different distorted phases of BaZrO₃. The energy of the cubic $Pm\bar{3}m$ phase was taken as the energy reference.

Unstable mode	Glazer rotations	Space group	Energy (meV)
R_{25}	$a^-a^-a^-$	$R\bar{3}c$	-9.17
R_{25}	$a^0b^-b^-$	$Imma$	-9.47
R_{25}	$a^0a^0c^-$	$I4/mcm$	-10.01

It should be noted that among the obtained phases there is no $P\bar{1}$ solution, which was considered as the ground-state structure in Ref. 14. This phase corresponds to the Glazer tilt system $a^-b^-c^-$, in which the rotation angles around three fourfold axes of the cubic structure are different. The testing of this solution showed that the $P\bar{1}$ structure very slowly relaxes to the $I4/mcm$ solution found above (the convergence to this result required over 400 iterations). This demonstrates that the use of the information on the symmetry of the total energy can significantly (by more than 10 times) reduce the computation time needed to find the ground-state structure and guarantees a correct result.

The lattice parameters and atomic coordinates in the ground-state structure of BaZrO₃ are given in Table 2.

4. Experimental Results

A typical EXAFS spectrum for the BaZrO₃ sample obtained at the Ba L_{III} -edge at 300 K is shown in Fig. 3. The data analysis shows that the spectra are consistent with a model in which the structure of the sample is cubic. The structural parameters (interatomic distances and the Debye–Waller factors) for the first three shells are given in Table 3. It is seen that the structural parameters obtained using two different measurement methods (transmission and fluorescence) agree within the experimental error.^a The Debye–Waller factor for the Ba–Zr pair is very close to the Zr–Ba Debye–Waller factor ($0.0072 \text{ \AA}^2$) obtained at the Zr K -edge at 300 K.¹¹ The discrepancy between the R_1 values obtained by EXAFS and X-ray methods, in our opinion, is due to anharmonicity effects. For Gaussian distribution of interatomic distances describing the thermal disorder, the effective shortening of this distance resulting from the thermal vibrations parallel to the bond direction is given by the formula $\Delta R_1 \approx -2\sigma_1^2/R_1$ ²⁷ and is close to $\approx -0.01 \text{ \AA}$ in our case. However, for a system exhibiting the structural instability, the actual distribution usually have two maxima, and the effective shortening of the

^aThe data for fluorescence mode were corrected for the self-absorption using the FLUO program by Haskel (<http://www.aps.anl.gov/~haskel/fluio.html>).

Table 2. Calculated lattice parameters and atomic coordinates in the ground-state structure of BaZrO₃.

Phase	Lattice parameters (Å)	Atom	Wyckoff position	x	y	z
I4/mcm	a = 5.8722 c = 8.3577	Ba	4b	0.00000	0.50000	0.25000
		Zr	4c	0.00000	0.00000	0.00000
		O	4a	0.00000	0.00000	0.25000
		O	8h	0.22315	0.72315	0.00000

Fig. 3. (Color online) A typical raw EXAFS spectrum of BaZrO₃ obtained at the Ba *L*_{III}-edge at 300 K after removal of the background and normalization (thin, black line) and the results of its fitting with three nearest shells (thick, blue line).

EXAFS bond length can be much larger. For the third shell, the discrepancy between the EXAFS and X-ray data can be explained by a parasitic contamination of the data for this shell by multiple scattering contributions from Ba–Zr–O–Ba and Ba–O–O–Ba paths with half-path lengths of 4.35 and 4.45 Å (both *R*₃ and *σ*₃² data may be subject to errors).

In Table 3, it should be noted that the Debye–Waller factor for the first shell is much higher than the values for the second and third shells (usually the values of this factor increase monotonically with increasing interatomic distance).

The values of the Debye–Waller factors are determined by two components: (1) static distortions of the structure and

(2) thermal vibrations. As our measurements are performed at a temperature above the temperature of the expected phase transition, the static distortions of the structure are absent. Furthermore, the optical modes responsible for the deformation of the oxygen octahedron are high-energy modes in the phonon spectrum of BaZrO₃ and are not excited at 300 K.^b Therefore, we can consider the octahedron ZrO₆ as a rigid unit. The thermal motion of the center of the octahedron relative to the Ba atom is characterized by the Debye–Waller factor *σ*₂². Since (as result of the rigidity of the octahedron) the oxygen atoms are strongly bound to the Zr atoms, the only way to explain why *σ*₁² ≫ *σ*₂² is to take into account the rotation of the octahedra. The estimation of the *σ*₁² value for the case where the octahedral rotations are absent is not an easy task. The contribution of acoustic modes to *σ*₁² should be smaller than that to *σ*₂² because there is a strong correlation between the displacements of neighboring atoms. For optical modes, the information on the frequencies of these modes and their eigenvectors in the whole Brillouin zone is needed to calculate their contribution to the Debye–Waller factors, but we can expect that their contributions to *σ*₁² and *σ*₂² are close. The experimental data^{28,29} confirm our reasoning. So, we can consider the *σ*₂² value as an upper limit for *σ*₁². Assuming that *σ*₁² = *σ*₂², the excess part of the Debye–Waller factor in the first shell, Δ*σ*₁² = *σ*₁² – *σ*₂², can be associated with the thermal rotations. Then, using the formula

$$\Delta\sigma_1^2 = \frac{a_0^2\theta^2}{12},$$

which describes the dependence of Δ*σ*² on the octahedral rotation angle *θ* about the fourfold axis of the cubic structure, we can estimate the amplitude of the thermal rotations. For the lattice parameter of *a*₀ ≈ 4.2 Å, the mean rotation angle is √*θ*² ≈ 4°. Taking into account the results of Ref. 30 in which the experimental value of the rotation angle in SrTiO₃ at 50 K (well below the temperature of the structural phase transition) is 2.01°, we can conclude the existence of the structural instability in BaZrO₃. We note that a similar behavior of the Debye–Waller factors, *σ*₁² ≫ *σ*₂²,³¹ was observed in SrTiO₃ both below and above the temperature of the real structural phase transition.

Table 3. Structural parameters for the first three shells in cubic BaZrO₃ at 300 K obtained from the EXAFS data.

Measurement method	First shell (Ba–O)		Second shell (Ba–Zr)		Third shell (Ba–Ba)	
	<i>R</i> ₁ (Å)	<i>σ</i> ₁ ² (Å ²)	<i>R</i> ₂ (Å)	<i>σ</i> ₂ ² (Å ²)	<i>R</i> ₃ (Å)	<i>σ</i> ₃ ² (Å ²)
Fluorescence	2.916(8)	0.0149(15)	3.640(8)	0.0073(9)	4.244(13)	0.0094(15)
Transmission	2.914(6)	0.0145(13)	3.635(3)	0.0068(7)	4.244(8)	0.0087(13)
X-ray data	2.963	—	3.630	—	4.191	—

^bIn experiment, this is confirmed by small values of the Debye–Waller factor for the Zr–O pair.^{9,11}

5. Discussion

Now, we discuss why the long-range order in the octahedral rotations is absent in BaZrO₃ at low temperatures. As was mentioned in Sec. 1, one of the reasons for this behavior was the suppression of the long-range order by zero-point vibrations. In Ref. 32, a criterion was proposed, which enables, using a set of parameters obtained entirely from first principles, to estimate the stability of a structure with respect to zero-point vibrations. According to this criterion, zero-point vibrations prevent the system to be localized in one of the local minima of the potential if $h\nu/E_0 > 2.419$, where ν is the unstable phonon frequency and E_0 is the depth of the local minimum of the potential. In our calculations, for the unstable R_{25} mode $h\nu = 81.2 \text{ i cm}^{-1} \approx 10 \text{ meV}$ and $E_0 \approx 10 \text{ meV}$ (Table 1); therefore, zero-point vibrations should not suppress the structural distortions in BaZrO₃. The phonon frequency of 79 i cm^{-1} and the local minimum depth of 8 meV obtained for BaZrO₃ in Ref. 14 give the ratio $h\nu/E_0 \approx 1.2$, which is close to our value. The parameters $h\nu \approx 27 \text{ i cm}^{-1}$ and $E_0 = 1.5 \text{ meV}$ obtained in Ref. 10 are much lower and give $h\nu/E_0 \approx 2.2$, which is anyway lower than the critical value. Therefore, the explanation proposed in Refs. 10, 13 and 15 that the suppression of the long-range order in BaZrO₃ is caused by zero-point vibrations seems unlikely. The fact that the influence of zero-point vibrations on the phase transition in BaZrO₃ is weaker than in SrTiO₃ is not surprising because the masses of both metal atoms in BaZrO₃ are larger.

The theoretical calculations performed in this work enable to propose another explanation for the absence of the long-range order in BaZrO₃ crystals in which the structural instability is expected. The closeness of the total energies of the $R\bar{3}c$, $Imma$, and $I4/mcm$ phases (Table 1), which can result from the condensation of the R_{25} mode, but do not satisfy the group-subgroup relation, enables to suggest the appearance of a quenched rotational disorder when cooling the samples. In this state, the positions of Ba and Zr atoms are practically the same as in the parent cubic phase, but the local rotation angles ϕ_x , ϕ_y , and ϕ_z are the parameters that vary randomly in space. The internal strains and defects cause the appearance of fragments of different phases with close energies at different points of the sample, obviously resulting in the absence of the long-range order in the octahedral rotations. Moreover, the oxygen vacancies, which can be generated in BaZrO₃ quite easily, disturb the three-dimensional connectivity of the perovskite structure and can also contribute to the formation of the quenched rotational disorder.

The uniqueness of BaZrO₃ among crystals with the perovskite structure and rotational instability is the small difference between the energies of phases with different rotation patterns in this compound. The comparison of the energies of these phases (Table 4) shows that in all compounds with moderate rotational instability this difference is about 10% of the ground-state energy (for CdTiO₃ and CaZrO₃ with

Table 4. The energies of phases resulting from the condensation of rotational R_{25} mode in some perovskite crystals and the maximum difference of these energies. The energies of the ground-state structures are shown in boldface.

Compound	Unstable mode	Space group	Energy (meV)	ΔE (meV)
BaZrO ₃	R_{25}	$R\bar{3}c$	-9.17	0.84
	R_{25}	$Imma$	-9.47	
	R_{25}	$I4/mcm$	-10.01	
SrTiO ₃	R_{25}	$R\bar{3}c$	-27.6	3.3 ²⁰
	R_{25}	$Imma$	-28.9	
	R_{25}	$I4/mcm$	-30.9	
SrZrO ₃	R_{25}	$I4/mcm$	-298	34
	R_{25}	$R\bar{3}c$	-311	
	R_{25}	$Imma$	-332	
CaTiO ₃	$R_{25} + M_3$	$Pbnm$	-367	47 ²⁰
	M_3	$P4/mbm$	-321	
	R_{25}	$I4/mcm$	-365	
	R_{25}	$R\bar{3}c$	-385	
	R_{25}	$Imma$	-412	
	$R_{25} + M_3$	$Pbnm$	-497	

stronger instability, the energy difference is larger, about 25%). This difference is independent of the presence of the phonon instability at the M point in the cubic phase. Therefore, BaZrO₃ can be considered as a normal crystal in which the small difference between the energy of phases with different rotation patterns results from a rather weak rotational instability. In our opinion, this small energy difference may explain the tendency of BaZrO₃ to the formation of the quenched rotational disorder. We find a close analogy between this phenomenon and the appearance of a glass-like behavior in ferroelectric $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ solid solutions in which the energy difference between the $P4mm$, $Amm2$, and $R3m$ ferroelectric phases becomes small when decreasing x , and the system transforms into the dipolar glass state at low temperatures.³³

Further experiments on BaZrO₃, such as studies of the temperature dependence of the diffraction line width, diffuse scattering, elastic properties, and other physical phenomena sensitive to the rotations of the octahedra, could provide additional information on the cause of the discrepancy between theory and experiment and to confirm or refute our explanation. We think that the low-temperature Raman studies of BaZrO₃ can also be very useful; our calculations show that five first-order Raman lines located at 16–36, 104–111, 121–128, 350–361, and 547–548 cm^{-1} should appear in three possible distorted phases ($R\bar{3}c$, $Imma$, and $I4/mcm$) with the octahedral rotations.

6. Conclusion

First-principles calculations of the phonon spectrum of BaZrO₃ performed in this work and experimental observation

of the enhanced Debye–Waller factor for the Ba–O bonds in the EXAFS study of BaZrO₃ suggest that BaZrO₃ actually exhibits the structural instability associated with the rotations of the oxygen octahedra. It is shown that zero-point lattice vibrations are not the factor that prevents establishing of the long-range order in the octahedral rotations. Very close energies of the phases with the different rotation patterns, which can result from the condensation of the R_{25} phonon, suggest a possible transition to the quenched rotational disorder state when cooling BaZrO₃ samples. This explains the apparent contradiction between the theoretical predictions and the absence of the long-range order in the octahedral rotations observed in the experiment.

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