

PROCEEDING OF THE XVIII ALL-RUSSIA CONFERENCE
ON PHYSICS OF FERROELECTRICS (VKS-XVIII)
(St. Petersburg, Russia, June 9–14, 2008)

Lattice Dynamics of BiFeO₃ under Hydrostatic Pressure

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Abstract—The vibrational frequencies of the BiFeO₃ crystal lattice in the cubic phase (*Pm3m*) and the rhombohedral paraelectric phase (*R3c*) are calculated in terms of the ab initio model of an ionic crystal with the inclusion of the dipole and quadrupole polarizabilities. In the ferroelectric phase with the symmetry *R3c*, the calculated spontaneous polarization of 136 $\mu\text{C cm}^{-2}$ agrees well with the experimental data. The dependences of the unit cell volume, the elastic modulus, and the vibrational frequencies on the pressure are calculated. It is found that the frequency of an unstable ferroelectric mode in both the cubic (*Pm3m*) and rhombohedral (*R3c*) phases are almost independent of the applied pressure, in contrast to classical ferroelectrics with a perovskite structure, where the ferroelectric instability is very sensitive to a variation in the pressure.

PACS numbers: 63.20.-e, 62.50.-p

DOI: 10.1134/S1063783409070208

In recent years, much attention has been focused on the study of multiferroics, i.e. compounds in which magnetic, ferroelectric, and (or) ferroelastic orders exist. Among them is bismuth ferrite BiFeO₃ with a perovskite-like structure.

As is known from the experimental data, BiFeO₃ undergoes a ferroelectric phase transition at a temperature T_c approximately equal to 1100 K and an antiferromagnetic phase transition at a temperature T_N approximately equal to 640 K [1]. Above T_c , the crystal belongs to the rhombohedral system with space group *R3c*, where its structure is a distorted form of the ideal

perovskite structure and the distortions are due to the rotation of the FeO₆ octahedra around the spatial diagonal of the cubic perovskite unit cell. In the ferroelectric phase with symmetry *R3c*, additional distortions related to the displacements of bismuth, iron, and oxygen ions occur.

In this work, the crystal-lattice vibrational frequencies, dynamic Born charges, elastic constants, and their dependences on the external hydrostatic pressure are calculated using ab initio methods for a bismuth ferrite crystal. The calculations are carried out in terms of the model of an ionic crystal with inclusion of the dipole and

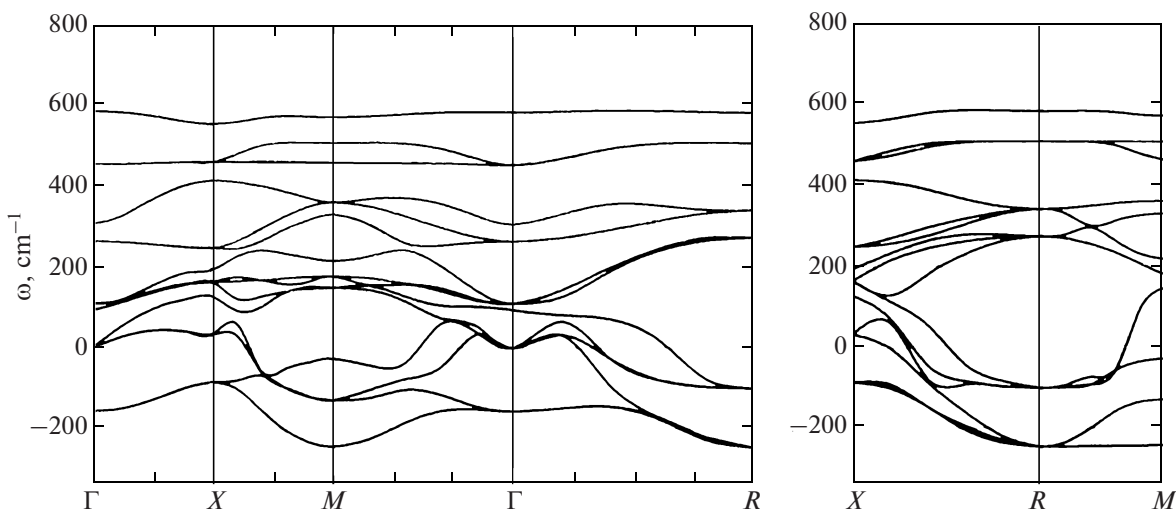


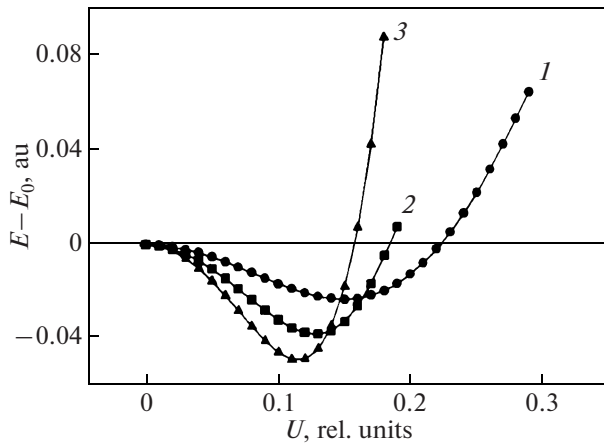
Fig. 1. Phonon spectrum of the BiFeO₃ crystal in the cubic phase. Imaginary frequencies are represented by negative values.

Table 1. Dynamic charges of atoms and the elastic moduli of the BiFeO₃ crystal in the cubic phase (lattice parameter $a_0 = 3.96 \text{ \AA}$, permittivity $\epsilon_\infty = 6.892$)

Atom	Z_{din}
Bi	4.644
Fe	5.735
O	-5.088
O _⊥	-2.646
Elastic moduli, GPa	
C_{11}	249.9
C_{12}	71.0
C_{44}	71.9

quadrupole polarizabilities of the ions. The calculation method is described in detail in the review [2].

For the cubic phase of the BiFeO₃ crystal, we calculated the equilibrium lattice parameter, dynamic charges of the atoms, permittivity, elastic moduli (Table 1), and also the complete phonon spectrum (Fig. 1). The presence of the imaginary modes over the entire Brillouin zone and their large magnitudes are indicative of a strong instability of the cubic phase of the compound under study. The unstable threefold degenerate mode Γ_{1u} at the Brillouin zone center with a frequency of $157i \text{ cm}^{-1}$ is the polar ferroelectric mode. The eigenvector of a component of this mode is given in Table 2. Figure 2 shows the calculated dependences of the change in the total energy of the crystal on the atomic displacement amplitude in the eigenvectors of the unstable polar mode along the [100], [110], and [111] directions of the crystal. As is seen from the plot, the distortion of the initial cubic unit cell due to the atomic displacement in the eigenvector

**Fig. 2.** Dependences of the change in the total energy of the crystal on the amplitude of atomic displacement in the eigenvectors of the unstable polar mode along the (1) [100], (2) [110], and (3) [111] directions of the crystal.**Table 2.** Component x of the eigenvector of the unstable threefold ferroelectric mode Γ_{1u} ($y = z = 0$)

Atom	x
Bi	0.7565
Fe	0.1537
O	-0.0114
O _⊥	-0.4494

Table 3. Lattice parameters and fractional atomic coordinates of the BiFeO₃ crystal in the rhombohedral phase with space group $R3c$

	Calculation	
	this work	[3]
$a_0, \text{ \AA}$	5.60	5.513
$\alpha, \text{ deg}$	60	61.432
	Bi: $2b[x, x, x]$	
x	1/4	1/4
	Fe: $2a[x, x, x]$	
x	0	0
	O: $6b[x, y, z]$	
x	-0.330	0.3358
y	-0.170	0.1641
z	1/4	1/4

along the [111] direction is energetically most favorable. The calculated spontaneous polarization of such a distorted structure is $109.54 \mu\text{C cm}^{-2}$.

However, the most unstable mode in the cubic phase of BiFeO₃ is the threefold degenerate mode R_{25} of the boundary point R of the Brillouin zone equal to

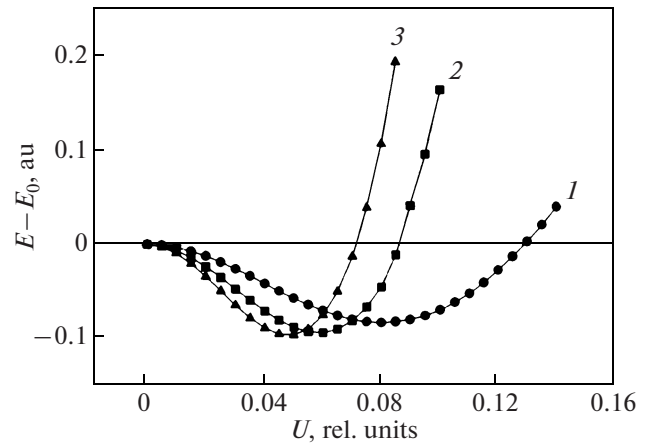
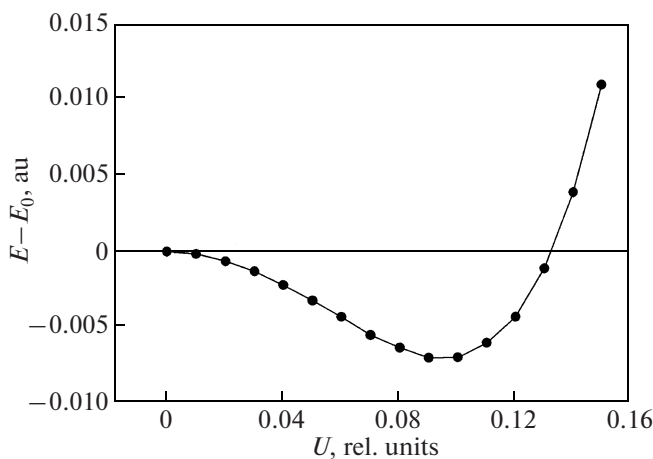
**Fig. 3.** Dependences of the change in the total energy of the crystal on (1) one, (2) two, and (3) three components of uniform displacements in the local mode R_{25} .

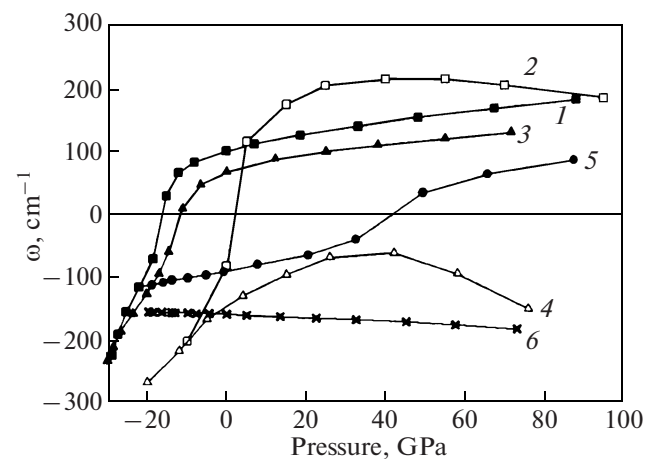
Table 4. Vibrational frequencies of the lattice of the BiFeO₃ crystal in the rhombohedral phase with space group *R3c*

Mode	Frequency, cm ⁻¹
<i>A</i> _{1g}	198
<i>A</i> _{2g}	65 <i>j</i>
	270
	552
<i>E</i> _g	117 <i>i</i>
	88
	276
	437
<i>A</i> _{1u}	254
	314
<i>A</i> _{2u}	90 <i>i</i>
	273
	385
<i>E</i> _u	60 <i>i</i>
	161
	262
	312
	395

247i cm⁻¹. The eigenvector of this mode corresponds to the rotation of the FeO₆ octahedron. Figure 3 shows the dependences of the change in the total energy of the crystal on one, two, and three components of uniform displacements in the local mode *R*₂₅ corresponding to the rotations of the oxygen octahedra along the

**Fig. 4.** Dependence of the total energy of the crystal on the amplitude of atomic displacement in the eigenvector of the unstable ferroelectric mode *A*_{2u}.

[100], [110], and [111] cube axes. As is seen from this plot, the rotation around the [111] cube axis is most favorable. The lattice distortion due to the rotation of the oxygen octahedra around the [111] cube axis with the atomic displacements corresponding to the energy minimum, permits us to obtain the rhombohedral phase with space group *R3c*. The fractional atomic coordinates are given in Table 3, where the atomic coordinates calculated in [3] are presented as well. Further calculation of the lattice dynamics of the BiFeO₃ crystal in this phase shows the existence of unstable polar ferroelectric *A*_{2u} modes and twofold *E*_u mode (Table 4) into which the unstable threefold Γ_{1u} mode of the initial cubic phase is split. The *A*_{2u} mode eigenvector corresponds to the atomic displacements in parallel to the third-order axis of the rhombohedral unit cell: the bismuth and iron atoms move to a direction and the oxygen atoms move in the opposite direction. In the polar mode *E*_u, atoms move similarly in the plane perpendicular to the third-order axis. The calculated dependence of the total energy of the crystal on the amplitude of the atomic displacement in the eigenvector of the unstable ferroelectric mode *A*_{2u} is presented in Fig. 4. Thus, to obtain the low-temperature ferroelectric rhombohedral phase with space group *R3c*, the lattice must be distorted by the atomic displacement in the eigenvector of the mode *A*_{2u} to a value corresponding to the total-energy minimum. The obtained fractional atomic coordinates for this phase are given in Table 5 where, for comparison, the atomic coordinates calculated in [3] and the experimental data from [4] are presented as well. As is seen, the distortion character and its value satisfactorily agree with the experiment. The subsequent calculation of the lattice dynamics of the BiFeO₃ crystal in

**Fig. 5.** Dependence of the frequency of the ferroelectric mode (imaginary frequencies are represented by negative values) on the hydrostatic pressure for the cubic phase of the crystals: (1) BaTiO₃, (2) BaTiO₃ (calculation from [8]), (3) PbTiO₃, (4) PbTiO₃ (calculation from [9]), (5) BiAlO₃, and (6) BiFeO₃.

this phase showed the absence of imaginary modes over the entire Brillouin zone, which indicates that this phase is stable. For the compound under study in the $R3c$ phase, we calculated the spontaneous polarization, which is equal to $136.42 \mu\text{C cm}^{-2}$, whereas the calculation performed in [5] gives a spontaneous polarization equal to $101.2 \mu\text{C cm}^{-2}$ and, furthermore, according to the experimental data for a 300-nm-thick polycrystalline film [6], it is $158 \mu\text{C cm}^{-2}$.

As was shown earlier in [7], the ferroelectric instability in the cubic phase of bismuth ferrite is almost independent of applied hydrostatic pressure (Fig. 5). It is shown also in [7] that the high-temperature rhombohedral phase with space group $R3c$ contains the ferroelectric unstable mode A_{2u} which also is almost independent of applied pressure and, in the rhombic phase with space group $Pnma$ which was theoretically predicted in [3], there are the imaginary polar modes B_{1u} , B_{2u} , and B_{3u} which slightly depend on applied pressure and retain large magnitudes up to pressures of 80 GPa (Fig. 5). For the BiFeO₃ crystal in the low-temperature polar phase with space group $R3c$, we calculated the dependence of the unit cell volume on the applied pressure (Fig. 6; here, the experimental data from [10] are presented as well). Figure 7 shows the calculated dependence of the elastic moduli and the bulk modulus on applied pressure for the polar compound under study. According to the experimental data from [10], the bulk modulus is 75.5 ± 15.5 GPa at pressures 0–40 GPa and 292 ± 9 GPa at pressures 54–70 GPa. However, our calculations give 133 GPa at a zero pressure and 286 GPa at a pressure of 73 GPa. As is seen, the results obtained for the ferroelectric phase

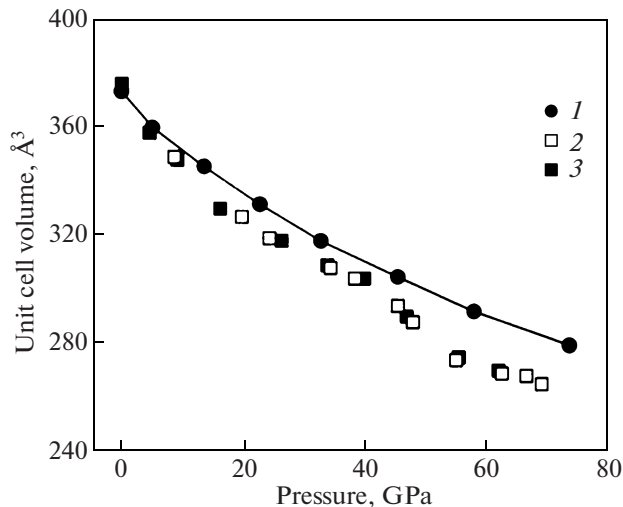


Fig. 6. Pressure dependence of the unit cell volume of the polar rhombohedral phase of BiFeO₃ according to (1) our calculation, (2) the experimental data taken from [10] (increase in the pressure), and (3) the experimental data taken from [10] (decrease in the pressure).

Table 5. Lattice parameters and fractional atomic coordinates of the BiFeO₃ crystal in the polar rhombohedral phase with space group $R3c$

	Calculation (this work)	Experiment [1]	Calculation [2]
$a_0, \text{Å}$	5.60	5.63	5.697
α, deg	60	59.35	59.235
Bi: $2b[x, x, x]$			
x	0	0	0
Fe: $2a[x, x, x]$			
x	0.227	0.221	0.2232
O: $6b[x, y, z]$			
x	0.546	0.538	0.5342
y	0.951	0.933	0.9357
z	0.386	0.395	0.3865

of the bismuth ferrite crystal satisfactorily agree with the available experimental data.

In this work, in terms of the ab initio calculation, we calculated the vibrational frequencies of the bismuth-ferrite crystal in the cubic and rhombohedral phases. It is established that the cubic phase of this compound is unstable with respect to the lattice vibrational modes occupying all the phase space in the Brillouin zone. The calculation of the vibrational frequencies for the paraelectric phase with space group $R3c$ shows that this phase contains unstable ferroelectric modes. The coordinates of the atoms of the stable ferroelectric phase with space group $R3c$ are found. The calculated unit cell parameters, ion coordinates,

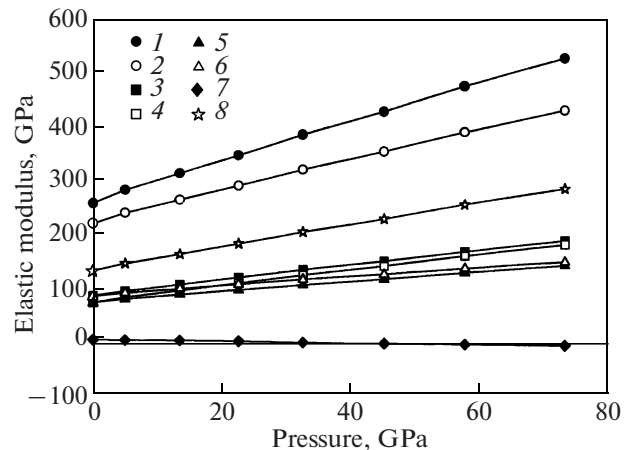


Fig. 7. Pressure dependences of the elastic moduli and the bulk modulus of the BiFeO₃ crystal in the polar rhombohedral phase (space group $R3c$): (1) C_{11} , (2) C_{33} , (3) C_{12} , (4) C_{13} , (5) C_{44} , (6) C_{66} , (7) C_{14} , and (8) bulk modulus.

spontaneous polarization, the dependences of the bulk modulus and unit cell volume on applied pressure in the ferroelectric rhombohedral phase of BiFeO_3 agree satisfactorily with the experimental data. Thus, we can say that the used ab initio model of an ionic crystal with inclusion of the dipole and quadrupole polarizabilities of the ions describes quite adequately the structural properties and lattice dynamics of the BiFeO_3 crystal.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 06-02-016091) and the Council on Grants from the President of the Russian Federation for Support of Leading Scientific Schools of the Russian Federation (grant no. NSh-1011.2008.2).

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Translated by Yu. Ryzhkov