

# Lattice Dynamics of BiFeO<sub>3</sub>: The Untypical Behavior of the Ferroelectric Instability under Hydrostatic Pressure

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Within a nonempirical model of an ionic crystal with the inclusion of the dipole and quadrupole ion polarizations, the lattice vibrational frequencies, high-frequency dielectric constant, Born dynamic charges, and the elasticity moduli of the BiFeO<sub>3</sub> crystal have been calculated and their dependencies on the hydrostatic pressure in the cubic, rhombic, and rhombohedral phases have been determined. The results indicate the presence of the ferroelectric instability, which depends weakly on the pressure in all of the phases investigated. The dependence of the crystal lattice dynamics on the applied pressure for the cubic phases of BiAlO<sub>3</sub>, BaTiO<sub>3</sub>, and PbTiO<sub>3</sub> has been calculated for comparison.

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Perovskite BiFeO<sub>3</sub> belongs to the so-called multiferromagnetic materials, which are the compounds where the magnetic and ferroelectric and/or the ferroelastic orders exist. In recent years, these compounds have been the focus of attention in view of their possible application as multifunctional materials essential for modern microelectronics.

Perovskite BiFeO<sub>3</sub> undergoes the ferroelectric phase transition at  $T_c$  of about 1100 K and the antiferromagnetic phase transition at  $T_N$  of about 640 K. The phase diagram and properties of this compound have been thoroughly studied both experimentally and theoretically. The structures of the paraelectric and ferroelectric phases are determined by the x-ray and neutron diffraction methods [1, 2]. At temperatures above  $T_c$ , the crystal belongs to the rhombohedral system with the space group  $R\bar{3}c$  and its structure is a distorted form of the ideal perovskite structure. Here, the main distortions are associated with the “rotation” of the FeO<sub>6</sub> octahedron about the space diagonal of the perovskite cubic unit cell. In the ferroelectric phase with  $R3c$  symmetry, additional distortions caused by the displacements of Bi, Fe, and O ions appear. The values of the spontaneous polarization, the Born dynamic charges, and the high-frequency dielectric constant of BiFeO<sub>3</sub> were calculated by the density functional method (DFM) both for the bulk crystal [3] and for thin films [4]. The effect of the hydrostatic pressure on the phase diagram and properties of BiFeO<sub>3</sub> were theoretically and experimentally studied in [3, 5]. In particular, the DFM calculations performed in [3] using the VASP program showed that the nonpolar rhombic phase with

$Pnma$  symmetry at a pressure of about 13 GPa becomes more energetically favorable than the ferroelectric  $R3c$  phase. However, it seems that the effect of the hydrostatic pressure on the ferroelectric instability in BiFeO<sub>3</sub> has not yet been investigated, although its importance was demonstrated for some ferroelectric oxides with the perovskite structure [6, 7]. Samara et al. [8] showed that the ferroelectric instability in classical perovskite ferroelectrics, such as BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, KNbO<sub>3</sub>, etc., is extremely sensitive to the external pressure, which reduces and even fully suppresses the ferroelectric transition in these compounds. This phenomenon was explained in a simple model as follows: the short-range repulsion forces, which stabilize the cubic structure, increase faster with a decreasing distance than the long-range ones destabilizing the structure. In the ab initio calculations [9] of the lattice dynamics of BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, KNbO<sub>3</sub>, and other oxides with the perovskite structure, it was also shown that the sign and value of the squared frequency of the “soft” polar mode are rather sensitive to a slight variation of the lattice parameter.

In this work, the lattice vibrational frequency, the Born dynamic charges, and the elastic constants, as well as their dependencies on the external hydrostatic pressure in the BiFeO<sub>3</sub> crystal, are calculated. The calculation was performed in a nonempirical model of an ionic crystal with the inclusion of the dipole and value of quadrupole ion polarizabilities. The calculation details are presented in the review in [10] and the references therein.

We first discuss the calculation results for the cubic phase. Table I presents the equilibrium unit cell parameter, dielectric constant, Born dynamic charges, and

elastic constants. For comparison, the dynamic charges calculated in [11] are presented in parentheses. The values of the lattice vibrational frequency for the two points of the Brillouin zone are presented in Table 2. The table implies that the cubic phase of BiFeO<sub>3</sub> is unstable to both polar vibrations and to  $R_{25}$  and  $R_{15}$  vibrations at the boundary point  $R$ . The displacements in the  $R_{25}$  mode corresponds to the rotation of the FeO<sub>6</sub> octahedron. Figure 1 shows the frequency of the transverse polar mode as a function of the applied hydrostatic pressure for BiFeO<sub>3</sub>, as well as for BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, and BiAlO<sub>3</sub>. To compare, this figure also presents this dependence for BaTiO<sub>3</sub> and PbTiO<sub>3</sub> calculated by DFM [6, 7]. Clearly, the behavior of the frequency of the soft polar mode in BiFeO<sub>3</sub> is fundamentally different from that in BaTiO<sub>3</sub> and PbTiO<sub>3</sub>. In the latter two compounds, the ferroelectric instability at low applied pressures is very sensitive to pressure (accordingly, to the lattice parameter). This result qualitatively agrees with the DFM calculations as seen in Fig. 1. However, note that our calculation for BaTiO<sub>3</sub> and PbTiO<sub>3</sub> does not provide any softening of the polar mode frequency at high positive pressures in contrast to [6, 7]. The frequency of the unstable polar mode in the BiFeO<sub>3</sub> crystal is almost independent of the pressure up to sufficiently high values. The ferroelectric instability in BiAlO<sub>3</sub> vanishes at a pressure of about 40 GPa, but the dependence of the soft polar mode frequency on the pressure is less sharp than that for BaTiO<sub>3</sub> and PbTiO<sub>3</sub>.

To date, the dipole–dipole mechanism seems to be the most commonly accepted mechanism of the ferroelectric instability in the perovskite oxides. In this mechanism, the long-range dipole–dipole interactions destabilize the cubic structure [12]. Actually, if we exclude the contributions of the Coulomb dipole–dipole interactions between the Bravais lattices in the dynamic matrix, then all of the polar modes become rigid [13]. For BiFeO<sub>3</sub>, this is shown in column 3 of Table 2, which presents the vibrational frequencies at  $q = 0$  disregarding the long-range dipole–dipole interactions. As discussed in [13], the ferroelectric instability in the perovskite oxides is determined by a fine balance of all of the interactions depending on the chemical composition and the ion–ion distances. In particular, it was shown in [13] that the contribution to the dynamic matrix from the short-range interaction between the dipole electron density of the oxygen ion and the spherically distributed electron density of the ion at the octahedron center stabilizes the cubic structure. This interaction magnitude depends both on the charge of the cation at the octahedron center and on the cubic unit cell parameter. According to the estimate of the cubic structure stability in terms of the magnitude of the short-range dipole–charge interaction, BaTiO<sub>3</sub> and PbTiO<sub>3</sub> are more stable than BiFeO<sub>3</sub> and BiAlO<sub>3</sub>. In fact, the cubic structure stability to polar vibrations is determined by a fine balance between all of the contri-

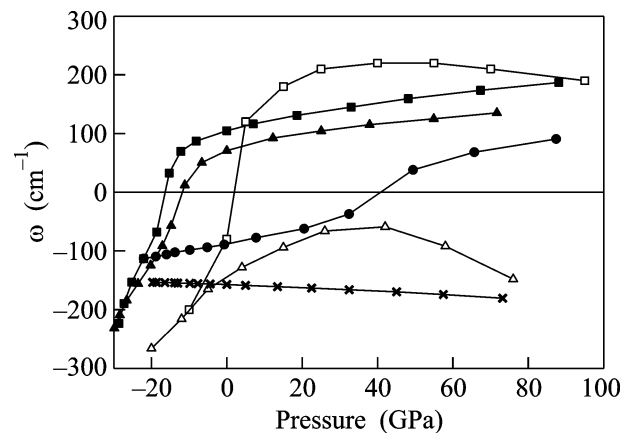
**Table 1.** Unit cell parameter (in Å), dielectric constant, dynamic charges (in elementary charge  $e$ ), and elastic constants (in GPa) in the cubic phase of the BiFeO<sub>3</sub> crystal

$a_0$	$\epsilon_\infty$	$Z_{\text{Bi}}^{\text{eff}}$	$Z_{\text{Fe}}^{\text{eff}}$	$Z_{\text{O}\parallel}^{\text{eff}}$	$Z_{\text{O}\perp}^{\text{eff}}$	$C_{11}$	$C_{12}$	$C_{44}$
3.96	6.892	4.644 (6.32)	5.735 (4.55)	-5.088	-2.646	238	69	69

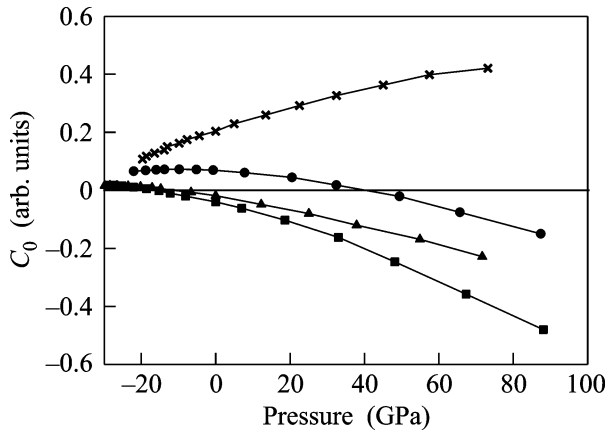
**Table 2.** Calculated vibrational frequencies (in cm<sup>-1</sup>) at the center and boundary point  $R = \pi/a(1, 1, 1)$  of the Brillouin zone in the cubic phase of the BiFeO<sub>3</sub> crystal. The third column presents the frequencies calculated disregarding the long-range dipole–dipole interactions

	$q = 0$		$q = R$	
$\Gamma_{1u}$	157i(2)	99(2)	$R_{25}$	247i(3)
$\Gamma_{1u}$	93	136	$R_{15}$	101i(3)
$\Gamma_{2u}$	109(3)	109(3)	$R_{15}$	273(3)
$\Gamma_{1u}$	264(2)	314(2)	$R_{25'}$	341(3)
$\Gamma_{1u}$	307	338	$R_{12'}$	507(2)
$\Gamma_{1u}$	454(2)	555(2)	$R_{2'}$	583
$\Gamma_{1u}$	585	625		

butions to the dynamic matrix, as discussed in [13]. In the first order of the perturbation theory, the squared frequency of the low-energy polar mode can be written as  $\omega_{TO}^2 \approx -C_0/C_1$ , where  $C_0$  and  $C_1$  are sufficiently lengthy combinations of the dynamic matrix elements [13]. Figure 2 presents the  $C_0$  value for BiFeO<sub>3</sub>, BiAlO<sub>3</sub>, BaTiO<sub>3</sub>, and PbTiO<sub>3</sub> as a function of the pressure. According to this figure, the ferroelectric instabil-



**Fig. 1.** Hydrostatic-pressure dependence of the ferroelectric mode frequency (imaginary frequencies are shown by negative values) for the cubic phase of the crystals of (squares) BaTiO<sub>3</sub> (light symbols, calculation [7]), (triangles) PbTiO<sub>3</sub> (light symbols, calculation [6]), (closed circles) BiAlO<sub>3</sub>, and (crosses) BiFeO<sub>3</sub>.



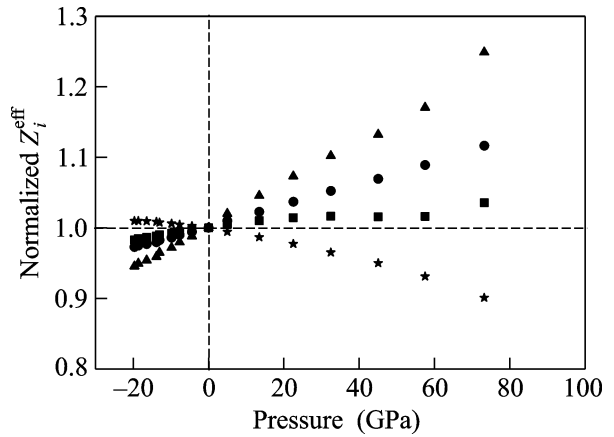
**Fig. 2.** Hydrostatic-pressure dependence of the quantity  $C_0$  for the cubic phase of the compounds of (squares)  $\text{BaTiO}_3$ , (triangles)  $\text{PbTiO}_3$ , (closed circles)  $\text{BiAlO}_3$ , and (crosses)  $\text{BiFeO}_3$ .

ity is determined by the sign of  $C_0$ . It is known that the competition between the short- and long-range interactions in the perovskite crystals is also important for the Born dynamic charges. Figure 3 illustrates the calculated pressure dependence of  $Z_i^{\text{eff}}$  for  $\text{BiFeO}_3$ . It is seen that, as the pressure increases, the dynamic charge  $Z_{\text{O}\parallel}^{\text{eff}}$  for oxygen increases and  $Z_{\text{O}\perp}^{\text{eff}}$  decreases. In  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$ , the situation is reversed, as follows from our calculations and the calculations of [6, 7]. Therefore, the insensitivity of the ferroelectric instability to pressure in  $\text{BiFeO}_3$  agrees with the anomalous pressure dependence of the Born dynamic charges in this compound in contrast to their behavior in normal ferroelectrics.

As mentioned above, the  $\text{BiFeO}_3$  cubic phase is not likely realized and the crystal at temperatures above 1100 K has rhombohedral symmetry with the space group  $R\bar{3}c$  ( $z = 2$  and  $z$  is the number of molecules in the unit cell). This structure is a distorted form of the perovskite structure, and the distortions are due to the condensation of the  $R_{25}$  mode of the boundary point  $R = \pi/a(1, 1, 1)$  of the Brillouin zone ( $a$  is the unit cell parameter of the cubic phase). In this mode, only oxy-

**Table 3.** Calculated vibrational frequencies (in  $\text{cm}^{-1}$ ) at the center of the Brillouin zone in the rhombohedral phase ( $R\bar{3}c$ ) of the  $\text{BiFeO}_3$  crystal

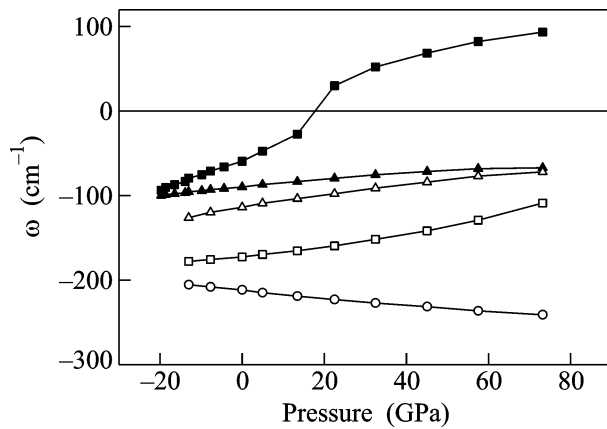
$A_{1g}$	$A_{2g}$	$E_g$
198	65i 270 552	117i 88 276 437
$A_{1u}$	$A_{2u}$	$E_u$
254 314	90i 273 385	60i 161 262 312 395



**Fig. 3.** Normalized Born dynamic charges  $[Z_i^{\text{eff}}(P)/Z_i^{\text{eff}}(0)]$  of the atoms of the  $\text{BiFeO}_3$  crystal in the cubic phase: (circles)  $Z_{\text{Bi}}^{\text{eff}}$ , (squares)  $Z_{\text{Fe}}^{\text{eff}}$ , (triangles)  $Z_{\text{O}\parallel}^{\text{eff}}$ , and (stars)  $Z_{\text{O}\perp}^{\text{eff}}$ .

gen ions are displaced, and these displacements correspond to the rotation of the  $\text{FeO}_6$  octahedron about the cube space diagonal. Here, we have calculated the oxygen displacements in the rhombohedral phase from the minimum of the total energy of the crystal and obtained the following values:  $U = \sqrt{2}(-v_{1x}^{\text{O}} = -v_{1y}^{\text{O}} = -v_{2x}^{\text{O}} = v_{2z}^{\text{O}} = v_{3y}^{\text{O}} = v_{3z}^{\text{O}}) = 0.4483 \text{ \AA}$ . Unfortunately, we have not found any experimental values of the oxygen ion displacements in the  $R\bar{3}c$  phase, and we here present the value of this displacement  $U = 0.4835 \text{ \AA}$  calculated in [3]. The calculated values of the lattice vibrational frequency at  $q = 0$  in the  $R\bar{3}c$  phase are presented in Table 3.

The ferroelectric instability holds in the  $R\bar{3}c$  phase, and the experimentally observed ferroelectric transition  $R\bar{3}c \rightarrow R3c$  is attributed to the condensation of the  $A_{2u}$  mode. The triply degenerate mode  $\Gamma_{1u}$  of the cubic phase in  $R\bar{3}c$  splits into the doubly degenerate mode  $E_u$  and the nondegenerate mode  $A_{2u}$ , as seen in Table 3. The frequencies of the  $E_u$  and  $A_{2u}$  modes are shown in Fig. 4 as functions of the pressure. It is seen from the figure that the frequency of the unstable polar mode  $A_{2u}$ , in the eigenvector of which the Bi, Fe, and O ions are displaced along the third-order axis of the  $R\bar{3}c$  phase, depends weakly on the external pressure, and the ferroelectric instability associated with the  $E_u$  mode, in the eigenvectors of which the ions are displaced in the plane perpendicular to the third-order axis, vanishes at a pressure of about 20 GPa. Figure 4 also shows the calculated pressure dependencies of the frequencies of soft ferroelectric modes  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  for  $\text{BiFeO}_3$  in



**Fig. 4.** Hydrostatic-pressure dependence of the ferroelectric mode frequency (imaginary frequencies are shown by negative values) for the BiFeO<sub>3</sub> crystal in (closed symbols) the rhombohedral phase: (squares) the  $E_u$  mode and (triangles) the  $A_{2u}$  mode, and in (open symbols) the rhombic phase: (squares) the  $B_{1u}$  mode, (triangles) the  $B_{2u}$  mode, and (circles) the  $B_{3u}$  mode.

the rhombohedral phase with the  $Pnma$  symmetry ( $z = 4$ ). This phase was experimentally observed in [5] and was theoretically predicted in [3]. To calculate the vibrational frequencies in this phase, the data on the lattice parameters and atomic coordinates were taken from [3]. It is seen that the ferroelectric instability holds in this phase, and the frequencies of the unstable non-degenerate polar modes vary slightly with the pressure. This result contradicts the conclusions made in [5], where it was proposed that the ferroelectric instability at pressures above 10 GPa is suppressed. It is desirable to experimentally verify in more detail the presence of the ferroelectric phase transition in the rhombic phase.

Thus, the nonempirical calculation of the lattice vibrational frequencies as functions of the hydrostatic pressure in the BiFeO<sub>3</sub> crystal indicates that the ferroelectric instability in this crystal in the cubic, rhombic, and rhombohedral phases depends weakly on the

applied pressure in contrast to the normal perovskite ferroelectrics.

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