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LETTER TO THE EDITOR

Analysis of soft optical modes in hexagonal BaTiO$_3$: transference of perovskite local distortions

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Abstract.   We have performed detailed first-principles calculations to determine the eigenvectors of the zone-centre modes of hexagonal BaTiO$_3$ and shown that the experimentally relevant soft modes can be represented as suitable combinations of basic local distortions taken directly from the better known perovskite phase. The hexagonal structure provides a testing ground for the analysis of the influence of the stacking of TiO$_6$ octahedra; in particular, its effect on the energetics of the chains of dipoles which are the essential element in the instabilities of the perovskite BaTiO$_3$.

Barium titanate has two structural polymorphs: the cubic perovskite type (c-BT) and its hexagonal modification (h-BT) with six formula units per unit cell. While c-BT has been one of the best studied ferroelectric materials for decades [1], most of the work on the structural and dielectric properties of h-BT is quite recent [2–4]. As shown in figure 1(*a*), h-BT is also composed of TiO$_6$ groups, albeit with a different stacking than the perovskite form. It seems well established that the hexagonal polymorph undergoes two zone-centre structural phase transitions: at 222 K from the high temperature $P6_3/mmc$ hexagonal phase to a second non-polar $C222_1$ phase, and at 74 K to a ferroelectric $P2_1$ phase. The first transition is associated with the softening of an optical mode and the second attributed to a shear strain instability; but a detailed analysis is lacking due to the absence of structural information on the two low-symmetry phases, and little is known about the microscopic origin of the instabilities.

On the other hand, the discovery of a giant LO–TO splitting in h-BT by Inoue *et al* [5] suggested that its ferroelectric modes have the same origin as those of c-BT. In the cubic phase the ferroelectric instabilities can be essentially described as chains of dipoles that originate in the displacement of Ti ions relative to the surrounding O$_6$ octahedra with a minor distortion of the latter. The basic correctness of this view is supported by the successful use of polar local modes by Zhong *et al* [6] in the construction of an effective Hamiltonian for c-BT.

In view of the basic structural similarities between the cubic and hexagonal forms of BaTiO$_3$, it is meaningful to ask whether the local modes that describe the unstable branches in c-BT can somehow be transferred to h-BT and serve as a basis to discuss the low-energy distortions of the structure.

We have performed first-principles calculations that provide structural information on the low-symmetry phases of the hexagonal polymorph of BaTiO$_3$. The analysis of the results proves that the structure of the experimentally found zone-centre optical low-energy modes in
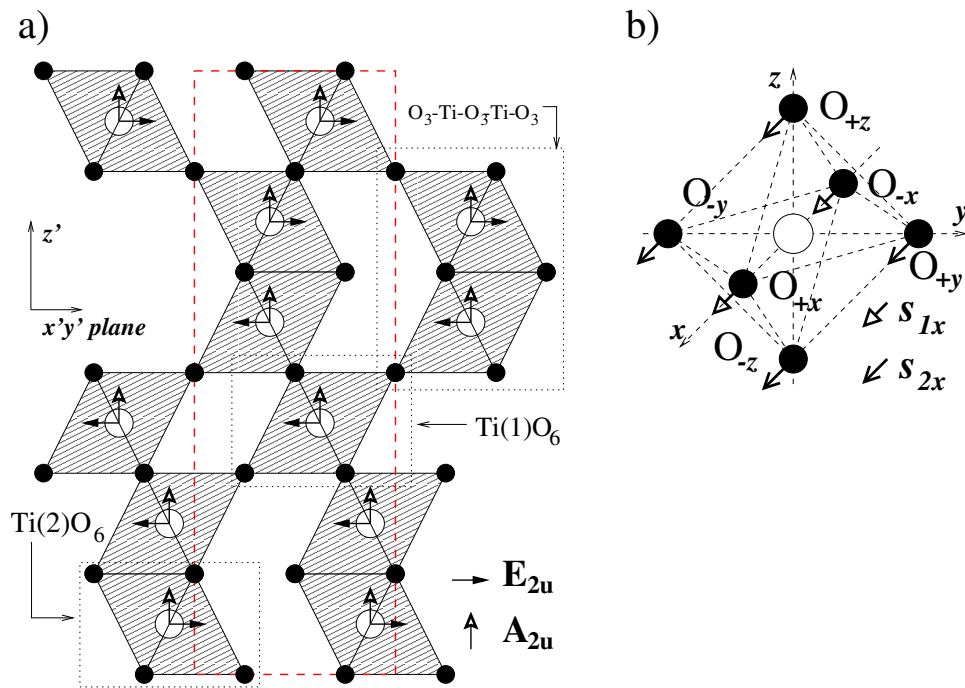
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a)

b)

Figure 1. Panel (*a*): Symbolic representation of the unit cell (broken-line box) of h-BT. Ti and O ions are depicted by empty and full circles respectively. For clarity, only 4 of the 6 O ions in the octahedra are drawn, and Ba ions are not shown. The distributions of local dipoles corresponding to the E_{2u} and A_{2u} soft modes are indicated. Panel (*b*): Polar (vector like) deformations of the $m3m$ (regular) octahedra of c-BT. Only the modes polarized along x are indicated. The y and z sets are analogous.

h-BT is indeed characterized by the same distortions of the TiO_6 octahedra that are relevant in c-BT, leading to similar chains of dipoles in the hexagonal structure.

In h-BT, the optical modes found experimentally to be soft are: a zone-centre instability that drives the phase transition at 222 K and transforms according to the E_{2u} irreducible representation (irrep) of $6/mmm$, and an A_{2u} ferroelectric mode that softens (though remaining stable) in the temperature range of the $C222_1$ phase and is responsible for the giant LO–TO splitting. Our calculations agree with this experimental evidence. We performed a full *ab initio* (the technical details are essentially the same as those in [7]) relaxation of the thirty-atom h-BT structure, resulting in lattice parameters $a = 10.68$ and $c = 26.053$ a.u. (to be compared with experimental values of 10.77 and 26.451 [8], respectively). The five free internal coordinates are also in excellent agreement with the experimentally determined ones (within 1%). After computing the force-constant matrix at Γ and diagonalizing it within the subspaces of the appropriate symmetries, we found an unstable E_{2u} mode and a low-energy but not unstable A_{2u} mode. (The fact that the A_{2u} mode is very close to being unstable could be particularly relevant for the phase transition at 74 K.)

A first analysis of the eigenvectors for both modes reveals that the Ba contribution is small (around 10% of the total mode norm, compared to 4% in the perovskite soft mode). Moreover, we confirmed that if the Ba ions are frozen at their high-symmetry positions the modes are still soft, so we do not consider them in the following discussion, and focus on the distortions of the TiO_6 groups. To make the comparison to the perovskite quantitative, let us consider the polar

deformations of the TiO_6 groups of c-BT. These are shown in figure 1(*b*), where we assume that the Ti ion is located at the origin of coordinates, so only the displacement patterns of the O ions need to be considered. For each spatial direction $\alpha = x, y, z$ we have two symmetry-adapted distortions denoted by $\hat{s}_{1,\alpha}$ and $\hat{s}_{2,\alpha}$ and transforming according to the T_{1u} (vector like) irrep of $m3m$, the point group of the regular octahedra of c-BT. For example, in terms of this basis, the tetragonal ferroelectric distortion in c-BT along x can be written as $0.69\hat{s}_{1x} + 0.73\hat{s}_{2x}$, with the distorted octahedra exhibiting point group symmetry $4mm$. In h-BT there are two kinds of octahedra: those centred around Ti ions at $2a$ Wyckoff positions with $\bar{3}m$ point symmetry (denoted by $Ti(1)O_6$ in figure 1 (*a*)) and those arranged around Ti ions at $4f$ Wyckoff positions with $3m$ point symmetry ($Ti(2)O_6$). The octahedra in the first set are coordinated in the same way as in c-BT, i.e., by sharing O ions with six other octahedra. Those in the second set are linked to other $1 + 3$ octahedra by sharing one O_3 face and single O ions, respectively. Due to the low (as compared to the case of c-BT) symmetry of the octahedra in h-BT, their distortions associated to general E_{2u} and A_{2u} modes can be decomposed in a relatively large number of symmetry-adapted displacement patterns. Among all the possible ones, we restrict ourselves to those of c-BT type and check if they can actually account for the structure of the low-energy modes. For instance, a general A_{2u} distortion leads the crystal to a phase with space group $P6_3mc$, in which the $Ti(1)O_6$ groups reduce their point symmetry to $3m$ (see table 1). As shown in figure 2(*b*), c-BT type distortions in the $s_{ix} = s_{iy} = s_{iz}$ component combination (Ti ions moving towards O_3 faces as in the rhombohedral phase of c-BT) produce this symmetry breaking. In the case of an E_{2u} distortion, the $Ti(1)O_6$ groups reduce their point symmetry to 2, and the appropriate c-BT mode has the form $s_{ix} = -s_{iy}$ (orthorhombic), as shown in figure 2(*c*).
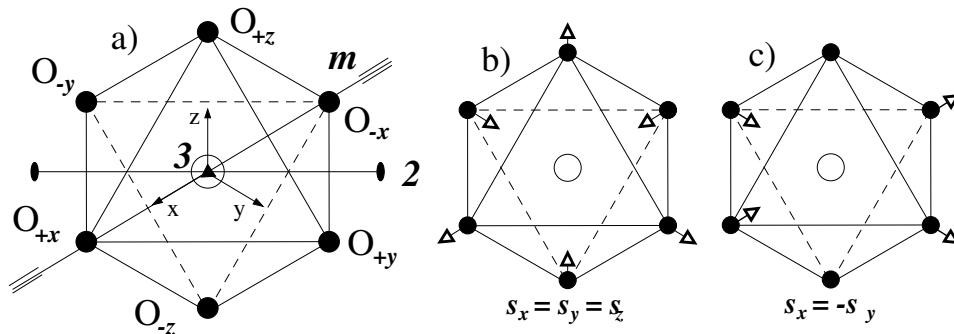

Figure 2. Combinations of $\hat{s}_{i,\alpha}$ modes that represent the symmetry breaking of the octahedra in h-BT by the soft modes. Panel (*a*) shows a conveniently oriented octahedron which will be assumed to have $\bar{3}m$ (resp. $3m$) symmetry. Oxygen ions are labelled as in figure 1(*b*) and the cartesian axes with origin in the Ti ion are indicated. Panel (*b*) shows the $s_x = s_y = s_z$ distortion that breaks the 2-fold axes (resp. no symmetry element) and is related to the A_{2u} mode. In panel (*c*), a $s_x = -s_y$ distortion results in a 2 (resp. 1) point-symmetry, which applies to the E_{2u} mode. Only $\hat{s}_1$ modes are shown, but the same combinations apply to $\hat{s}_2$.

For the two soft modes of h-BT, we considered separately the various classes of octahedra, computed from our *ab initio* eigenvectors the displacement of the O ions relative to the Ti ion, and performed a projection of the resulting distortion field into the c-BT type symmetry-adapted modes. The results (last column of table 1) present two main features: first, almost 100% of the total structural change associated with both soft modes can be described in terms of the c-BT type polar distortions (normalization is chosen in such a way that, for instance, for the first row in table 1 we have $(0.62^2 + 0.78^2) \times 100 = 99.3\%$). Second, the components

Table 1. Symmetry breakings of the h-BT phase TiO_6 groups caused by the A_{2u} and E_{2u} soft modes. The fourth column shows the combinations of symmetry-adapted c-BT type distortions that are compatible with the symmetry reduction (it applies to both s_1 and s_2). The last column shows the projections of the normalized total distortion of the TiO_6 groups onto the $\hat{s}$ modes of the second column, in the form s_1; s_2. The E_{2u} mode removes all symmetry elements from the $Ti(2)O_6$ octahedra, and any combination of s_α is possible. For this case we have listed in the last column the s_1 and s_2 projections along each of the three spatial directions as well as the modulus.

Mode	Octahedra type	Final symmetry	$s_{i,\alpha}$ distortion	Projection components
E_{2u}	$Ti(1)O_6\bar{3}m$	2	$s_x = -s_y$	0.62; 0.78
	$Ti(2)O_63m$	1	s_x, s_y, s_z	0.05; 0.01 (x)
				0.44; 0.50 (y)
				0.51; 0.53 (z)
				0.68; 0.73
A_{2u}	$Ti(1)O_6\bar{3}m$	$3m$	$s_x = s_y = s_z$	0.67; 0.70
	$Ti(2)O_63m$	$3m$	$s_x = s_y = s_z$	0.63; 0.74

s_1; s_2 are always similar in magnitude to those of c-BT (0.69; 0.73) and present a positive s_1/s_2 ratio, which implies that the O_6 octahedral cage moves almost rigidly relative to the Ti ion also in h-BT. Using the Berry's phase approach [9], we have computed the Born effective charge associated with the ferroelectric A_{2u} soft mode and found it unusually large ($Z^* = 11.29$), which further confirms the relation with the (rhombohedral) ferroelectric instability of c-BT (for which $Z^* = 9.956$).

We have proved then that at a local level the soft modes in h-BT can be described by the same distortion vectors that determine the c-BT polar instability. In the crystal as a whole, these local polar distortions lead to chains of dipoles, which suggests that the E_{2u} instability and the softness of the A_{2u} mode of h-BT are caused by Coulomb destabilizing forces, as happens in the cubic perovskite. The ferroelectric A_{2u} soft mode, polarized along z', is roughly depicted in figure 1(a). In the E_{2u} distortion the chains of dipoles lay on the $x'y'$ plane and alternate in orientation with a zero net polarization. From first-principles studies of the c-BT phase it is known that parallel dipole chains are weakly coupled, so that a transverse modulation of a chain-like instability is not energetically relevant, and, therefore, unstable TO normal modes exist almost in the whole Brillouin Zone (BZ) [10]. (The only exception are k points near $k_R = \frac{2\pi}{a}(1, 1, 1)$, for which we have an anti-phase modulation of the Ti displacements (Ti$\Rightarrow$O$\Leftarrow$Ti–O) in the three spatial directions, so the long-range destabilizing forces are always cancelled.) If this view is taken to its logical conclusion, we could expect to find more zone-centre soft modes in h-BT, corresponding to the other possible distributions of chains of dipoles. Table 2 enumerates all the possibilities. Apart from the already discussed A_{2u} and E_{2u} modes, our *ab initio* calculations show that there is one E_{1g} mode that is indeed rather low in energy, while the ferroelectric E_{1u} and the E_{2g} modes that are dominated by the movement of Ti ions are quite hard. In order to explain this result, let us remark that for the E_{2u} and A_{2u} soft modes the distortion is such that if an O ion is approached by one of its two Ti neighbours the second Ti ion moves away from it. This reflects the hybridization of the Ti $3d$ and O $2p$ electronic states, which has been shown to be essential for the occurrence of the c-BT ferroelectric instability [11]. It can be checked that any other zone-centre arrangement of the chains of dipoles results in either two Ti ions approaching one O ion (for example, if the two Ti ions in one of the $O_3-Ti-O_3-Ti-O_3$ groups depicted in figure 1(a) move in the same way in the $x'y'$ plane, there is at least one oxygen of the shared face that is approached by

Table 2. Symbolic description of the possible zone-centre chains of dipoles in h-BT, classified in terms of irreps of $6/mmm$. The layers of Ti ions are represented along the z' direction as in figure 1(a). Arrows indicate the orientation of the dipoles (horizontal ones symbolize any direction in the $x'y'$ plane), and those set in the same type are symmetry related. The superscript f marks the ferroelectric modes. The bottom line shows the mode force constants in atomic units (for B_{1g} an unambiguous assignment cannot be made).

Layer	A_{2u}^f	B_{1g}	E_{1g}	E_{1u}^f	E_{2g}	E_{2u}
Ti(2)	⇑	⇑	⇒	⇒*	⇒*	⇒
Ti(2)	⇑	⇑	⇐	⇒*	⇒*	⇐
Ti(1)	↑			→		←
Ti(2)	⇑	⇓	⇒	⇒*	⇐*	⇐
Ti(2)	⇑	⇓	⇐	⇒*	⇐*	⇒
Ti(1)	↑			→		→
	0.0074	($\geqslant$ 0.046)	0.0105	0.3305	0.2543	-0.0123

both) or in the second titanium not moving away from an oxygen. In the former case (E_{1u} and E_{2g}) the effect of the hybridization is lost and the corresponding modes are hard. In the latter (E_{1g} and B_{1g}), the hardening is not as strong. Thus, we conclude that the particular stacking of the TiO_6 groups in h-BT causes (through this local effect) the relatively high energy of some chain-like distortions.

In summary, first-principles calculations of the character of the zone-centre modes of hexagonal $BaTiO_3$ support the physically appealing idea that the experimentally relevant soft modes (including the non-polar instability) can be represented as combinations of local polar distortions transferred directly from the cubic perovskite form of the compound. Our results provide insight into the influence of the arrangement of TiO_6 octahedra on the low-energy dynamics of the structure and could be useful for the analysis of other materials composed of TiO_6 groups.

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