

# FIRST-PRINCIPLES INVESTIGATION OF $\text{SrBi}_2\text{Ta}_2\text{O}_9$

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The electronic structure of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) is investigated from first-principles, within the local density approximation, using the full-potential linearized augmented plane wave (LAPW) method. The results show that, besides the large Ta(5d)-O(2p) hybridization which is a common feature of the ferroelectric perovskites, there is an important hybridization between bismuth and oxygen states. The role played by these two covalent bonds for driving the ferroelectric instability in SBT is investigated.

Keywords: SBT, electronic structure, LDA .

$\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) is a member of the family of layered bismuth compounds. In recent years, this material has emerged as an important candidate for non-volatile ferroelectric memories [1, 2]. In spite of its technological importance, theoretical studies are limited due to the complexity of its structure. The crystal structure of SBT consists of perovskitelike ( $\text{SrTa}_2\text{O}_7$ ) slabs alternating with ( $\text{Bi}_2\text{O}_2$ ) layers. At room temperature, the structure is orthorhombic (space group  $A2_1am$ ) and the primitive cell

contains 28 atoms. The lattice parameters of the conventional unit cell are  $a = 5.531\text{\AA}$ ,  $b = 5.534\text{\AA}$  and  $c = 24.984\text{\AA}$  [3]. As a result, the ferroelectric properties are expected to be very anisotropic, and it is observed that the ferroelectricity along the  $c$  axis is absent or very low [4], being  $a$  the polar axis.

This complex structure can be described in terms of relatively small perturbations from a high-symmetry body-centered tetragonal structure (space group symmetry I4/mmm,  $a = b \approx \frac{5.53}{2^{1/2}} = 3.91\text{\AA}$ ), which contains only one formula unit per primitive cell (as in other orthorhombic structures, the  $a$  and  $b$  axes are rotated  $45^\circ$  from the tetragonal set).

Although the orthorhombic symmetry is responsible for SBT's ferroelectricity, the parent tetragonal structure shown in Figure 1 provides a convenient simplification for visualizing and dealing with the complex SBT structure. Two main distortions from the tetragonal prototype structure lead to the orthorhombic structure. First, the ions displace along the orthorhombic  $a$  axis ([110] axis of the tetragonal structure). Second, the  $\text{TaO}_6$  octahedra rotate around the  $a$  and  $c$  axes. The first factor is directly responsible for the observed macroscopic spontaneous polarization along the  $a$  direction.

The band structure of SBT was calculated by Robertson *et al.* using the tight-binding method [5]. A highly simplified orbital basis set was used to bring out the main features of the bonding. They showed that both the valence and conduction band extrema are comprised of states localized mainly on the Bi-O layer, arguing that while the Bi-O layer dominates the electronic response (band gap, effective masses, etc.), the ferroelectric response largely originates from the Sr-Ta-O perovskite blocks. Several other speculations have been made about the origin of ferroelectricity in SBT and related compounds: central role of  $\text{Sr}^{+2}$  ion displacements [6], off-center position of  $\text{Ta}^{+5}$  ion relative to its octahedron of surrounding oxygens [7], movement of the Ta-O plane relative to the Bi-O plane [3], etc.

In this work we present a first-principles study of the electronic structure and origin of ferroelectricity in SBT. The calculations were performed

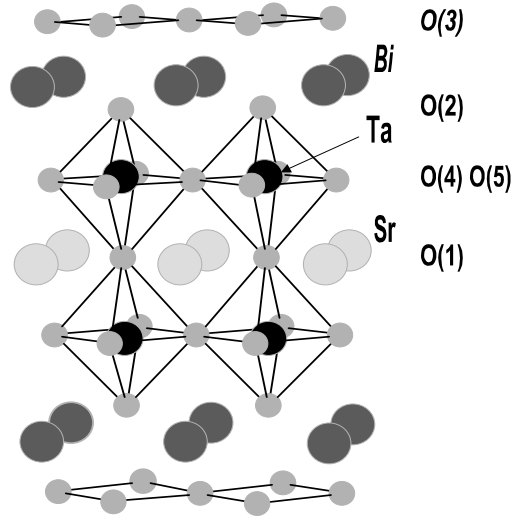


Figure 1: Tetragonal structure of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ . Only atoms between  $\frac{1}{4}c$  and  $\frac{3}{4}c$  are shown.

within the local density approximation (LDA) to density functional theory, using the full-potential LAPW method. We use the WIEN97 implementation of the method [8]. The Ceperley and Alder [9] exchange-correlation potential for the many body interactions between electrons was used.

The electronic structure of SBT is calculated for the tetragonal parent structure. The lattice constants we used are  $a = 3.91\text{\AA}$  and  $c = 24.984\text{\AA}$ . Since the internal parameters of this structure have not been determined experimentally, we evaluated the equilibrium positions of the atoms using a damping Newton dynamics method (the final force on each atom was less than  $\approx 1 \text{ mRy/a.u.}$ ).

The band structure of SBT is shown in Figure 2 along several high-symmetry lines in the Brillouin zone. Roughly speaking, the two bands centered at  $\approx -10\text{eV}$  are derived from Bi 6s orbitals while the manifold

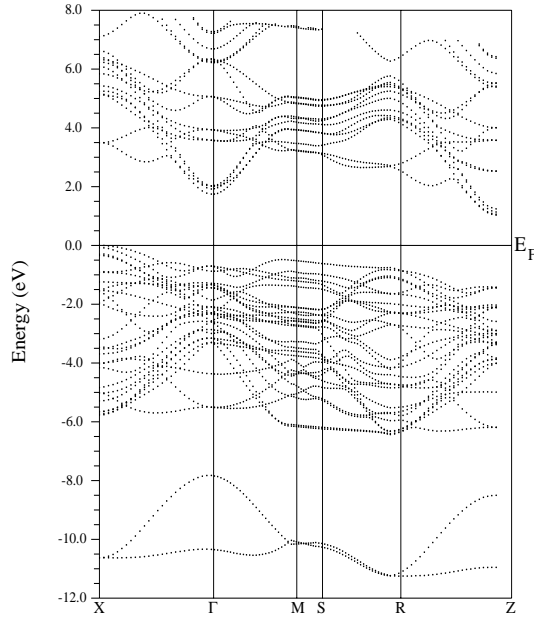


Figure 2: Band structure of tetragonal  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ .

of 27 valence bands are derived from O 2p orbitals. These are separated by an indirect (X- $\Gamma$ ) gap of  $\approx 2$  eV from the conduction bands. Although the conduction band edge is of primarily Bi 6p character, the conduction bands have strong contributions from both Bi 6p and Ta 5d states. The valence band maximum at X is of primarily O(1,4) 2p character. As is typical in LDA calculations for semiconductor oxides, the band gap is underestimated. The experimental band gap obtained from UV-absorbance measurements is  $4.2 \pm 0.2$  eV [10]. It is interesting to note that, in disagreement with our results, an indirect ( $\Gamma$ -M) band gap was obtained by the tight-binding calculation [5], which indicates important differences in the details of the dispersion.

Although the valence band presents mainly O 2p character, there is a quite strong hybridization with Bi and Ta states, as is evident from the sphere projected density of states (DOS) shown in Figure 3. Examination of the DOS reveals that there is substantial O 2p character in the conduction bands, rising from zero at the conduction band minimum with

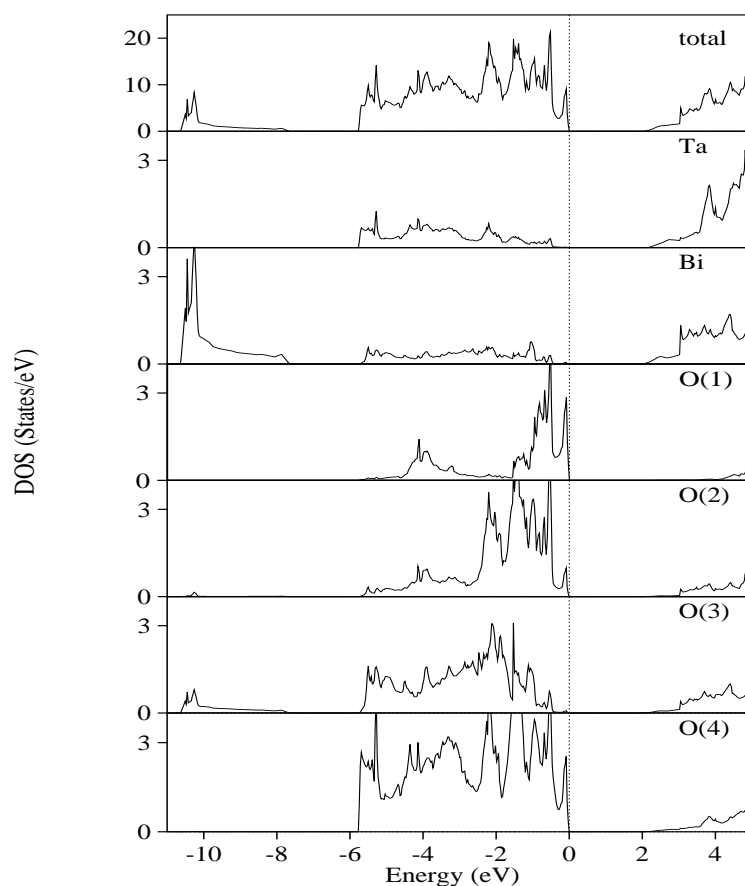


Figure 3: Total and projected electronic DOS for tetragonal  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ .

increasing energy. Conversely, there are strong Ta and Bi contributions to the valence band. The Ta 5d contribution is zero at the valence band maximum but rises strongly with decreasing binding energy, reflecting the Ta 5d-O 2p covalency (as it is common in  $\text{ABO}_3$  perovskites). The Bi contribution has both s-like (mainly in the upper part of the valence band) and p-like (mainly in the lower part) character. These contributions arise from a strong hybridization between O(2,3) 2p valence band states with Bi 6s (fully occupied) and Bi 6p (conduction) bands.

It is interesting to point out that the calculated total DOS is seen to be in reasonable agreement with XPS data, which show a valence band

Table 1: Frequencies and eigenvectors of the  $E_\mu$  modes, which are polarized perpendicular to the  $c$  axis.

Freq. ( $\text{cm}^{-1}$ )	Eigenvector							
	Sr	Ta+	Bi+	O1	O2 +	O3+	O4+	O5+
495	0.036	0.052	0.001	0.432	0.033	-0.001	-0.617	0.148
247	-0.051	0.064	0.053	-0.754	0.324	-0.205	-0.212	0.125
215	-0.032	0.053	-0.117	-0.360	-0.122	0.621	-0.113	0.073
113	-0.786	0.395	-0.026	0.019	-0.120	-0.066	-0.019	-0.122
100	0.147	0.037	0.031	0.010	0.239	0.108	-0.129	-0.634
73	0.502	0.301	-0.191	-0.232	-0.403	-0.199	-0.088	-0.103
i54	0.130	0.251	-0.489	0.213	0.360	0.035	0.147	0.120

width of  $\approx 7$  eV and a peak centered  $\approx 10$  eV below the valence band maximum (Bi 6s band) [10].

As was already highlighted by Robertson *et al.* [5], the main features of SBT described so far resembles the electronic structure of  $\text{PbTiO}_3$ . In this material, besides the large Ti 3d-O 2p hybridization, there is an important hybridization between Pb 6s and O 2p states; and this covalent bond plays a central role in the stabilization of the tetragonal ferroelectric structure of  $\text{PbTiO}_3$  [11].

The presence of quite strong Ta-O and Bi-O hybridizations in SBT opens fundamental questions about the origin of its ferroelectricity: what is the underlying static potential for the ferroelectric distortion? which is the primary source for ferroelectricity? We investigate these questions by a lattice dynamics study using a frozen-phonon approach.

To search for the presence of a possible lattice instability of the tetragonal structure, we determined the phonon frequencies and eigenvectors of the infrared active  $E_\mu$  modes, which are polarized perpendicular to the  $c$  axis. To this end, we calculated atomic forces for several small displacements ( $\sim 0.01$  Å) consistent with the symmetry of the mode. From the force as a function of displacement, the dynamical matrix was constructed and diagonalized.

The calculated frequencies and eigenvectors are listed in Table 1. Unfortunately, there is no experimental determination of phonon frequencies

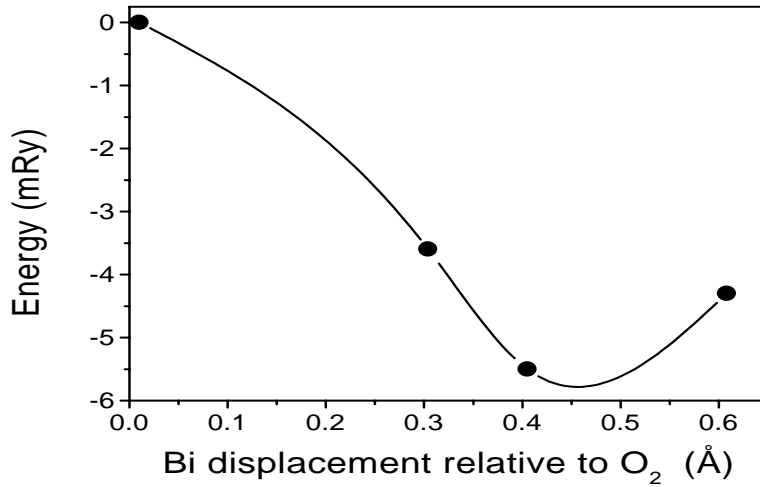


Figure 4: Energy as a function of the unstable mode distortion along the  $[110]$  direction. The normal coordinate is represented through the Bi relative to O(2) ionic shifts. The energies are referred to the perfect tetragonal structure.

for the tetragonal structure to compare with. The remarkable fact, however, is the presence of one unstable phonon mode. Roughly speaking, this mode mainly involves displacements of the Bi atoms with respect to rest of the lattice. Actually, its displacement pattern is (0.085, 0.114, -0.206, 0.325, 0.549, 0.053, 0.224, 0.182), showing large displacements of the  $\text{TaO}_6$  perovskitelike blocks relative to Bi atoms. This pattern is obtained from the eigenvector by dividing each component by the square root of the corresponding atomic mass and then normalizing to unity. So, the polarity of the mode can be described as a movement of the  $\text{TaO}_6$  perovskitelike block relative to Bi, with an additional contribution arising from the movement of Ta relative to its surrounding oxygens. Rae et al. [3] argued that the polarity of orthorhombic SBT can be quite well described as a movement of Ta, O(4) and O(5) relative to Bi and O(3) of the  $\text{BiO}_2$  layer with an additional movement of Ta relative to O(4) and O(5). Although the displacement pattern of the unstable mode is not directly related with the atomimic positions of the orthorhombic phase,

both pictures show some consistence.

Finally, the total energy is evaluated as a function of the unstable mode displacement pattern along the [110] direction. The result is shown in Figure 4. This figure shows the energy per formula unit as a function of the relative displacement of Bi with respect to O2. A ferroelectric instability with an energy lowering of  $\approx 5.7$  mRy/cell is observed. It is possible to conclude, from a detailed analysis of the calculated force constants, that such lattice instability primarily arises from the attractive Bi-O(2) interaction. Whether the origin of this attractive interaction is pure Coulombic or not deserves a detailed analysis which will be presented in a forthcoming paper.

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### References

- [1] C.A.Paz de Araujo, J.D.Cuchiaro, L.D.McMillan, M.C.Scott and J.F.Scott , Nature, **374**, 627 (1995).
- [2] O.Auciello, J.F.Scott and R.Ramesh , Physics Today, **51(7)**, 22 (1998).
- [3] A.D.Rae, J.G.Thompson and R.L.Withers, Acta Cryst., **B48**, 418 (1992).
- [4] S.B.Desu, D.P.Vijay and B. He, Appl. Phys. Lett., **69**, 1719 (1996).
- [5] J.Robertson, W.Chen, W.L.Warren and C.D.Gutleben , Appl. Phys. Lett., **69**, 1704 (1996).
- [6] J.Lui, G.Zou, H.Yang and Q.Cui, Solid State Comm., **90**, 365 (1994).
- [7] R.E.Newnham, R.W.Wolfe, R.S.Horsey, F.A.Diaz-Colon and M.I.Kay, Mater. Res. Bull., **8**, 1183 (1973).
- [8] P. Blaha, K. Schwarz, P. Dufek and R. Augustyn, WIEN97, Technical University of Vienna 1997. (Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin and S.B. Trickey, Comput. Phys. Commun., **59**, 399 (1990).
- [9] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett., **45**, 566 (1980).
- [10] A.J.Hartmann, R.N.Lamb, J.F.Scott and C.D.Gutleben, Integ. Ferroelec., **18**, 101 (1997).
- [11] R.E.Cohen, Nature, **358**, 136 (1992).