

## PAPER DETAILS

TITLE: CALCULATION OF ELECTRONIC BAND STRUCTURE OF FERROELECTRIC  
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# Calculation of Electronic Band Structure of Ferroelectric Semiconductor Bismuth Niobium Oxyfluoride ( $\text{Bi}_2\text{NbO}_5\text{F}$ ) Crystal

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## ABSTRACT

In this study, the geometric structural optimization, electronic band structure and density of states (DOS) for electrons of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  structure with space group  $\text{Pca}2_1$  have been investigated using the density functional theory (DFT) under the local density approximation (LDA). The ground state properties of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  structure are studied. The computed ground state properties and experimental results are consistent. The energy band structure of  $\text{Bi}_2\text{NbO}_5\text{F}$  compound below  $T_c$  shows that it is a ferroelectric semiconductor with narrow band gap of 0.0589 eV. Unfortunately, there is neither experimental nor theoretical electronic band structure study of  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal in the literature, so we could not compare our results.

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**Keywords:** Density functional theory; Electronic band structure; Optical properties.

## 1. INTRODUCTION

Aurivillius compounds are in a class of layered bismuth oxide crystals. Aurivillius materials were first investigated using X-ray diffraction by Aurivillius in 1952 [1]. Aurivillius defined the crystal structures such as  $\text{Bi}_2\text{TiO}_4\text{F}$ ,  $\text{Bi}_2\text{NbO}_5\text{F}$  and  $\text{Bi}_2\text{TaO}_5\text{F}$ . Previously, the structures of Aurivillius oxide-fluoride compounds were investigated only with X-ray diffraction [1]. Later, using X-ray diffraction, neutron powder diffraction and electron diffraction, the structures of Aurivillius layered bismuth oxides crystals were investigated in different structural phases [2, 3]. Many of these crystals exhibit ferroelectric properties [4]. The ferroelectric crystal structures are prevalent in scientific and technological areas due to their electro-optic and electro-mechanic

properties, non-linearity and large dielectric constants. Large numbers of ferroelectric materials are being used in areas such as sensor applications, optical devices and optical memories. For example, widespread commercial optical devices are mainly ferroelectric optical devices. In fact, there has been an effort toward the production of ferroelectric optical films recently. The  $\text{Bi}_2\text{TaO}_5\text{F}$  structure has been reported in orthorhombic space group  $\text{Pca}2_1$  showing polar properties below  $T_c$  [5]. It was demonstrated that the  $\text{Bi}_2\text{TaO}_5\text{F}$  phase structure was ferroelectric at Curie temperatures of 284 K [6] and it has a polar phase at room temperature in space group  $\text{Pca}2_1$  [1]. In contrast to this phase, other phases of  $\text{I4/mmm}$  and  $\text{Pbca}$  are non-polar [1]. Formation of solid solutions in the  $\text{Bi}_2\text{W}_{1-x}\text{Nb}_x\text{O}_{6-x}$  and  $\text{Bi}_2\text{W}_{1-x}\text{Ta}_x\text{O}_{6-x}$  ( $0 < x < 1$ ) compounds was reported in detail and the

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effects of Ta and Nb on these crystals were investigated [7]. Lai *et al.* studied effects of N- and Mo- monodoped and N/Mo-codoped on electronic structure of  $\text{Bi}_2\text{WO}_6$  compound using first-principles calculations [8]. Voronkova *et al.* reported the physical properties such as polymorphism, synthesis, electrical conductivity and dielectric properties of  $\text{Bi}_2\text{W}_{1-x}\text{Mo}_x\text{O}_6$  ( $0 < x < 1$ ) [9]. Kharitonova *et al.* investigated phase transition and electrical properties of Ga and In doped  $\text{Bi}_{10}\text{Ti}_3\text{W}_3\text{O}_{30}$  [10]. Tsujimoto *et al.* reviewed recent progress of bismuth oxyfluoride perovskite of Aurivillius type perovskite families [11].

There were only a few studies for this compound in literature. Therefore, investigation of physical properties such as structural optimization, DOS and electronic band structure of  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal showing ferroelectric property in space group  $\text{Pca}2_1$  at room temperature is main subject of our article.

## 2. RESULTS AND DISCUSSION

### 2.1. Method

ABINIT software based on the ab-initio method can be applied under different approaches. One of these approaches based on DFT is LDA [12]. The success of this approximation has been confirmed from the investigated studies. We used ABINIT package [13] based on DFT under LDA for calculations. The structural optimization, electronic band structure and total density of states of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  structure are calculated using Ceperley-Alder Perdew-Wang LDA functional (CAPW-LDA-1992) format produced self-consistent norm-conserving pseudo-potentials. For electronic wave functions, the plane wave basis sets are used. Kohn-Sham equation solutions [14] were done with the ABINIT software. Both in production of pseudopotential and band structure calculations, the exchange-correlation effects in LDA are taken into account. For Bi:  $6s^2 6p^3$ , for Nb:  $4d^4 5s^1$ , for O:  $2s^2 2p^4$  and for F:  $2s^2 2p^5$  were considered as the true valence. To be consistent with the experimental study, the calculations of structural optimization should be done first. It is crucial to know total energy of a material because all physical properties of materials are related to total energy. If the total energy of a material is, somehow, calculated, then any physical quantity depending on total energy can be obtained.

### 2.2. STRUCTURAL OPTIMIZATION

The unit cell of orthorhombic  $\text{Bi}_2\text{NbO}_5\text{F}$  contains thirty-six atoms of which the positions are given in table 1. To calculate the electronic band structure and DOS of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  orthorhombic crystal, we

performed structural optimization. First of all, total energy was optimized with respect to cut-off energy and given in figure 1. As seen in figure 1, total energy converges about 35 Ha of cut-off energy value. All calculations were carried out using this cut-off energy.

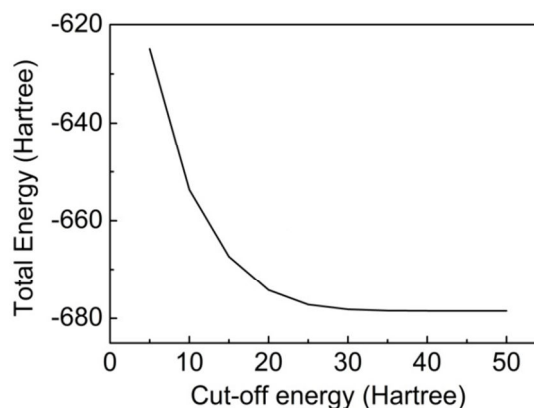


Figure 1. Cut-off energy-total energy optimization for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal.

In many theoretical calculations, we have to integrate over wave vector in Brillouin zone. This is considerably a difficult job. However, instead of too many k points, since the values of k points close to each other are the almost same in Brillouin zone, a few k points are sufficient. Therefore, instead of integrating over the all Brillouin zone, applying integration over certain k points will be enough. Secondly, the obtained value of the cut-off energy was used to optimize numbers of k point. Increasing k point mesh from  $2 \times 2 \times 2$  to  $12 \times 12 \times 12$ , total energy corresponding k point numbers were calculated and given in figure 2, in which total energy converges about 27 k point numbers and  $6 \times 6 \times 6$  k point mesh. All calculations were performed using 27 k point numbers in Brillouin zone.

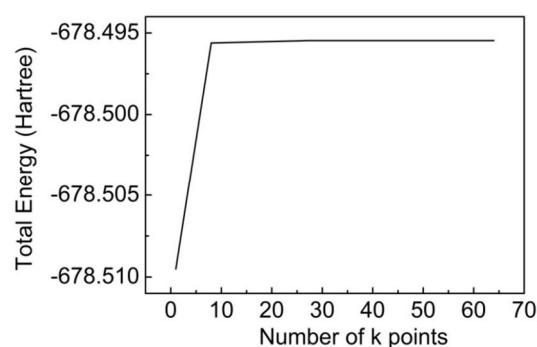


Figure 2. Number of k points-the calculated total energy graph for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal.

Table 1. Crystal structure data of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal.

Space group			Pca2 <sub>1</sub> (29)				
$\text{Bi}_2\text{NbO}_5\text{F}$	Calculated (LDA)	Experimental [2]	Atom	Wyckoff	x	y	z
$a$ (Bohr)	10.176	10.2555	Bi1	4a	0.511	0.4228	0.000
			Bi2	4a	0.479	0.0748	-0.009
$b$ (Bohr)	31.3996	31.4791	Nb	4a	0.009	0.2464	0.000
$c$ (Bohr)	10.2574	10.2574	O1	4a	0.004	0.1340	0.063
			O2	4a	0.244	-0.001	0.254
			O3	4a	0.264	0.5059	0.254
			O4	4a	0.713	0.2288	0.227
Volume (Bohr) <sup>3</sup>	3252	3311	O5	4a	0.210	0.2490	0.310
$E_g$ (eV)	0.0589	unknown	F	4a	0.539	0.3685	0.525

Thirdly, the obtained value of cut-off energy and the calculated k point numbers were used for total energy versus volume optimization. To find the equilibrium lattice constants of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal compound, the total energy of the crystals for different lattice constants were calculated. The total energy-volume graph is given in figure 3. As seen in figure 3, the lattice constant of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal can be extracted from total energy-volume optimization. The obtained values of lattice constants are corresponding to the most stable total energy. All obtained results of the physical properties of  $\text{Bi}_2\text{NbO}_5\text{F}$  in orthorhombic phase are given in table 1. As seen in table 1, calculated ground state properties and experimental results are consistent.

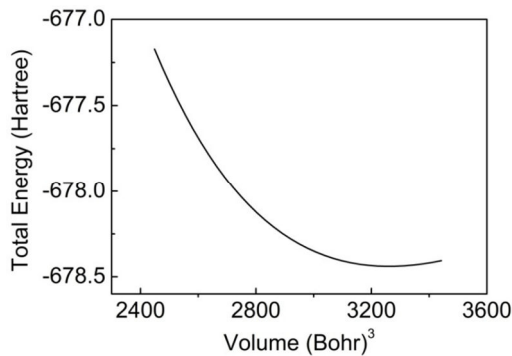


Figure 3. Volume-total energy graph for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$ .

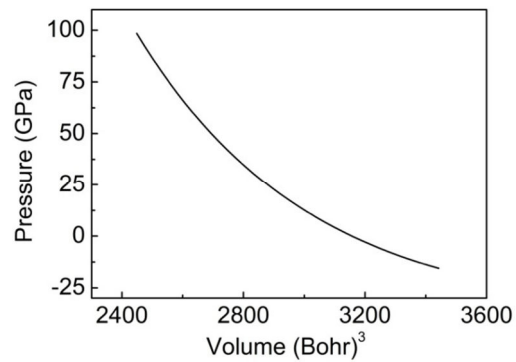


Figure 4. Pressure-volume graph for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$ .

Then, pressure-volume and total energy-pressure graphs of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal are given in figure 4 and figure 5, respectively. Figure 4 shows calculated pressure as a function of volume of unit cell for this crystal, which is about the calculated total energy as a function of pressure of unit cell for this compound.

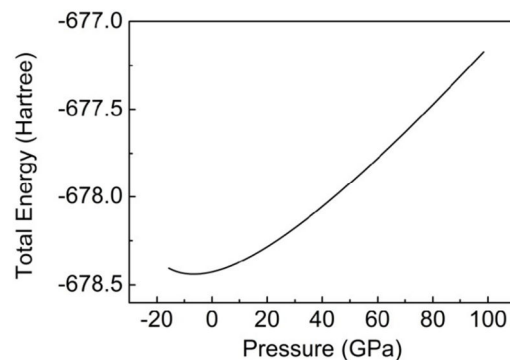


Figure 5. Pressure-total energy graph for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$ .

### 2.3. Electronic band structure

The energy band structure of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal corresponding to the high symmetry directions,

$\Gamma$ , Y, T, Z, X, U, R and S in the BZ are obtained using the lattice constants calculated from the equilibrium position. The energy band structure and DOS curve are plotted in figure 6 and figure 8, respectively. Ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal has 104 valence states. Additional 46 conduction states were used for band structure calculation. As seen in figure 6, energy band gap between valence and conduction bands is too small. Thus, in order to measure the band gap value, we adjusted y axis of figure 6 and re-plotted as in figure 7. The computed results of the direct band gaps at equilibrium,  $E_{\Gamma-\Gamma}$  is 0.275,  $E_{Y-Y}$  is 0.295,  $E_{T-T}$  is 0.749,  $E_{Z-Z}$  is 0.754,  $E_{X-X}$  is 0.632,  $E_{U-U}$  is 0.733,  $E_{R-R}$  is 0.734 and  $E_{S-S}$  is 6.626. The obtained results of the indirect band gaps at equilibrium:  $E_{\Gamma-U}$  is 0.0589 and  $E_{\Gamma-R}$  is 0.0595 eV. As seen in figure 6, conduction band minimum with the valence band maximum is located at  $\Gamma$ -U symmetry points. The band structure of this crystal is indirect and value of indirect band gap is 0.0589 eV between  $\Gamma$ -U high symmetry points. Obtained result shows that the studied compound is a semiconductor crystal. In the literature, because no experimental or theoretical studies were performed to obtain band gap of  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal, we could not make any comparison.

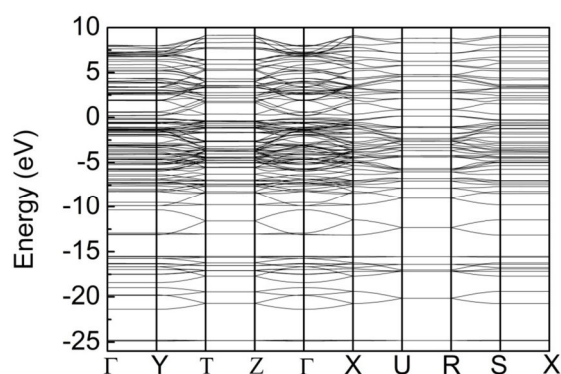


Figure 6. Band structure for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal.

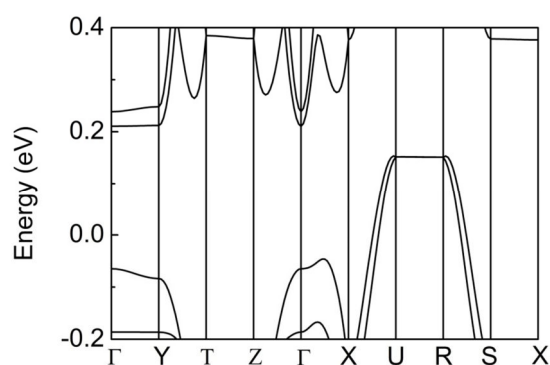


Figure 7. Enlarged band structure for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal

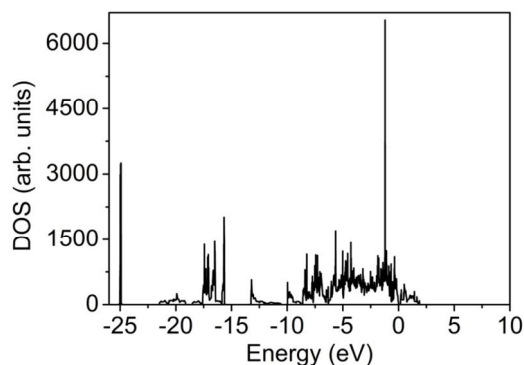


Figure 8. Density of states (DOS) for ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal.

### 3. CONCLUSIONS

In this work, we calculated the structural optimization, electronic band structure and DOS of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$  structure. We obtained the lattice constants of ferroelectric  $\text{Bi}_2\text{NbO}_5\text{F}$ . These lattice constants and experimental results are consistent. We obtained as 0.0589 eV the electronic band gap of  $\text{Bi}_2\text{NbO}_5\text{F}$  which is extremely important for more efficient technological instruments. Obtained band gap shows that the  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal is a semiconductor ferroelectric material. Since there is no work with band gap of  $\text{Bi}_2\text{NbO}_5\text{F}$  crystal, it could not be made any comparison.

### ACKNOWLEDGEMENTS

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### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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