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Ab initio study of structural, electronic and optical properties of the $Bi_{12}TiO_{20}$ sillenite crystal

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ABSTRACT

It is presented an analysis of some important structural, electronic and optical characteristics of the pure $Bi_{12}TiO_{20}$ sillenite crystal, based on the ab initio calculations of its electronic structure and complex dielectric tensor. The band gap is calculated to be 2.3 eV and found to be direct. The contributions to the valence band top and conduction band bottom come predominantly from O 2p- and Bi 6p-states, respectively. The optical absorption spectrum is calculated and interpreted in terms of electronic band structure for incident radiation energy up to 40 eV. The principal absorption occurs within the energy range from 2.5 to 10 eV, originating manly from the electronic transitions from the O 2p- to the Bi 6p-states.

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1. Introduction

Dodecabismuth titanium oxide, $Bi_{12}TiO_{20}$ (BTO) belongs to a family of sillenites crystals described by the general formula $Bi_{12}MO_{20}$ (M = Ge, Si, or Ti) [1]. These crystals are well known due to photorefractive properties, which are widely used in various optoelectronic devices [2]. The BTO crystal, particularly, has several optical properties (high electro-optical coefficients, low optical activity and high photosensitivity in the visible red region [3]) favorable for holographic interferometry applications [4], waveguides and fiber-like crystals [5]. This material has also been considered as a potential photocatalytic for the degradation of organic pollutants [6].

For holographic use of the BTO the defects play very important role providing the additional energy levels within the band gap and changing the optical properties of the pure compound. In spite of significant experimental efforts to characterize the various defect levels in the BTO and to identify their origin [7,8], it was concluded that there is no sufficient knowledge to reach conclusive picture about the photorefractive centers in this material [9]. Thus additional experimental and especially theoretical efforts must be made in order to resolve that problem. So far, however, just a few first-principles pseudo-potential calculations have been made on the pure BTO [10,11], with controversial results of its band structure and without discussing its optical properties. In the Ref. [10] the authors claim that the lowest unoccupied states of the BTO consist of the Ti-3d states, while in the Ref. [11] the authors characterize the conduction band bottom as a mixture of the Bi 6p- and the Ti-3d states.

In this paper we present the first principles calculations of the structural, electronic and optical properties of the pure BTO crystal, as a first and necessary step towards the future investigation of the impurity effects in the material. Our calculations were performed with the spin–orbit (SO) interaction taken into account. This relativistic effect is important for correct description of band structure and optical spectra of materials containing heavier elements (such as the Bi), as we demonstrated recently in the case of $Bi_4M_3O_{12}$ (M = Ge, Si) compounds [12]. The lattice parameters and atomic positions were computationally optimized by total energy minimization. We analyzed the BTO electronic structure, and on this basis determined its complex dielectric tensor as a function of the incident radiation energy up to 40 eV (far ultraviolet region), being able to identify the electronic transitions that govern the optical absorption.

2. Calculation details and structure optimization

The self-consistent calculations of pure BTO compound were performed by density-functional theory (DFT) [13] based, full potential linear augmented plane wave (FP-LAPW) method [14] as embodied in WIEN2k computer code [15]. In this method, the electronic wave functions, charge density and crystal potential are expanded in spherical harmonics inside the non-overlapping spheres centered at each nuclear position (atomic spheres with radii R_{MT}), and in plane waves in the rest of the space (interstitial region). The

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choice for the atomic sphere radii (in atomic units) was 2.3 for Bi, 1.8 for Ti and 1.4 for O. Inside atomic spheres the partial waves were expanded up to $l_{\max} = 10$, while the number of plane waves in the interstitial was limited by the cut-off at $K_{\max} = 7.0/R_{\mathrm{MT}}$. The charge density was Fourier expanded up to $G_{\max} = 14$. A mesh of 7 k-points in the irreducible part of the Brillouin zone was used. Exchange and correlation effects were treated by generalized-gradient approximation (GGA96) [16]. The Bi 5d, 6s, 6p, the O 2s, 2p, and the Ti 3s, 3p, 4s, 3d electronic states were considered as valence ones, and treated within the scalar-relativistic approach, whereas the core states were relaxed in a fully relativistic manner. The spin–orbit coupling has been taken into account for the heavy Bi atoms via a second variational procedure using scalar-relativistic eigenfunctions as basis [14]. This procedure consists of two steps in each iteration cycle. In the first one, the scalar-relativistic part of the Hamiltonian is diagonalized and scalar-relativistic eigenstates obtained. In the second step, some of these eigenstates (with lowest energy) are used to calculate a Hamiltonian matrix with spin–orbit term included. Diagonalization of this matrix finally gives the spin–orbit eigenvalues and eigenstates which are confined within atomic sphere.

The optical response of the BTO was determined by calculating its complex dielectric tensor ε. Imaginary part of this tensor is proportional to the optical absorption spectrum of the material. It can be computed from knowledge of the electronic band structure. In the limit of linear optics, neglecting electron polarization effects and within the frame of random phase approximation, the expression for the imaginary part of ε is the following [17]:

$$Im\,\varepsilon_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_{i,f} \int_{BZ} \frac{2dk}{(2\pi)^3} |\langle\varphi_{fk}|P_\beta|\varphi_{ik}\rangle||\langle\varphi_{fk}|P_\alpha|\varphi_{ik}\rangle| \cdot \delta(E_f(k) - E_i(k) - \hbar\omega) \tag{1}$$

for a vertical transition from a filled initial state $|\varphi_{ik}\rangle$ of energy $E_i(k)$ to an empty final state $|\varphi_{fk}\rangle$ of energy $E_f(k)$ with the same wave vector k. ω is the frequency of the incident radiation, m the electron mass, P the momentum operator, and α and β stand for the projections x, y, z. We computed the $Im(\varepsilon)$ up to incident radiation energy of $\hbar\omega = 40$ eV, with a mesh of 45 k-points in the irreducible wedge of the first Brillouin zone. Owing to the cubic symmetry the dielectric tensor is diagonal, with $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon$. Thus, in this particular case, it is reduced to scalar function $\varepsilon(\omega)$.

The crystal structure of the BTO exhibits a cubic symmetry, space group I23. The BTO unit cell contains one formula unit (33 atoms), without having a center of inversion. We started our calculations by optimizing the structure of this unit cell, i.e. its lattice parameter and positions of atoms within it, in order to reach the structure that corresponds to energy minimum in our computer experiment. The lattice parameter a is optimized by varying unit cell volume (a^3) and calculating total energy for each volume considered. The results are then plotted on a graph representing energy versus volume of the unit cell. The equilibrium lattice constant is determined from the minimum of this curve. As the point of the minimum was well resolved, no fitting procedure (as Birch–Murnaghan, for example) has been applied. The relaxation of the lattice parameter resulted in $a = 10.322$ Å, the value that corresponds to the 4% larger unit cell volume than determined by the experiment realized at the ambient temperature [1]. All atomic positions inside this unit cell were then optimized by moving the atoms according to forces which act on them (damped Newton scheme), and obeying the symmetry constraints of the space group. The procedure has been performed until these forces became less than 2.0 mRy/a.u. The resulting interatomic distances Bi–O and Ti–O are shown in Table 1. Each Bi ion is coordinated with seven oxygens at different distances, forming an irregular polyhedron. The Ti atoms are surrounded by four oxygens, all at the same distance, arranged in a perfect tetrahedron. We found the calculated values in good agreement with the experimental data [1], since the average values of the Bi–O and Ti–O bond lengths are only 1% and 3% bigger than experimental ones, respectively.

Table 1
Calculated interatomic distances (Å) within the first coordination sphere of Bi (7 O's) and Ti (4 O's), compared with the experimental data at ambient temperature [1]. The numbers in parenthesis denote a number of oxygens which refer to the given distance.

Nearest-neighbour distance	Theory (this work)	Experimental (Ref. [1])
Bi–O (1)	2.063	2.163
Bi–O (1)	2.234	2.205
Bi–O (1)	2.304	2.206
Bi–O (1)	2.592	2.514
Bi–O (1)	2.788	2.622
Bi–O (1)	2.968	3.131
Bi–O (1)	3.352	3.370
Ti–O (4)	1.842	1.809

3. Electronic structure

The Fig. 1 shows the calculated total density of states (TDOS) of the BTO. Band gap is found to be 2.3 eV, which is underestimated in comparison with the experimental values of 2.4, 2.8 and 3.2 eV estimated from the optical absorption thresholds [6,18] and photoconductivity experiment [9], respectively. The wrong size of the calculated gap is due to a well known effect of the GGA approximation implemented in the DFT. This discrepancy arises from the fact that GGA treats the exchange and correlation effects only approximately. In insulator materials, the correlation effects tend to be weaker than in electron gas, which GGA uses to estimate correlation energy of the electron system. Therefore, the calculated band gap of insulators is usually underestimated in comparison to the experiment [19]. The top of the valence band (−5 to 0 eV) is formed mainly from the O-2p and the non-bonding portion of the Bi-6s-states, but with dominancy of the O-2p states. This band has also a very little contribution of the Ti-3d states. The bonding portion of the Bi-6s states is concentrated within the isolated band centered at −9 eV, similarly to the case of the $Bi_4M_3O_{12}$ (M = Ge,Si) compounds [12]. The bands in the lower energy part of the TDOS spectrum are dominated by the Ti s- and p-states, O-2s states, and the Bi-5d states, which are split into the $j = 3/2$ and 5/2 components due to effect of the spin–orbit interaction. Above the Fermi level, the conduction band consists of two distinct blocks. The lower energy one (2.3–7.5 eV) accommodates mostly the Bi-6p states. These states are split into the $j = 1/2$ and $j = 3/2$ components, caused by the effect of SO coupling. The Bi-$6p_{1/2}$ component dominates the lower energy part (2.3–4.3 eV) of the block, while the upper part (4.3–7.5 eV) is composed of the Bi $6p_{3/2}$ states mixed with significant contribution of the Ti-3d states. The higher energy part of TDOS (above 9 eV) consists of the hybridized Bi-6p, O-2p and the Ti-3d states. Our results for the BTO electronic TDOS disagree with the results published in Ref. [10] in which the authors claim that the conduction band bottom is composed of the Ti-3d states. Instead, our calculated TDOS is very similar to that published in the Ref. [11].

The structure of electronic bands of the BTO crystal in the vicinity of the fundamental gap is shown in the Fig. 2. It is seen that the conduction band has its energy minimum at the same point Γ in the Brillouin zone as the energy maximum of the valence band. Thus, the band gap in the BTO crystal is found to be direct. The previous band-structure calculations [11], however, predicted an indirect band gap in the BTO (conduction band minimum at the Γ, and valence band maximum at the H point). The reason for this

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