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The first-principles study of electronic and optical properties of BGO and BSO scintillators

M.V. Lalic *, S.O. Souza

Universidade Federal de Sergipe, Departamento de Física, P.O. Box 353, 49100-000 São Cristóvão, SE, Brazil

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Abstract

In this paper we present electronic and optical properties of two important scintillating materials: the $Bi_4Ge_3O_{12}$ (BGO) and the $Bi_4Si_3O_{12}$ (BSO). These properties were calculated by first-principles, density-functional theory based full potential augmented plane wave method. We discuss the differences between the band structures and optical constants of the BGO and BSO, and analyze the process of absorption of the radiation energy in these materials. Our results indicate that the major part of this energy is absorbed by the O p-electrons and then transferred to the Bi p-electrons.

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1. Introduction

The bismuth ortho-germanate $Bi_4Ge_3O_{12}$ (BGO) and bismuth ortho-silicate $Bi_4Si_3O_{12}$ (BSO) are technologically important materials owing to their remarkable characteristics such as fast luminescent decay constant, large light output and radiation hardness [1,2]. Both are used as high-efficient scintillators in gamma ray spectroscopy and high energy physics, and widely applied in non-linear optical devices and nuclear medicine (X-ray and positron computer tomography) [3–5].

The BGO and BSO crystallize in the same cubic structure, known as eulytite. Although resembling in many aspects, they exhibit differences in some of the key scintillation properties: BSO has faster response but smaller light output then BGO, for example [6]. Thus the BSO is preferably used for some applications and BGO for others [7,8].

The theoretical studies of BGO and BSO, however, face difficulties due to complexity of their crystal structure (38 atoms in primitive unit cell, absence of the inversion symmetry). This is the main reason why no theoretical calculations considering a full crystal structure has been reported so far.

In this paper we present such calculations for the first time. It is the first-principles study of pure BGO and BSO crystals, in which the whole crystal structure was taken into account. We calculated and compared the electronic structures of both compounds, and on this basis determined their complex dielectric tensors. Then we calculated their optical constants as a function of the incident radiation energy. By analysis of obtained results we were able to clarify the process of optical absorption in BGO and BSO. Our conclusion is that the oxygen atoms absorb the energy of incoming radiation, and then transfer it to Bi ion which is the luminescent center in both materials.

2. Calculation details and structure optimization

The self-consistent band-structure calculations of pure BGO and BSO compounds were performed by density-functional theory based [9], full potential linear augmented plane wave (FP-LAPW) method [10] as embodied in WIEN2k computer code [11]. In this method, the electronic

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* Corresponding author.
E-mail address: mlalic@fisica.ufs.br (M.V. Lalic).

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wave functions, charge density and crystal potential are expanded in spherical harmonics inside the non-overlapping spheres centered at each nuclear position (with radii R_{MT}), and in plane waves in the rest of the space (interstitial region). The choice for the atomic sphere radii R_{MT} (in atomic units) was the following: 2.3 for Bi, 1.8 for Ge and 1.45 for O, in case of BGO, and: 2.3 for Bi, 1.6 for Si and 1.4 for O, in case of BSO. Inside the atomic spheres, the partial waves were expanded up to $l_{\max} = 6$, while the number of plane waves in the interstitial was limited by the cut-off at $K_{\max} = 7.0/R_{\mathrm{MT}}$. The augmented plane wave basis set was utilized in both cases. The charge density was Fourier expanded up to $G_{\max} = 14$. For a Brillouin zone integration, a mesh of 6 k-points in the irreducible part of the zone was used. Exchange and correlation effects were treated by generalized-gradient approximation (GGA96) [12]. The Bi 5d, 6s, 6p, the O 2s, 2p, the Ge 3d, 4s, 4p and the Si 2p, 3s and 3p electronic states were considered as valence ones, and treated within the scalar-relativistic approach, whereas the core states were treated in a fully relativistic manner.

The crystal structure of both BGO and BSO has a cubic symmetry, space group *I*-43*d*, where the Bi, Ge (or Si), and O atoms occupy 16c, 12a and 48e positions, respectively, according to Wyckoff's notation. The primitive unit cell contains two formula units, i.e. 38 atoms, and does not have a center of inversion. While the Ge (Si) position is fixed by the symmetry, the Bi and O positions are determined by internal parameters. To initiate the calculations we used the experimental values for these parameters from reference [13] for the BGO, and from reference [14] for the BSO compound. The lattice parameters are taken from the same references: $a = 10.524$ Å for the BGO, and $a = 10.278$ Å for the BSO. Then, series of calculations were performed in order to relax these values and to find a structure that corresponds to energy minima. This was a necessary step since the density-functional theory applies only for a fundamental state of solid. For the BGO the relaxed value of the lattice parameters is found to be $a = 10.594$ Å, corresponding to 2% bigger volume of the unit cell in comparison with the experiment [13]. For the BSO the calculated relaxed lattice parameter is 10.379 Å, 3% bigger than the experimental one [14]. All atomic positions inside these unit cells were also optimized using the damped Newton scheme, until the forces acting on each atom became less than 5.0 mRy/a.u. These were the final BGO and BSO unit cells utilized in our theoretical study. All the results presented below refer to these structures.

3. Electronic structure

The resulting electronic structure of BGO and BSO crystals, in an energy region situated around the band gap, is shown in Fig. 1.

Similarity of the electronic density of states (DOS) in both compounds is remarkable, especially within a valence band. One could notice, however, some differences, two of which are especially important:

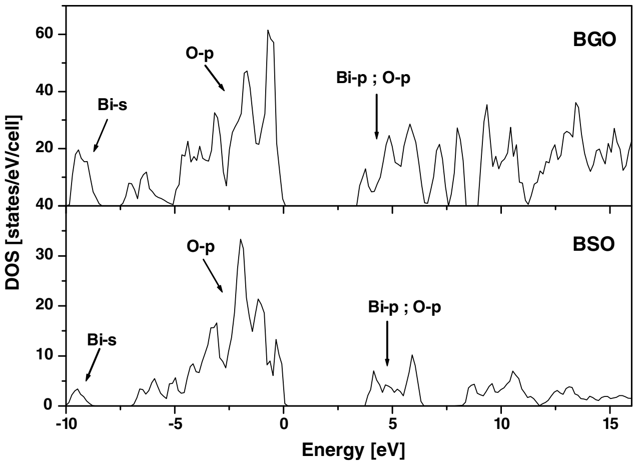

Fig. 1. Calculated total DOS for the pure BGO and BSO scintillators. The Fermi level is fixed at 0 eV. Predominant orbital characters of some bands are indicated.

1. Band gap in BGO is calculated to be 3.54 eV, while in the BSO the calculated band gap is substantially wider: 4.04 eV.
2. The BGO conduction band is very compact, while in the case of the BSO there is a group of bands between 3.8 and 6.5 eV that is isolated from the rest of the conduction band.

These differences refer to the fundamental properties of the gap, its width and the bands situated at its ends – the properties which determine the optical absorption, and can lead to different characteristics of the scintillation process. A more detailed analysis of the band structures shows that in both BGO and BSO the band gap is indirect [15].

The experimental values for the BGO and BSO band gaps were extracted from their corresponding transmission spectra presented in the literature: 4.13 eV for the BGO [16] and 4.34 eV for the BSO [17]. These values are larger than the calculated ones due to a well known effect of underestimation of the band gap owing to the GGA approximation implemented in the density-functional theory.

The total DOS of the BGO and BSO (Fig. 1) can be decomposed to the DOS of each atomic type in the compounds (so-called projected DOS, PDOS). A careful analysis of this decomposition [15] leads to conclusion that the Bi and O states mostly determine the electronic properties of both compounds. Although some Ge s- and Si p-states are also present in the vicinity of the gap, their density is negligible in comparison with the Bi and O.

In the case of the BGO, the peak centered around −9 eV consists of the Bi s-states. The valence band top (from −5 to 0 eV) is dominated by the O p-states, hybridized with some small amount of the Bi s-states. The conduction band bottom (up to 6.5 eV) is formed by hybridized Bi-p and O-p states. In this mixture, the Bi-p states dominate. The O s-states are situated in the upper part of the conduction band.

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