



Electronic and optical properties of BGO:Nd: The role of localized and delocalized f electrons



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ABSTRACT

We have studied BGO:Nd electronic structure in the energy region around the band gap, treating f electrons in two different ways, first as localized (using the open-core approximation), and second as delocalized. The aim is to investigate the changes in electronic properties of the BGO:Nd by analyzing the character and the position of the electronic states introduced by Nd. DFT was used within LAPW basis functions. The effects of exchange and correlation were simulated according to the GGA. Optical properties of BGO:Nd were also analyzed. The absorption spectrum is found to be similar for both treatments.

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1. Introduction

Bismuth germanium oxide or bismuth germanate (BGO, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$) is a well-known luminescent material that emits light in the visible region after being exposed to ionizing radiation. It is used in computed tomography scanners and high-precision calorimeters for detecting electromagnetic radiation. The efficiency of the BGO scintillator can be improved with the inclusion of impurities [1]. The Nd doped BGO (BGO:Nd) called a special attention because it behaves as a waveguide with the generation of harmonics of the second order, i.e., it exhibits a nonlinear optical process in which the photons that interact with the material are effectively 'combined' to form new photons with doubled energy and frequency. This property is shown in the study of Jazmati et al. [2] who investigated BGO:Nd samples implanted at LNT ($\text{LiNb}_x\text{Ta}_{1-x}\text{O}_3$ for $0 \leq x \leq 0.3$) at 77 K with He ions for manufacturing waveguides. They observed a phase change in the BGO, modifying its cubic structure to an anisotropic guide layer generated from the 'stress' of the He beam deployment and, at the same time, the optical activity, i.e., rotation of the polarization plane of linearly polarized light [2–6]. Besides, the BGO:Nd demonstrates the properties that allow its use in the construction of solid-state laser [5]. All these features, together with the lack of theoretical knowledge of the electronic and microscopic properties of BGO:Nd [7] system, were the main motivations for this study.

Many compounds containing rare earths are characterized by the simultaneous presence of localized and delocalized (itinerant) f electrons interacting with each other [8]. Delocalized f electrons

have their orbitals extended, overlapping with the electronic orbitals of the neighboring atoms. This way they participate in the chemical bonding. In this situation, the f electrons must be treated as the other valence electrons (s or p). In the opposite case, the f electrons are confined within the layers that are shielded by external electron layers and do not participate in chemical bonding, and they are treated as the other core electrons.

The electronic properties of the pure BGO were recently studied [9–11], while the structural properties of BGO:Nd were studied by Farias and Lalic [12]. In this Letter we are focused to study the electronic structure of the BGO:Nd in the energy region around the band gap, treating the f electrons in two different ways: (1) as localized (using the open-core approximation), and (2) as delocalized.

Our first objective is to investigate the changes in electronic properties of BGO:Nd by analyzing the character and the position (in relation with the valence band top) of the electronic states introduced by the Nd with localized and delocalized f electrons. The second objective is to analyze and compare optical properties of the compound with Nd f electrons.

As a computational tool we have used density functional theory (DFT), implemented in WIEN2k computer code [13]. The basis functions used were the Linearized Augmented Plane Waves (LAPW). The effects of exchange and correlation were simulated according to the generalized gradient approximation (GGA) [14].

2. Computational details

BGO crystallizes in a cubic structure of eulytite, belonging to $\bar{1}43d$ space group [15]. The primitive unit cell contains two formula units of BGO (38 atoms) without inversion symmetry, having a crystal cell parameter of $a = 10.54 \text{ \AA}$. In this structure, each atom

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Ge⁴⁺ is surrounded by four oxygen ions, O²⁻ at a distance of 1.740 Å [15], arranged at the vertices of a slightly distorted tetrahedron. At the same time, each Bi³⁺ ion is coordinated to six oxygen ions which form a strongly distorted octahedron around it: the closest three of them are situated at a distance of 2.605 Å from the Bi [15,16]. For self-consistent calculations of the BGO, the density functional theory [17] was used, with the (L)APW [18] method implemented in the WIEN2k package [13]. 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 or ‘muffin-tin’ (MT) spheres) and in plane waves in the rest of the space (interstitial region). The radii of the MT spheres (R_{MT}) were chosen as follows: 2.3 a.u. for Bi, 1.8 a.u. for Ge, 1.30 a.u. for O and 2.20 a.u. for Nd. Within the MT spheres, the partial waves were expanded up to $l_{\text{max}} = 10$, while the number of plane waves in the interstitial region was limited by the cutoff parameter $k_{\text{max}} = 6.63/R_{\text{MT}}$. The charge density was expanded in Fourier series up to $G_{\text{max}} = 14$. The number of k points was equal to 6 in the irreducible wedge of the first Brillouin zone. The exchange and correlation potential was approximated by means of GGA [14]. Typical electronic configuration of lanthanide is [Xe] 4 f^n ($0 \leq n \leq 14$), with a formal valence state of +3. Chemical bonds occur predominantly involving their 5d and 6s orbitals, making the trivalent oxidation state the most stable one. Therefore, the simultaneous presence of delocalized and localized f states and the interaction between them [8] are of fundamental importance to describe these f systems.

Delocalized f -electrons refer to the extended f -shell which overlaps with the electronic orbitals of neighboring atoms and participates in the chemical bonding. DFT method calculates this case treating f -electrons in the same manner as the other valence electrons. The localized f -electrons are screened by outer shells and do not participate in the chemical bonding. The local spin density approximation and GGA cannot treat reliably the ground state properties of highly correlated systems with 4f electrons [19]. A tool for this is the ‘open-core’ approximation in which the localized 4f orbitals are not contained in a set of valence basis functions, but are treated as part of the core atomic type [20]. A more sophisticated approach to this problem is provided by applying the LDA + U [21] schemes. As the degree of localization (or delocalization) of the 4f electrons is not well known, two types of calculations were performed, simulating two extreme situations that can occur with these electrons. The first one is the completely localized 4f³ configuration, which is treated using open-core approach, while the second is the completely delocalized 4f³ configuration where f electrons are treated as a part of valence panel.

The following electronic states are chosen as valence ones: (Bi) 5d, 6s, 6p, (O) 2s, 2p, (Ge) 3d, 4s, 4p, and (Nd) 5d, 6s, in both types of calculations, and treated by a scalar relativistic approach, while the core states were treated with full relativistic approach. The doped system was simulated using the primitive unit cell of pure BGO (38 atoms), in which one Bi atom was substituted by the Nd atom. When the Nd atom is introduced in the unit cell of the BGO, it substitutes the Bi atom due to the valence chemistry and similar ionic radii, 0.104 nm for Nd³⁺ and 0.096 nm for the Bi³⁺, without any compensation of charges [22]. In this periodic calculation Nd is present in the BGO with a concentration of 1/38 (2.56%). The unit cell of the BGO is large enough to prevent interaction between the impurities, with the Nd–Nd distance of 9.174 Å. The space group of the doped system is changed to R3.

The lattice parameters and atomic positions of doped BGO were relaxed using as the initial values the lattice parameters of the pure BGO [10]. The method used for geometry optimization was based on damped Newtonian, which seeks equilibrium of the atomic positions by minimizing the forces felt by each atom. The

calculations were performed until the forces were less than 5.0 mRy/a.u. for each atom [12].

Optical characteristics of the BGO:Nd system were analyzed by calculating the complex dielectric tensor ϵ , whose imaginary part $\text{Im}(\epsilon)$ is directly proportional to its optical absorption spectrum. The $\text{Im}(\epsilon)$ is computed within the frame of random phase approximation (RPA), in the limit of linear optics and neglecting electron polarization effects, using the following formula [23]:

$$\text{Im } \epsilon_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{if} \int_{\text{BZ}} \frac{2dk}{(2\pi)^3} |\langle \phi_{fk} | P_{\beta} | \phi_{ik} \rangle| |\langle \phi_{fk} | P_{\alpha} | \phi_{ik} \rangle| \cdot \delta E_f(k) - E_i(k) - \hbar\omega \quad (1)$$

for a vertical transition from a filled initial Kohn–Sham state $|\phi_{ik}\rangle$ of energy $E_i(k)$ to an empty final Kohn–Sham state $|\phi_{fk}\rangle$ 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 in the x , y , and z directions.

On the basis of calculated electronic structure (i.e. the Kohn–Sham orbitals) of BGO:Nd we computed the $\text{Im}(\epsilon)$ up to incident radiation energy of $\hbar\omega = 40$ eV. The real part of dielectric tensor is then determined using Kramers–Kronig relation. Both real and imaginary parts of ϵ were calculated with a mesh of 68 k -points in the irreducible block of the first Brillouin zone. Owing to cubic symmetry the dielectric tensor is diagonal, with $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \epsilon$. It is thus reduced to a scalar function $\epsilon(\omega)$.

3. Results and discussions

3.1. Electronic structure of BGO:Nd

Figure 1 shows the relaxed structure of the BGO:Nd. Since the ionic radii of the Bi and the Nd ions are similar and the concentration of Nd is small, it is not expected that the unit cell volume be significantly changed due to the substitution of the Bi by the Nd. Thus, in our calculations we used the value of the lattice parameter of pure BGO calculated by Lalic and Souza [9], via DFT, which is only 2% larger than the experimental value [15].

Figure 2 shows the total density of electronic states for pure BGO (a), BGO:Nd system with delocalized (b) and localized (c) 4f electrons. The fundamental band gap calculated in the BGO:Nd with delocalized 4f electrons is 3.36 eV, while with localized 4f electrons is 3.48 eV. The experimental value for the band gap of the pure BGO estimated from optical absorption measurement is 4.13 eV [24], and the calculated value for pure BGO at the same level of theory is 3.54 eV [10]. It is well known that the band gap values are underestimated due to an effect of GGA approach. Therefore, the delocalized f -electrons reduce the band gap more than the localized f -electrons, probably due to the fact that the first are making part of the valence panel. To the best of our knowledge there is no experimental value for the fundamental gap of BGO doped with neodymium.

Figures 2b and c show similarity of the valence bands in both treatments of the Nd 4f electrons. In the case of the pure BGO, the principal part of valence band (from -7.0 to 0.0 eV) is dominated by the p states of the oxygen which hybridize with a small amount of the Bi s states, while the bottom of the conduction band is formed by hybridization of the Bi p states with the O p states, where the Bi p states are the dominant ones [10]. Nd introduces its f -states within the band gap and at the conduction band bottom, influencing very little in the intensity and the form of the principal valence band.

Figure 3 shows the partial density of states (PDOS) for the delocalized and localized f electrons. For the BGO:Nd with delocalized Nd 4f electrons the populated states accommodate about three 4f electrons with spin up, while other states are empty and available

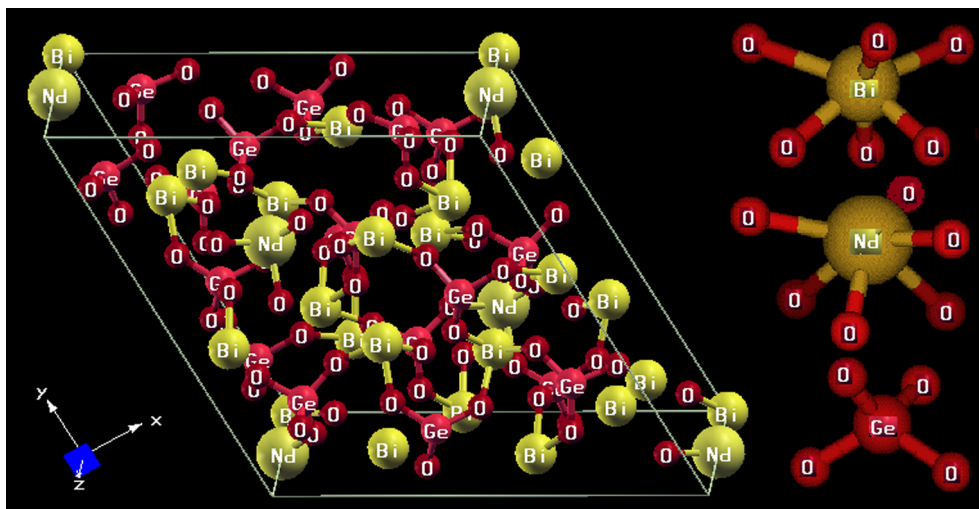


Figure 1. Cubic structure of doped BGO with Nd. Local structure around Bi ion (BiO_6), of Nd ion (NdO_6) and Ge ion (GeO_4) in BGO:Nd.

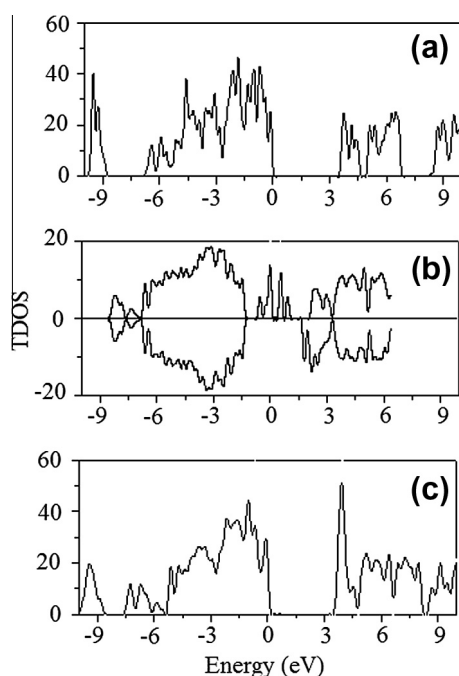


Figure 2. The total density of electronic states (a) of pure BGO, (b) with spin polarized of BGO doped with Nd (delocalized f electrons) and (c) of BGO doped with Nd (localized f electrons). The Fermi level passes through zero eV.

to four f electrons with spin up and seven with spin down. In the case of the BGO:Nd with the three localized f-electrons, the empty f-states are situated within the conduction band.

A detailed analysis of the density of states (DOS) demonstrates that in the treatment with delocalized 4f electrons, there are 2.96 electrons with spin-up and 0.07 electrons with the spin-down per atom of Nd within the populated states. On the other hand, in the treatment with localized 4f electrons, we found 0.18 f-electrons of Nd accommodated within the valence band. That is, the f electrons of Nd are not effectively treated in the calculation with the open-core approach. This causes internal inconsistency of the open-core treatment [25,26], since the fixed occupation of the 4f orbitals ($4f^3$) with an integer often violates the Kohn–Sham rule to occupy the lowest state of an electron in the construction of charge density and spin [20]. The total magnetic moment per unit

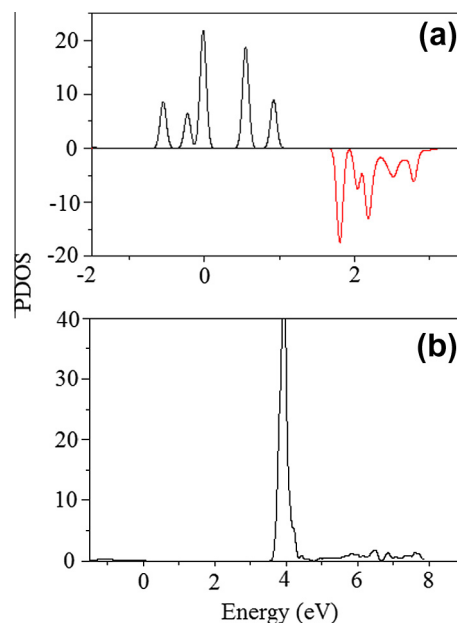


Figure 3. (a) Refers to the PDOS of f orbital delocalized in Nd atom that is at the Bi site in BGO and (b) refers to the PDOS with the 4f electrons located in the Nd atom. The Fermi level passes through zero eV.

cell is $+3.01 \mu_B$ in the calculation with delocalized electrons, and $+2.89 \mu_B$ in the calculation with localized 4f electrons.

The calculations with inclusion of spin–orbit (SO) interaction for the Bi and the Nd atoms were also carried out. The results do not show a significant difference in relation to the study without SO inclusion. Basically, the SO interaction only introduces some differences in a region of low energy, between -20 and -16 eV, where the 5p states of Nd were separated in the $J = 1/2$ and $J = 3/2$ components, while in the gap region the splitting of the Nd 4f states into the components of $J = 5/2$ and $J = 7/2$ was negligible. The effects of SO inclusion for the atoms of Bi were identical to those already published [10].

3.2. Optical properties of BGO:Nd

Figure 4 shows the imaginary part of dielectric tensor (which is directly proportional to optical absorption spectrum of the material)

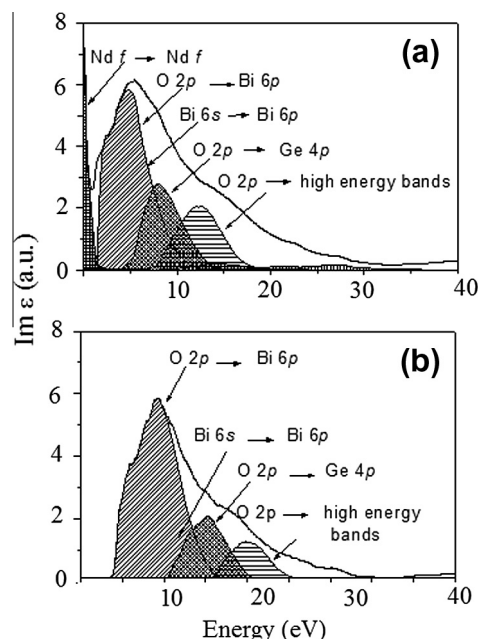


Figure 4. Imaginary part of dielectric tensor calculated for BGO:Nd. (a) refers to BGO:Nd with delocalized 4f electrons and (b) refers to BGO:Nd with localized 4f electrons.

calculated for localized and delocalized 4f electrons of the Nd atom. It is interpreted in terms of electronic structure of Figures 2 and 3.

The form of the principal part of absorption spectrum is very similar for BGO:Nd with localized and delocalized f-electrons and consists of very intensive, broad peak centered at 5 and 8 eV, respectively, and of a shoulder centered at 15 and 17 eV. The peak is generated by electronic transitions within the BiO_6 octahedron, from O 2p- to the Bi 6p-states and from the Bi 6s- to the Bi 6p-states. The shoulder is influenced by electronic transitions within the GeO_4 tetrahedron, between the O 2p- and the Ge 4p-states, although the transitions within the BiO_6 octahedron cannot

be neglected in its formation. In the case when the Nd f-electrons are delocalized, there exist additional peaks whose energy range is from 0 eV to approximately 3 eV. These peaks are due to transitions between occupied and empty f-states of the Nd which are not forbidden, since the f-states do not have clearly defined parity when there is no center of inversion in the unit cell. The peak at zero energy originates from intra-band f–f transition (a band which is pinned at the Fermi energy in Figure 3).

Figure 5 depicts the calculated refractive index and extinction coefficient for the pure BGO (Figures 5a and b) and BGO:Nd treated with delocalized (Figures 5c and d) and localized 4f electrons (Figures 5e and f). All figures show decay in the region of ultra-violet. Both refractive index and extinction coefficient show similarities for the cases of pure BGO and the BGO:Nd with localized Nd f-electrons. The case of BGO:Nd with delocalized f-electrons of Nd is very different due to a presence of Nd occupied f-states within the BGO band gap. The question of which theoretical treatment of the Nd f-electrons is more realistic can be judged only by appropriate comparison with experimental study. Theoretical calculations of the extinction coefficient of BGO:Nd showed an increase between 32 and 40 eV, while experimental values [27] show increase to a value around of $7.5 \times 10^5 \text{ cm}^{-1}$ between 30 and 32 eV. The result for the 4f electrons not participating in chemical bonds is more similar to the experimentally measured absorption coefficient and that calculated for the pure BGO.

4. Conclusions

In this Letter was conducted a theoretical study of electronic and optical properties of the bismuth germanate scintillator $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ doped with the Nd (BGO:Nd). As a computational tool we used the method (L)APW based on DFT and implemented in the WIEN2k code.

The investigation of the compound BGO:Nd began with the computational optimization of crystal structure. Owing to the low concentration of impurities (Nd) (1/38) considered in this simulation, it was not necessary to optimize the lattice parameters, but all the atomic positions were relaxed. The Nd 4f electrons were

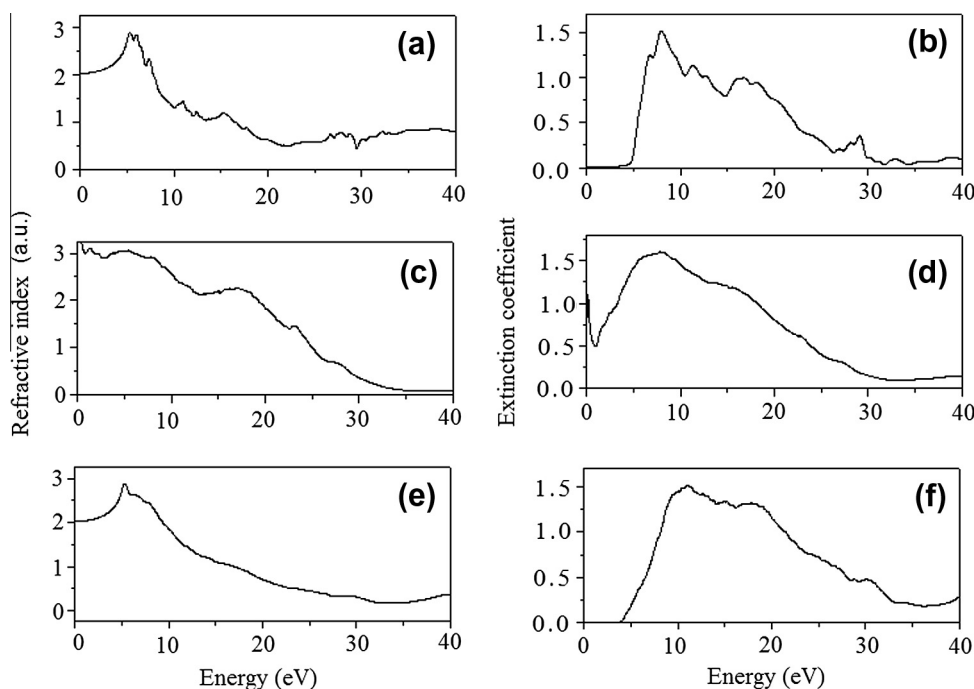


Figure 5. Calculated refractive index and extinction coefficient for pure BGO (a and b), BGO:Nd with delocalized (c and d) and localized (e and f) Nd 4f electrons.

treated in two different ways: as localized (using the open-core approach) and delocalized (treated as the other valence electrons). Electronic structure in both cases were analyzed and compared. In the case of localized treatment, the $4f^3$ configuration of the Nd was relatively correctly described since only small fraction of 0.18 extra f-electrons is found within the valence band. At the same time, the empty f-states are positioned at the bottom of the conduction band. The delocalized treatment also succeeded to describe the Nd $4f^3$ configuration showing the presence of almost three 4f electrons in the valence band. In this case majority spin states are positioned within the fundamental gap, while the minority spin states are localized at the conduction band bottom. It is also shown that the Nd–O bond stems partly from hybridization of Nd-s, Nd-p and O-p electronic states, suggesting a significant degree of covalence.

Optical properties of the BGO:Nd have been also investigated, and the results for two different treatments of the Nd 4f-electrons analyzed and compared. The principal part of absorption spectrum is found to be similar for both treatments, consisting of one broad, intensive peak and one shoulder. The peak originates from electronic transitions within the BiO_6 octahedron while the shoulder is influenced by electronic transitions within the GeO_4 tetrahedron. The significant influence of the Nd 4f electrons on optical absorption is found only in a region of very low energy, and only in the case of delocalized f-electrons. The similar trend is observed in the case of calculated refractive index and extinction coefficient. This fact should be a clue for eventual future experimental measurements to discover which theoretical treatment of the Nd 4f-electrons is more realistic.

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