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# The local structure around the Nd impurity incorporated into the $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$ crystal matrix: An ab initio study 

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#### Abstract

The local structure around the Nd impurity introduced at the Bi site in the $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$ compound is theoretically investigated by density-functional theory based augmented plane wave method. A set of parameters that completely describes the Nd neighborhood is calculated by treating the Nd 4 electrons either as localized or as delocalized. In both cases the local structure was dominantly determined by the Nd departure from the ideal host position along the trigonal axis. Displacement occurs in the direction towards the center of the Oxygen octahedron around the Nd.


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## 1. Introduction

Bismuth Ortho-Germanate $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$ (BGO) is a well known scintillator with a wide variety of applications in high energy physics, nuclear medicine and non-linear optical devices [1-3]. When doped with a transition metal and rare-earth ions, it shows potential for use as a solid state laser host [4,5]. Nd is an especially interesting dopant, because the BGO:Nd system presents good electro-optical properties such as second harmonic generation and optical rotation [6]. It also exhibits medium laser amplification characteristics [7], being recently investigated as a possible laser system which can be pumped by laser diode [8,9].

The optical properties of the BGO:Nd system were experimentally studied by Kaminskii et al. [7] and more recently by Loro et al. [10]. In order to understand and manipulate these properties, it is important to know the position of the Nd impurity within the host crystal matrix, as well as the local structure around it, i.e. the positions of its neighboring atoms. As the Nd and the Bi ions have the same valence ( $3+$ ) and very similar ionic radii ( 0.104 and 0.096 nm respectively), it is expected that the $\mathrm{Nd}^{3+}$ ion substitutes the $\mathrm{Bi}^{3+}$ ion. This fact has been confirmed by electron paramagnetic resonance (EPR) investigation, in which the determined EPR parameters were associated to the $\mathrm{Nd}^{3+}$ impurity located exactly at the octahedral $\mathrm{Bi}^{3+}$ site with trigonal symmetry [11]. Using the perturbation formulas of the EPR parameters for a $4 f^{3}$ ion

[^0]in a trigonally-distorted crystal field, Wu and Dong concluded that the Nd impurity does not occupy exactly the host Bi site, but dislocates from it along the $C_{3}$ symmetry axis [12]. The authors, however, stress that their semi-empirical calculations contain various approximations and need to be verified either experimentally or by using more accurate calculations based on density functional theory (DFT).

The DFT description of the structural and, especially, electronic properties of f-electron systems, however, faces serious difficulties due to a strong correlation between f-electrons which causes their localization. This fact is not properly described by LDA or GGA exchange-correlation potentials, which apply much better to delocalized s -, p- or d-states [13]. Most f-electron systems are characterized by the simultaneous presence of itinerant (delocalized) and localized f states and the interaction between them [14]. The situation of delocalized f-electrons refers to the extended f-shell which overlaps with the electronic orbitals of neighboring atoms and participates in chemical bonding. DFT calculations simulate this situation by treating the f-electrons in the same manner as the other valence electrons. On the other hand, the localized f-electrons are confined within the shell which is screened by outer shells (free-atom-like) and do not participate in chemical bonding. This situation is approximated in the DFT calculations by the so-called open-core treatment, in which the f -electrons are removed from the valence band and treated as the core electrons. A more sophisticated approach to this problem is provided by applying the LDA +U [15] or LDA + SIC [16] schemes.

The objective of the present study is to theoretically investigate the local structure around the Nd impurity incorporated into the BGO crystal matrix. To achieve this objective we employed first-principles DFT calculations on a BGO compound doped with
an isolated Nd impurity which substituted the Bi atom. Since the degree of localization (or delocalization) of the Nd 4f-electrons is not known, two types of calculations were performed, simulating two extreme situations that can occur with these electrons. Namely, they were considered either completely localized (via open-core approach) or fully delocalized. By relaxing the atomic positions around the impurity, all parameters that describe the Nd surrounding were determined, which can be useful in eventually improving the modeling of the crystal field parameters for the BGO:Nd system [10]. Both types of calculations confirmed the off-site displacement of the Nd along the $C_{3}$ axis, but in the direction which is opposite to the predictions of Wu and Dong [12].

## 2. Crystal structure

The crystal structure of pure BGO is know as eulytite and belongs to the cubic space group I43d. The primitive unit cell contains two formula units ( 38 atoms), without having a center of inversion. In this structure, each Bi atom is coordinated by six Oxygen atoms which form a strongly distorted octahedron around it: three of them are situated nearer to the Bi than the other three. The Bi senses the $C_{3}$ (trigonal) point symmetry with the threefold axis pointing along a (111) direction of the cubic cell. The Ge atoms are surrounded by four Oxygens, all at the same distance, forming perfect tetrahedrons around them. They experience the $S_{4}$ point symmetry. In practice, these tetrahedrons are very slightly compressed along one of their fourfold axes [4]. When the Nd atom is introduced into the BGO unit cell, it substitutes the Bi atom due to the same chemical valence and similar ionic radius, without a need of any charge compensation. The space group of the system, however, changes to R3 (no. 146).

## 3. Computational details

The self-consistent calculations of the BGO:Nd system were performed by density functional theory based [17], linear augmented plane wave (LAPW) method [18] as embodied in WIEN2k computer code [19]. 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 (with radii $R_{M T}$ ), and in plane waves in the rest of the space (interstitial region). The choice for the atomic sphere radii $R_{M T}$ was the following: 2.3 for $\mathrm{Bi}, 1.8$ for $\mathrm{Ge}, 1.30$ for O and 2.20 for Nd . Inside the atomic spheres, the partial waves were expanded up to $l_{\max }=10$, while the number of plane waves in the interstitial was limited by cutoff at $K_{\max }=6.63 / R_{M T}$. The augmented plane waves were utilized for the basis set. The charge density was Fourier expanded up to $G_{\max }=14$. For Brillouin zone integration, a mesh of $6 k$-points in the irreducible part of the zone was used. Exchange and correlation effects were taken into account by generalized-gradient approximation (GGA) [20]. The Nd 4f states were treated in two manners: (1) as localized (simulating $4 f^{3}$ configuration), utilizing the open-core approach, and (2) as delocalized, belonging to the set of the valence states. In both types of calculations the $\mathrm{Bi}: 5 \mathrm{~d}, 6 \mathrm{~s}, 6 \mathrm{p}$, the $\mathrm{O}: 2 \mathrm{~s}, 2 \mathrm{p}$, the Ge: $3 \mathrm{~d}, 4 \mathrm{~s}, 4 \mathrm{p}, \mathrm{Si}: 2 \mathrm{p}$, $3 \mathrm{~s}, 3 \mathrm{p}$ and Nd : 5 d , 6 s 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 doped system was simulated using a primitive unit cell of pure BGO from which the central Bi atom had been removed and replaced by a Nd atom. The crystal is then generated by infinite repetition of this unit cell. Thus, we have effectively considered the doped BGO compound with Nd concentration of the 1/38 (2.6\%). Since the BGO unit cell is very extensive, the Nd-Nd distance ( $9.174 \AA$ ) is large enough to prevent interaction between the impurities.

We started calculations of the BGO:Nd system using the lattice parameter $a=10.594 \AA$ and atomic positions as determined by computational relaxation of the structure of pure BGO [21]. Since atomic radii of the Bi and the Nd ion are similar and the Nd concentration is small, it is not expected that the unit cell volume significantly changes due to substitution of the Bi by Nd. Thus, we did not additionally relax the lattice parameter. We performed, however, a series of long-lasting calculations in order to optimize all atomic positions within the BGO unit cell perturbed by the Nd presence. The utilized method was the geometry optimization based on a damped Newton scheme, which searches for the equilibrium atomic positions by minimization of the forces sensed by each atom. The calculations were carried on until these forces became less than $5.0 \mathrm{mRy} /$ au for every atom.

## 4. Results and discussion

In order to understand and interpret the optical and EPR spectroscopic data, knowledge of accurate local structures around the atoms is highly desirable. In the BGO:Nd system we are primarily interested in the local structures which depict the Bi and the Nd neighborhood. They are usually described in terms of two parameters: (1) the metal-oxygen distance $R_{M-0}$, and (2) the angle $\beta$ between the $R_{\mathrm{M}-\mathrm{o}}$ and the $C_{3}$ axis. In the Table 1 we present these parameters calculated in the present work, together with the parameters previously calculated and experimentally determined for pure BGO.

The Nd presence perturbs the atomic positions in the whole unit cell. Thus, the Bi-O bond lengths in BGO:Nd depend on the chosen Bi atom. Table 1 presents the local structure around the Bi atom that is most distant from the impurity, and thus suffered the weakest perturbations. It is seen that the bond lengths that characterize this structure do not differ too much in comparison with the theoretical bond lengths around the Bi in pure BGO [21], as well as with the ones determined experimentally [22,23]. The Nd surrounding, on the contrary, suffered much more significant changes.

The calculated local structure around the Nd results from the movement of not just the nearest neighbor oxygens, but also the Nd itself. The Table 2 shows the positions of the Nd and its six neighboring oxygens before and after the structure was relaxed.

The data shown in Table 2 imply that the difference between the optimized and initial positions is about one order of magnitude larger in the case of Nd movement than in the case of O movements. Therefore, a displacement suffered by the Nd is much more significant than displacements experienced by the neighboring Oxygens. This fact leads to the conclusion that the local structure around the Nd is dominantly determined by the Nd displacement from the ideal host (i.e. Bi ) position. This displacement occurs along the $\left(\begin{array}{ll}1 & 1\end{array}\right)$ direction, which coincides with the trigonal $C_{3}$ axis.

With the data presented in Tables 1 and 2 at our disposal, we are in a position to discuss more thoroughly the structural changes which occur when the Nd substitutes the Bi. The ideal host position for the Nd is the Bi site, situated at the axis of highest $\left(C_{3}\right)$ symmetry inside the imaginary irregular octahedron with the Oxygen ions in the vertices (Fig. 1). Searching for equilibrium, the Nd dislocates from this position, moves along the $C_{3}$ axis away from its three nearest Oxygens $\left(\mathrm{O}_{1}\right)$ and approximates to its second nearest ones $\left(\mathrm{O}_{2}\right)$. This is evident by comparing the $\mathrm{Bi}-\mathrm{O}$ bond lengths for the ideal host position of the Nd (3rd or 4th column of the Table 1) with the $\mathrm{Nd}-\mathrm{O}$ bond lengths for the relaxed position of the Nd (1st and 2nd column of the Table 1). As a consequence of relaxation, both angles $\beta$ which correspond to the $\mathrm{Nd}-\mathrm{O}$ bonds diminish, which is consistent with the described movement of the Nd. Table 1 shows that the $\mathrm{Nd}-\mathrm{O}_{1}$ and $\mathrm{Nd}-\mathrm{O}_{2}$ bond lengths in $\mathrm{BGO}: \mathrm{Nd}$ differ less than the corresponding $\mathrm{Bi}-\mathrm{O}_{1}$ and $\mathrm{Bi}-\mathrm{O}_{2}$ bond lengths in the pure BGO .

Table 1
Calculated equilibrium metal-oxygen bond lengths (in $\AA$ ) and the angles $\beta$ between them and the $C_{3}$ axis in BGO:Nd, compared to the previous theoretical and experimental data for pure BGO. The labels $\mathrm{O}_{1}$ and $\mathrm{O}_{2}$ denote the three nearest and the three second nearest $\mathrm{Bi}(\mathrm{Nd})$ neighbors respectively. The numbers in parentheses denote the number of oxygens which correspond to the given length and the angle.

|  | BGO:Nd <br> Localized f-states <br> (This work) | BGO:Nd <br> Delocalized f-states <br> (This work) | Pure BGO <br> DFT <br> (Ref. [21]) | Pure BGO <br> Experimental <br> (Refs. [22,23]) |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{Bi}-\mathrm{O}_{1}$ | $2.153(3) \beta=49.67^{\circ}$ | $2.145(3) \beta=43.26^{\circ}$ | $2.221(3) \beta=50.11^{\circ}$ | $2.149(3) \beta=51.38^{\circ}$ |
| $\mathrm{Bi}-\mathrm{O}_{2}$ | $2.589(3) \beta=114.67^{\circ}$ | $2.593(3) \beta=116.97^{\circ}$ | $2.584(3) \beta=102.77^{\circ}$ |  |
| $\mathrm{Nd}-\mathrm{O}_{1}$ | $2.344(3) \beta=48.97^{\circ}$ | $2.393(3) \beta=43.63^{\circ}$ |  |  |
| $\mathrm{Nd}-\mathrm{O}_{2}$ | $2.439(3) \beta=101.12^{\circ}$ | $2.435(3) \beta=94.41^{\circ}$ |  |  |

Table 2
Atomic positions of the Nd and its neighboring oxygens before and after the structure relaxation. The labels $\mathrm{O}_{1}$ and $\mathrm{O}_{2}$ denote the nearest and the second nearest Nd neighbors respectively. The atomic coordinates are given in atomic units, with respect to the rhombohedral coordinate system $\left(\vec{a}_{1}, \vec{a}_{2}, \vec{a}_{3}\right)$, where $\vec{a}_{1}=\frac{a}{2 \sqrt{3}} \vec{e}_{x}-\frac{a}{2} \vec{e}_{y}+\frac{c}{3} \vec{e}_{z}$; $\vec{a}_{2}=\frac{a}{2 \sqrt{3}} \vec{e}_{x}+\frac{a}{2} \vec{e}_{y}+\frac{c}{3} \vec{e}_{z} ; \vec{a}_{3}=-\frac{a}{\sqrt{3}} \vec{e}_{x}+\frac{c}{3} \vec{e}_{z} ; a=28.311 \mathrm{au} ; c=17,337$ au and $\vec{e}_{x}, \vec{e}_{y}, \vec{e}_{z}$ are Cartesian axes.

|  | Local structure around the Nd in BGO:Nd | Optimized positions <br> (Delocalized f-states) |  |
| :--- | :--- | :--- | :--- |
| Nd | $(0.5,0.5,0.5)$ | Optimized positions <br> (Localized f-states) | $(0.4639,0.4639,0.4639)$ |
| $\mathrm{O}_{1}$ | $(0.6927,0.7455,0.5275)$ | $(0.4860,0.4860,0.4860)$ | $(0.6781,0.7341,0.5202)$ |
| $\mathrm{O}_{1}$ | $(0.5275,0.6927,0.7455)$ | $(0.6833,0.7433,0.5221)$ | $(0.5202,0.6781,0.7341)$ |
| $\mathrm{O}_{1}$ | $(0.7455,0.5275,0.6927)$ | $(0.5221,0.6838,0.7433)$ | $(0.7341,0.5202,0.6781)$ |
| $\mathrm{O}_{2}$ | $(0.4193,0.2795,0.6144)$ | $(0.7433,0.5211,0.6838)$ | $(0.4029,0.2885,0.6076)$ |
| $\mathrm{O}_{2}$ | $(0.6144,0.4193,0.2795)$ | $(0.4125,0.2851,0.6048)$ | $(0.6076,0.4029,0.2885)$ |
| $\mathrm{O}_{2}$ | $(0.2795,0.6144,0.4193)$ | $(0.6048,0.4125,0.2851)$ | $(0.2885,0.6076,0.4029)$ |



Fig. 1. The local structure around the Nd in the BGO:Nd compound in a hypothetical situation when the Nd occupies the ideal ( Bi ) host position. The octahedron of Oxygens around it is irregular: the three O ions above the Nd are its nearest neighbors $\left(O_{1}\right)$, while the $O$ ions below the Nd are its second nearest neighbors $\left(\mathrm{O}_{2}\right)$. During the process of structure relaxation, the Nd impurity suffers inward displacement $\Delta d_{N d}$ towards the center of the octahedron along the $C_{3}$ axis.

This clearly means that the Nd suffered off-site dislocation towards the center of the oxygen octahedron along the $C_{3}$ axis (Fig. 1).

In their recent work, Wu and Dong [12] arrived at a different conclusion. They applied perturbation formulas on the EPR parameters for an $\mathrm{f}^{3}$ ion in a trigonally-distorted octahedral environment, and predicted that the Nd should move along the $C_{3}$ axis away from the center of the octahedron. The calculated displacement was 0.08 Å. The authors explained this result by assuming that the $\mathrm{Nd}^{3+}$, having a slightly larger ionic radius, feels a tense environment at the $\mathrm{Bi}^{3+}$ position, which pushes it away from the center of the oxygen octahedron. Our DFT calculations, however, do not support their conclusion. We think that the reason of this disagreement might be the fact that the authors of Ref. [12] put too much reliance on the concept of ionic radius. This concept works much better for highly ionic compounds, which is not the case of BGO. The Nd-O bond in BGO has significant covalent character, which originates from the hybridization of the Nd s and p -, and O p- electronic states. Thus, assigning any definite value for the size of the Nd and the Bi ions in BGO might be questionable. The value of the Nd displacement, calculated for both types of f-electron treatments and compared to the displacement calculated in the Ref. [12] is presented in Table 3.

Table 3
The off-site displacement, in angstroms, of the Nd ion substituting the Bi site in BGO. The displacement occurs along the $C_{3}$ axis. The signal + denotes the direction pointing towards the center of the oxygen octahedron, and -, away from the center of this octahedron.

|  | BGO:Nd <br> Localized f-states | BGO:Nd <br> Delocalized f-states | BGO:Nd <br> Ref.[12] |
| :--- | :--- | :--- | :--- |
| $\Delta d_{N d}$ | +0.21 | +0.42 | -0.08 |

Finally, different treatments of the Nd 4 f electrons resulted in slightly different local structures around the Nd. The off-site displacement is more significant when the $4 f$ electrons are treated as localized. In this case the distance between the Nd and the three $\mathrm{O}_{1}$ neighbors is about $0.05 \AA$ longer in comparison with the case of delocalized f-states, making the $\mathrm{Nd}-\mathrm{O}_{1}$ and $\mathrm{Nd}-\mathrm{O}_{2}$ interatomic distances almost equal. Our main conclusion about the local structure around the Nd , its off-site displacement towards the center of the oxygen octahedron, stays however the same for both type of treatments of the Nd f-electrons.

## 5. Conclusions

The local structure around the trigonal Nd center substituting the Bi atom in the $\mathrm{Bi}_{4} \mathrm{Ge}_{3} \mathrm{O}_{12}$ is theoretically investigated by density functional theory. The Nd 4 f electrons are treated in two different ways: as localized (in the open-core) and delocalized (in the valence panel). As a result of structure relaxation, a set of parameters which describes the local surrounding of the Nd, consisting of six Oxygens situated at the vertices of a distorted octahedron, is determined. It was found that the principal structural changes were caused by the Nd departure from the ideal host position along the $C_{3}$ symmetry axis, and not by the Oxygen's movement. The Nd displacement occurred in the direction which points towards the center of the oxygen octahedron around it.

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