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First principles study of electronic and optical properties of the chromium doped BGO crystal

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Abstract. Ab-initio calculations based on density functional theory have been employed to study electronic properties of Cr doped $Bi_4Ge_3O_{12}$ (BGO), as well as its optical absorption spectra in ultraviolet region. Two different situations have been analyzed: when the Cr is situated at the Ge position (Cr^{4+}), and when it resides at the Bi site (Cr^{3+}). For each case the band structure and absorption spectra were calculated, and the Cr contributions identified and interpreted. Comparison with the experimental data indicates that the Cr enters both the Ge and Bi sites during the doping.

1. Introduction

The bismuth ortho-germanate $Bi_4Ge_3O_{12}$ (BGO) has been the focus of numerous studies due to its excellent scintillation properties suitable for technological applications. As a pure crystal it is utilized as high-efficient scintillator in scientific research, as well as in non-linear optical devices and nuclear medicine [1,2]. When doped with Cr, the BGO exhibits enhanced photorefractive response [3] and shows potential to be used as a near infrared (NIR) solid state laser host [4]. Several experimental studies have been performed on this system so far, focusing its optical properties and the possible Cr accommodation within the lattice. It was not unambiguously determined which position the Cr impurity occupies in the BGO: the octahedral Bi^{3+} site (with trigonal symmetry) or tetrahedral Ge^{4+} site (tetrahedron symmetry). The EPR study of Bravo et al [4] indicates the Cr presence in both sites, with the approximately the same concentration of the Cr^{3+} and Cr^{4+} ions. Using the same technique, Chernei et al [5] concluded that the Cr should reside at the Ge position, and the same conclusion has been drawn from the optical absorption study of Mello et al. [6].

The objective of the present study is to calculate the optical characteristics of the Cr doped BGO in the ultra-violet region, as well as to discuss the possible Cr accommodation within its crystal lattice. We utilized the first-principles, density-functional theory based calculations in order to analyze the electronic and some optical properties of the BGO doped with substitutional Cr impurities situated either at the Ge^{4+} or at the Bi^{3+} site. By comparing these properties with the ones recently calculated for the pure BGO crystal [7] we were able to extract the effects caused by the Cr presence. The results of our study indicate that the Cr should be present at the both Bi and Ge sites in the BGO, thus supporting the conclusions of the experimental work of Bravo et al [4].

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2. Calculations

The BGO crystallizes in cubic symmetry, space group *I-43d.* Primitive unit cell contains two formula units (38 atoms) and does not have a center of inversion. Each Bi ion is surrounded by six oxygens arranged in a strongly distorted octahedron: three of them are situated nearer to the Bi than the other three. The Ge atoms are surrounded by four oxygens, all at the same distance, arranged in the vertices of a perfect tetrahedron.

In this work we have treated two systems: the BGO with the Cr substituting the Bi atom (BGO:Cr→Bi case) and the BGO with the Cr residing at the Ge position (BGO:Cr→Ge case). The doped systems were simulated using the primitive unit cell of the pure BGO from which the central Bi (Ge) atom has been removed and replaced by the Cr atom. The crystal is then generated by infinite repetition of this unit cell. Therefore, we have calculated doped systems with Cr concentration of the 1/38 (2.6%).

The spin-polarized, self-consistent band-structure calculations were performed by density-functional theory [8] based, full potential linear augmented plane wave (FP-LAPW) method [9] as embodied in WIEN2k computer code [10]. 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), and in plane waves in the rest of the space (interstitial region). The choice for the atomic sphere radii (in atomic units) was 2.3 for the Bi, 1.8 for the Ge, 1.45 for the O and 1.8 for the Cr atom. Inside 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 $K_{max}=7.0/R_{MT}$. The augmented plane waves were utilized as a basis set. The charge density was Fourier expanded up to $G_{max}=14$. For the k-space integration a mesh of 12 k-points in the irreducible part of the Brillouin zone was used. Exchange and correlation effects were treated by generalized-gradient approximation (GGA96) [11]. The Bi 5d, 6s, 6p, the O 2s, 2p, the Ge 3d, 4s, 4p and the Cr 3s, 3p, 3d and 4s 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 crystal structure of the doped systems was computationally optimized: all atomic positions around the impurity were allowed to relax by total energy minimization, while the optimized unit cell parameter was taken from the recently performed theoretical study of the pure BGO [7].

The optical response of the Cr doped BGO is determined by calculating its complex dielectric tensor ε. Imaginary part of this tensor is directly 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 [12]:

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

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(ε) up to incident radiation energy of $\hbar\omega$ = 40 eV, with a mesh of 55 (BGO:Cr→Ge case) and 68 k-points (BGO:Cr→Bi case) 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 ε(ω).

3. Results and the discussion

3.1. Electronic structure

In the figure 1 it is presented the total density of states (TDOS) for the BGO:Cr→Ge system.

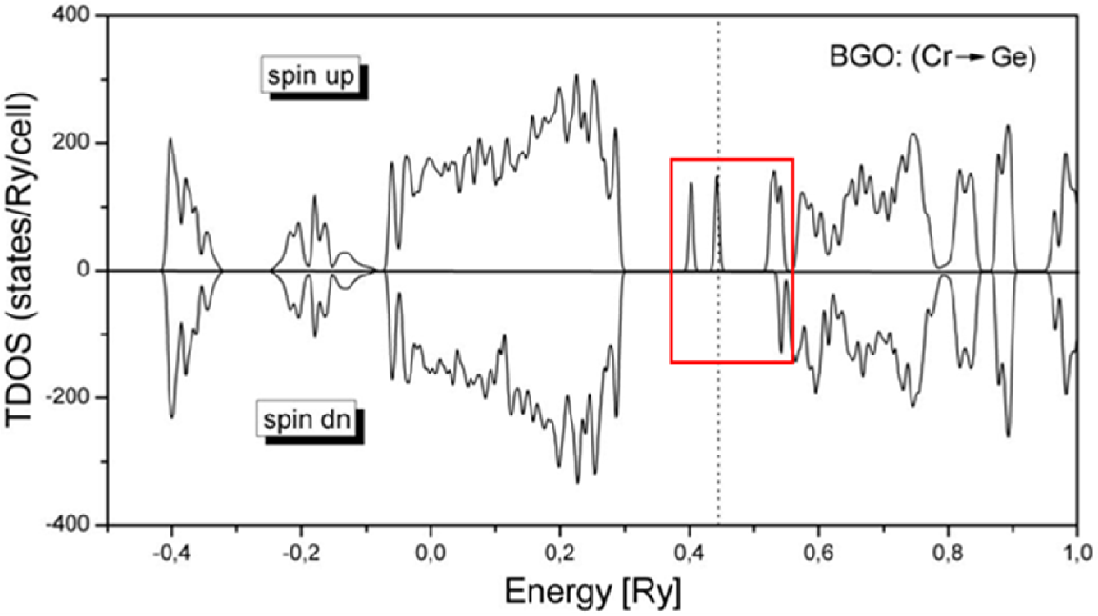

Figure 1: Total spin-polarized electronic density of states of the BGO doped with the Cr residing at the Ge position. The dashed line denotes Fermi level.

The basic difference between the TDOS of the doped BGO and the TDOS of the pure BGO (ref. [7]) consists of a presence of the bands situated within the fundamental gap of the pure system. These bands are emphasized by the square in the Fig. 1. When the Cr substitutes the Ge, it introduces two deep and one shallow band within the gap (the last is superposition of the spin up and down states). Deep bands are populated, and the shallow one is empty. The deep band of lower energy consists of the Cr d_z^2 states, where the z-axis is a symmetry axis of the tetrahedral surrounding of the Cr. The deep band of higher energy is superposition of the Cr d_{xy} and d_{x2-y2} states, while the shallow band is formed from the Cr d_{xz} and d_{yz} spin-up states and the d_z^2 spin-down states. All the Cr d-states within the gap are strongly hybridized with the p-states of nearest neighbor oxygen's, a fact which causes the broadening of bands. The majority states are the spin-up states, and the calculated magnetic moment of the Cr atom is $+1.58\mu_B$.

In the figure 2 it is presented the total density of states (TDOS) for the BGO:Cr→Bi system.

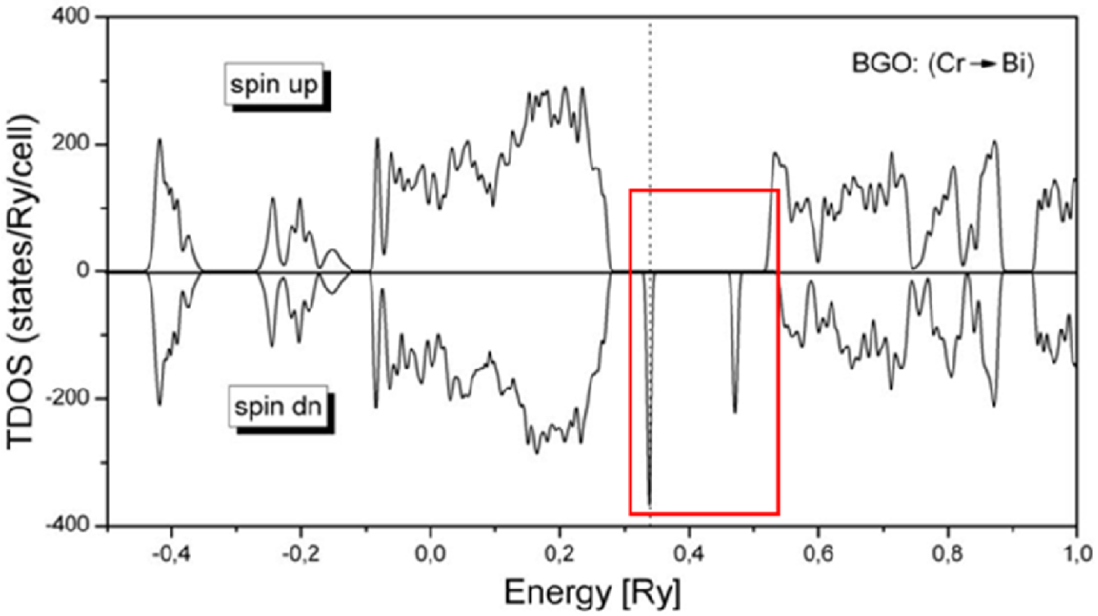

Figure 2: Total spin-polarized electronic density of states of the BGO doped with the Cr residing at the Bi position. The dashed line denotes Fermi level.

In the case when the Cr substitutes the Bi, it introduces two shallow bands within the gap and positions its states at the bottom of the conduction band (emphasized by the square in the Fig. 2). Both shallow bands are composed of the superposition of the Cr spin-down d_{xy} ,d_{x2-y2}, d_{xz} and d_{yz} states, strongly hybridized with the neighboring O's p-states. The spin-up states at the bottom of the conduction band have the dominant Cr $d_z{}^2$ character. Majority states are the spin-down states, and the calculated magnetic moment of the Cr atom is $-2.44\mu_B$.

3.2. Optical absorption spectra

Figure 3 shows intensity of the optical absorption of the BGO:Cr→Ge system as a function of the wavelength of the incident light. In the region above the absorption threshold of the pure BGO there are three prominent peaks (structures) centred at the 355, 710 and 1080 nm. All the three are caused by the Cr presence. A more detailed analysis [13] shows that the 355 nm band originates from the electronic transitions from O-p (valence band top) to the Cr-d states (shallow band within a gap). The 710 nm band is dominated by the transitions from the Cr-d states (deep band of lower energy) to the Cr-d (shallow band) and the O-p states (conduction band bottom), while the 1080 nm band is due to Cr-d (deep band of higher energy) to Cr-d states (shallow band). It should be stressed that the d-d transitions are not forbidden owing to the fact that the BGO unit cell does not possess the inversion centre.

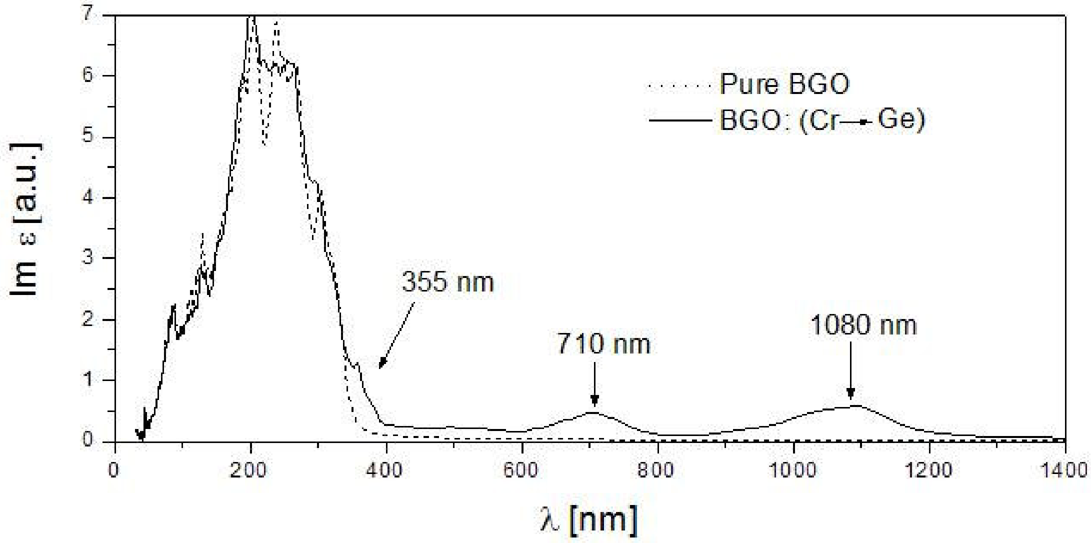

Figure 3: Optical absorption spectrum of the BGO:Cr→Ge system (in arbitrary units). The dashed curve represents the optical absorption of the pure BGO.

The absorption spectrum of the BGO doped with the Cr residing at the Bi site is shown in the figure 4. It is seen that the Cr presence induces three absorption bands above the absorption threshold of the pure BGO. The first two, centred at the 380 and 420 nm, originate from the electron transitions from the O-p states (valence band top) to the Cr-d states (empty shallow band within a gap). The 680 nm band is dominated by the transitions between the Cr-d states of different symmetry (from semi-populated shallow band to the empty shallow band).

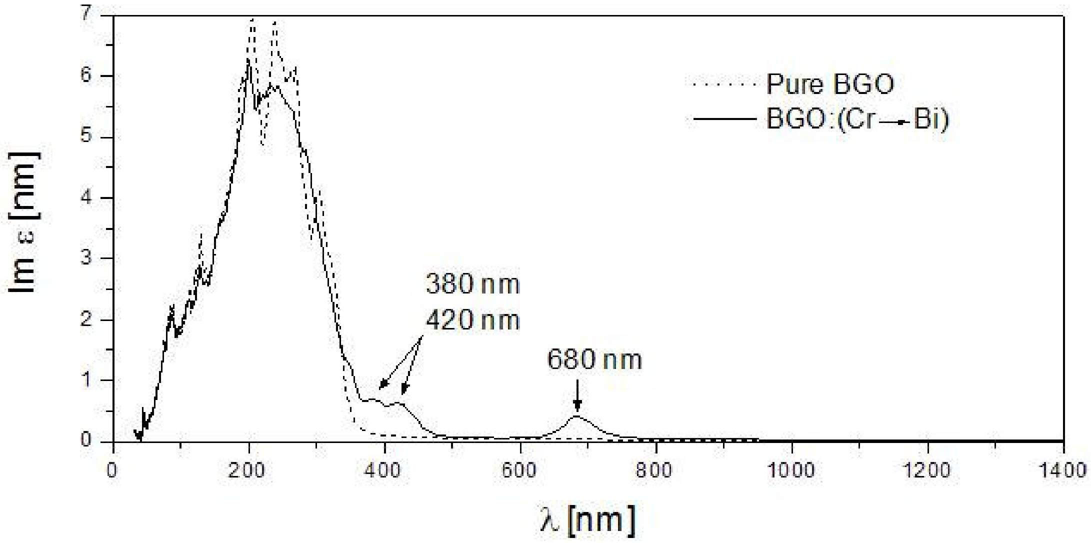

Figure 4: Optical absorption spectrum of the BGO:Cr→Bi system (in arbitrary units). The dashed curve represents the optical absorption of the pure BGO.

The experimentally recorded absorption spectrum of the Cr doped BGO at ambient temperature is characterized by the 6 peaks above the absorption threshold of the pure BGO [5]. Three of them lie in the range of 300-600 nm, relatively near the absorption threshold (which is about 300 nm), and the other three are positioned between the 600 and 900 nm. All the peaks are found to be very broad.

Tempting to directly compare the theoretical and experimental absorption spectra of the Cr doped BGO one should be cautious. The theoretical spectra refer to the ground state of the system, i.e. strictly speaking to the T=0K. Besides, the calculated band gap of the pure BGO is underestimated [7] due to the well known deficiency of DFT to correctly describe exchange and correlation effects. Thus, the calculated peak positions cannot be directly comparable with the experiment. On the other side, the electronic band structure is not expected to change very much from T=0 to T=300K if there is no phase transition in this temperature range. Since the absorption spectrum depends crucially on this band structure, it is also not expected to be much different at the ambient temperature. Therefore, one could trust that at ambient temperature the calculated absorption spectra would be more or less the same as presented in the figures 3 and 4, with eventual slight dislocation and rearrangement of the peaks. The superposition of the two Cr optical responses, from the Ge and the Bi site, would result in the 6 peaks above the absorption threshold. Keeping this in mind, we conclude that our calculations indicate that the experimental spectrum shown in the ref. [5] is probably composed of the optical response of the Cr residing at the both Ge and Bi positions, supporting thus the conclusion of the experimental work of Bravo et al [4].

4. Conclusions

We have analyzed theoretically the electronic and optical properties of the Cr doped BGO scintillator, taking into account the fact that Cr can substitute either Ge or Bi atom in the BGO lattice. As a computation tool it was employed the DFT based, full potential linear augmented plane wave method. The results show that the Cr modifies the electronic structure of the pure BGO introducing its states within the band gap: two deep and one shallow band if it resides at the Ge position and two shallow bands if it resides at the Bi position. In the first case the Cr magnetic moment is calculated to be $+1.58\mu_B$, while for the second $-2.44\mu_B$. Thus, in the external magnetic field the Cr moments are expected to align oppositely. The optical absorption spectra were calculated as functions of the incident light energy up to 40 eV. The absorption peaks caused by the Cr presence were identified and interpreted in terms of calculated electronic structure, for both possible positions of the Cr impurity. Comparison with the experimental data indicate that the Cr doped BGO should contain the Cr atoms in both Ge and Bi substitution sites.

Acknowledgements

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