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First-principles study of the $\text{Bi}_M\text{O}_4$ antisite defect in the $\text{Bi}_{12}\text{MO}_{20}$ ($M=\text{Si}, \text{Ge}, \text{Ti}$) sillenite compounds

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Abstract

Structural, electronic and optical properties of the antisite $\text{Bi}_M\text{O}_4$ defect in $\text{Bi}_{12}\text{MO}_{20}$ sillenites ($\text{BMO}, M=\text{Si}, \text{Ge}, \text{Ti}$) were investigated using density functional theory. The defect is studied in neutral, positively and negatively charged states. It is demonstrated that within the neutral defect the $\text{Bi} 6s^2$ lone pair is broken and the valence state of the $\text{Bi}$ is $4+$ ($6s^1$). Within the charged defects, the $\text{Bi} 6s$ orbital is found to be either full ($\text{Bi}^{3+}: 6s^2$) or empty ($\text{Bi}^{5+}: 6s^0$). All three charged states introduce energy bands within the BMO gap. By analyzing possible transitions between them we deduced a simple model of functioning of the $\text{Bi}_M\text{O}_4$ defect that is able to explain the photochromic and photorefractive effect in sillenites and that reproduces almost all known experimental facts.

1. Introduction

The sillenite crystals with chemical formula $\text{Bi}_{12}\text{MO}_{20}$ ($\text{BMO}, M=\text{Ti}, \text{Ge}, \text{Si}$) attract significant scientific attention mostly because of their pronounced photorefractive (PR) effect that is used in many applications such as multi-wavelength holography [1], real-time holographic surface imaging [2, 3], optical information processing [4] and in various metrological problems [5]. Besides, the sillenites also exhibit pronounced optical activity and Faraday rotation, very useful properties for development of fiber optic current sensors [6, 7] and a variety of photocatalytic applications [8, 9].

A simple optical recording in PR materials requires the presence of photoconductive centers, usually defects or impurities, which provide additional energy levels within the band gap. They serve as traps for electrons which, under coherent illumination, migrate from bright to dark regions of crystal space, changing electrical and optical properties of the perfect compound [10]. Characterization of these levels and comprehension of their origin are necessary tasks for efficient manipulation and technological application of PR materials.

The nominally pure sillenites possess a complex structure of intrinsic defects [11–15], a fact proven by observation of the PR effect in undoped materials [16–18]. Summarizing [11–15], the majority of them involve wrong population of the $M$ site (with nominal valence $4+$) which can be partially (I) occupied by the $\text{Bi}^{3+}$ ion tetrahedrally coordinated by the $\text{O}$ ions ($\text{Bi}_M\text{O}_4$), (II) occupied by the $\text{Bi}^{3+}$ ion coordinated with three $\text{O}$ ions ($\text{Bi}_M\text{O}_3$) and with the $\text{Bi} 6s^2$ lone pair pointing in the direction of the fourth absent $\text{O}$, or (III) vacant ($\text{VO}_4$). The $\text{Bi}_M\text{O}_4$ and $\text{Bi}_M\text{O}_3$ defect centers are commonly known as antisite $\text{Bi}$ defects ($\text{Bi}_M$) in sillenites.

Even though is possible that all three types of defect coexist simultaneously, the PR effect is always justified on the basis of the $\text{Bi}_M\text{O}_4$ defect center [16–18]. The latter has been studied experimentally in two different states of the host crystal: (1) a bleached state (reached by thermal exposure or red light illumination of the sample), and (2) a colored state (realized by blue light illumination of the bleached sample). The following facts were established. Within the bleached state the BMOs do not exhibit any absorption from the near-infrared to ultraviolet range (the band gap in all three
for the Bi and the excited electron is captured by other defects. In which the Bi ion appears in paramagnetic configuration $6s^1$ conduction band, transforming the host into the colored state. Light illumination excites one of the Bi $6s$ electrons into the neutral with the Bi ion in diamagnetic configuration $6s^0$.

The MCD and optically detected magnetic resonance (ODMR) studies correlate this shoulder with the paramagnetic defect [10, 20]. The fact magnetic circular dichroism (MCD) measurements do not register this shoulder means that it is provoked by diamagnetic defect [10]. Within the colored state of the BMOs [19] the optical absorption measurements register a very intense and broad shoulder in the visible and near-infrared region [10, 20]. The bleached state of the BMOs should contain these two kinds of diamagnetic defect. The blue (or more energetic) light illumination excites electrons or holes from these defects, creating again the paramagnetic Bi$^{0+}$ defect and transforming the host into the colored state. In the rest of the paper we will detail the theoretical foundation of this model and demonstrate that it is able to explain most of the established experimental facts.

2. Computational procedure

2.1. Simulation of isolated intrinsic defect and structural relaxation

The BMO’s crystal structure is body-centered cubic, with space group I23 (no 197) [22]. The primitive unit cell contains 1 f.u. (33 atoms) without having a center of inversion. It contains three nonequivalent O atoms, one at the position 24f (O(1)), and two at the position 8c (O(2) and O(3)). The M$^{4+}$ ion occupies 2a site, being bonded with four O(3) atoms. The local structure can be viewed as a regular tetrahedron with the M$^{4+}$ at its center and O$^{2-}$ at its vertices. The Bi$^{3+}$ ions occupy the 24f site, being surrounded by eight O atoms that form a distorted BiO$_8$ polyhedron [32]. Within the unit cell the MO$_4$ tetrahedra are located at the body-centered and corner sites. Connection between the BiO$_8$ polyhedron and the MO$_4$ tetrahedron is established via the O(3) ion (figure 1).

The Bi$^{3+}$O$_4$ defect center was simulated using the primitive unit cell of the perfect Bi$_{12}$TiO$_{20}$ (BTO) crystal, whose lattice parameter has been computationally relaxed.
in our recent work ($\alpha = 10.322$ Å) [23]. The BTO (and not the Bi$_2$GeO$_2$O$_5$ (BGO) or Bi$_2$SiO$_5$O$_2$ (BSO)) unit cell was chosen because the calculated gap agrees best with the experimental value [18]. Within this unit cell the central Ti$^{4+}$ ion has been replaced by the Bi$^{3+}$ ion generating the neutral antiseite defect Bi$_0^0$Ti$_0$. The defective periodic system BTO:Bi$_0^0$Ti$_0$ is then generated by infinite repetition of this unit cell, which actually does not contain the Ti ions and simulates all three BMO:Bi$_0^0$ compounds. We estimated that this unit cell is large enough to prevent significant interaction between defects and to correctly simulate their neighborhoods (see the discussion at the end of section 4). The antiseite defect is also studied in two ionization states: positively charged Bi$^{3+}_M$ is simulated by removing one electron from the unit cell of the BMO:Bi$_0^0$M and negatively charged Bi$^{3+}_M$ by adding one electron to it. In both cases a charge compensating homogeneous jellium background charge is assumed to preserve overall neutrality.

For all three differently charged defective systems all atomic positions inside respective unit cells were relaxed by moving the atoms according to forces which act on them (damped Newton scheme) [24]. The process was repeated until these forces became less than 2.0 mRyd/a.u. During relaxation the symmetry constraints of the space group have been obeyed because of strong experimental evidence that the M site experiences a perfect tetrahedral crystal field [13].

2.2. Calculations of electronic structure and optical response

All calculations were carried out using a full potential linear augmented plane wave (FP-LAPW) method [25] based on DFT [26] and implemented in the WIEN2k computer code [27]. The electronic wavefunctions, charge density and crystal potential were expanded in terms of partial waves inside the non-overlapping atomic spheres centered at each nuclear position (with radii $R_{MT}$) and in terms of the plane waves in the rest of the space (interstitial). The choices for the Bi and O $R_{MT}$ were 2.3 and 1.4 a.u. respectively. The partial waves were expanded up to $l_{\text{max}} = 10$, while the number of plane waves was limited by the cut-off at $K_{\text{max}} = 7.0/RMT$ (O). As a basis, the augmented plane waves were used. The charge density was Fourier expanded up to $G_{\text{max}} = 14$. A mesh of seven $k$-points in the irreducible part of the Brillouin zone was used. The Bi 5d, 6s, 6p and the O 2s, 2p 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.

Exchange and correlation effects were treated in a twofold manner. The relaxation of atomic positions has been performed using the generalized gradient approximation with Perdew–Burke–Ernzerhof parameterization (GGA-PBE) [28]. While this functional is very useful in calculating structural and other properties related to total energies, it severely underestimates the band gaps of most semiconductors and insulators. Thus, electronic bands and optical response have been calculated using the semi-local modified Becke–Johnson (mBJ) functional recently proposed by Tran and Blaha [29]. This functional has been shown to reproduce better the band gaps, electronic and optical properties for a variety of semiconductors and insulators [30–32]. The spin–orbit coupling has been taken into account just for heavy Bi atoms via a second variation procedure, using scalar-relativistic eigenfunctions as a basis. Electronic structure was calculated up to an energy of 4.0 Ryd. The self-consistent calculations of all three defective systems were performed on the same level of precision and successfully converged within the energy precision of $10^{-5}$ Ryd.

The linear optical properties were determined by the WIEN2k optical package [33], which calculates the imaginary part of the complex dielectric tensor $\varepsilon_2$, directly proportional to the optical absorption spectrum, on the basis of the following formula [34]:

$$
\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2\omega^2} \sum_{i,f} \int_{BZ} \frac{2d}{(2\pi)^3} |\langle \varphi_i | P | \varphi_f \rangle |^2 \delta(E_f(k) - E_i(k) - \hbar\omega). \tag{1}
$$

Formula (1) is valid within the frame of the random phase approximation and does not account for electron polarization effects. It therefore cannot describe excitonic effects, but in the case of sillenites there are no experimental proofs of their importance. Instead, it describes electric dipole allowed transitions from populated Kohn–Sham states $|\varphi_i\rangle$ of energy $E_i(k)$ to empty Kohn–Sham states $|\varphi_f\rangle$ of energy $E_f(k)$ with the same wavevector $k$ ($\omega$ is the frequency of incident radiation, $m$ the electron mass, $P$ the momentum operator, and $\alpha$ and $\beta$ stand for the projections $x$, $y$ or $z$). $\varepsilon_2$ was computed in the energy range from 0 to 3 Ryd (0–40 eV), taking into account electronic transitions from $-1.2$ to 2.0 Ryd. The number of empty states considered was approximately 254, for all three defective systems. A mesh of 45 $k$-points in the irreducible wedge of the first Brillouin zone was used. Owing to their cubic symmetry, the sillenite’s dielectric tensor is diagonal, with $\varepsilon_{2xx} = \varepsilon_{2yy} = \varepsilon_{2zz} = \varepsilon_2$, and thus reduced to scalar function $\varepsilon_2(\omega)$.

3. Results and discussion

3.1. Electronic structure of defective systems

Resulting total and partial densities of electronic states (TDOS and PDOS) of the three BMO:Bi$_{3+}^{1+}, 1^-$ defective systems are presented in figure 2, together with the TDOS of the perfect BTO (calculated recently by our group [32]), which is shown for comparison.

For the perfect BTO the calculated gap was 0.243 Ryd (3.3 eV), very close to the experimental value of 3.2 eV [18]. The peak at the very top of the valence band (marked by letter A) is predominantly composed of the 2p states of the O(3) and the Bi 6s states. The peak at the very bottom of the conduction band (marked by B) is dominated by the Bi 6p states hybridized with the 2p states of the O atoms [32].

For the defective systems, figure 2 reveals two principal differences relative to the perfect one: (1) significant change of intensity, form and composition of the TDOS at the top of the valence band, and (2) formation of one extra band, situated within the fundamental gap and composed of the hybridized Bi$_M$ 6s and O(3) 2p states.
Figure 2. Top: calculated TDOS of the perfect BTO (a) and the BMO containing the neutral (b), positively (c) and negatively (d) charged antisite Bi\textsubscript{M} defect. The letters A and B denote the peaks at the valence band top and conduction band bottom, respectively. The letters C, C′ and C″ denote bands within the gap introduced by the antisite defect. The dashed line indicates the Fermi energy. Bottom: calculated PDOS of the three defective BMO crystals. A band due to the antisite Bi defect is composed of a mixture of the Bi\textsubscript{M} 6s and the O(3) 2p states.

The first difference can be related to the relaxation of atomic positions in defective systems. In perfect BMOs the shortest bonds are the M–O(3) ones, so the occupied O(3) states have high energy and dominate the very top of the valence band [32]. In defective systems the Bi\textsubscript{M}–O(3) bonds are significantly elongated (see table 1), and the Bi–O(1) bonds become the shortest ones (since the neighborhood around the regular Bi sites in defective systems does not change much we did not find it necessary to represent a table with the Bi–O interatomic distances; this table for the pure BMOs can be consulted in [32]). As a consequence, the dominant orbital character of the valence band top in defective systems changes from the O(3) to the O(1) 2p states, while the TDOS intensity increases because there are more O(1) than O(3) atoms within the BMO unit cell.

Table 1. Calculated equilibrium distances between the Bi\textsuperscript{0}\textsubscript{M} defects and their nearest and next-nearest (NN and NNN) neighboring O atoms, as well as between the Bi\textsuperscript{0}\textsubscript{M} and the nearest regular Bi ions. The same distances in the pure BTO are shown in the last line, taken from [23].

<table>
<thead>
<tr>
<th>Distances (Å)</th>
<th>NN O atoms</th>
<th>NNN O atoms</th>
<th>Bi\textsuperscript{0}\textsubscript{M}–Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(3)</td>
<td>O(2b)</td>
<td>Bi\textsuperscript{0}\textsubscript{M}–Bi</td>
</tr>
<tr>
<td>Bi\textsuperscript{0}\textsubscript{M}</td>
<td>2.112</td>
<td>3.901</td>
<td>3.925</td>
</tr>
<tr>
<td>Bi\textsuperscript{+}\textsubscript{M}</td>
<td>2.026</td>
<td>3.988</td>
<td>3.980</td>
</tr>
<tr>
<td>Bi\textsuperscript{−}\textsubscript{M}</td>
<td>2.200</td>
<td>3.645</td>
<td>3.836</td>
</tr>
<tr>
<td>Ti</td>
<td>1.842</td>
<td>3.443</td>
<td>3.913</td>
</tr>
</tbody>
</table>

The second difference is a fundamental one, resulting in formation of a new permitted energy band within the gap. In all three defective systems this band can admit up to two
electrons, but its actual occupation and energy depend on the charge state of the defect.

The neutral defect (figure 2(b)) forms a deep, half-occupied band, placed in the middle of the gap. Since this band has the dominant Bi 6s character (figure 2(c)), it can be concluded that the Bi releases one electron from its 6s² lone pair to satisfy bonding with all four neighboring O(3) ions. Thus, four of the five valence electrons of the Bi (6s⁷6p⁶ in free-atom configuration) are used to form the tetrahedral covalent bonds with the neighbors, while the fifth electron remains within the BiM atomic sphere. This fact can be interpreted as if the Bi ion within the Bi⁰ defect exhibits approximately the 6s¹ configuration, being in the valence state 4+. It introduces both donor and acceptor states into the BMO’s gap.

The positively charged Bi⁺ Mü defect forms an acceptor band (figure 2(c)). Since it has predominantly the Bi 6s character (figure 2(g)), this result indicates that one electron has been removed from the Bi 6s orbital, leaving the Bi without any valence electrons. This situation describes the 5+ valence state of the Bi (6s⁰ configuration). It is physically realized when the Bi 6s¹ electron is excited to the conduction band by, for example, an optical absorption process.

The negatively charged Bi⁻ Mü defect introduces a donor band within the BMO gap (figure 2(d)). Again, the fact that the band exhibits predominant Bi 6s character (figure 2(i)) leads to the conclusion that one extra electron is accommodated into the Bi 6s² orbital, recuperating the Bi 6s² lone pair. Thus, the formal valence of the Bi ion within the Bi⁻ Mü defect is 3+ (6s² configuration). This defect is realized when the neutral Bi⁰ Mü defect captures an electron from somewhere, either by excitation from the valence band top or by de-excitation from the conduction band bottom. In the first case the 2p electron is transferred to the Bi from the O(3) surrounding it, while in the second case the additional electron is captured from other regions of the crystal (possibly originating from other defects).

Contrary to existing models, our theoretical results predict vulnerability of the Bi 6s² lone pair within the BiM₆O₄ defect. Our calculations clearly indicate that within the Bi⁽⁰⁰⁾ Mü defect the Bi uses one of its 6s electrons to satisfy the missing (fourth) bond with neighboring O atoms without producing an electron hole but, instead, changing its valence state from 3+ to 4+. The results of simulation of the charged defects additionally support ‘vulnerability’ of the Bi 6s² states (in the sense of their facility to be occupied or unoccupied).

Figure 3. Valence electron density of the BiM₆O₄ defect projected onto the (111) crystal plane. In the left picture the black frame emphasizes the TiO₄ cluster within the perfect BTO: the Ti ion is in the center, and its three neighboring O atoms have density projections around it (they are actually slightly above the plane). The fourth O is exactly below the Ti and therefore not seen. The three pictures on the right refer to the differently charged BiM defects and demonstrate deterioration of the BiM 6s² lone pair. The sketch below these pictures illustrates the form of the 6s² electronic cloud, facilitating the visualization of its projection onto the plane formed by the Bi and three neighboring O atoms.

3.2. Energetic and structural characteristics of the BiM₆O₄ defect

In order to check if all three Bi⁽³⁾ Mü defects are physically realizable and to estimate their relative stabilities, we need to calculate their formation energies. In the present study the reference pure system is the BTO (see discussion in the section 2.1), and thus we are able to discuss only defect formation energies in this compound: Bi⁽³⁾ Mü. The results, however, could be somewhat generalized for the antisite defects in the other two sillenites (BGO and BSO), considering the fact that the Ge and Si ions have the same valence state (4+) and the same surroundings as the Ti ions in the BTO. Formation energies of the Bi⁽³⁾ Mü defects are calculated on the basis of the following formula [35, 36]:

$$E_f (\text{BTO:Bi}^{3+}_{\text{Bi}}) = E_f (\text{BTO:Bi}^{3+}_{\text{Ti}}) - E_f (\text{BTO}) + \mu_{\text{Ti}}$$

$$= -\mu_{\text{Bi}} + q(E_{\text{VB,M}} + E_{\text{F}} + \Delta V(q))$$

where the first two terms on the right-hand side represent the total energies of the perfect and defect-containing BTO...
defects were determined as 13 as well as the distances between Bi nearest and next-nearest (NN and NNN) neighboring O atoms, between differently charged antisite Bi defects and their positively charged defect is the most difficult to realize over favorable for Fermi energies between 2 and 3.3 eV . The 0 to 2 eV , while the negative defect becomes energetically 2p to the Bi 3+ defects, but not for the BiM defect, for which the second neighborhood consists of the 12 Bi atoms at the distance of 3.980 Å, while four O(2b) appear at the distance of 3.988 Å as the third neighbors.

Table 1 summarizes the calculated inter-ionic distances of all defective systems. First, it shows that all defects induce considerable expansion of their first and second coordination spheres as compared with the perfect system. Second, it expresses a clear dependence of interatomic distances on the charge state of the defects. If the neutral defect BiM is considered as a referent system for comparison, then the BiM produces smaller expansion of its first and larger expansion of its second coordination sphere. On the other hand, the BiM defect induces larger expansion of its first and smaller expansion of its second coordination sphere. The BiM-Bi distances exhibit the same trend as the BiM-O(2b) ones.

All these characteristics can be understood on the basis of electronic configurations of three BiM defects deduced from electronic structure calculations presented in section 3.1. Within the neutral BiM defect the Bi appears in the formal valence state 4+. It repels the NN and the NNN O atoms for two reasons: (1) the ionic radius of the Bi is much larger than the M, and (2) the presence of a spatially extended 6s negative cloud additionally repels the negative oxygen ions. Within the negatively charged BiM defect, the Bi is in the formal valence state 3+. A spatially extended 6s electron cloud is more negative, thus the Bi3+ repels the NN O atoms farther away than the Bi4+. At the same time, the Bi4+ repels the NNN O(2b) atoms less than the Bi3+ due to a weaker electrostatic interaction with the neighboring Bi3+ ions at the regular crystallographic sites (the Bi3+-Bi3+ electrostatic repulsion is weaker than the Bi4+-Bi3+ one). The O(2b) atoms, being the NNs of the regular Bi3+, are simply dragged together with the regular Bi3+ since they are bound much more strongly to it. Within the positively charged BiM defect the valence state of the Bi is 5+. Owing to the lack of the 6s negative electron cloud the Bi5+–O(3) bonds are shorter in comparison with the neutral defect. At the same time, the Bi5+–Bi3+ electrostatic repulsion is stronger than the Bi3+-Bi3+ repulsion, and the Bi5+–O(2b) bonds are considerably longer than in the case of the neutral defect.

3.3. Optical absorption spectra of defective systems

The presence of antisite defects causes changes in the absorption spectrum of the BMOs, and these changes are most pronounced near the optical absorption edge of the perfect system. Figure 5 shows the calculated imaginary part of the dielectric function ε2 of the three BMO:BiM defective systems, as well as of the perfect BTO, as a function of incident radiation energy in the range of 1.5–4.0 eV.

As can be seen from figure 5, the perfect material starts to absorb the photons at the energy of 3.3 eV, while the spectra of all defective systems are characterized by prominent peaks below this energy. These peaks can be interpreted in terms of electronic structures presented in figure 2. The peaks I, I’ and I” in the BMO:BiM spectrum are formed by electronic transitions from band A to band C and from band C to band B. Taking into account the distance between atoms and predominant orbital character of the bands A, B and C, these structures are mainly determined by transitions from the O(3) 2p to the BiM 6s, from the O(3) 2p to the BiM 6p, and from the Bi 6s to the O(3) 2p and the BiM 6p states. All these
transitions transform the Bi electronic configuration from 6s\(^{1}\) to 6s\(^{2}\) (Bi\(^{3+}\) ion) and 6s\(^{0}\) (Bi\(^{5+}\) ion), creating the Bi\(_{M}\) and the Bi\(_{M}^{\text{q}}\) antisite defects. The optical spectrum of BMO:Bi\(_{M}\) also exhibits three prominent peaks (III, III' and III'') below the absorption threshold of the perfect BTO. These structures are due to electronic transitions from the top of the valence band to the unoccupied band C' within the gap. The electronic transitions involved are those between the O(3) 2p and the Bi 6s states. The optical spectrum of the BMO:Bi\(_{M}\) defect exhibits only one peak, numbered as V, below the absorption edge of the pure BTO. It is formed by electron transfer from band C' (occupied Bi 6s and O(3) 2p states) to band B (unoccupied O(3) 2p and the Bi 6p states).

Figure 5 also demonstrates that optical absorption above the 3.3 eV is more intense in defective systems than in the perfect BMOs. This characteristic is emphasized by peaks II (figure 5(a)), IV (figure 5(b)) and VI (figure 5(c)). It can be related to the existence of the higher DOS at the top of the valence band of defective systems (figures 2(b)–(d)) compared to the perfect BTO (figure 2(a)). This occurs because the O(1) 2p states become dominant at the valence band top of the defective systems (as discussed in section 3.1), increasing the probability of optical transition between the Bi and O(1) within the regular BiO\(_{8}\) polyhedron.

4. Model of the Bi\(_{M}\)O\(_{4}\) defect

On the basis of results presented in section 3.3, it is possible to construct a model of the functioning of the antisite Bi\(_{M}\)O\(_{4}\) defect that is able to explain the photochromic and PR effect in sillenites and that agrees with most of the basic experimental facts established so far. Deduction of the model can be assisted by a schematic representation of energy bands within the BMO gap originated from the Bi\(_{M}\) defects, as shown in figure 6. The scheme is constructed on the basis of the electronic structure presented in figures 2(b)–(d).

The neutral Bi\(_{M}^{0}\) is the defect that exists in the BMOs which are not subjected to any treatment, i.e. in their so-called colored state. This defect is paramagnetic (Bi\(^{4+}:\text{Bi}\(^{5+}\))

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The presented model emphasizes the importance of the Bi\textsubscript{3}M\textsubscript{2}X\textsubscript{3} defect for explanation of the PR effect in sillenites. Under coherent illumination of the crystal this defect acts as a donor and acceptor of the electrons at the same time (Bi\textsubscript{3}M\textsuperscript{0}), providing the traps for electrons (Bi\textsubscript{3}M\textsuperscript{−}) and holes (Bi\textsubscript{3}M\textsuperscript{+}) throughout the lattice, fulfilling in this way essential conditions required for optical recording via space–charge modulation [16–18].

Considering the optical absorption process caused by antisite defects, the presented model predicts the following features.

In the bleached state, optical absorption of the BMO’s below gap energy should be composed of superposition of the Bi\textsubscript{3}M\textsuperscript{−} and the Bi\textsubscript{3}M\textsuperscript{+} ε\textsubscript{2} spectra shown in figure 5. This superposition results in peaks centered at approximately 2.50, 2.75 and 3.00 eV. The experiment, however, observes just the shoulder at the energy of ∼3 eV [10]. There are two possible reasons for this disagreement: (1) optical calculations overestimated the transition probability from the O(3) 2p to the Bi\textsubscript{3} 6s states (those which generate peaks at 2.5 and 2.75 eV), resulting in higher absorption intensity than measured; (2) owing to the relatively small supercell size and approximate treatment of exchange–correlation effects in our calculations the energy of the acceptor band is slightly underestimated; if this band were positioned ∼0.5 eV higher in energy, the peak at 2.5 eV would be centered on 3 eV while other peaks would be immersed into the host absorption.

In the colored state, the BMO’s optical absorption edge should be influenced only by neutral defects and absorption described by the ε\textsubscript{2} spectrum of the Bi\textsubscript{3}M\textsuperscript{+} (figure 5). In the literature, however, the optical absorption spectrum of the BMOs at room temperature is sometimes presented [20], in which case it should be composed of a superposition of all three spectra shown in figure 5 (since all three differently charged defects should coexist in the host). In both cases our theoretical model predicts formation of a broad shoulder in the optical absorption spectrum of the BMO, as shown in figure 7, which explains the coloration of the material provoked by proper illumination (photochromism). It also demonstrates good qualitative agreement with experimental results.

It is worth mentioning that several experimental studies of doped sillenites have discussed the change of valence state of the impurities after illumination and its influence on the photoconductivity and photochromicity of the material. Montenegro et al [37] and Carvalho et al [38] studied optical absorption of nominally pure BTO doped with V atoms. They suggested that some of the tetrahedral sites occupied by Bi\textsuperscript{3+} defects may be substituted by either V\textsuperscript{3+} or V\textsuperscript{5+} ions. A similar conclusion is also drawn from works of Marquet et al [19] and McCullough et al [39], who investigated the optical absorption of BGO doped with Cr. Our theoretical study clearly substantiates their suggestions.

Finally, let us briefly discuss the reliability of the calculations presented in this paper. It is a fact that the size of the supercell used to simulate antisite defects was not very large (this is especially valid for consideration of the charged defects). This size is, however, sufficient to constrain the geometric influence of the defects within the supercell, as can be seen from the following facts.

Figure 7. Calculated optical absorption spectra of the BMO in the colored state (green line) and in the state in which all three Bi\textsubscript{3}M\textsuperscript{+} defects coexist (black line). They are compared to measured absorption spectra of nominally undoped BTO (red curve, [21]) and BGO (blue curve, [10]). The theoretical spectra are calculated in the energy range 0–3 eV, simulating measurements which were made up to this energy.

(1) Analysis of interatomic distances has shown that the lattice deformation is localized nearby the defect. Table 1 demonstrates that the distances between the defect and its neighboring O atoms are changed very much, which is not the case with distances between the defect and its third-neighboring Bi. The distances between the defect and the atoms situated farther away (not shown in the paper due to economy of space) are quite similar to the distances in the pure compound, for all three kinds of defect considered.

(2) Electronic bands of the defects, introduced within the band gap, are narrow. The thicknesses of the neutral and the charged defects’ bands are similar (figure 2). This fact indicates very small overlap between the wavefunction of the defect and its periodic images in other supercells.

(3) According to the distribution of the valence charge density, shown in figure 3, an extra or a missing electron charge (within the charged defects) is concentrated nearby the defect, populating or emptying the 6s states of the Bi.

The supercell size used in the present study is also sufficient to significantly reduce the magnitude of the Coulomb interaction between the charged defect and its periodic images. This effect can be estimated by calculating the first term of the Makov–Payne correction to the energy of the ionic crystals [40] (written in SI units):

$$E_{\text{corr}}^{\text{MP}} = \frac{1}{4\pi \varepsilon_0 \varepsilon_r} \frac{q^2 \alpha}{2L}$$

where $q = \pm e$ (charges), $\alpha = 3.64$ (Madelung constant for bcc lattice), $L = 10.322$ Å (supercell lattice constant) and $\varepsilon_r \approx 50$ (static dielectric constants of the BTO, BSO and BGO are 48, 56 and 47 respectively [41]). The result obtained is $E_{\text{corr}} = 50$ meV. Thus, even though the supercell is not large, due to the high dielectric constant of the sillenites the Coulomb interaction between defects is strongly screened and, consequently, errors in calculated total energies and positions of the Kohn–Sham bands within the gap are small.
5. Conclusions

In this paper we performed a thorough theoretical study of the antisite Bi&Msub;Osub;4 defect in the Bi2Msub;2Osub;20 (M = Si, Ge, Ti; BMO) sillenite compounds, which is formed by wrong occupation of the M4+ sites by the Bi3+ ions (Bi&Msub;M). As a tool we used the first-principles FP-(L)APW method, based on DFT and implemented in the WIEN2k computer code. We discussed the structural, electronic and optical properties of the Bi&Msub;M defect in its neutral (Bi&Msub;M0), negative (Bi&Msub;M-) and positive (Bi&Msub;M+) charge state.

The results of our study demonstrate that within the neutral defect (Bi&Msub;M0) the Bi 6s2 lone pair is broken and the Bi electron configuration is 6s1. By capturing or emitting one electron, the Bi assumes 6s2 or 6s0 configurations respectively, forming the Bi&Msub;M- and Bi&Msub;M+ charged defects. All three Bi&Msub;M+ defects introduce bands inside the BMO gap: the Bi&Msub;M+ a half-occupied deep band, the Bi&Msub;M- a donor band and the Bi&Msub;M+ an acceptor band. By analyzing the interplay of possible transitions between them we deduced a model of functioning of the Bi&Msub;M defect in sillenites which is substantially different from the existing ones. In brief, our model predicts that the Bi&Msub;M+ defect should be dominant in the colored state of the BMOs and should act simultaneously as a donor and an acceptor. Under proper excitation it can create traps for electrons (Bi&Msub;M+) and holes (Bi&Msub;M-) throughout the lattice, transforming the host into the bleached state and fulfilling the basic conditions required for optical recording via space–charge modulation. The model explains the domination of paramagnetic defects in the colored and diamagnetic defects in the bleached state, and accurately reproduces conditions that are necessary to transform the colored state into the bleached one and vice versa. Additionally, it correctly predicts the formation of the broad and intense shoulder below the optical absorption edge of the BMOs, explaining their coloration under appropriate illumination.

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