

**DFT study on electronic, optical, and photocatalytic properties of  
mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ )**

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## Abstract

The structure, electronic band structure, density of state, projected wave function and optical properties of mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) crystals have been studied using density functional theory framework with the plane wave pseudo-potential in the frame of the generalized gradient approximation proposed by Perdew, Burke, Ernzerhof. Satisfactory agreement between experimental and theoretical results indicates that the used method and conditions are suitable. M-O bonds in tetrahedral  $\text{MO}_4$  environments are stronger and more covalent respect to octahedral  $\text{MO}_6$ , also Bi-O bonds in both studied structures are almost ionic in nature. The photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is enhanced due to unequal values of Mulliken charges on the O atoms in  $\text{MO}_4$ ,  $\text{MO}_6$ , and  $\text{BiO}_6\text{E}$  groups.  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are direct and indirect band gap semiconductors with band gaps 2.71 and 2.86 eV, respectively. Higher photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  is inferable from lighter effective masses of electrons and holes around the CBM and VBM, in comparison with  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . Presence of M and O orbitals in the valence and conduction bands states that symmetry breaking in the  $\text{MO}_4$  and  $\text{MO}_6$  units has an important role in separating charges and increasing of photocatalytic activity. Photocatalytic activities of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  for decomposition of organic pollutants and generation of hydrogen from water splitting are confirmed from band edge potentials.

**Keywords:** GGA/PBE; Effective mass; DOS; Projected wave function; Tauc plot; Photocatalytic activity

## 1. Introduction

Ceramic semiconductors have received considerable interest because of their potential applications in solid oxide fuel cells, electrochemical reactors and sensors, gas separation membranes, photocatalytic, multi ferroelectric, and scintillating materials <sup>1</sup>. Mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}$ ) <sup>2, 3</sup> with the space group *Pbam* are attractive research subjects due to useful properties such as high thermal stability under extreme conditions, excellent creep resistance, low thermal expansion, low thermal conductivity, photo-luminescence (green-yellow and red emission bands for both  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ ), photocatalytic activity, etc <sup>4-6</sup>.

The whole structure of  $\text{Bi}_2\text{M}_4\text{O}_9$  ceramics (see Figure 1-a) is characterized by the linear Zweier single chains of edge-sharing  $\text{MO}_6$  octahedral (green polyhedral) which is extended along the crystallographic *c*-axis <sup>1, 6, 7</sup>. The octahedral  $\text{MO}_6$  chains are connected together via  $\text{M}_2\text{O}_7$  diortho-groups formed by corner-sharing  $\text{MO}_4$  tetrahedral (blue polyhedral) in which half of the  $\text{M}^{3+}$  cations are octahedrally coordinated and the other half cations are tetrahedrally coordinated. The  $\text{M}_2\text{O}_7$  dimers are arranged in (0 0 1) planes and alternate with planes of  $\text{BiO}_6\text{E}$  groups (E refers to a  $6s^2$  lone electron pair, LEP) along the *c*-axis in which oxygen vertex atoms on  $\text{M}_2\text{O}_7$  dimers form linear M-O-M bonds <sup>1, 8, 9</sup>. The environment of the  $\text{Bi}^{3+}$  cation in  $\text{BiO}_6\text{E}$  groups is highly asymmetric with three strong bonds and one weaker Bi-O bond on one side, and the LEP and two long, very weak Bi-O bonds on the other side <sup>8</sup>.

Mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  semiconductors have been invoked in the literatures as active photocatalyst for water photocatalytic splitting and photocatalytic degradation of toxic organic pollutants. Compared with typical photocatalysts such as  $\text{TiO}_2$  (3.2 eV),  $\text{SrTiO}_3$  (3.2 eV),  $\text{ZnO}$  (3.3 eV),  $\text{BiOCl}$  (3.5 eV), and  $\text{ZnS}$  (3.6 eV) <sup>10, 11</sup>, mullite-type  $\text{Bi}_2\text{M}_4\text{O}_9$  semiconductors have adequate band gap ( $< 3.0$  eV) which can absorb photons in the visible region. The experimental and theoretical results indicated that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  has a narrow band gap near the range of visible and ultra violet light spectra <sup>1, 12, 13</sup>. Recent investigations indicated that  $\text{Bi}_2\text{Fe}_4\text{O}_9$  is an interesting alternative material for water photocatalytic splitting <sup>14</sup>, photodegradation of methyl orange <sup>15</sup>, phenol and aqueous ammonia <sup>16</sup>. Photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  for degrading of methylene blue has been studied experimentally by Curti and coworkers <sup>17</sup>. They observed that photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  was decreased after exchanging of Al atoms by Fe atoms. In addition to the band gap, photocatalytic activity are

related to the dielectric constant, effective masses of photogenerated carriers and band edge positions of semiconductors<sup>18</sup>. First principles methods are optimistic approaches which can provide suitable information about these parameters economically.

To the best of our knowledge photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  has not been studied basically yet. In this work, detailed systematic theoretical investigations are presented on the structural properties, electronic band structure, density of states (DOS), optical and photocatalytic properties of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  using the first principles calculation based on density functional theory (DFT). Furthermore, covalence/ionic nature of M-O bonds, effective mass tensors of photogenerated holes and electrons, and band edge positions of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  have been studied.

## 2. Computational methodology

The experimental crystal structural data of  $\text{Bi}_2\text{Al}_4\text{O}_9$ <sup>19</sup> and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ <sup>8</sup> were taken as initial geometries. All calculations are performed using plane wave pseudo-potential method by **employing** the Cambridge Serial Total Energy Package (CASTEP) code<sup>20</sup>. The electronic exchange-correlation interactions were treated according to the Perdew, Burke, Ernzerhof (PBE) **density** functional within the generalized gradient approximation (GGA)<sup>21</sup>. The electron-ion interactions were taken into account by means of Vanderbilt ultrasoft pseudo-potential (VUPP)<sup>22</sup> with the valence configurations  $6s^2 6p^3$  for Bi,  $3s^2 3p^1$  for Al,  $3d^{10} 4s^2 4p^1$  for Ga and  $2s^2 2p^4$  for O, in order to allow calculations to be performed with the lowest possible cut-off **kinetic** energy with minimum contribution from the core region. **All scalar relativistic effects were included in the current ultrasoft pseudopotentials, and spin-orbital coupling was not considered.** The crystal reciprocal-lattice and integration over the Brillouin zone were performed using the Monkhorst-Pack<sup>23</sup> grid of  $4 \times 4 \times 6$ , in which spacing of grid points are smaller than  $0.03 \text{ \AA}^{-1}$ . The Broyden-Fletcher-Goldfarb-Shanno (BFGS)<sup>24</sup> algorithm has been used for geometry optimizations and convergence parameters were as follows: the plane wave basis set energy cut-off 380 eV, total energy convergence tolerance  $1 \times 10^{-5}$  eV/atom, self-consistent field tolerance  $1 \times 10^{-6}$  eV/atom, maximum force  $0.03 \text{ eV/\AA}$ , maximum stress 0.05 GPa and maximum displacement  $0.001 \text{ \AA}$ .

### 3. Results and discussion

First, crystal structures of orthorhombic  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  with space group *Pbam* have been optimized using BFGS algorithm. The calculated lattice parameters are listed in Table 1 and compared with available experimental values. The calculated equilibrium lattice parameters are satisfactory in comparison with the experimental data<sup>8, 19, 25</sup>. The maximum and minimum deviation of lattice parameters are 2.7% and 0.2%, respectively. The main difference between the theoretical and experimental values is due to two factors: i) the experimental measurements were performed at 300 K, while the theoretical calculations were performed in the ground state condition at 0 K, and ii) known DFT limitation due to certain simplifications and approximations in exchange-correlation functionals. Structural results show that the computational method and parameters used in this work are reasonable. It should be noted that results of GGA-PBE method have been acceptable for prediction of structural and electronic properties of other member of mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{Bi}_2\text{Fe}_4\text{O}_9$ )<sup>26</sup>. The calculated bond lengths of M-O ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) in tetrahedral  $\text{MO}_4$  and octahedral  $\text{MO}_6$  units are given in Tables 2 and 3. The calculated and experimental<sup>8, 19</sup> M-O bond lengths show that tetrahedral  $\text{MO}_4$  and octahedral  $\text{MO}_6$  are distorted and their symmetries are reduced in which the center of gravity is deviated from the position of the M ion.

Unequal values of Mulliken charges (Tables 2 and 3) on the O atoms in  $\text{MO}_4$ ,  $\text{MO}_6$ , and  $\text{BiO}_6\text{E}$  groups are important factor to generation of dipole moment. The local internal fields due to generated dipole moment promotes the separation of electron-hole pairs in the very initial process of photo-oxidation which can enhance photocatalytic activity<sup>27</sup>. To understand the bonding nature of each M-O bond, bond populations are calculated according to the Mulliken population analysis<sup>28, 29</sup>. Mulliken bond population is a measure of spatial charge density between bonding atoms, and this quantity does not totally depend on the valence charge transfer along the bond axis. The percentage of covalence nature of a bond is related to the bond population and can be calculated using population ionicity ( $P_i$ ) from the following equation<sup>30</sup>:

$$P_i = 1 - e^{-\left| \frac{P_c - P}{P} \right|} \quad (1)$$

where  $P$  is the bond population of a bond and  $P_c$  is the bond population for a purely covalent bond. The lower limit, i.e.,  $P_i = 0$  indicates a pure covalent bond, while the upper limit i.e.,  $P_i = 1$  indicates a purely ionic bond. Here, the value of  $P_c$  is assumed equal to 1<sup>31</sup>. The calculated bond populations and their ionicity index of each M-O and Bi-O bonds are reported in Tables 2 and 3. Mulliken bond population analysis and ionicity index values confirm that Bi-O bonds in both studied crystals have ionic nature more than 92%. On the other hand the M-O bonds ( $M = Al^{3+}, Ga^{3+}$ ) in tetrahedral  $MO_4$  are stronger and more covalent with respect to octahedral  $MO_6$ .

Band structures of  $Bi_2Al_4O_9$  and  $Bi_2Ga_4O_9$  are calculated with  $0.001 \text{ \AA}^{-1}$  separation along the high symmetry directions in the first Brillouin zone (Figure 1-b) and the results are presented in Figure 2. The Fermi energy level,  $E_F$ , is chosen to be located at the top of valence band (0 eV). Coordinates of the special points of the Brillouin zone in term of unit vectors of the reciprocal lattice are G (0, 0, 0), X (1/2, 0, 0), S (1/2, 1/2, 0), Y (0, 1/2, 0), Z (0, 0, 1/2), U (1/2, 0, 1/2), R (1/2, 1/2, 1/2), and T (0, 1/2, 1/2). The valence bands are apparent from -6.08 eV and -6.33 eV to 0 eV for  $Bi_2Al_4O_9$  and  $Bi_2Ga_4O_9$ , respectively, whereas the conduction bands are apparent from 2.71 eV and 2.86 eV onward. For  $Bi_2Al_4O_9$  the valence band maximum (VBM) and conduction band minimum (CBM) are found at Z point, indicating that  $Bi_2Al_4O_9$  is a direct band gap semiconductor (Z-Z) with electronic band gap 2.71 eV. While, for  $Bi_2Ga_4O_9$  VBM and CBM are located at different points of the Brillouin zone, in the segment between G and X, and Z, respectively, indicating that  $Bi_2Ga_4O_9$  is an indirect band gap semiconductor (GX-Z) with electronic band gap 2.86 eV. The calculated band gap values of  $Bi_2Al_4O_9$  and  $Bi_2Ga_4O_9$  are in agreement with reported experimental findings which are ~2.25-2.84 eV for  $Bi_2Al_4O_9$ <sup>17, 32</sup> and 2.75 eV for  $Bi_2Ga_4O_9$ <sup>32</sup>. Band gaps energies of  $Bi_2Al_4O_9$  and  $Bi_2Ga_4O_9$  can be tuned and reduced by partially substitution of transition metals such as Fe or Cr at aluminum and gallium sites<sup>17, 32</sup>. In previous researches, it has been reported that for  $Bi_2Fe_4O_9$  the calculated band gap using GGA-PBE method is close to experimental values ~1.91-2.13 eV<sup>12, 14, 26, 33</sup> and is narrower than  $Bi_2Al_4O_9$  and  $Bi_2Ga_4O_9$ . As can be seen from Figure 2, the valence bands are less dispersive compared to conduction bands. The effective mass of the electrons and holes are related to the dispersion property of conduction and valence bands, respectively. The mobility of photo-induced carriers influence on the activity of a photocatalyst. The higher the mobility of electrons and holes the better is the performance

of the photocatalyst <sup>34</sup>. Inverse effective masses of photo-induced electron and hole is proportional to the mobility of photo-generated carriers <sup>35</sup>. Consequently, a low effective mass promotes the migration and suppresses the recombination of carriers. Since, the top of the valence band and the bottom of the conduction band are not symmetrical, VBM and CBM can be calculated as follows <sup>36, 37</sup>:

$$E(\vec{\mathbf{k}}) = E(\vec{\mathbf{k}}_0) \pm \frac{\hbar^2(\vec{\mathbf{k}}_x - \vec{\mathbf{k}}_{0,x})}{2m_x^*} \pm \frac{\hbar^2(\vec{\mathbf{k}}_y - \vec{\mathbf{k}}_{0,y})}{2m_y^*} \pm \frac{\hbar^2(\vec{\mathbf{k}}_z - \vec{\mathbf{k}}_{0,z})}{2m_z^*} \quad (2)$$

where  $E(\vec{\mathbf{k}})$  is the energy at wave-vector  $\mathbf{k}$  in the band and  $E(\vec{\mathbf{k}}_0)$  is a constant giving the edge of energy of the band.  $m_x^* = \frac{m_x}{m_e}$ ,  $m_y^* = \frac{m_y}{m_e}$ , and  $m_z^* = \frac{m_z}{m_e}$  are effective masses of electrons or holes in the [1 0 0], [0 1 0], and [0 0 1] directions, respectively. For crystal structures with orthorhombic symmetry effective masses of carriers along [1 0 0], [0 1 0], and [0 0 1] directions are  $m_x^* \neq m_y^* \neq m_z^*$ . The effective masses of electrons and holes are obtained by parabola fitting of the band dispersions of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  in three principal directions near the band extremes. The calculated effective masses of holes and electrons are shown in Table 4. Meanwhile, we also calculate the spherical averaged electron and hole effective masses using the following expressions <sup>37, 38</sup>.

$$\bar{m} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi m(\theta, \varphi) \sin(\theta) d\theta d\varphi, \quad (3)$$

$$m(\theta, \varphi) = \frac{1}{S_{11}n_1^2 + S_{22}n_2^2 + S_{33}n_3^2}. \quad (4)$$

where,  $S_{11} = \frac{1}{m_{100}^*}$ ,  $S_{22} = \frac{1}{m_{010}^*}$  and  $S_{33} = \frac{1}{m_{001}^*}$ . The directional cosines are given by  $n_1 = \sin(\theta) \cos(\varphi)$ ,  $n_2 = \sin(\theta) \sin(\varphi)$ , and  $n_3 = \cos(\theta)$  in spherical coordinates. From the calculated values given in Table.4, both structures have large hole and electron effective masses, compared to some widely known semiconductors. We further illustrate the anisotropy of hole or electron effective mass in three-dimensional space using contour plots. For orthorhombic symmetry, we employ Eq.(4) in the calculation. The results for the two structures are depicted

in Figure 3. As implied by tensor elements, the hole and electron are anisotropic in two structures.

Smaller **average** effective masses of electrons and holes for  $\text{Bi}_2\text{Al}_4\text{O}_9$  compared to  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is due to more **dispersive** feature of conduction and valence bands of  $\text{Bi}_2\text{Al}_4\text{O}_9$ , implying that the photo-generated electrons and holes in  $\text{Bi}_2\text{Al}_4\text{O}_9$  migrate rapidly with respect to  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . Therefore, the photo-generated electrons and holes in  $\text{Bi}_2\text{Al}_4\text{O}_9$  have more probability to reach the surface reaction sites within their life-time and participate in the photocatalytic reaction, indicating a higher photocatalytic performance of  $\text{Bi}_2\text{Al}_4\text{O}_9$ . On the other hand, effective mass of electrons are lighter than holes for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ , suggesting that electrons have higher probability to participate in the photocatalytic process with respect to photogenerated holes<sup>39</sup>. However, it should be mentioned that production of electron-hole pairs in a direct band gap semiconductor is easy but in the indirect band gap semiconductors electron must interact with photon to gain energy, and with lattice vibration (phonon) to gain or lose momentum. On the other hand recombination of photo-generated carriers is much more efficient for direct than for indirect band gap semiconductors<sup>35</sup>.

The composition of the calculated electronic bands can be assigned using the total, site- and angular projected density of states (DOS) diagrams which are plotted in Figures 4 and 5. It should be noted that the use of the plane wave basis set and ultrasoft pseudo-potential presents only the wave functions of the **valence** electrons  $6s^2 6p^3$  for Bi,  $3s^2 3p^1$  for Al,  $3d^{10} 4s^2 4p^1$  for Ga and  $2s^2 2p^4$  for O. Also, the chemical bonding feature in each band structure region are

examined using projected electronic wave function (PEWF) in the  $(\bar{1} 1 0)$  plane which are presented in Figures 6 and 7, to illustrate the interactions of M-O and Bi-O bonds. DOS diagram of  $\text{Bi}_2\text{Al}_4\text{O}_9$  can be divided into four parts. The lowest-lying state from -19 to -15.5 eV ( $E_1$  region) is essentially contributed by O 2s states with a small admixture of Al and Bi orbitals, in which the portion of Al states are slightly more than Bi states. PEWF of this region shows a very weak hybridization between O 2s and Al 3p states. The second region in a higher energy range ( $E_2$  region) from -10.5 to -8 eV is mainly composed of Bi 6s and O 2p states, so that bonding states arise from hybridization between them, also the role of Al electronic states in this energy region is very minor. The states from -6.5 to 0 eV ( $E_3$  region) mainly come from O 2p states with a few contribution of Bi and Al orbitals. PEWF of this

region shows strong hybridization between O 2p with Al 3s/3p and Bi 6s/6p states, which are clearly shown in its PEWF. The conduction band region lies between 2.5 to 8 eV (E<sub>4</sub> region), is mainly composed of Bi 6p and O 2p states with a small mixture of Al 3s/3p and Bi 6s states. In this energy region the role of Al electronic states is insignificant as the same as in the E<sub>2</sub> energy region.

DOS diagram of Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub> has five energy part in such a manner that the valence band is divided into four sub-bands. The lowest-lying state is located from -19 to -16 eV (E<sub>1</sub> region) mainly consist of O 2s and a few Ga 3d states so that contribution of Ga 4s/4p and Bi states in this region is insignificant. PEWF in this region demonstrate that hybridization between O 2s and Ga 3d states yielding bonding states between O and Ga atoms. Second energy range is located at about -13 to -11 eV (E<sub>2</sub> region) predominantly is due to Ga 3d state. Contribution of other states are very low, and a very weak hybridization between Ga 3d and O states is inferable from PEWF in this region. The E<sub>3</sub> region from -8 to -10 eV is mainly composed of Bi 6s and O 2p states and its PEWF shows a weak hybridization between these states. The high energy set of valence band (E<sub>4</sub> region) extending from -7 to 0 eV mainly formed by O 2p states with a few contribution of Bi and Ga orbitals. Represented bonding state in PEWF is from hybridization of O 2p and Ga 3d/4p states. States of conduction band (E<sub>5</sub> region) in a range from -2.5 to 7 eV mainly come from Bi 6p, Ga 4s and O 2p states. In the total PEWF of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub> orientation of Bi 6s<sup>2</sup> lone electron pair (LEP) is clearly observable.

Since the valence band and conduction band of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub> are mainly composed of O and Al/Ga states, distortions at tetrahedral MO<sub>4</sub> and octahedral MO<sub>6</sub> units can induce changes in the band structure, affect the band gap, and play a significant role in the photocatalytic activity of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub>.

Light sensitivity of Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub> can be described by optical properties. Optical properties of a matter is related to the transverse dielectric function  $\epsilon(q,\omega)$ , where q is the momentum transfer in the photon-electron interaction and  $\omega$  is the energy transfer. If the effect of momentum transfer from the initial state to the final state isn't taken into consideration (**direct inter-band transition**), the complex dielectric function can be written in terms of the real  $\epsilon_1(\omega)$  and imaginary  $\epsilon_2(\omega)$  part as <sup>40</sup>:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (5)$$

The imaginary part of dielectric function can be calculated from direct numerical evaluations of the momentum matrix elements of the electric dipole operator between the occupied and unoccupied wave functions<sup>35, 41</sup>:

$$\varepsilon_2(\omega) = \frac{2e^2\pi}{\omega\varepsilon_0} \sum_{\mathbf{k}, v, c} \left| \langle \psi_{\mathbf{k}}^c | \mathbf{u} \cdot \mathbf{r} | \psi_{\mathbf{k}}^v \rangle \right|^2 \delta(E_{\mathbf{k}}^c - E_{\mathbf{k}}^v - E) \quad (6)$$

where  $\mathbf{u}$  is the polarization vector of the incident electric field,  $\mathbf{r}$  and  $e$  are the electron's radius vector and electric charge, respectively,  $\psi_{\mathbf{k}}^c$  and  $\psi_{\mathbf{k}}^v$  are the conduction band and valence band wave functions at  $\mathbf{k}$ , respectively,  $\omega$  is the electromagnetic radiation striking (angular frequency of the incident photon) and  $\varepsilon_0$  is the vacuum permittivity. The summation of the equation is applied over all states from the occupied and empty bands, with their wave functions obtained in a numerical form after optimization of the crystal structure. The real part of the dielectric function can be obtained from the imaginary part by using the Kramers-Krönig dispersion relation<sup>35, 42</sup>:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \text{P} \int_0^{\infty} \frac{\Omega \varepsilon_2(\Omega)}{\Omega^2 - \omega^2} d\Omega \quad (7)$$

where P is the Cauchy principal value of the integral. Optical properties are calculated with calculation geometry polycrystalline, and instrumental smearing 0.5 eV. Considering that experimental reports on the optical gap of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are close to the DFT results, therefore scissor operator correction was not applied. The imaginary and real parts of dielectric constant of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are plotted in Figure 8-a. The real part of dielectric function at zero frequency shows that the static dielectric constant for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are 3.17 and 3.36, respectively. The negative values of the real part of dielectric function in the energy range from 6.65 to 11.31 eV for  $\text{Bi}_2\text{Al}_4\text{O}_9$ , and 6.04 to 10.92 eV for  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are due to damping of electromagnetic wave, and zero values indicate that longitudinally polarized waves are possible<sup>40</sup>. In the imaginary part of dielectric function there are two peaks located at 5.72 and 13.68 eV for  $\text{Bi}_2\text{Al}_4\text{O}_9$ , whereas the positions of these peaks for  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are at 5.07 and 13.57 eV. The main peak for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  corresponds mainly to the interband electronic transition from O 2p(VB) to Bi 6s(CB).

Since the crystal structure of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  belong to the space group  $Pbam$ , so the calculated static optical dielectric tensor along three polarization direction can be written as

Eq. (8). Therefore, three diagonal tensor components might be different. The anisotropy in static dielectric constant in an arbitrary crystallographic direction is calculated by Eq. (9).

$$\begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix} \quad (8)$$

$$\varepsilon_{\alpha\beta} = \sum_{i=1}^3 \sum_{j=1}^3 \lambda_{\alpha i} \lambda_{\beta j} \varepsilon_{ij} \quad (9)$$

where,  $\lambda_{ij}$  represents the matrix of directional cosines. Regarding the orthorhombic symmetry, Eq.(9) is further simplified as Eq. (10) <sup>43</sup>.

$$\varepsilon(\theta, \varphi) = \varepsilon_{[100]}n_1^2 + \varepsilon_{[010]}n_2^2 + \varepsilon_{[001]}n_3^2 \quad (10)$$

In Eq. (10), the directional cosines  $n_1$ ,  $n_2$  and  $n_3$  are the same as those given in Eq. (4). Figures 8-b and 8-c illustrate that the calculated static optical dielectric constant of  $\text{Bi}_2\text{Al}_4\text{O}_9$  at the frequency approaching zero along the three directions [1 0 0], [0 1 0], [0 0 1] are 3.371, 3.136, and 3.023, respectively. Similarly, related values along the three polarization directions for  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are 3.376, 3.430, and 3.279, respectively. However, the peaks intensities along the polarization directions of the studied crystals in Figures 8-b and 8-c show that the optical anisotropy character of  $\text{Bi}_2\text{Al}_4\text{O}_9$  is **stronger** than  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . The feature of the real part of dielectric constant along the polycrystalline direction are similar to that exhibited along the polarization directions. As illustrated in Figure 9, the three-dimensional contour plots do not imply a strong anisotropy in static dielectric tensor of both phases.

Collective oscillations of the free electron gas density is plasmon and the corresponding energy, which is so-called plasmon energy, can be found from the energy loss spectrum  $L(\omega)$  that is calculated by <sup>44</sup>:

$$L(\omega) = \text{Im} \left( \frac{-1}{\varepsilon(\omega)} \right) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} \quad (11)$$

The point at which highest loss function occur corresponds to the plasmon energy ( $E_p$ ). The energy loss functions of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are depicted in Figure 10-a. The plasmon energies for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  appear at 11.36 eV and 10.95 eV, respectively. Optical band gap of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are calculated using the conventional Tauc method from

the optical absorption spectra. The absorption coefficient  $\alpha(E)$  indicates the fraction of energy lost by the wave when it passes through the material, and **which** is written as <sup>35</sup>:

$$\alpha(\omega) = \frac{\sqrt{2}\omega\sqrt{\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)}}{c} \quad (12)$$

**here**  $c$  is the velocity of light. Two types of optical transitions, direct and indirect, can be investigated by following relation expression which is proposed by Tauc <sup>45</sup>:

$$\alpha(E)E = A(E - E_g^{\text{direct}})^{0.5} + B(E - E_g^{\text{indirect}} \pm E_{\text{phonon}})^2 \quad (13)$$

where  $A$  and  $B$  are fitting parameters,  $E_g^{\text{direct}}$  and  $E_g^{\text{indirect}}$  are direct and indirect optical gaps,  $E_{\text{phonon}}$  is the phonon energy and  $E$  is incident photon energy. The straight line segment in  $(\alpha E)^2$  indicates direct optical gap whereas straight line segment in  $(\alpha E)^{0.5}$  indicates indirect optical gap. The calculated optical absorption curves for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are shown in Figure 10-b. Based on ISO standard ISO-21348 <sup>46</sup>, the first peak for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is located at the extreme ultra violet region (70-100 nm). The second peak starts from extreme ultra violet region and the tail of absorption are extended till visible region, 430 nm and 480 nm for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ , respectively. It is clear that the main part of absorption for  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is located at the ultra violet region. Consequently,  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are poor absorber of visible light or in other words are ultra violet light response photocatalysts. Tauc plots of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are sketched using optical absorption curves (see Figure 10-c). Extrapolation of the linear portion of the graphs with the abscissa clearly indicate that  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are indirect band gap semiconductor. Direct and indirect band gaps for  $\text{Bi}_2\text{Al}_4\text{O}_9$  are 4.95 eV and 2.82 eV, respectively, on the other hand its values for  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are 4.35 eV and 2.71 eV, respectively. Reasonable agreement between the calculated indirect optical band gaps and electronic band gaps indicates that optical and electronic gaps coincide.

The band edge positions of a semiconductor and the redox potentials of an adsorbate are effective parameters on the ability of the semiconductor to undergo photoinduced electron transfer to the adsorbed species on its surface. **The suitable potential level of the acceptor species is thermodynamically required to be more positive than the conduction band potential of the semiconductor ( $E_{\text{CB}}$ ), while the potential level of the donor needs to be more negative than the valence band position of the semiconductor ( $E_{\text{VB}}$ ) in order to donate an electron to**

the vacant hole<sup>47</sup>. The band edge positions of a semiconductor can be expressed empirically by<sup>10, 35</sup>:

$$E_{VB} = \chi - E_e + 0.5E_g^{Optical} \quad (14)$$

$$E_{CB} = E_{VB} - E_g^{Optical} \quad (15)$$

where  $E_e$  is the energy of free electrons on the hydrogen scale (approximately 4.50 eV) and  $\chi$  is absolute electronegativity of semiconductor, which is the geometric mean of the electronegativities of the isolated component atoms and is expressed as<sup>48</sup>:

$$\chi \approx \left( \prod_{k=1}^P \chi_k \right)^{\frac{1}{P}} \quad (16)$$

where P is the number of atoms in the semiconductor and  $k=1, 2, 3, \dots, P$ . Electronegativity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  without considering the crystal structures and surface polarizations are 5.64 eV and 5.63 eV, respectively, which are calculated from experimental values of electronegativity (i.e. Bi=4.69 eV, Al=3.23 eV, Ga=3.20 eV, and O=7.54 eV)<sup>49</sup>. The CB edge potential of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  respect to the NHE (normal hydrogen electrode) are -0.27 and -0.23 eV, respectively, while the VB edge potentials are 2.55 eV and 2.48 eV. Relative disposition of VB and CB potentials of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  respect to vacuum scale and NHE are displayed in Figure 11. The VB potentials of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are more positive than the redox potential of  $\text{O}_2/\text{H}_2\text{O}$  (1.23 V),  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  (1.77 V), and  $\text{O}_3/\text{H}_2\text{O}$  (2.07 V). Therefore, photogenerated holes can oxidize  $\text{H}_2\text{O}$  to produce active species  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$ . These active species can oxidize/decompose organic pollutants and dye molecules. Since the CB potentials of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are more negative than the redox potential of  $\text{H}^+/\text{H}_2$  (0.0 V), the photogenerated electrons can reduce produced  $\text{H}^+$  to  $\text{H}_2$ . The deep VB potential of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  cause both compounds be strong oxidative material without the need to add co-catalyst. It should be noted that  $\text{O}_2^{\bullet-}$  and  $\text{OH}^{\bullet}$  are other active kind that can be produced using photogenerated electrons, since the CB potentials of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are not negative enough and adding of suitable co-catalyst to  $\text{Bi}_2\text{Al}_4\text{O}_9$  or  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is necessary for increasing of photocatalytic activity. Finally, the position of the conduction band edge of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  makes these materials as suitable solids for photocatalytic hydrogen generation from water splitting.

### 3. Conclusion

In summary structure, electronic, optical, and photocatalytic properties of mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) have been elucidated using the density functional theory (DFT) method with the plane wave pseudo-potential in the frame of the generalized gradient approximation (GGA) proposed by Perdew, Burke, Ernzerhof (PBE) as implemented in CASTEP code. The optimized crystallographic parameters are in **acceptable** agreement with experimental results. Ionicity index values of Bi-O bonds in both studied crystals are more than 92%. Also, M-O bonds ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) in tetrahedral  $\text{MO}_4$  environments are stronger and more covalent respect to octahedral  $\text{MO}_6$ . The photocatalytic activity of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is enhanced due to unequal values of Mulliken charges on the O atoms in  $\text{MO}_4$ ,  $\text{MO}_6$ , and  $\text{BiO}_6$  groups. **The band structure shows that  $\text{Bi}_2\text{Al}_4\text{O}_9$  is a direct band gap 2.71 eV semiconductor while  $\text{Bi}_2\text{Ga}_4\text{O}_9$  is an indirect band gap 2.86 eV semiconductor which are satisfactory values in comparison with experimental findings 2.84 and 2.75 eV, respectively.** Lighter effective masses of electrons and holes around the CBM and VBM of  $\text{Bi}_2\text{Al}_4\text{O}_9$  facilitate the migration of photogenerated carriers and improve photocatalytic activity of its respect to  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . The density of states at different electronic energies and their projected electronic wave functions are studied to illustrate the composition of the calculated electronic bands.  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are ultraviolet light response photocatalysts with plasmon energies 11.36 eV and 10.95 eV, respectively. Optical band gaps of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  are obtained using Tauc plots which show that they have indirect optical gaps 2.82 eV and 2.71 eV, respectively. Both  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  have strong activity to oxidize or decompose organic pollutants and dye molecules. Also they have excellent property for photocatalytic hydrogen generation from water splitting.

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## Caption for figures

**Figure 1.** (a) Crystal structure of mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}, \text{Fe}^{3+}$ ). The Bismuth and oxygen atoms are represented by purple and red spheres, respectively.  $\text{MO}_6$  octahedral and  $\text{MO}_4$  tetrahedral environments are showed by green and blue colors, respectively. (b) The first Brillouin zone of mullite-type orthorhombic  $\text{Bi}_2\text{M}_4\text{O}_9$  ( $\text{M} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) in the reciprocal lattice. The Bradley-Cracknell notation is used for the high-symmetry points. G (0, 0, 0), X (1/2, 0, 0), S (1/2, 1/2, 0), Y (0, 1/2, 0), Z (0, 0, 1/2), U (1/2, 0, 1/2), R (1/2, 1/2, 1/2), and T (0, 1/2, 1/2). The red line corresponds to the path of the band structure diagram and  $g_1$ ,  $g_2$ , and  $g_3$  denote the reciprocal vectors.

**Figure 2.** The calculated band structures of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . The Fermi energy ( $E_F$ ) is set to be 0 eV and is marked by horizontal dashed line.

**Figure 3.** Three-dimensional contour plots of hole and electron effective masses. (a) and (b): electron and hole of  $\text{Bi}_2\text{Al}_4\text{O}_9$ ; (c) and (d): electron and hole of  $\text{Bi}_2\text{Ga}_4\text{O}_9$ .

**Figure 4.** Total and partial density of states for  $\text{Bi}_2\text{Al}_4\text{O}_9$ . Red, blue and black lines represent p orbitals, s orbitals and all orbitals, respectively. The Fermi energy ( $E_F$ ) is set to be 0 eV and is marked by vertical dashed line.

**Figure 5.** Total and partial density of states for  $\text{Bi}_2\text{Ga}_4\text{O}_9$ . Green, red, blue, and black lines represent d orbitals, p orbitals, s orbitals, and all orbitals, respectively. The Fermi energy ( $E_F$ ) is set to be 0 eV and is marked by vertical dashed line.

**Figure 6.** Projected wave function contour plots for  $\text{Bi}_2\text{Al}_4\text{O}_9$  at four different energy ranges in the  $(\bar{1} 1 0)$  plane.

**Figure 7.** Projected wave function contour plots for  $\text{Bi}_2\text{Ga}_4\text{O}_9$  at five different energy ranges in the  $(\bar{1} 1 0)$  plane.

**Figure 8.** (a) The real (solid line) and imaginary (dashed line) parts of the dielectric function of  $\text{Bi}_2\text{Al}_4\text{O}_9$  (blue line) and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  (red line). (b) The real part of the dielectric function of

$\text{Bi}_2\text{Al}_4\text{O}_9$  for different polarization vector. (c) The real part of the dielectric function of  $\text{Bi}_2\text{Ga}_4\text{O}_9$  for different polarization vector.

**Figure 9.** Anisotropy in static optical dielectric tensor. (a):  $\text{Bi}_2\text{Al}_4\text{O}_9$ ; (b):  $\text{Bi}_2\text{Ga}_4\text{O}_9$ .

**Figure 10.** (a) Energy loss functions of  $\text{Bi}_2\text{Al}_4\text{O}_9$  (blue line) and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  (red line) as a function of photon energy. (b) Absorption spectra of  $\text{Bi}_2\text{Al}_4\text{O}_9$  (blue line) and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  (red line). (c) Tauc plots of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$ .  $(\alpha E)^{0.5}$  for indirect gap (blue line) and  $(\alpha E)^2$  for direct gap (red line).

**Figure 11.** Relative disposition of VB and CB potentials of  $\text{Bi}_2\text{Al}_4\text{O}_9$  and  $\text{Bi}_2\text{Ga}_4\text{O}_9$  respect to vacuum scale and NHE.