First-principles study on electronic structure, phase stability, and optical properties of $\text{In}_2\text{X}_2\text{O}_7$ ($\text{X}=$ C, Si, Ge or Sn)

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A B S T R A C T

In$_2$Ge$_2$O$_7$ and In$_2$Si$_2$O$_7$ are commonly used as scintillation materials. More studies on In$_2\text{X}_2\text{O}_7$ ($\text{X}=$ C, Si, Ge, or Sn) are important to explore the possibility of using these materials for optoelectronic devices. This work presents results dealing with structural properties, electronic structure, chemical bonding, carrier effective masses, and optical spectra of polymorphs of In$_2$X$_2$O$_7$ obtained from first-principles calculations. The monoclinic phase of In$_2$Ge$_2$O$_7$, cubic and monoclinic phases of In$_2$Si$_2$O$_7$, as well as cubic phase of In$_2$Sn$_2$O$_7$ are known in scientific literature. From the total energy calculations at high pressure/strain we have found that the monoclinic phase of In$_2$Si$_2$O$_7$, In$_2$Ge$_2$O$_7$, and In$_2$Sn$_2$O$_7$ can be transformed into the cubic phase. The cubic phase of In$_2$Ge$_2$O$_7$ and In$_2$Sn$_2$O$_7$ is found to be more stable than the monoclinic phase. However, the monoclinic phase of In$_2$C$_2$O$_7$ and In$_2$Si$_2$O$_7$ is more stable than the cubic phase. The phase stability study suggests that In$_2$C$_2$O$_7$ is not stable, and that it might dissociate into corresponding binary oxides. Effective masses of electrons and holes have been estimated. Analysis of optical properties shows that in Si solar cells In$_2$Sn$_2$O$_7$ and In$_2$Sn$_2$O$_{7-x}$ can be used as antireflection coating layer.

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1. Introduction

Studies on indium-rich compounds In$_2\text{X}_2\text{O}_7$ ($\text{X}=$ C, Si, Ge, and Sn) became attractive because of the possibility for their use in many technological applications such as high density, high light output scintillators [1], and photovoltaics (PV) [2–4]. They can be formed as an intermediate layer at the interface between In$_2$O$_3$ and the host lattice. For example, in studies of the role of the Ge based quantum dots embedded into indium-tin-oxide (ITO) In$_2$O$_3$:Sn, an intermediate layer has been detected by X-ray diffraction in between Ge dots and ITO, which is suggested to be In$_2$Ge$_2$O$_7$ [3]. There are many reports about In$_2$Sn$_2$O$_7$ formed in between ITO and glass [5], in the In$_2$O$_3$-SnO$_2$ [6], and CdTe/CdS/ITO/glass [7] systems, etc. Some of the In$_2\text{X}_2\text{O}_7$ compounds have been synthesized and characterized. Tubes of In$_2$Ge$_2$O$_7$ have been synthesized with sub-micrometer diameters [8]. Large-scale In$_2$Ge$_2$O$_7$ nanobelts have been synthesized by a simple thermal evaporation method without the presence of a catalyst, and a strong as well as broad violet emission peak at about 410 nm has been observed [9]. In$_2$Si$_2$O$_7$ and In$_2$Ge$_2$O$_7$ are suggested [1,10] for the use as radiation detectors with high light output, good attenuation power, low level of afterglow, and fast scintillation decay time. Monoclinic In$_2$Si$_2$O$_7$ prepared by firing the mixture of In$_2$O$_3$ with SiO$_2$ has been reported [11] to be an efficient phosphor. Such films have also been formed upon deposition of In$_2$O$_3$ on glass by sol-gel with subsequent annealing at 900 °C [12]. In the study of Ge doped In$_2$O$_3$ it is found [13] that In$_2$Ge$_2$O$_7$ can be formed at concentrations of Ge exceeding 0.5 atom%. Polycrystalline cubic In$_2$Sn$_2$O$_7$ has been prepared [14] by a chemical process for optical devices. Mixed crystallites of In$_2$Sn$_2$O$_7$ and In$_2$Sn$_2$O$_{7-x}$ have been observed [15] in the deposition of In$_2$O$_3$ by reactive evaporation on glass upon annealing at 150 °C. Different structural modifications of In$_2$Si$_2$O$_7$ and In$_2$Ge$_2$O$_7$ have been observed experimentally. In$_2$Si$_2$O$_7$ can be in monoclinic phase [10] and cubic phase, whereas, In$_2$Ge$_2$O$_7$ can be in two different varieties of monoclinic phases [16,17]. In$_2$Sn$_2$O$_7$ is reported to be stable in the cubic phase [18]. There is no structural information available for In$_2$C$_2$O$_7$, and also the possibility of phase transitions between different polymorphs of In$_2$X$_2$O$_7$ has not yet been studied. The aim of this work is to study ground state properties, electronic structure and optical properties of In$_2$X$_2$O$_7$, and compare our results with available experimental studies.

2. Computational details

The structural properties, electronic band structure, and optical properties of In$_2$X$_2$O$_7$ are studied using the Vienna ab initio simulation package (VASP) [19], which calculates the Kohn-Sham eigenvalues within the framework of density functional theory (DFT). The calculations have been performed with the use of the local density

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approximation. The exchange and correlation energy per electron have been described by the Perdew-Zunger parametrization [20] with the quantum Monte Carlo procedure of Ceperley-Alder [21]. The interaction between electrons and atomic cores is described by means of non-norm-conserving pseudopotentials implemented in the VASP package [19]. The pseudopotentials are generated in accordance to the projector-augmented-wave method [22–24]. The use of the pseudopotentials addresses the problem of the inadequate description of the wave functions in the core region common to other pseudopotential approaches. The In-4d, -5s, and -5p, O-2s and -2p, C-2s and -2p, Si-3s and -3p, Ge-4s, -3d, and -4p, as well as Sn-5s, -4d, and -5p electrons have been considered as the valence electrons.

We have considered four different structural modifications of In$_2$X$_2$O$_7$. Three of them with space group (SG) C12/m1 (SG number 12), B112/m (SG number 12), and P121/c1 (SG number 14) possess monoclinic structure. Among them the most stable one is denoted hereafter as phase (-I). The fourth structural modification is of SG Fd$ar{3}$m with SG number 227 denoted as phase (-II). The crystal structures are schematically presented in Fig. 1. In these structural modifications, the atomic arrangement around In and X cations are in InO$_6$ and XO$_6$ octahedra. The Wyckoff positions, calculated and experimentally established lattice parameters are provided in Table 1.

Using the experimentally determined crystal structure information as input, the structural optimization has been performed by the following procedure: Atomic positions, cell volume, and shape have been relaxed by force and stress minimization. The optimized crystal structure information obtained from the above approach was used as input for calculation of the total energy ($E_{tot}$) as a function of the cell volume ($V$). The magnitude of $V$ corresponding to minimum ($E_{min}$) of the total energy is taken as the equilibrium volume. Structural optimization has been performed using a 2×2×2 mesh of the k-points and the plane-wave cutoff energy 500 eV. The convergence was achieved when the forces acting on the atoms were <20 meV Å$^{-1}$ and the total energy difference between two consecutive iterations was <10$^{-6}$ eV. The electronic structure is calculated using the 4×4×4 mesh of the k-points and the plane-wave cutoff energy 500 eV. By fitting the calculated pressure-volume dependency to the Birch–Murnaghan equation of state, bulk modulus ($B_0$) and its pressure derivative $B_0$ has been calculated.

The effective masses for the conduction band (CB) electrons $m_e$ and holes in the valence band (VB) $m_h$ normalized to the free electron mass $m_0$ are calculated by:

$$\frac{1}{m_{e,h}} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2} \bigg|_{k=k_0}$$

for a direction $k$ about an extreme point $k_0$ in the Brillouin zone. As demonstrated below, the band at the CB minimum is well dispersive whereas the topmost VB is almost flat. Furthermore, the CB and VB extremes are located at the $\Gamma$ point. For this reason the effective masses have been studied in the close vicinity of the $\Gamma$ point. For the monoclinic phases the masses have been calculated along the directions $\Gamma \rightarrow Z$ and $\Gamma \rightarrow A$. For the cubic phases the masses have been studied along $\Gamma \rightarrow X$ and $\Gamma \rightarrow L$ directions. The band edge energies $E(k)$ have been extracted from well converged DFT calculations, and a polynomial of order higher than 2 was used to achieve best fitting. The second derivative of the polynomial was calculated for the $\Gamma$ point, which was then used in the effective mass calculations using Eq. (1).

The imaginary part of the dielectric function $\varepsilon_2(\omega)$ was calculated using the random phase approximation by integrating the allowed interband optical transitions.

$$\varepsilon_2^{\|}(\omega) = \frac{V^2 e^4 k}{2 \pi \hbar m_0 \omega^2} \int d^3 k \sum_{mn} \langle kn | p_i | k\prime n \rangle \langle k\prime n | p_j | kn \rangle \frac{\delta (\varepsilon_{k\prime n} - \varepsilon_{kn} - \hbar \omega)}{\varepsilon_{k\prime n} - \varepsilon_{kn} - \hbar \omega)}.$$

Here $\langle p_i p_j p_k \rangle = \rho$ is the momentum operator, $f_{kn}$ is the Fermi distribution, and $| kn \rangle$ is the crystal wave function, corresponding to energy $\varepsilon_{kn}$ with momentum $k$. For cubic In$_2$X$_2$O$_7$ the optical spectra are isotropic; consequently, only one component of the dielectric function is analyzed. However, for monoclinic In$_2$X$_2$O$_7$ six components of the optical spectra have been calculated in order to understand the anisotropy in the optical spectra. We have focused our attention to the diagonal components of the optical dielectric tensor to study the optical transitions when the electric field polarized along the crystal axes i.e. only on the three directions $E (a, b, \text{and } c)$. The real part of the dielectric function $\varepsilon_1(\omega)$ is then calculated using the Kramers-Kronig transformation. These two spectra were then used to calculate all the other optical spectra for the energy range 0–20 eV. In this paper, we presented the reflectivity $R(\omega)$, the absorption coefficient $\alpha(\omega)$, the refractive index $n(\omega)$, and the extinction coefficient $k(\omega)$. More details about the optical calculations are discussed in Ref. [25,26].

The heat of formation ($\Delta H^\circ$) of In$_2$X$_2$O$_7$-I and -II has been calculated for the solid state reaction

$$\text{In}_2\text{X}_2\text{O}_7 \leftrightarrow \text{In}_2\text{O}_3 + 2\text{X}_2\text{O}_2.$$
using the relation
\[
\Delta H = E_{[In_2X_2O_7-I]} - E_{[In_2X_2O_7-II]} - 2 \times E[XO_2].
\]
(4)

Here \( E \) is the total energy corresponding to ground state of \( In_2X_2O_7-I \) and -II, \( In_2O_3 \), and \( XO_2 \) (\( X=Si, Si, Ge, \) and Sn).

3. Results and discussion

3.1. Ground-state properties

We have calculated the equilibrium structural properties of \( In_2X_2O_7 \) using structural optimization. For these computations, the experimentally determined lattice parameters are used as input, which are available for \( In_5Si_2O_7-I \) and -II, \( In_5Ge_2O_7-I \), and \( In_5Sn_2O_7-II \). However, there are no experimental data for crystal structures of \( In_5C_2O_7-I \) and -II and \( In_5Sn_2O_7-II \). So, for phase stability studies of the compounds respective structural information of the \( In_5Si_2O_7-I \) and -II have been used as the input. Total energy \( E_{tot} \) per formula unit (f.u.) has been estimated for different polymorphs of \( In_2X_2O_7 \) and compared with each other. The one with smallest \( E_{tot} \) has been considered as the most stable structure, which is the ground state. The equilibrium atomic positions and lattice parameters are derived from the lattices in ground state [Table 1], which have been compared with the experimentally determined ones. Analysis of the Table 1 shows that the deviation of the calculated and the experimentally measured equilibrium volumes is by -1.2% for \( In_2Si_2O_7-I \), -1.0% for \( In_2Si_2O_7-II \), and -0.4% for \( In_2Ge_2O_7-I \). The calculated equilibrium positional parameters are found to be in good agreement with the experimental data. The symmetry of the optimized lattices is found to be the same as that determined experimentally.

The calculated total energy as a function of the cell volume \( (E_{tot}V) \) for \( In_5X_2O_7-I \) and -II is presented in Fig. 2. Difference between the equilibrium volumes for \( In_5X_2O_7-I \) and -II is 13.21 Å² for \( In_5C_2O_7 \), 25.81 Å² for \( In_5Si_2O_7 \), 25.74 Å² for \( In_5Ge_2O_7 \), and 28.74 Å² for \( In_5Sn_2O_7 \). The relative stability of these compounds has been analyzed by comparing \( E_{tot}V \) for \( In_5X_2O_7-I \) and -II. The present calculations show that \( In_5C_2O_7-I \) is more stable than \( In_5C_2O_7-II \). The difference in \( E_{tot}V \) between these two polymorphs is -10.8 eV. Similarly, \( E_{tot}V \) for \( In_5Si_2O_7-II \) and -II is -0.28 eV. Hence, \( In_5Si_2O_7-I \) can be said to be more stable than \( In_5Si_2O_7-II \). Therefore, \( In_5Ge_2O_7-II \) and \( In_5Sn_2O_7-II \) are more stable than \( In_5Ge_2O_7-I \) and \( In_5Sn_2O_7-I \).

Analysis of Fig. 2 shows that the dependence \( E_{tot} \) vs volume for \( In_5X_2O_7 \) (\( X=Si, Ge, \) and Sn) and -II exists, which is the ground state. Analysis of the Table 1 shows that the deviation of the calculated and the experimentally measured equilibrium volumes is by -1.2% for \( In_2Si_2O_7-I \), -1.0% for \( In_2Si_2O_7-II \), and -0.4% for \( In_2Ge_2O_7-I \). The calculated equilibrium positional parameters are found to be in good agreement with the experimental data. The symmetry of the optimized lattices is found to be the same as that determined experimentally.

The calculated total energy as a function of the cell volume \( (E_{tot}V) \) for \( In_5X_2O_7-I \) and -II is presented in Fig. 2. Difference between the equilibrium volumes for \( In_5X_2O_7-I \) and -II is 13.21 Å² for \( In_5C_2O_7 \), 25.81 Å² for \( In_5Si_2O_7 \), 25.74 Å² for \( In_5Ge_2O_7 \), and 28.74 Å² for \( In_5Sn_2O_7 \). The relative stability of these compounds has been analyzed by comparing \( E_{tot}V \) for \( In_5X_2O_7-I \) and -II. The present calculations show that \( In_5C_2O_7-I \) is more stable than \( In_5C_2O_7-II \). The difference in \( E_{tot}V \) between these two polymorphs is -10.8 eV. Similarly, \( E_{tot}V \) for \( In_5Si_2O_7-II \) and -II is -0.28 eV. Hence, \( In_5Si_2O_7-I \) can be said to be more stable than \( In_5Si_2O_7-II \). Therefore, \( In_5Ge_2O_7-II \) and \( In_5Sn_2O_7-II \) are more stable than \( In_5Ge_2O_7-I \) and \( In_5Sn_2O_7-I \).
One of the parameters of interest in semiconductors that can be determined from the band structure is the fundamental band gap $E_g$. For this purpose knowledge of the experimentally measured band gap values is needed. Due to lack of such experimental data, rigid shift technique has not been applied. One of the parameters that characterize transparency of n-type conducting material is the difference of energies ($E_g^0$) between the nearest two minima in the bottommost part of CB (Table 2). Our calculations show that $E_g^0 \geq 2.8$ eV for In$_2$Si$_2$O$_7$-II, In$_2$Ge$_2$O$_7$-I, and In$_2$Sn$_2$O$_7$-II. It indicates that if heavy doping with shallow donors is possible, then the materials can still be transparent to the visible part of the solar spectra.

We have calculated the CB electron effective masses (Table 3). The calculated CB electron effective masses are of the same order of magnitude as ZnO and In$_2$O$_3$. We have found that the CB electron effective masses are almost isotropic along all directions. The topmost VB for In$_2$Si$_2$O$_7$-I and In$_2$Ge$_2$O$_7$-I is dispersive along $\Gamma \rightarrow \text{A}$. The effective masses corresponding to the topmost VB are found to be anisotropic.

The calculated total densities of states (TDOS) for In$_2$X$_2$O$_7$ are presented in Fig. 5. The VB for In$_2$C$_2$O$_7$-I, -II consists of four major regions, whereas the VB for the rest of In$_2$X$_2$O$_7$-I and -II consists of only three regions. As demonstrated below by the analysis of orbital and site projected DOS (PDOS), the lowest energy region in the VB (to

respectively. In scientific literature there is no report regarding phase transitions in these oxides. $B_0$ and its derivative $B'_0$ have been calculated [Table 1]. $B_0$ for In$_2$X$_2$O$_7$-I is larger than that for In$_2$X$_2$O$_7$-II. This result is because of the smaller equilibrium volume of In$_2$X$_2$O$_7$-I than -II.

Using the calculated ground state structural parameters, we have estimated the heat of formation $\Delta H_f$ for stable phases of In$_2$X$_2$O$_7$ [Table 1]. The analysis shows that $\Delta H_f$ is positive for In$_2$C$_2$O$_7$-I and is negative for all the other compounds considered in the present study. The observation of negative value of $\Delta H_f$ indicates that these compounds are stable and will not dissociate into corresponding binary oxides. The observation of positive value of $\Delta H_f$ for In$_2$C$_2$O$_7$-I may be associated with the hypothetical structures assumed in the present study, which will not be stabilized experimentally. This could also explain why In$_2$C$_2$O$_7$ is not yet identified experimentally.

### 3.2. Electronic structure

The calculated band structures are plotted in Fig. 4 for In$_2$X$_2$O$_7$-I and -II. It is seen in Fig. 4 that the bottommost CB is well dispersive whereas topmost VB is almost dispersionless for all these compounds. The narrow band dispersion at the VB maximum indicates that the effective mass of the holes will be large and hence the hole mobility will be smaller. On the one hand it means that contribution to the electrical current of the CB electrons will be much larger than that by the same concentration of holes. On the other hand it indicates that the electrons in the VB are tightly bound to the O anions and that predominant ionic type of chemical bonding is present in the compounds.

One of the parameters of interest in semiconductors that can be determined from the band structure is the fundamental band gap $E_g$, which is the difference of energies of the bottommost CB and topmost VB. We have estimated the $E_g$ values of all these compounds from Fig. 4 and summarized them in Table 2. Analysis of Fig. 4 and Table 2 shows that In$_2$X$_2$O$_7$-I and -II, except In$_2$C$_2$O$_7$-II, are wide band gap oxides possessing large fundamental band gaps. Here it should be mentioned the systematic DFT error in calculation of the fundamental band gap. So, the real bandgap values for In$_2$X$_2$O$_7$-I and -II are expected to be larger than the calculated values presented in Table 2. Often rigid shift technique is used to correct the error in calculated band gaps to compare the calculated optical spectra with correspond-
be called VB1 hereafter) of In$_2$Sn$_2$O$_7$-I and -II comes from the Sn-4d electrons, which are not available in other In$_2$X$_2$O$_7$ compounds. They are located in the energy range 17.0–18.5 eV. The energy region located above VB1 to be called as the VB2 is in the energy range from −17.0 to −13.5 eV. It is split into narrow sharp sub-bands. The other region is VB3 located at higher energies than VB2 and it covers the range from −13.5 to 11.0 eV. It is localized and narrow. The topmost part of the VB is the fourth region to be denoted as VB4. It is located in a broad energy range −8.0 to 0.0 eV.

Analysis of PDOS has been performed. Since PDOS for In$_2$X$_2$O$_7$-I and -II are similar to each other in Fig. 6 we present the result only for In$_2$Sn$_2$O$_7$-I and -II. It is seen that VB2 consists of O 2p strongly hybridized with s and p electrons of In and group-IV atoms. The VB2 band is split into three distinct sharp peaks. Among the In$_2$Sn$_2$O$_7$-I and -II this feature is especially well defined in In$_2$Sn$_2$O$_7$-I and -II. The VB3 consists of the well-localized very sharp peaks centered at −12.5 eV, which are coming from In 4d electrons slightly hybridized with s and p electrons of O and group-IV atoms. The topmost part of the VB, called VB4, consists of two parts: the first one is located at lower energies. Strong contribution to VB4 is coming from the In-5s and -5p as well as s and p electrons of group-IV atoms. The other one formed by the O-2p electrons is located at higher energies. The CB edge is well dispersed and consists of In 5s electrons, s electrons of group-IV atoms and O 2s electrons.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_g$ (eV)</th>
<th>$E_F$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$C$_2$O$_7$</td>
<td>2.91</td>
<td>1.87</td>
</tr>
<tr>
<td>In$_2$Si$_2$O$_7$</td>
<td>3.20</td>
<td>2.26</td>
</tr>
<tr>
<td>In$_2$Ge$_2$O$_7$</td>
<td>2.81</td>
<td>2.37</td>
</tr>
<tr>
<td>In$_2$Sn$_2$O$_7$</td>
<td>2.16</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Table 3: The calculated effective masses of electrons and holes (in units of the free-electron mass $m_0$) for In$_2$X$_2$O$_7$-I and -II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$m_e$ (eV)</th>
<th>$m_0$ (eV)</th>
<th>$m_h$ (eV)</th>
<th>$m_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$Si$_2$O$_7$-I</td>
<td>0.37</td>
<td>0.33</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>In$_2$Ge$_2$O$_7$-I</td>
<td>0.38</td>
<td>0.36</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>In$_2$Ge$_2$O$_7$-II</td>
<td>0.37</td>
<td>0.33</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>In$_2$Sn$_2$O$_7$-I</td>
<td>2.86</td>
<td>1.40</td>
<td>2.77</td>
<td>1.07</td>
</tr>
<tr>
<td>In$_2$Sn$_2$O$_7$-II</td>
<td>2.86</td>
<td>14.0</td>
<td>2.77</td>
<td>1.07</td>
</tr>
</tbody>
</table>

### 3.3. Charge density, electron-localization function, Bader and Voronoi charge analysis

For qualitative characterization of chemical bonding between In and O as well as between O and group-IV atoms in In$_2$X$_2$O$_7$-I and -II, the charge-density and electron localization function (ELF) have been analyzed [27-29]. Fig. 7 (a) and (b) presents the charge-density and ELF for In$_2$Sn$_2$O$_7$-I and -II. It is found that the largest charge density is residing at O atoms, indicating that electrons are transferred from the cations to the O site. As in the computations we have considered the semicore In 4d electrons as valence electrons, large amount of localized electrons are residing around In. The charge density around group-IV atoms is smaller than that around In. Based on the analysis one can say that the bonding interaction between In/X and O is mixed ionic–covalent with pronounced ionic character. ELF [Fig. 7(c) and (d)] analysis shows that the charge is concentrated mainly around O atoms with spherical symmetric ELF distribution. This picture once again confirms the dominant ionic nature of the chemical bonding. This result is consistent with analysis of PDOS [Fig. 4], which shows that valence charge population at the In and X sites is much smaller than that at the
O site. This result is reasonable, because, the spectroscopic electronegativity of In, Si and O are 1.78, 1.90 and 3.44 [30], respectively. Since the electronegativity of O is larger, the ionic interaction between In and O is dominantly ionic. For quantitative analysis of charge transfer between constituents we have performed Bader and Voronoi charge analysis [Table 4]. As expected, In and group-IV atoms (X=C, Si, Ge, and Sn) donate electrons, while O atoms accept them. Based on the amount of the transferred charges one can conclude that chemical bonding between In and O is more pronounced than the covalent bonding.

3.4. Optical properties of In$_2$X$_2$O$_7$

We have calculated both diagonal and off-diagonal components of the dielectric response function for In$_2$X$_2$O$_7$-I. Among the six components for In$_2$X$_2$O$_7$-I, the off-diagonal components are found to be negligible, and hence the analysis is made for just the three diagonal components corresponding to the electric field $E$ parallel to the crystallographic a, b and c axes. Since the optical properties of In$_2$X$_2$O$_7$-II are isotropic, only one of the diagonal components has been analyzed. Fig. 8 displays the imaginary part of the optical dielectric response function for In$_2$Ge$_2$O$_7$-I along $E \parallel a$, $E \parallel b$, and $E \parallel c$, and one of the diagonal components for In$_2$X$_2$O$_7$-II as a function of the photon energy. Analysis shows that because of the deficiency of DFT to underestimate band gaps, the calculated optical spectra are shifted toward lower energies relative to the corresponding experimental spectra. Due to lack of experimentally determined band gaps and optical spectra for In$_2$X$_2$O$_7$-I and -II, rigid shift of the optical spectra toward higher energies up to the experimentally determined location is not applied. The $\varepsilon_2(\omega)$ spectra for In$_2$Ge$_2$O$_7$-I are isotropic in the energy range 0.0–4.5 eV and anisotropic at larger photon energies. In the energy range 0.0–4.2 eV optical properties of In$_2$Si$_2$O$_7$-II are isotropic and are almost the same for both In$_2$Si$_2$O$_7$-I and -II. The dependency of optical spectra on the crystallographic directions and lattice type becomes evident at larger energies of photons.

Further analysis of the optical spectra of In$_2$X$_2$O$_7$ other than $\varepsilon_2(\omega)$ has been performed only for one direction $E \parallel a$. The absorption coefficient $\alpha(\omega)$, reflectivity $R(\omega)$, refractive index $n(\omega)$, and extinction coefficient $k(\omega)$ are presented in Fig. 9 for In$_2$Si$_2$O$_7$-I, -II,
and In$_2$Sn$_2$O$_7$-I are found to be the most stable polymorphs. Possibility of aligning with other semiconductors will be the subject of future studies. We hope that our theoretical results will motivate experimental studies on these materials.

4. Conclusion

Ground state properties, electronic structure, and optical properties of In$_2$X$_2$O$_7$ (X=C, Se, Ge, and Sn) in monoclinic (-I) and cubic (-II) phases have been studied by DFT. In$_2$C$_2$O$_7$-II and In$_2$Se$_2$O$_7$-II as well as In$_2$Ge$_2$O$_7$-I and In$_2$Sn$_2$O$_7$-II are found to be the most stable polymorphs. Possibility of phase transition between phases -I and -II of In$_2$X$_2$O$_7$ is shown, and bulk modulus, transition pressure, and volume shrinkages at the phase transition point have been estimated. From the charge density, ELF, density of states, and Bader charge analysis, the chemical bonding is analyzed between constituents in In$_2$X$_2$O$_7$. Bottommost conduction band is found to be strongly dispersive whereas the topmost valence band is slightly dispersive. Effective masses of the conduction band electrons are found to be much smaller than those of the holes in the valence band, and comparable with the well known transparent conducting oxides. The In$_2$X$_2$O$_7$ compounds are found to be transparent in the visible part of the solar spectra. Based on the magnitude of the refractive index and the reflectivity, In$_2$X$_2$O$_7$-I and -II are suggested to be used as antireflection coating layer in solar cells.

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