Electronic structure and optical spectra of $\text{ZnX}_2\text{O}_4$ ($X = \text{Al}, \text{Ga}, \text{In}$) have been studied by density functional calculations. It is shown that $\text{ZnX}_2\text{O}_4$ possesses a large fundamental band gap and a second gap defined as the energy difference between the two lowest conduction band (CB) energies. The second gap is found to be $\sim 2$ eV for $\text{ZnAl}_2\text{O}_4$ and $> 2.8$ for $\text{ZnGa}_2\text{O}_4$ and $\text{ZnIn}_2\text{O}_4$. The bottommost CB for $\text{ZnX}_2\text{O}_4$ is well dispersive, which means that these materials possess the feature to conduct electrical current by CB electrons. Effective masses of electrons and holes are of the same order as those of the well-known $\text{ZnO}$ and $\text{In}_2\text{O}_3$. Optimized equilibrium structural parameters and bulk modulus for $\text{ZnAl}_2\text{O}_4$ and $\text{ZnGa}_2\text{O}_4$ are found to be in good agreement with the available experimental values and these values for $\text{ZnIn}_2\text{O}_4$ are predicted. Chemical bonding is found to be mixed ionic–covalent with predominant ionic character.

I. Introduction

Because of their robust properties such as high melting temperature, high strength, high resistance to chemical attack, large fundamental band gap, good electrical conductivity, and luminescence, $\text{ZnX}_2\text{O}_4$ ($X = \text{Al}, \text{Ga}, \text{In}$) have been studied by density functional calculations. Compared with the other transparent conducting oxides (TCO), such as, e.g., $\text{In}_2\text{O}_3:\text{Sn}$, $\text{SnO}_2$, $\text{ZnO}(\text{Al}, \text{Ga}, \text{etc})$, the band gap of $\text{ZnX}_2\text{O}_4$ is $> 4.0$ eV. Consequently, $\text{ZnX}_2\text{O}_4$ can be transparent to the UV part of the solar spectra whereas $\text{In}_2\text{O}_3:\text{Sn}$, $\text{SnO}_2$, and $\text{ZnO}(\text{Al}, \text{Ga})$ are transparent only in the visible part of the solar spectra. Hence, $\text{ZnX}_2\text{O}_4$ can present an interest for applications in violet to near UV-optoelectronic devices. Moreover, $\text{ZnX}_2\text{O}_4$ are highly reflective for the UV photon wave lengths, which is preferable for reflective optical coating in aerospace applications. Room-temperature resistivity of the order of $30 \text{ m}\Omega \times \text{cm}$ has been reported for polycrystalline $\text{ZnGa}_2\text{O}_4$.

The perspectives of usage of $\text{ZnX}_2\text{O}_4$ in the above and other applications have stimulated extensive theoretical and experimental studies. Pressure-induced phase transition of $\text{ZnAl}_2\text{O}_4$ and $\text{ZnGa}_2\text{O}_4$ has been found in Lopez et al.\(^9\) which shows that at ambient pressures a cubic spinel modification of these compounds is more stable and the phase transition can occur at high pressures. This finding can be important because of the occurrence of the compounds in geological settings of the earth’s crust and mantle.

Ground-state structures of $\text{MgAl}_2\text{O}_4$, $\text{ZnAl}_2\text{O}_4$, $\text{ZnGa}_2\text{O}_4$, and $\text{ZnIn}_2\text{O}_4$ are found\(^10\) to be normal spinels with a cubic lattice.

From the study of optical and electrical properties, it is reported\(^1\) that $\text{ZnGa}_2\text{O}_4$ is an interesting UV TCO with a wide energy band gap of about 4.4 eV and a moderate conductivity can be achieved by annealing under a reducing atmosphere at a high temperature. Electrical conductivity of $\text{ZnGa}_2\text{O}_4$ was $3 \times 10^4 \text{ S/cm}$. From the study of the optical properties of $\text{ZnAl}_2\text{O}_4$, $\text{ZnGa}_2\text{O}_4$, and $\text{ZnAlGaO}_4$ powders, a broad absorption band has been observed\(^2\) in the UV region from 260 to $\sim 270$ nm for $\text{ZnAl}_2\text{O}_4$ and 240 to 260 nm for $\text{ZnGa}_2\text{O}_4$ occurring, probably, due to fundamental band-to-band transitions.

One of the interesting features of the class of spinels is the possibility of modulation of electrical, optical, and magnetic properties by that of cation distributions.\(^12\) A systematic study of this question has been performed\(^13\) for $\text{A}^{\text{III}}\text{B}^{\text{II}}\text{O}_4$ and $\text{A}^{\text{IV}}\text{B}^{\text{III}}\text{O}_4$ with Mg, Zn, and Cd as group II atoms, Al, Ga, and In as group III atoms, and Si, Ge, and Sn as group IV atoms. It is reported that the group II atoms prefer to occupy the tetrahedral site rather than the octahedral site, in part, because of the preference of the group II atoms to form a covalent tetrahedral bond. Furthermore, the cation distribution is suggested to provide the opportunity for band gap engineering for $\text{A}^{\text{III}}\text{B}^{\text{II}}\text{O}_4$ and $\text{A}^{\text{IV}}\text{B}^{\text{III}}\text{O}_4$.

As it is well known, tuning of the electrical and optical properties of semiconductors can be provided by external and/or internal defects. A study of thermodynamic properties of point defects has also been studied\(^18\) by the inelastic neutron scattering and first-principles calculations. Despite these research efforts, many questions are still open. One of them is that the experimental determined band gap value for $\text{ZnGa}_2\text{O}_4$ was widely scattered with an energy range of 4.1–5.0 eV. Band parameters for $\text{ZnAl}_2\text{O}_4$ and $\text{ZnIn}_2\text{O}_4$ are not yet available. There are no experimental or theoretical data on the optical properties of $\text{ZnIn}_2\text{O}_4$ available in the literature. The main aim of this paper was to make a systematic study of the electronic structure and optical properties of $\text{ZnX}_2\text{O}_4$ ($X = \text{Al}, \text{Ga}, \text{and In}$).
II. Methods

The ZnX2O4 in face-centered cubic spinel phases are studied using the Vienna *ab initio* simulation package (VASP), which calculate the Kohn-Sham eigenvalues within the framework of DFT. The calculations have been performed with the use of the local-density approximation (LDA) and the LDA plus multiorbital mean-field Hubbard potential (LDA + U), which includes the on-site Coulomb interaction in the Hamiltonian. The latter approximation has been used to suppress partially the error in the computations within LDA related to the description of the d-electrons of the Zn, Ga, and In. As it is well known in the LDA calculations, energy bands of the d-electrons might be delocalized, located inappropriately close to the topmost VB, and be hybridized with O p-electrons, thus falsifying the band gap and band dispersion, and the spin-split of energy. For the LDA + U calculation, explicit values of the parameters U and J are required. These parameters have been estimated for ZnO to adjust partially the position of the Zn 3d bands, crystal-field energy, splitting energy, and the order of states at the top of the VB to experimental data. Similar experimental data are not available for ZnX2O4. However, a study of the electronic structure for ZnX2O4 within LDA showed that similar to ZnO, the Zn 3d bands are located close to the topmost VB, are not well localized, and hybridized with the O-2p bands. Hence, the U = 6 eV and J = 1 eV used for ZnO have been adopted in the present band structure calculations.

The exchange and correlation energy per electron have been described by the Perdew-Zunger parametrization with the quantum Monte Carlo procedure of Ceperley–Alder. The interaction between electrons and atomic cores is described by the Perdew–Zunger parametrization with the projector-augmented-wave (PAW) method. The use of the PAW pseudopotentials addresses the problem of the inadequate description of the wave functions in the core region common to other pseudopotential approaches. Also, it allows us to construct orthonormalized all-electron-like wave functions for the Zn-3d, -s, O-2s and -2p, Al-3s and -3p, Ga-3d, -s, and -4p as well as In-4d, -5s, and -5p valence electrons. Self-consistent calculations were performed using a 10 × 10 × 10 k mesh frame according to the Monkhorst–Pack scheme. The semicore Zn-3d, Ga-3d, and In-4d states have been considered as valence states. In order to understand the role of the spin-orbit (SO) coupling in electronic structure, the computations have been performed with and without SO coupling within LDA. Structural optimization has also been performed within LDA. For knowledge of the role of Coulomb correlation effects, a study of the electronic structure and optical properties has been performed within both LDA and LDA + U.

The equilibrium lattice parameters and bulk modulus of ZnX2O4 are determined by a total energy calculation through fitting into the Birch–Murnaghan equation of state. The calculations have been performed on a Γ-centered 10 × 10 × 10 k grid in the entire Brillouin zone. The computations are confined to the primitive unit cell consisting of 14 atoms. For the studies of antisite defects, a unit cell consisting 56 atoms has been considered. The antisite defects in ZnIn2O4 such as Zn at the In site (ZnIn) and In at the Zn site (InZn) have been considered. The diagonal elements of the effective mass tensor for the conduction band (CB) electrons are calculated by

\[
\frac{1}{m^*_k(k)} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial^2 k} \mid_{k=k_0}
\]

for a direction \( k \) about an extremum point \( k_0 \) in the Brillouin zone. For ZnX2O4, we have studied effective masses along the [001] and [111] directions in the vicinity of the Γ point. We use this to give an indication of the conduction, because the CB minimum of the band dispersions of all the compounds considered are located at the Γ point of the Brillouin zone. The band edge energies \( E(k) \) have been extracted from DFT calculations and a polynomial of an order > 2 was used to achieve the best fitting. From the fitted polynomial, the second order derivative was calculated for the Γ point, which was then used in the effective mass calculations by Eq. (1). Throughout the paper, the masses are presented in the unit of the free-electron rest mass \( m_0 \).

An imaginary part of the dielectric function \( \epsilon_2(\omega) \) was calculated from interband transitions through the following relation within LDA and LDA + U approximations

\[
\epsilon_2^\omega(\omega) = \frac{2e^2}{\pi \hbar^2 m^*_k} \int dk \sum_{\alpha} \langle \alpha | p | \alpha \rangle \langle \alpha | p | \alpha \rangle \times f_{\alpha}(1 - f_{\alpha}) \delta(h\omega - E_k)
\]

Here \( (p, p_e, p_p) = p \) is the momentum operator, \( f_{\alpha} \) is the Fermi distribution, and \( | k\rangle \) is the crystal wave function, corresponding to energy \( E_k \) with momentum \( k \). Owing to the cubic structure of ZnX2O4, the optical spectra are isotropic; consequently, only one component of the dielectric function is analyzed. The real part of the dielectric function \( \epsilon_1(\omega) \) is then calculated using the Kramer-Kronig transformation. These two spectra were then used to calculate all the other optical spectra. In this paper, we present and analyze the reflectivity \( R(\omega) \), the absorption coefficient \( \alpha(\omega) \), the refractive index \( n(\omega) \), the extinction coefficient \( k(\omega) \), and the electron energy loss spectra. More details about the optical calculations are discussed in Karazhanov and colleagues. The optical spectra are calculated by DFT within LDA and LDA + U for the energy range of 0–12 eV.

III. Results

1) Ground-State Properties

ZnX2O4 are ternary compounds, that belong to the space group \( Fd\bar{3}m \) (227) with stoichiometry \( AB_2O_4 \) (Fig. 1). The A cations are tetrahedrally coordinate whereas the B cations are in BO6 octahedra. The Zn atoms are located at Wyckoff positions, 8a \( (1/8, 1/8, 1/8) \) tetrahedral sites whereas X (\( X = Al, Ga, \) and In) atoms are located at the 16d \( (1/2, 1/2, 1/2) \) octahedral sites and the O atoms at 32e \( (u,u,u) \) face-centered cubic structure (Fig. 1) with the space group \( Fd\bar{3}m \). The spinels are characterized by the lattice parameter \( a \) and the internal parameter \( u \).

Using the experimentally determined structural parameters as input, structural optimization has been performed for ZnX2O4 by the following procedure: first, atomic positions have been relaxed by the force minimization method keeping the volume and shape of the crystal fixed. Using the relaxed atomic positions as input, the crystal volume and shape have been relaxed using stress minimization freezing out atomic positions. Then,

![Fig. 1. Crystal structures of ZnX2O4](image-url)
these optimized parameters have been used as input to relax atomic positions, cell volume, and shape altogether. Crystal structure information obtained by this way was used as input for the calculation of the total energy \( E_{\text{tot}} \) as a function of the cell volume \( V \) (Fig. 2). For each points in the total energy versus volume \( E_{\text{tot}}(V) \) atom, the positions have been relaxed in order to account the variation in the internal parameter \( u \) with volume change. The structural parameters corresponding to minimum (\( E_{\text{tot min}} \)) of the dependence \( E_{\text{tot}}(V) \) are taken as the ground-state parameters. Positional and lattice parameters derived from the DFT calculations for the equilibrium lattices are given in Table I together with experimentally determined values. Analysis of the Table I shows that deviation of the calculated equilibrium volumes are smaller than the experimentally determined values by 2.56% for ZnAl\(_2\)O\(_4\) and 2.5% for ZnGa\(_2\)O\(_4\), which indicates that the theoretical calculations are reliable to predict equilibrium structural parameters for such complex systems. Furthermore, symmetry of the thus optimized lattices is checked and found that it is the same as that of the experimentally determined one. The values of the oxygen internal parameters for optimized lattices are equal to \( u = 0.2638 \) for ZnAl\(_2\)O\(_4\), \( u = 0.2612 \) for ZnGa\(_2\)O\(_4\), and \( u = 0.2557 \) for ZnIn\(_2\)O\(_4\) which are in good agreement with experimental results of 0.2599 and 0.2654 for ZnAl\(_2\)O\(_4\) and ZnGa\(_2\)O\(_4\), respectively.

In order to understand the compressibility of studied systems, the bulk modulus \( B_0 \) and its pressure derivative \( B'_0 \) have been calculated for Zn\(_x\)O\(_y\). The results are presented in Table I. Analysis shows that the calculated \( B_0 \) are in good agreement with experimental results and other theoretical results. However, the calculated \( B'_0 \) are smaller than those determined from the experiment, which might be related to the experimental nonhydrostatic conditions.

### (2) Band Structure

For an insight into the electrical and optical properties of solids, analysis of band structure is important. Band structures for Zn\(_x\)O\(_y\) have been calculated within LDA and LDA+\( U \). Figure 3 presents band structure calculations within LDA+\( U \) including the SO coupling into account and neglecting it. Analysis of Fig. 3 shows that ZnAl\(_2\)O\(_4\) and ZnIn\(_2\)O\(_4\) are direct band gap solids with CB minimum and VB maximum located at the \( \Gamma \) point. However, ZnGa\(_2\)O\(_4\) is an indirect gap material with CB minimum and VB maximum located in between \( L \) and \( U \) points. The indirect nature of the band gap remained in the LDA+\( U \) calculations also. This result is consistent with findings of Lopez et al.\(^{16}\) Compared with bottommost CB, the topmost VB of ZnX\(_2\)O\(_4\) is almost dispersionless, which means that the VB electrons are tightly bound into respective atoms. However, the bottommost CB is well dispersive for ZnX\(_2\)O\(_4\). Consequently, one can expect electrical current transport through CB by electrons.

From the band structure analysis calculated by LDA and LDA+\( U \), the following band parameters have been determined: (i) fundamental band gap \( (E_g) \), which is the difference between the bottommost CB and topmost VB, (ii) the second band gap \( E'_g \), which is the difference between energies of the bottommost and next nearest CB, and (iii) spin-splitting energy \( (E_{\text{SO}}) \). These parameters are presented in Table II. As it is well known, the band gap values obtained from usual DFT calculations are systematically underestimated. However, the magnitude of \( E_g \) calculated for ZnAl\(_2\)O\(_4\) by LDA and LDA+\( U \) are larger than the corresponding experimentally determined values of 3.80–3.90 eV.\(^4\) However, our theoretical results agree with other theoretical findings.\(^{9,15}\) It is suggested in Lopez et al.\(^{15}\) that the band gap of ZnAl\(_2\)O\(_4\) estimated in Sampath and Cordaro,\(^4\) probably, is incorrect. It may be noted that the presently calculated band gap parameters are in good agreement with experimentally determined values of 3.80–3.90 eV.\(^4\) However, our theoretical results agree with other theoretical findings.\(^{9,15}\)

### Table I. Equilibrium Lattice Parameter (\( \AA \)) and volume (\( \AA^3 \)), Structural Parameters, Bulk Modulus (\( B_0 \)), As Well As The Derivative of Bulk Modulus (\( B'_0 \)) for Zn\(_x\)O\(_y\) Derived from the Present DFT Calculations by a Search of the Total Energy Minimum

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit cell dimensions</th>
<th>Atom</th>
<th>Site</th>
<th>( x )</th>
<th>( y )</th>
<th>( Z )</th>
<th>( B_0 ) (GPa)</th>
<th>( B'_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAl(_2)O(_4)</td>
<td>( a = 8.0215 ) (8.0912)</td>
<td>Zn</td>
<td>8a</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>219 (202)(^1)</td>
<td>4.3</td>
</tr>
<tr>
<td>Fd(_{3m})</td>
<td>( V = 516.14 ) (529.70)</td>
<td>Al</td>
<td>16d</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>218(^1)</td>
<td>(5.52)(^g)</td>
</tr>
<tr>
<td>ZnGa(_2)O(_4)</td>
<td>( a = 8.2657 ) (8.3358)</td>
<td>Zn</td>
<td>8a</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>205 (233)(^f)</td>
<td>4.5 (8.3)(^l)</td>
</tr>
<tr>
<td>Fd(_{3m})</td>
<td>( V = 564.72 ) (579.22)</td>
<td>Ga</td>
<td>16d</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>163</td>
<td>5.0</td>
</tr>
<tr>
<td>ZnIn(_2)O(_4)</td>
<td>( a = 8.8424 ) (8.8370)</td>
<td>Zn</td>
<td>8a</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>0.1250 (0.1250)</td>
<td>223 (202)(^d)</td>
<td>3.5 (8.3)(^d)</td>
</tr>
<tr>
<td>Fd(_{3m})</td>
<td>( V = 691.36 ) (690.10)</td>
<td>In</td>
<td>16d</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>0.5000 (0.5000)</td>
<td>324</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Values given in parentheses refer to experimental data.\(^{10}\) For ZnIn\(_2\)O\(_4\), theoretical data of Seko et al.\(^{10}\) are used.\(^{1} \) Experiment.\(^{14}\) \(^{1} \) Experiment.\(^{18}\) \(^{1} \) Experiment.\(^{16}\) \(^{1} \) Experiment.\(^{16}\) DFT, density functional theory.
The second band gap $E_g^n$ is also one of the important parameters, which shows whether the material can remain transparent to the visible spectra, if it is heavily doped by shallow donors. Although DFT underestimates the fundamental band gap, it calculates accurately $E_g^n$. Analysis of Table II shows that the magnitudes of $E_g^n$ calculated within LDA and LDA+U are close to each other thus indicating that the Coulomb correlation effects do not play an important role in the parameter. It should be noted that $E_g^n<2.8$ eV for ZnAl$_2$O$_4$ and $>2.8$ eV for ZnIn$_2$O$_4$. These results indicate that if ZnGa$_2$O$_4$ and ZnIn$_2$O$_4$ can possess good $n$-type electrical conductivity, then they still can remain transparent in the visible spectra and can, respectively, be considered as $n$-type TCOs. This result indicates that the transparency of the compound will increase upon increasing the atomic number from Al to In.

Without the SO coupling, the topmost VB of ZnX$_2$O$_4$ is triple degenerate at the $\Gamma$ point. Upon inclusion of the SO coupling, these three states are split and form two groups of states. In ZnAl$_2$O$_4$, one of these groups located at higher energy is double degenerate. It is split from the fourfold degenerated one by about 1 eV. In ZnGa$_2$O$_4$ and ZnIn$_2$O$_4$ the order is reversed, i.e. the fourfold degenerated states forms the topmost VB, whereas the double-degenerated states is split toward lower energies. There are no experimental data about $\Delta_{SO}$ for ZnX$_2$O$_4$. Analysis of the Table II shows that $\Delta_{SO}$ estimated for the $\Gamma$ point increases upon moving from Al to In and this is due to the increase in SO coupling by the increase in atomic number. Not only $\Delta_{SO}$, but the band structure of ZnX$_2$O$_4$ is very sensitive to choice of the approximation used in the computations. This is demonstrated in Fig. 4, which displays the band structure of ZnIn$_2$O$_4$ calculated within LDA and LDA+U including the SO coupling and neglecting it. Systematic experimental research is needed to clarify the origin of the VB and proper selection of the computational approximation.

### (3) Density of States

Figure 5 presents total DOS (TDOS) calculated by DFT within LDA and LDA+U methods. Analysis shows that the VB consists of two regions for ZnAl$_2$O$_4$, three regions for ZnGa$_2$O$_4$, and four regions for ZnIn$_2$O$_4$. The lowest bands are located ≈17 eV below the topmost VB and it is well localized. The Ga- and In-derived $d$-bands are well separated from these lowest bands and are located at higher energies. The Zn-$3d$ localized bands are separated from the Ga- and In-derived $d$-bands. They are combined with topmost VBs in ZnAl$_2$O$_4$ and ZnGa$_2$O$_4$ and slightly separated in ZnIn$_2$O$_4$. Analysis of Fig. 5 shows that the Zn-$3d$ bands calculated within LDA+U are shifted toward

### Table II. Fundamental ($E_g$) and Optical ($E'_g$) Band Gaps (eV) of ZnX$_2$O$_4$ Calculated Neglecting the SO Coupling within LDA and LDA+U, with SO Coupling within LDA Along with Computed Results of Other Authors and Experimental Data

<table>
<thead>
<tr>
<th></th>
<th>ZnAl$_2$O$_4$</th>
<th>ZnGa$_2$O$_4$</th>
<th>ZnIn$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No SO</td>
<td>3.99</td>
<td>4.11</td>
<td>3.80–3.90</td>
</tr>
<tr>
<td>SO</td>
<td>4.23</td>
<td>3.80–3.90</td>
<td>3.99</td>
</tr>
<tr>
<td>$U = 6$</td>
<td>4.53</td>
<td>4.30</td>
<td>4.27</td>
</tr>
<tr>
<td>LDA+U</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No SO</td>
<td>2.73</td>
<td>2.76</td>
<td>3.38</td>
</tr>
<tr>
<td>SO</td>
<td>2.94</td>
<td>2.77</td>
<td>3.37</td>
</tr>
<tr>
<td>$U = 6$</td>
<td>3.09</td>
<td>2.76</td>
<td>3.42</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_g$</th>
<th>VASP$^1$</th>
<th>TB-LMTO$^4$</th>
<th>FP-LAPW$^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'_g$</td>
<td>Experiment$^4$</td>
<td>Experiment$^1$</td>
<td>Experiment$^1$</td>
</tr>
</tbody>
</table>

Energy of spin-orbit coupling ($\Delta_{SO}$) is in meV. $^1$Calculated by VASP package. $^4$Calculated by TB-LMTO method. $^8$Calculated by FP-LAPW method. LDA, local-density approximation; VASP, Vienna ab initio simulation package; SO, spin-orbit.
lower energies and become more localized compared with those by LDA. Consequently, the LDA computations artificially enhance strong hybridization of the O-2p bands located at the top of the VB with the Zn-3d bands. This might influence the dispersion of the topmost VB. Consequently, the effective masses calculated by LDA and LDA+U are expected to differ each from other, which demonstrates the importance of the Coulomb correlation in band parameters of ZnX₂O₄ in agreement with the results in Table II.

The information regarding the origin of the bands and chemical bonding can be obtained from the analysis of orbital and site-projected DOS (PDOS). The results are presented in Fig. 6. In ZnAl₂O₄, the lowest bands originate mainly from the O-2s electrons slightly hybridized with Zn-4s electrons. In ZnGa₂O₄ and ZnIn₂O₄, they are also hybridized with Ga and In s valence electrons. As expected, the topmost VB consists of strongly hybridized Zn-3d, X(X = Al, Ga, and In)p-π and O2p valence electrons. Chemical bonding between O and Zn as well as between O and X (X = Al, Ga, and In) can be said as mixed ionic-covalent with a predominant ionic character. The lowest CB minimum mainly originates from Zn-4s electrons.

(4) Charge Density, Electron-Localization Function, Bader and Voronoi Charges

For the quantitative characterization of chemical bonding of a solid, Bader and Voronoi charge analyses²⁶–³⁰ are widely used. In the Bader charge analysis, each atom of a compound is surrounded by a surface (called Bader regions) that run through minima of the charge density and the total charge of the atom is assigned to the nearest atom, but each of these distances are not scaled by the radius of each atom, and hence, the Voronoi charges in the present article is used just for a sanity check.

Table III presents the atomic charges for ZnX₂O₄ calculated according to Bader and Voronoi schemes. As expected, Zn, Al, and Ga atoms donate electrons, while O atoms accept them. Based on the amount of the transferred charges one can conclude that chemical bonding is of mixed covalent–ionic type.

(5) Effective Masses

One of the parameters characterizing transport properties through VB and CB are the effective masses of electrons and holes. As demonstrated in Fig. 3, topmost VB of both ZnX₂O₄ is almost flat compared with bottommost CB. So, holes are well localized within their respective atoms and indicate the dominance of ionicity in the chemical bonding of these compounds. However, bottommost CB is well dispersive, which shows that current can be transported by CB electrons. To characterize quantitatively, we have calculated the CB electron effective masses for ZnX₂O₄. The results are presented in Table IV. It is seen in the Table IV that the CB electron effective masses calculated within LDA and LDA+U for ZnAl₂O₄ are larger whereas those for ZnIn₂O₄ are smaller than 0.23m₀ of ZnO calculated by us within LDA and 0.30m₀ determined experimentally for the well-known TCO In₂O₃:Sn.³⁹ The small values of calculated CB electron effective masses indicate that these materials can be considered as good electron conductors. The CB electron effective masses for ZnX₂O₄ calculated within LDA+U is found to be slightly different from that within

![Fig. 4. Fine structure at the topmost VB for ZnIn₂O₄ calculated by DFT within LDA and LDA+U including the SO coupling into computations (dashed lines) and neglecting it (continuous lines).](image)

![Fig. 5. Total density of states for ZnX₂O₄ calculated by DFT within LDA and LDA+U.](image)

![Fig. 6. Orbital and site projected DOS for ZnX₂O₄ calculated within LDA+U for U = 6 eV and J = 1 eV.](image)

![Table III. Atomic Charges (in Units of the Electron Charge e⁻) Around Zn, Al, Ga, In, and O Atoms Calculated According to Voronoi and Bader Topological Analysis for Different Phases of ZnX₂O₄](table)

<table>
<thead>
<tr>
<th>ZnX₂O₄</th>
<th>ZnAl₂O₄</th>
<th>ZnGa₂O₄</th>
<th>ZnIn₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bader</td>
<td>Voronoi</td>
<td>Bader</td>
</tr>
<tr>
<td>Zn</td>
<td>1.30</td>
<td>1.14</td>
<td>1.33</td>
</tr>
<tr>
<td>O</td>
<td>−1.80</td>
<td>−1.00</td>
<td>−1.22</td>
</tr>
<tr>
<td>Al,Ga,In</td>
<td>0.50</td>
<td>1.43</td>
<td>1.84</td>
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</table>
LDA results thus demonstrating that the Coulomb correlation effects are in band dispersion.

(6) Optical Spectra

Optical spectra have been calculated for ZnX₂O₄ by DFT within LDA and LDA+U. Figure 8 presents the results calculated from LDA+U calculations. It is seen that in the energy range from 3 to 5 eV, absorption and reflectivity of ZnX₂O₄ are quite small. Hence, if the optical spectra will not be modulated much by doping, and if the compounds can possess high electrical conductivity, they can be classified as candidates for TCOs. The calculated refractive index is ≥1.8 in the visible and UV parts of the photon energies, so these compounds can be used as antireflection coatings in Si-based solar cells. As is well known, the band gap values calculated from DFT is smaller than the experimentally determined values. Consequently, absorption is expected to start at larger photon energies than 3 eV (Fig. 8). To partially fix the error, commonly the rigid shift technique is used, which shifts the optical spectra calculated by DFT toward larger energies until the experimentally determined location. Due to lack of such experimental results the rigid shift technique has not been applied. To know whether the scissors can be applied or not one need experimentally determined optical spectra in a wider energy range. Comparative analysis of the optical spectra coming from LDA and LDA+U shows that the difference between the two sets of the results is negligible. Consequently, the Coulomb correlation effects do not play an important role in direct optical transitions.

(7) Defects in ZnX₂O₄

It is well known that electrical and optical properties of solids can be tuned by internal and/or external defects. A great number of internal defects are expected to present in ZnX₂O₄. One of them is the antisite defect when, e.g., group III(II) atoms located at the site of group II(III) atoms being thus donors(acceptors). Such antisite defects ZnₓIn₀ and InₓZn₀ have been studied in the ZnₓIn₂O₄ unit cell. Analysis shows that, as expected, ZnₓIn₂O₄ with one ZnₓIn and one InₓZn can be an insulator. When the concentration of ZnₓIn is equal to that of InₓZn and if suppose that there are no other impurities/defects, then the acceptor ZnₓIn is compensated by the donor InₓZn, and ZnₓInₓZn becomes the insulator.

IV. Conclusion

From density functional calculations, it is found that ZnX₂O₄ poses large fundamental band gap values. The second gap, in which the energy difference is between the two lowest CB energies is ~2 eV for ZnAl₂O₄ and ~2.8 for ZnGa₂O₄ and ZnIn₂O₄. Bottommost CB for ZnX₂O₄ is well dispersive, which means that in these materials electrical current can be transported by CB electrons. Effective masses of electrons and holes are of the same order as those of the well-known ZnO and In₂O₃. Chemical bonding is found to be mixed ionic-covalent with predominant ionic character. Absorption and reflectivity spectra for ZnX₂O₄ are found to be small in the energies >3 eV whereas the refractive index is ≥1.8 in the visible and UV parts of the photon energies, and hence these compounds can be used as antireflection coatings in Si solar cells.

Acknowledgment

S. Z. K. has received partial financial support from the Academy of Sciences of Uzbekistan.

Table IV. Effective Masses of Electrons and Holes (in Units of the Free-Electron Mass m₀) for ZnX₂O₄ Calculated within LDA and LDA+U

<table>
<thead>
<tr>
<th>Direction</th>
<th>ZnAl₂O₄</th>
<th>ZnGa₂O₄</th>
<th>ZnIn₂O₄</th>
<th>LDA</th>
<th>LDA+U</th>
<th>LDA+U</th>
<th>LDA</th>
<th>LDA+U</th>
<th>References</th>
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<tbody>
<tr>
<td>me(Γ→↓)</td>
<td>0.35</td>
<td>0.33</td>
<td>0.25</td>
<td>0.22</td>
<td>0.17</td>
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<tr>
<td></td>
<td>0.36</td>
<td>0.22</td>
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<td></td>
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<tr>
<td>me(Γ→↑↑)</td>
<td>0.40</td>
<td>0.31</td>
<td>0.29</td>
<td>0.22</td>
<td>0.18</td>
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<tr>
<td></td>
<td>0.38</td>
<td>0.21</td>
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</tbody>
</table>

*Calculated by the TB-LMTO method. LDA, local-density approximation.

References


