

Electronic and Optical Properties of Spinel TCOs: SnZn_2O_4 , SnCd_2O_4 , and CdIn_2O_4

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ABSTRACT

Using the band-structure method, we have studied the electronic and optical properties of the transparent conducting oxides SnZn_2O_4 , SnCd_2O_4 , and CdIn_2O_4 . We analyzed the atomic and orbital characters of the band edge states and explained the general trends observed in the fundamental band gap, the optical band gap, the energy difference between the first and the second conduction bands, and the electron effective mass. General rules for designing more efficient transparent conducting oxides are proposed.

1. Objectives

SnZn_2O_4 , SnCd_2O_4 , and CdIn_2O_4 are ternary compounds that can exist in the spinel structure. They have emerged as promising transparent conducting oxides (TCOs), which are transparent and at the same time conductive, thus are suitable for solar cell applications. However, despite many recent studies of these compounds, many of their physical properties are still unknown. Their band structure and optical properties are not well established, nor are the reasons for their combined transparency and conductivity.

2. Technical Approach

Using first-principles band structure and total energy methods as implemented in the VASP code, we studied the structural, electronic, and optical properties of the three compounds in normal and inverse spinel structures [1]. In particular, we investigated the wavefunction characters of the band edge states and the relationship between the crystal structures and the combined transparency and n-type conductivity in these compounds.

TABLE I: Calculated total energy difference ΔE_g^{tot} (in eV, referenced to the normal spinel structure), fundamental band gap E_g , optical band gap E_g^{opt} , energy difference E_{12} between the first and the second conduction state at γ , and electron effective masses of SnZn_2O_4 , SnCd_2O_4 , and CdIn_2O_4 in the normal (N) and inverse (I) spinel structures. The LDA correction (about 1.4 eV for the band gap and $0.05 m_0$ for the effective masses) are included for easier comparison with experimental data.

	ΔE_g^{tot}	E_g	E_g^{opt}	E_{12}	m^*
SnZn_2O_4 N	0.00	1.9	3.1	2.3	0.24
SnZn_2O_4 I	-0.68	2.5	3.6	3.08	0.28
SnCd_2O_4 N	0.00	1.6	2.5	2.36	0.19
SnCd_2O_4 I	-0.71	1.7	2.7	3.80	0.22
CdIn_2O_4 N	0.00	2.5	2.9	4.02	0.22
CdIn_2O_4 I	-0.45	1.5	2.7	3.02	0.20

3. Results and Accomplishments

3.1 Crystal Structure

In the “normal” spinel oxide AB_2O_4 with O_h^7 symmetry, 1/8 of the tetrahedral voids in a face-centered-cubic (fcc) close-packed oxygen sublattice are occupied by A atoms and 1/2 of the octahedral voids are occupied by B atoms. There exists also an “inverse” spinel structure, where the tetrahedral sites are occupied by B atoms and octahedral sites are occupied randomly by an equal number of A and B atoms. From the total energy calculations (Table I), we find that SnZn_2O_4 and SnCd_2O_4 are more stable in the inverse spinel structure, whereas CdIn_2O_4 is more stable in the normal spinel structure. The relative stability between the normal and the inverse structures can be explained by the Coulomb interaction, and by the tendency for Zn to form four-fold covalent bond [2].

3.2 Band Structure

A high-performance n-type TCO should simultaneously satisfy two requirements: (i) large optical band gap as well as energy separation between the CBM and the second conduction band (SCB), for transparency; (ii) a low CBM with respect to the vacuum level, and a small effective mass, for high dopability and good conductivity. As a consequence of the second condition, a low VBM, which is a common characteristic of oxides, is also required.

For the three compounds in the spinel structure, we find that (a) the $_{12v}$ valence band maximum (VBM) state consists mostly of O p and cation d states of the octahedral site, with some d character also from the cation at the tetrahedral site. (b) The $_{1c}$ conduction band minimum (CBM) state consists predominantly of O s and cation s states of the tetrahedral site, with some s character from the cation at the octahedral site. (c) The SCB state has the $_{2c}$ representation, and consists mostly of O s and cation s states of the tetrahedral site only. (d) The $_{15v}$ state, which determines the optical band gap (see below), consists of mostly O p and cation d states of the tetrahedral site. With this analysis, we can now explain the changes in the band gap and the splitting between the first two conduction bands, $E_{12} = E_{\text{SCB}} - E_{\text{CBM}}$, as a function of the crystal structures.

The results for E_g and E_{12} are listed in Table I. We find that when SnZn_2O_4 changes from the normal to the inverse spinel structure, i.e., when Sn and half of the Zn change sites, both the band gap and E_{12} increases. This is because when Sn moves to the octahedral site, the VBM energy decreases, due to the lower Sn 4d orbital energy compared to that of the Zn 3d orbital, and, hence, the reduced p-d repulsion at the octahedral site. Moreover, since Zn has a much higher 4s orbital energy than the Sn 5s orbital, the

energies of both first two conduction bands increase. However, the energy of the SCB increases more than that of the CBM state because the former contains only Zn 4s orbital but no Sn 5s orbital.

The band structure and variation of E_g and E_{12} of SnCd_2O_4 are similar to those in SnZn_2O_4 , except that the band gap of SnCd_2O_4 is smaller than that of SnZn_2O_4 , due mostly to the larger volume of SnCd_2O_4 , and that the difference in the band gap between the normal and inverse structures is smaller in SnCd_2O_4 than in SnZn_2O_4 . This can be explained by the fact that the atomic size of Cd is much larger than that of Zn and Sn, while Sn and Zn have similar atomic sizes. When Cd moves to the tetrahedral site in the inverse spinel SnCd_2O_4 , the strain-induced deformation effect partially cancels the chemical effect in SnCd_2O_4 .

The band gap of CdIn_2O_4 in the normal spinel structure is larger than that of SnZn_2O_4 and SnCd_2O_4 , due to reduced hybridization between the O p and the cation d states at the octahedral site in the normal spinel CdIn_2O_4 . The trend in the band gap variation and E_{12} energy separation of CdIn_2O_4 is also opposite to that of SnZn_2O_4 and SnCd_2O_4 . This can be understood by noticing that in the inverse spinel structures of SnZn_2O_4 and SnCd_2O_4 , a low valence atom (Zn or Cd) moves to the tetrahedral site and a high valence atom (Sn) moves to the octahedral site. Consequently, in the inverse spinel structure of CdIn_2O_4 , the change is opposite. Finally, we remark that normal spinel CdIn_2O_4 is very much like the inverse spinel SnCd_2O_4 [$\text{Cd}(\text{Sn,Cd})\text{O}_4$]. However, the band gap of normal CdIn_2O_4 is much larger than that of inverse SnCd_2O_4 . This is because in SnCd_2O_4 the CBM becomes more localized on the Sn atom, which has a lower s orbital energy than that of In and because the O p and Cd d coupling is larger than that of O p and In d .

Based on the analysis above of the atomic characters of the band edge states, and on the effects of the volume deformation on the CBM and VBM levels, we propose

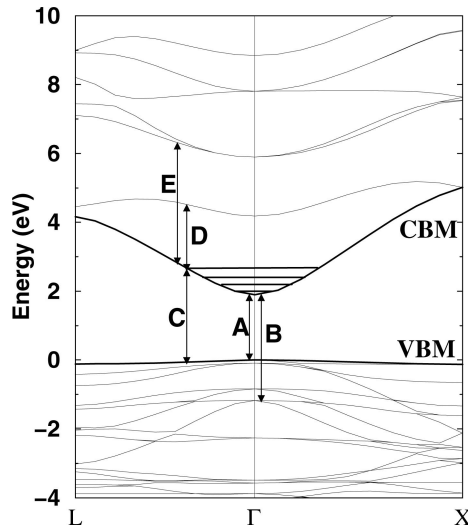


Fig. 1. Band Structure and transitions of normal spinel SnZn_2O_4 . The occupied levels in the conduction band are indicated for the n-type doped case.

here some general rules for designing TCOs with better transparency and higher carrier concentration. (i) The cations should have a relatively large atomic size and a low-lying s orbital, especially at the tetrahedral site. (ii) The d orbital binding energy of the cations should be large, especially at the octahedral site. (iii) A large energy difference should exist between the s orbitals of the cation at the tetrahedral site and that at the octahedral site. Finally, (iv) The high valence cation should occupy the octahedral site, and the low valence atom the tetrahedral site.

3.3 Effective Mass

A good TCO should also have a small electron effective mass to yield a high conductivity. The calculated electron effective masses at the Γ point of the CBM are shown in Table I. We find that the effective masses increase as the band gap increases. Furthermore, we find that for n-type doped systems the effective masses increase as the carrier (or Fermi energy) increases [1].

3.4 Optical Properties

In n-type TCOs, the optical properties are determined not only by the optical transitions between the valence bands and conduction bands, but also between the occupied conduction states and the other conduction band states. We find that for this system, the transition from the VBM to the CBM, which defines the fundamental band gap at Γ (A in Fig. 1), is forbidden by symmetry. The transition at L is allowed only between the $1c$ state and the $15v$ valence states (B in Fig. 1), which defines the optical band gap. We find that the optical band gap is usually about 1 eV larger than the fundamental band gap (see Table I). Furthermore, as carrier density increases, new features will start to appear in the absorption spectrum. First, the optical band gap shifts toward higher energy due to the Moss-Burstein effect (C in Fig. 1). Second, a new peak will appear (D in Fig. 1) below the fundamental band gap, which is related to allowed transitions between the occupied conduction band and the second conduction band. Furthermore, a feature in the absorption spectrum (E in Fig. 1) related to transitions between the first conduction band and other conduction band with higher energy may appear. In contrast to the C transition, the energy of the D and E transition decreases with increasing carrier concentration, and thus could exhibit an inverse Moss-Burstein shift at very high concentration.

4. Conclusions

We have studied the structural, electronic, and optical properties of SnZn_2O , SnCd_2O_4 and CdIn_2O_4 . General trends are observed and explained. The finding will help us in future design of high-performance TCOs.

REFERENCES

- [1] D. Segev and S.-H. Wei, Submitted to Phys. Rev. B.
- [2] S.-H. Wei and S. B. Zhang, Phys. Rev. B 63, 45112 (2001).

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