May 2002 • NREL/CP-520-32199

Conference Paper

Electronic Structure and Doping of P-Type Transparent Conducting Oxides

Preprint

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To be presented at the 29th IEEE PV Specialists Conference
New Orleans, Louisiana
May 20-24, 2002

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

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Contract No. DE-AC36-99-GO10337

ELECTRONIC STRUCTURE AND DOPING OF P-TYPE TRANSPARENT CONDUCTING OXIDES

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ABSTRACT

Transparent conducting oxides (TCOs) are a group of materials that are widely used in solar cells and other optoelectronic devices. Recently, Cu-containing p-type TCOs such as $M^{II}Cu_2O_2$ (M^{II}=Mg, Ca, Sr, Ba) and $CuM^{III}O_2$ (M^{III}=Al, Ga, In) have been proposed. Using first-principles band structure methods, we have systematically studied the electronic and optical properties of these p-type transparent oxides. For $M^{II}Cu_2O_2$, we predict that adding a small amount of Ca into $SrCu_2O_2$ can increase the transparency and conductivity. For $CuM^{III}O_2$, we explained the doping and band gap anomalies in this system and proposed a new approach to search for bipolar dopable wide-gap materials.

INTRODUCTION

Transparent conducting oxides (TCOs) are materials that are widely used in solar cells and other optoelectronic devices [1]. Almost all of the well-known TCOs, such as ZnO, In_2O_3, SnO_2, and their alloys, have n-type conductivity. The lack of p-type TCOs has severely limited the potential applications of these materials. Consequently, considerable efforts have been devoted to develop p-type TCOs and to understand the doping mechanism in these materials [2-7].

Recently, several Cu-containing p-type TCOs such as $SrCu_2O_2$ and $CuM^{III}O_2$ (M^{III}=Al, Ga, In) have been proposed [2,5-7]. The idea is based on the observations that Cu has shallow, occupied $3d$ orbital that is close to the O $2p$ orbitals. The coupling between the Cu d states and the O p states can lead to smaller ionization energies (which is equivalent to higher VBM) for these Cu compounds than for conventional oxides, thus, making it easier to dope them p-type.

Besides showing p-type conductivity, these materials also show some unique and unexplained physical properties [5-7]. For example, the optically *measured* direct band gap increases from 3.5 eV ($CuAlO_2$), to 3.6 eV ($CuGaO_2$), and to 3.9 eV ($CuInO_2$). This trend is in sharp contrast to the trend found in other group III containing semiconductors, in which the band gap decreases as the atomic number of the group III elements increases [8]. Furthermore, bipolar doping is achieved, but only in $CuInO_2$ by extrinsic dopants [7]. This is quite puzzling because $CuInO_2$ has the largest reported band gap [7]. No similar trend has ever been observed in any other semiconductors.

We have systematically studied the electronic and optical properties of these p-type transparent oxides. For $M^{II}Cu_2O_2$ (M^{II}=Mg, Ca, Sr, Ba), the trend of band gap variation of $M^{II}Cu_2O_2$ as a function of M^{II} is explained in terms of atomic energy levels and atomic sizes of the M^{II} elements. For $SrCu_2O_2$, the calculated effective masses for the conduction band states are found to be larger than those for the valence states, opposite to the trend in conventional semiconductors and n-type TCOs. We predict that adding a small amount of Ca into $SrCu_2O_2$ can increase the band gap and reduce the hole effective mass of $SrCu_2O_2$, therefore, increase the transparency and conductivity. For $CuM^{III}O_2$, we show that the doping and band gap anomalies in this system are results of a large disparity between the fundamental gap and the apparent optical gap, a finding that could lead to breakthroughs towards bipolarly dopable wide-gap semiconductor oxides.

METHOD OF CALCULATION

The band structure calculations were performed using the first-principles local density approximation (LDA) as implemented by the general potential linearized augmented plane wave (LAPW) method [9]. We used the Ceperley-Alder exchange correlation potentials as parameterized by Perdew and Zunger [10]. The Ca $3p$, Sr $4p$, and Ba $5p$ states, as well as the Ga $3d$ and In $4d$ states, are treated as valence states. Spin-orbit coupling is included when calculating the effective mass. The optical properties of these materials are studied by calculating the dipole momentum matrix element $P_{i,j}(\mathbf{k}) = | < \psi_{i,\mathbf{k}}|\mathbf{P}|\psi_{j,\mathbf{k}} > |^2$ and the absorption coefficient using the optic package in WIEN97 code [11].

RESULTS AND DISCUSSIONS

$M^{II}Cu_2O_2$

$M^{II}Cu_2O_2$ has the tetragonal crystal structure with space group of $I4_1/amd$ (Fig. 1b). In this crystal structure, M^{II} atoms are at the center of a distorted octahedron formed by O atoms. The Cu atoms form the well-known O-Cu-O dumbbell configuration, which is similar to that of Cu_2O (Figure 1a). In fact, $M^{II}Cu_2O_2$ can be considered as being derived from Cu_2O_2, in which one Cu atom is removed for each unit of distorted Cu_2O, plus an inter-penetrating body-centered tetragonal Sr sublattice.

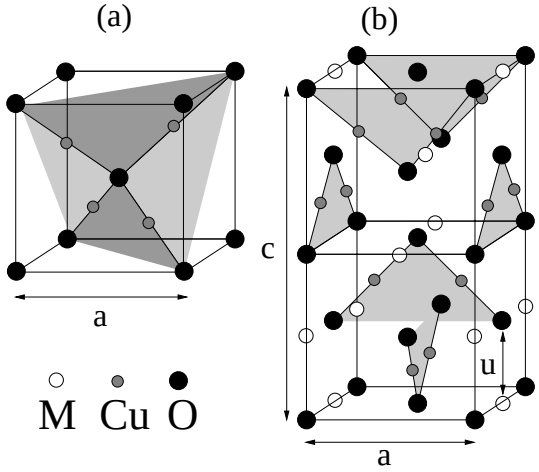

Fig. 1. Crystal structure of (a) Cu_2O and (b) $M^{II}Cu_2O_2$.

The calculated band structure of $SrCu_2O_2$ at the experimental lattice constants along some high symmetry directions is shown in Fig. 2c. It shows that $SrCu_2O_2$ has a direct band gap at Γ. Analysis of the electron density of states (DOS) [3] for $SrCu_2O_2$ indicates that the valence states consist of two major parts. The upper part from the valence band maximum (VBM) to $E_{VBM} - 3$ eV consists predominantly of the Cu $3d$ states. The lower part from $E_{VBM} - 3$ eV to $E_{VBM} - 6$ eV consists predominantly of the O $2p$ states. This is due to the fact that Cu $3d$ level is shallower than O $2p$. Thus, the Cu-containing oxides such as Cu_2O have much higher VBM than other conventional oxides such as ZnO, where the Zn $3d$ state is deeper than the O $2p$ state. Higher VBM also leads to higher p-type dopability, as suggested by the doping limit rule [12]. Comparing to Cu_2O, we find that adding SrO into Cu_2O reduces the $d-d$ coupling between the Cu atoms and raises the band gap by 1.31 eV, in good agreement with the experimental value of 1.22 eV.

In order to be transparent, a p-type TCO not only should have a large fundamental band gap, so no visible light absorption between the valence bands and the conduction bands can take place, but also should have no visible light absorption between the VBM and the bands below. We have calculated the momentum transition matrix elements between the VBM state and other states at Γ [3]. We find that, indeed, the dipole transition probabilities between the VBM and states within 4 eV below the VBM are negligible. This is because the on-site transition from the same angular momentum (such as O p to O p and Cu d to Cu d) is forbidden according to the classical selection rule. This explains the transparency for this p-type material.

A p-type TCO with good conductivity should also have high mobility, and thus, small hole effective mass. To test this, the electron and hole effective masses for the tetragonal $SrCu_2O_2$ are calculated along high symmetry lines parallel or perpendicular to the c directions. The results are shown in Table I. We find that for this p-type material, the effective mass of the conduction band minimum (CBM) is much larger than that of the VBM. Both the electron effective masses and the hole effective masses are anisotropic. The hole effective masses along the c-axis are much larger than the one perpendicular to the c axis. These results indicate that for single crystal, which could be obtained by epitaxial growth, hole conductivity perpendicular to the c-axis will be much larger than that parallel to the c-axis.

To search for better p-type TCOs we have also calculated the band structures of $M^{II}Cu_2O_2$ with M=Mg, Ca, Sr, and Ba. The calculated band structures are plotted in Fig. 2. All the four compounds show direct band gaps at Γ with E_g = 2.45, 3.01, 3.33, 3.30 eV, respectively, after the LDA correction [3]. We see that the variation of the band gaps of $M^{II}Cu_2O_2$ is non-monotonic. The band gaps increase from $MgCu_2O_2$ to $CaCu_2O_2$ to $SrCu_2O_2$, but becomes smaller when Sr is replaced by Ba. This trend of band gap variation of $M^{II}Cu_2O_2$ as a function of M^{II} can be understood by noticing that there are several states near the valence and conduction band edges, and each state has different dependence on atomic energy levels and volume deformation potentials [3]. The non-monotonic behavior is due to band crossing at the band edge: $MgCu_2O_2$, $CaCu_2O_2$, and $SrCu_2O_2$ all

Table I. Calculated effective masses (in m_0) of $SrCu_2O_2$ at Γ along high symmetry lines parallel ($\|$) or perpendicular ($\perp$) to the c directions. The results are calculated with spin-orbit coupling at experimental lattice constants. The states are labeled using semi-relativistic notations.

States	$m_\perp$	$m_\|$
Γ_2	2.40	0.44
Γ_5	0.48	2.12
	0.57	1.27
Γ_1	5.85	1.82
Γ_1'	0.32	0.79
Γ_3'	0.28	0.44

have the Γ_5 VBM state, whereas the VBM of $BaCu_2O_2$ is a Γ_2 state. Similarly, $MgCu_2O_2$ and $CaCu_2O_2$ have the Γ_3' CBM state and $SrCu_2O_2$ has the Γ_1 CBM state, whereas the CBM of $BaCu_2O_2$ has the Γ_1' symmetry.

We have also calculated the electron and hole effective masses at Γ for states near the band edge of the $M^{II}Cu_2O_2$ compounds. We find that, in general, all the $M^{II}Cu_2O_2$ compounds have similar effective masses as for $SrCu_2O_2$. Both the electron and hole effective masses are anisotropic. The hole effective masses perpendicular to c directions at VBM are relatively small for $MgCu_2O_2$, $CaCu_2O_2$, and $SrCu_2O_2$. Due to O-mediated coupling between Cu d states, the effective masses also decrease when the unit cell volumes decrease from $SrCu_2O_2$ to $CaCu_2O_2$ to $MgCu_2O_2$.

Our calculated results show that for pure $M^{II}Cu_2O_2$, $SrCu_2O_2$ has the largest band gap, thus is likely to be the most transparent. The band gap could be increased slightly if a fraction of Ca ($x \sim 16\%$) is mixed into $SrCu_2O_2$ to form $(Ca_xSr_{1-x})Cu_2O_2$ alloys. Furthermore, our calculations show that due to larger $p-d$ and $d-d$ couplings in $CaCu_2O_2$, its VBM is also slightly higher in energy ($\sim$ 0.1 eV) than the VBM of $SrCu_2O_2$. Based on the doping limit rule [12], $CaCu_2O_2$ should also be easier to dope p-type than $SrCu_2O_2$. Therefore, we predict that adding a small amount of Ca into $SrCu_2O_2$ can increase both the transparency and conductivity.

$CuM^{III}O_2$

$CuM^{III}O_2$ has a layered delafossite crystal structure with the space group of $R\bar{3}m$. It is composed of O-Cu-O dumbbell layers in a hexagonal plane separated by an $M^{III}O_6$ edge-sharing octahedra layer (see Fig. 3).

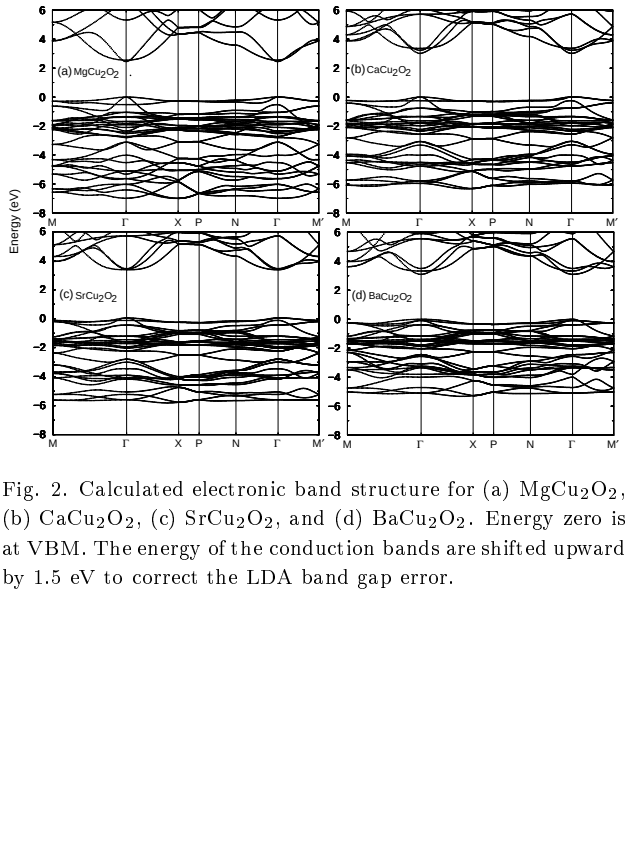

Fig. 2. Calculated electronic band structure for (a) $MgCu_2O_2$, (b) $CaCu_2O_2$, (c) $SrCu_2O_2$, and (d) $BaCu_2O_2$. Energy zero is at VBM. The energy of the conduction bands are shifted upward by 1.5 eV to correct the LDA band gap error.

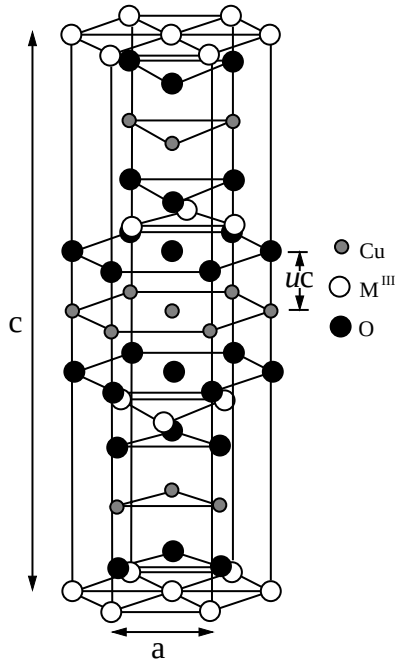

Fig. 3. The crystal structure of delafossite compounds $CuM^{III}O_2$.

The calculated band structures at experimental lattice constants for $CuM^{III}O_2$ (M=Al, Ga, and In) are shown in Fig. 4. The following general trends are observed:

(i) All three compounds have indirect fundamental band gaps with the CBM at Γ and the VBM on the Γ-F line near F, as indicated by the black circles in Fig. 4. The LDA-calculated indirect gaps are 1.97, 0.95, and 0.41 eV, respectively, for $CuAlO_2$, $CuGaO_2$, and $CuInO_2$.

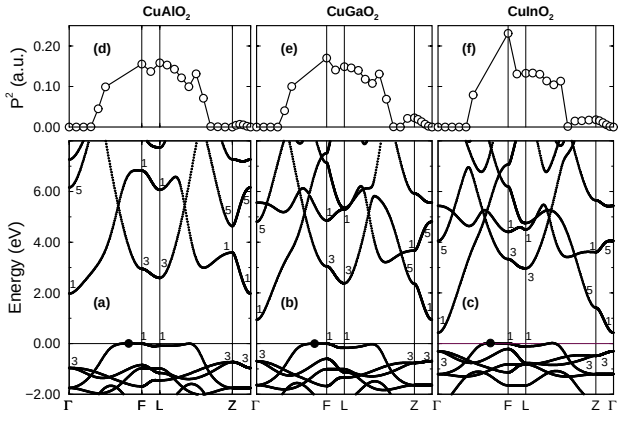

Fig. 4. (a) to (c) are the calculated LDA band structures for $CuAlO_2$, $CuGaO_2$, and $CuInO_2$, respectively. Energy zero is at the highest valence band at F. The VBMs are marked by the black circles. (d) to (f) are the corresponding transition matrix elements between the band edge states. The LDA band gap error of $\sim$ 0.8 eV is not added in this plot.

(ii) The direct band gap at Γ decreases considerably from 2.93 for $CuAlO_2$, to 1.63 for $CuGaO_2$, to 0.73 for $CuInO_2$. It also decreases at Z from 4.32 to 3.12 to 1.89 eV. This is consistent with the trend in other group III containing semiconductors. The decrease of the band gap from Al to Ga to In is mainly an atomic size effect: the CBM states at Γ_{1c} and Z_{1c} (or Z_{5c}) have significant antibonding s character. As the volume increases from the Al to Ga to In compounds, the energies of the antibonding states are lowered.

(iii) The direct band gap at F increases from 2.95 for $CuAlO_2$, to 3.05 for $CuGaO_2$, and to 3.34 for $CuInO_2$. A similar trend is observed at L: it decreases slightly from 2.68 for $CuAlO_2$ to 2.54 for $CuGaO_2$, then increases to 3.08 eV for $CuInO_2$. The increase of the gap at F (L) from Al or Ga to In is also a size effect. The conduction band edge states F_{3c} and L_{3c} have most of their charge densities in the interstitial region. Thus when the volume increases, the energy levels of F_{3c} and L_{3c} also increase.

The experimentally observed optical gaps increase from 3.5 ($CuAlO_2$), to 3.6 ($CuGaO_2$), to 3.9 eV ($CuInO_2$). This trend clearly contradicts the trend in the calculated fundamental direct gaps of 2.68 eV (L) for $CuAlO_2$, 1.64 eV (Γ) for $CuGaO_2$, and 0.73 eV (Γ) for $CuInO_2$, showing a decrease. To resolve this discrepancy, we have calculated the matrix elements for direct transitions between band edge states. The upper panel of Fig. 4 shows the results for $CuAlO_2$, $CuGaO_2$, and $CuInO_2$ at the Γ, F, L, and Z points and in between. It reveals that direct transitions between Γ_{3v} and Γ_{1c}, and between Z_{3v} and Z_{1c}, are forbidden in the delafossite structure because both states have the same (even) parity. An important consequence is that absorption *near* the fundamental gap at Γ for $CuGaO_2$ and $CuInO_2$ is very small and barely increases with energy until transitions at the next critical point take place (which define an apparent optical band gap). The calculated apparent gap [4] is very much unchanged from $CuAlO_2$ to $CuGaO_2$, but increases by +0.4 eV from $CuAlO_2$ to $CuInO_2$, in good agreement with experiment. The large differences in terms of the energy and transition matrix element between the fundamental direct gap and the apparent gap are the reason for the band gap anomalies seen in $CuM^{III}O_2$.

The p-type conductivity of $CuM^{III}O_2$ and the mysterious bipolar dopability of $CuInO_2$ can also be understood within the framework of equilibrium doping theory. According to the recently developed "doping limit rule" [12], the degree of self-compensation in a material correlates directly to its band edge positions with respect to others. A compound with higher VBM is easier to dope p-type, whereas a compound with lower CBM is easier to dope n-type. Our calculated band alignments [4] between the $CuM^{III}O_2$ show that the valence band offsets for this common-anion system are rather small. The VBMs for $CuGaO_2$ and $CuInO_2$ is about 0.17 eV higher than that for $CuAlO_2$ as a result of the coupling between the group III d orbitals and the O p orbital. Hence, p-type conductivity might be slightly easier to reach in $CuGaO_2$ and $CuInO_2$ than in $CuAlO_2$. However, the VBM for $CuGaO_2$ is 0.8 eV higher than ZnO, which explains why $CuM^{III}O_2$ can be made into p-type TCOs, whereas it is difficult to achieve p-type ZnO. On the other hand, due to a large volume deformation, the CBM of $CuInO_2$ is 1.48 eV lower than $CuAlO_2$. This explains why n-type conductivity can also be achieved in this nominally p-type material. Thus, a low CBM combined with a large apparent gap explains the puzzling combination of good transparency with bipolar dopability in $CuInO_2$. This finding provides a new avenue to achieving bipolar doping in wide-gap materials.

ACKNOWLEDGMENTS

This work was supported in part by U.S. Department of Energy, Grant DE-AC36-99-GO10337.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 2002	29th IEEE PVSC-Conference Paper May 20-24 2002

4. TITLE AND SUBTITLE
Electronic Structure and Doping of P-Type Transparent Conducting Oxides: Preprint

5. FUNDING NUMBERS
PVP22401

6. Author(S)
S.-H. Wei, X. Nie, and S.B. Zhang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/CP-520-32199

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

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14. SUBJECT TERMS: PV; transparent conducting oxides (TCOs); optoelectronic devices; bandga0 anomalies; linearized augmented plane wave (LAPW); spin-orbit coupling; crystal structure;

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL