

First principle study of bandgap modification of doped transparent conducting oxide CdO

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ABSTRACT

Transparent conducting oxide CdO has a wide range of applications in optoelectronics. We present the results of electronic and optical properties of pure and transition metal ions Sc, Y and Ti- doped CdO. The electronic structure is calculated within the full-potential linearized augmented plane wave (LAPW) + local orbitals (lo). The calculated band gap for pure CdO is 0.51 eV and changes significantly with doping. The calculated bandgap for Sc-doped CdO (CSO) is 2.67 eV, for Y-doped CdO (CYO) is 2.93 eV, and for Ti-doped CdO (CTO) is 2.53 eV. The effect of doping is clearly seen in the optical absorption profiles as well as in the enhanced electrical conductivities. Due to the widened optical transparency window, doped TCO has nearly 75-80% transmittance in the optical region. There is possibility of greater multiple direct and indirect interband transitions due to availability of more states compared to pure CdO. Copyright © 2011 VBRI press.

Keywords: Bandgap; transparent conducting oxide; doped CdO,



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Introduction

CdO has been studied by photoemission spectroscopy and ellipsometry and also by linear combination of atomic orbitals (LCAO) and many body perturbation theoretical methods [1-4]. Doping of CdO system by Sc and Y has been investigated using the sX-LDA FLAPW scheme [5-7]. Titanium doped CdO has been fabricated and characterized by studying the optical and electrical properties [8-9]. Due to its high electrical conductivity and transparency in the optical region, CdO has been subject of study for some time. In an effort to study the enhancement of these properties for more applications, we compute the electronic properties of CdO doped with transition metal ions with ionic radii smaller than Cd^{2+} . From a survey of literature it is seen that not much is known about the electronic structure of these doped transparent conducting oxides (TCO). To the best of our knowledge, the electronic band structure for Ti-doped CdO is not available in literature. In the present study we investigate the electronic structure, optical and transport properties of Sc, Y and Ti doped CdO (CSO, CYO, CTO) using full potential linear augmented plane wave method.

Computational methodology

We carry out this investigation using one of the most accurate band structure methods, the Wien2k code [10].

This method is based on the density functional theory which employs the full potential linearized augmented plane wave and local orbitals (lo). The latest GGA proposed by Wu and Cohen [11] was used for the exchange and correlation potential. The $R_{\text{MT}}K_{\text{max}}$ was set equal to 7 for the convergence parameter for which the calculation stabilizes and energy convergence is achieved. Here R is the smallest Muffin-tin radius and K_{max} is the cut-off wave vector of the plane-wave. The maximum radial expansion l_{max} is set to be 10. A mesh with 47 k -points in the irreducible Brillouin zone (IBZ) were used for CdO as well as Sc-, Y- and Ti- doped CdO. The energy cut-off between the core and valence states was set at -6.0 Ry. We construct a $2 \times 2 \times 1$ super cell to obtain 32 atoms in the unit cell. Cadmium ion is replaced by transition metal ion Scandium, Yttrium and Titanium to get the 1.6 % doped materials.

Results and discussion

Electronic properties

Cadmium oxide adopts a face-centered-cubic rocksalt structure (space group no. 225) based on octahedral coordination around Cd with lattice parameters $a=4.6953 \text{ \AA}$ [2]. In the unit cell of CdO we have two nonequivalent Cd atoms and two kinds of O atoms. The radii for Sc^{2+} , Y^{2+} and Ti^{3+} are 0.745, 0.9 and 0.605 \AA respectively, which is relatively smaller than 1.09 \AA which is the ionic radius of Cd^{2+} .

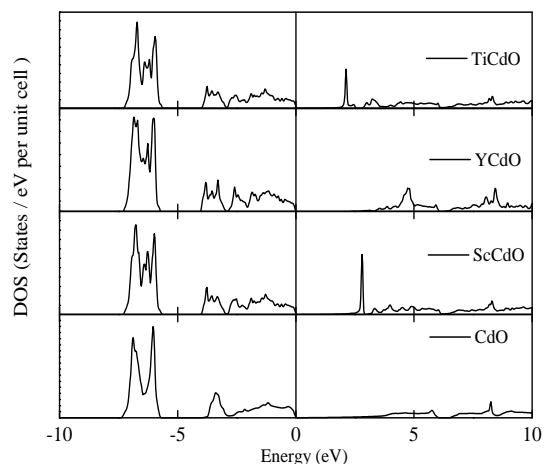


Fig. 1. Total density of states for Sc, Y and Ti-doped.

The effect of tuning of the electronic structure through doping of 1.6 % atom of transition metal ions, Sc-, Y- and Ti of differing ionic radii is clearly observed in the total density of states (TDOS) as shown Fig. 1. The zero of the energy was set at the top of the valence band. The topology of the calculated bands (not shown here) is similar to earlier calculations [1, 3, 6, 7]. In the valence band, from the partial density of states (not shown here) 4d-states of Cd are found in the lowermost energy range -7.33 to -5.73 eV, whereas the 2p-states of O mainly contribute between -3.89 eV to Fermi level E_F . Some s, p and d states of Cd also contribute in this region. Conduction band of hybridized 5s

and 5p states of Cd are spread from 0.5 to 5.99 eV. Higher p-states of Cd and O are found above 6.61 eV.

From the computed density of states for Sc, Y and Ti-doped CdO, it is observed that the lowermost energy states in the valence band (VB) region appear for the same energies -7.33 to -5.73 . However, in the valence band region from -3.89 to 0 eV, due to replacement of the Cd ion by the dopant ions, d states of Cd contribute nearest to the Fermi level E_F . Additional bonding p-states of dopant ions with Cd p-states are also found within the VBM, at slightly lower energies. The s-states of Cd, O and Sc/Y/Ti also contribute to the energy states.

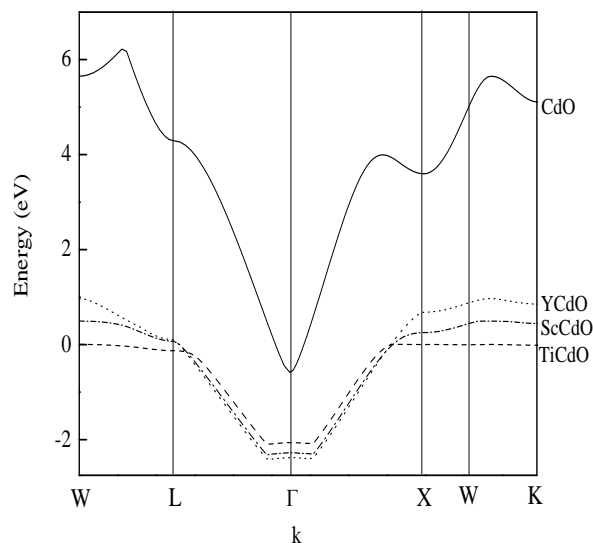


Fig. 2. Dispersion of Cd s-band due to doping with Sc/ Y/Ti atoms.

In the conduction band (CB) there is substantial mixing of s, p and d states of Cd, O and dopant ion Sc/Y/ Ti leading to hybridized states. Due to the additional d-states of Sc-, Y- and Ti- in doped CdO, the states in the conduction band minimum (CBM) are blocked which leads to the well known Moss-Burstein (MB) effect or shift [12, 13]. This shift is also called band filling, and results from the Pauli Exclusion principle. This shift is seen in semiconductors with increasing doping. For n-type doping as is seen in this case, the conduction band becomes significantly filled due to finite density of states. Due to the presence of antibonding p-states of the dopant ion, the s-states of Cd are repelled strongly, which results in the shifting of the Cd s-band as shown in Fig. 2.

Linear optical properties

It is known that the optical response can be described by a complex frequency dependent dielectric function $[\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)]$ [14]. The imaginary part $\varepsilon_2(\omega)$, which arises from intraband and interband transitions, depends on density of states (DOS) and the momentum matrix \mathbf{p} , and is calculated by considering all the possible transitions from occupied to unoccupied states (with fixed \mathbf{k} -vectors) over the Brillouin zone (BZ). The absorption coefficient $\alpha(\omega)$ are derived from $\varepsilon_2(\omega)$.

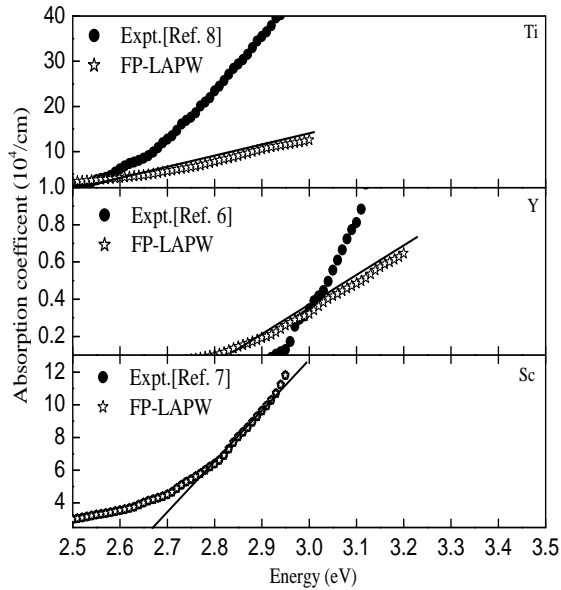


Fig. 3. Calculated and experimental absorption coefficient of doped CdO.

In **Fig. 3**, the absorption coefficient $\alpha(\omega)$ is plotted for photon energies from 0-15 eV. In the optical regions between 1.6 to 3.1 eV, there is very low absorption $\sim 10 \times 10^4/\text{cm}$ for doped CdO, which implies that because of the above described B-M shift, the interband transitions in the visible region are not possible. The filled states therefore block thermal or optical excitation. Consequently the measured band gap determined from the onset of interband absorption moves to higher energy (i.e. suffers "a blue shift"). Ti doped CdO shows some anomalous behavior since some weak absorption peaks in the IR region are found. **Fig. 3** shows the close agreement of the FP-LAPW calculations with experimental absorption coefficients. The bandgap estimates are obtained from the extrapolating the linear portion of calculated $\alpha(\omega)$. The calculated as well as experimental bandgap are listed in **Table 1**. The bandgap show an increasing trend with increasing ionic radii i.e. $Y > \text{Sc} > \text{Ti}$. Larger ionic radius dopant results in a larger optical band gap. About 75-80% transmittance is observed for pure CdO, whereas for doped-CdO, an average enhanced transmittance of 80-85% in the UV-Vis-NIR regions.

The refractive index n measured at frequencies above the lattice vibrational frequency is also related to $\epsilon(0)$ by the relation $n(0) = \sqrt{\text{Re} \epsilon(0)}$. We have also listed the calculated refractive indices in **Table 1**, which can be derived from the real ϵ_1 .

Transport properties

Amongst the transparent conducting oxides, CdO has very low electrical resistivity. In order to see the effect of doping, the transport properties are also calculated. The calculations relies on a Fourier expansion of the band energies where the space group symmetry is maintained by

using star functions. Properties such as conductivity, Hall and Seebeck coefficients can be obtained from the Boltzmann theory [15]. The density of states energy projected conductivity tensor is given in terms of

$$\sigma_{\alpha\beta}(i, k) = e^2 \tau_{i,k} v_{\alpha}(i, k) v_{\beta}(i, k) \quad \text{-----(1)}$$

where, τ is the relaxation time which depends on the band index i and k vector direction, and v is the group velocity.

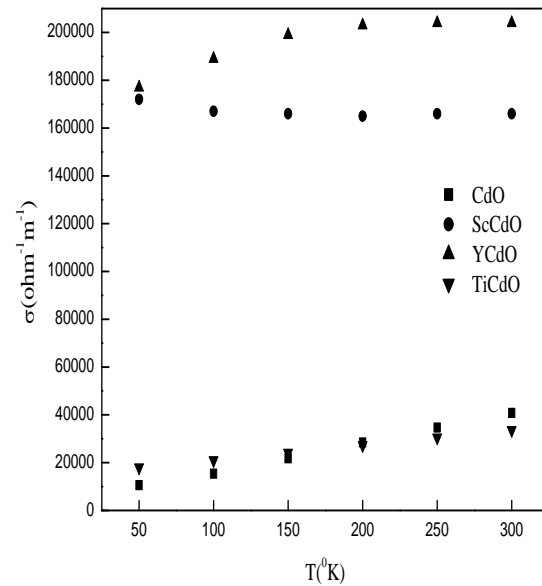


Fig. 4. Calculated electrical conductivity of doped CdO using BoltzTrap.

The electrical conductivity of CdO is enhanced due to the substitution of 1.6 % atom of dopant ion with ionic radii smaller than Cd ion, on doping. The most important charge transport property, the electrical conductivity as a function of temperature is shown in **Fig. 4**. Yttrium doped CdO shows maximum conductivity, whereas Ti-doped CdO shows anomalous behavior. The Sc-, Y- and Ti- doped CdOs exhibit n-type conductivity as determined from the negative Hall coefficients as shown in **Table 1**.

Conclusion

In this paper, we have presented the electronic and optical properties of pure and Sc-, Y-, Ti- doped CdO compound using the FP-LAPW method. The width of the 5s-Cd band is affected by the ionic radii of the dopant Sc/ Y/ Ti which can be seen from the width of the dispersed band. The optical absorption profiles clearly indicate that the doped-TCO has possibility of greater multiple direct and indirect interband transitions compared to pure CdO. Thus doping of CdO with metallic ions of smaller radius than that of Cd^{2+} like Sc, Y, Ti etc. improves its optical and electrical properties and increases the optical gap. Calculation with

different doping concentrations and ionic radii are urgently required in order to improve the optical response.

Table 1. Electronic and optical properties of pure and doped CdO.

Properties	CdO	ScCdO	YCdO	TiCdO
Ionic Radii (\AA)	1.09	0.74	0.9	0.6
	This Work	0.51	2.67	2.93
	1.0 [6] sX-LDA			
E_g (eV) Previous Work	1.61 [1] LCAO			
	6.56 [3] HF			
	0.5 [16] FP-LAPW			
Refractive Index (n)	2.68	2.82	2.28	12.34
Hall Coefficient (R_H)(cm^3/C)(10^{-4})	-3.81	-	-0.120	-0.124
Electrical Conductivity (σ)($1/\Omega^{-1}\text{m}^{-1}$)(10^4)	3.966	16.6	20.38	3.57
		8		

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