# Electronic structure of binary and ternary components of CdTe:O thin films

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We report first-principles calculations of the electronic structure of the simplest compounds that may be present in Cd–Te–O mixtures: CdTe, CdO, $\alpha$-TeO$_2$, CdTeO$_3$ and Cd$_3$TeO$_6$. The calculations are carried out in the Local Density Approximation (LDA) and predict the insulating character of these compounds, underestimating the optical bandgaps by nearly 1 eV, as usual for LDA. In the four oxides, the top valence bands originate mainly from the O 2p atomic levels.

## 1 Introduction

Oxidized CdTe thin films, obtained by r.f. sputtering, have been extensively studied in the last decade [1–9], using mainly optical spectroscopy, X-ray photoemission spectroscopy and Auger electron spectroscopy. These thin films present an amorphous structure, and are transparent insulators with an optical gap that can be tuned between 1.5 and 4 eV, depending on the O content. This material could play in CdTe solar cells technology a role similar to that of SiO$_2$ in Si technology. Most of the work up to date has been devoted to the optimization of growth techniques, element quantification and description of the optical properties.

A good understanding of the electronic and optical properties of the CdTe oxides needs the use of theoretical computations of the electronic properties and simulation of the structural properties. As a first step, the crystalline compounds of Cd, Te, and O should be carefully studied, as they provide information about the short range order and local electronic properties that are determinant in the amorphous regime. The simplest compounds CdTe and CdO have been extensively studied in the past, but others, including TeO$_2$, Cd$_3$TeO$_6$, CdTeO$_3$, and CdTe$_2$O$_5$ have not. Here, we report the first calculation of the electronic properties of crystalline $\alpha$-TeO$_2$, monoclinic CdTeO$_3$, and Cd$_3$TeO$_6$. In order to analyze the nature of the chemical bond in these materials, and to evaluate the systematic errors inherent to the theory, we also analyze the electronic structures of the simpler compounds CdTe and CdO.

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The electronic structure calculations presented here have been performed in the framework of the Local Density Approximation (LDA) of Density Functional Theory (DFT) [10, 11], as implemented in the Vienna Ab-initio Simulation Program (VASP) [12].

## 2   Structural and electronic properties

Amorphous CdTe:O films should present the same types of chemical bonds as present in the binary crystalline compounds. CdTe presents tetrahedral coordination of both Cd and Te species (zinc-blende structure) and degrees of oxidation +2 and −2, respectively. CdO presents octahedral coordination of Cd and O (rocksalt structure), and degree of oxidation +2 and −2, respectively. $\alpha$-TeO$_2$ (paratellurite) presents a tetragonal lattice with 12 atoms per unit cell [13]. The structural units of paratellurite are TeO$_4$ distorted trigonal bipyramids (tbp). In each tbp, a Te atom is surrounded by two O atoms in axial positions, and two O atoms in equatorial positions. The third equatorial position around Te is occupied by a lone pair of electrons.

In Figs. 1c and 2c, the central Te and the four O atoms below it form the above mentioned trigonal bipyramid, shown in dashed lines. The tbps form a spatial network, interconnected through an equatorial and an axial oxygen. This short-range order can be understood as produced by Te sp$^3$ hybridization, sharing four of the six valence electrons, and repulsion of the four bonds by a lone pair of Te electrons. Alternatively, the basic unit can be considered as a TeO$_6$ distorted octahedra, which is obtained adding to a tbp the following nearest pair of O at 2.86 Å from the central Te (above the tbp in Figs. 1c and 2c). From this point of view the crystal structure of paratellurite is considered as a deformation of the structure of rutile. This approximation has been used in early band structure calculations [14, 15]. Figure 1c and 2c show the above described local order.

Crystalline CdTeO$_3$ has been obtained in a cubic and several monoclinic phases [16, 17]. The cubic phase has also been reported in oxidized CdTe surfaces [18, 4, 7, 19]. The crystalline structure has been totally determined for only one monoclinic phase [16]. Figures 2d and 2d show a cluster O$_5$−Cd−O−TeO$_2$ that displays the basic short-range order. The basic units are TeO$_3$ trigonal pyramids
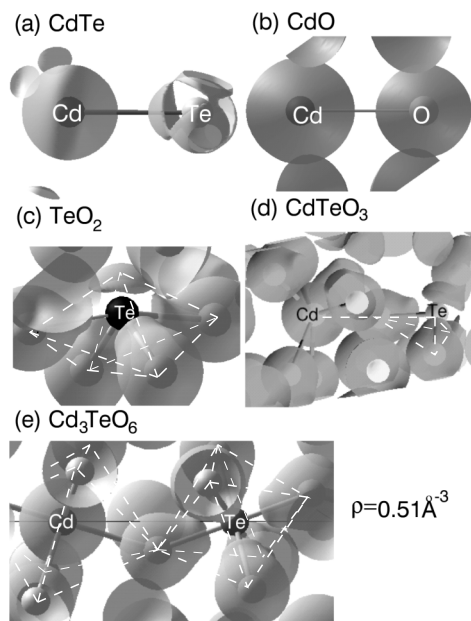
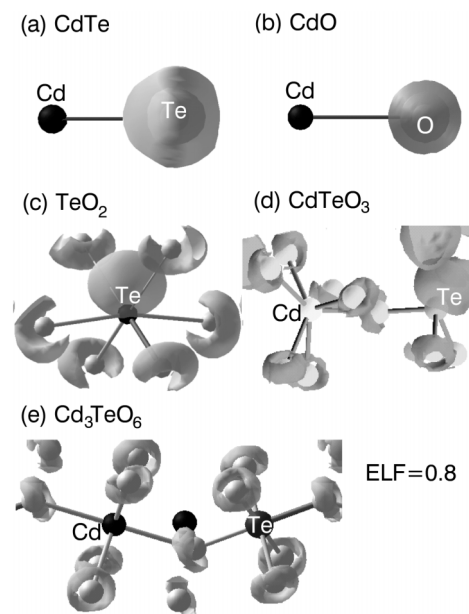

**Fig. 1** Isosurfaces of the electronic charge density ($\rho$).



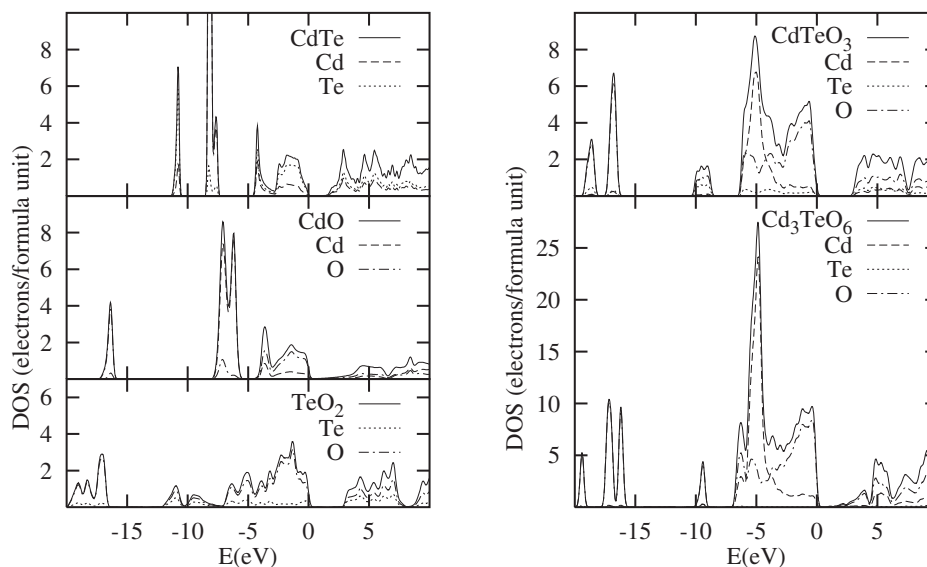**Fig. 2** Isosurfaces of the electron localization function (ELF).

**Fig. 3** Comparative plot of the density of states of CdTe, CdO, $TeO_2$, $CdTeO_3$ and $Cd_3TeO_6$.

that are linked through Cd atoms. This arrangement is similar to that found in tellurite glasses [20]. O atoms always link one Te atom with one, two, or three Cd atoms, the average coordination of O being three.

$Cd_3TeO_6$ structure [21] is described as a deformed perovskite-type in which the B-sites are occupied by Cd and Te, and the A-sites by Cd. Figures 1e and 2e show a typical cluster $O_5-Cd-O-Te-O_5$. There are also clusters that share two O atoms. The greatest difference between $CdTeO_3$ and $Cd_3TeO_6$ is that tellurium is 3-fold oxygen coordinated in the first case, and 6-fold octahedrally coordinated in the second case. This Te octahedral coordination is typical in compounds where Te has a degree of oxidation of +6. O atoms always bridge one Te with two, three or four Cd.

Figures 1 and 2 show the charge density and the electron localization function (ELF) for all the compounds analyzed. The ELF [22] is a measure of the electron localization relative to the homogeneous electron gas, and is able to resolve the atomic shell structure better than the electron density. By definition, ELF values range between 0 and 1. An ELF value near 1 at a given point indicates a high degree of localization of the electrons at that point, and that no other electron with the same spin is to be found in the vicinity. Hence, it indicates the regions where spin-paired electrons are found.

As can be seen in the Figs. 1 and 2, CdTe and CdO present a charge distribution rather centered around each atom, although in CdTe it is evident that the charge distribution around Te shows asymmetry related to the tetrahedral bonds. Note that the Cd electron density includes the full semicore 4d level, and the depopulated 5s level, which produces an overall spherical symmetry around Cd. In CdO, the charge around the anion O is spherically symmetric, thus confirming the more ionic character of the Cd−O bond than the Cd−Te one. The ELF, however, shows electron localization at the anion.

In $\alpha$-$TeO_2$ and $CdTeO_3$ the electron distribution around Te atoms present common features: (1) Directionality of the Te−O bonds; (2) A lone pair over the Te atom, opposite to the Te-O bonds; (3) There are two regions of high localization: one over the Te atom, which corresponds to the electrons lone pair, and other around O atoms in the plane perpendicular to the O−Te bonds. (4) For $TeO_2$, the two upper oxygens, which do not belong to the tbp, are not bound to Te, and must be considered as bound to other tbps.

In $Cd_3TeO_6$ there is no lone pair at Te, in agreement with the nominal degree of oxidation of Te +6. The ELF shows charge localization around O atoms, in the planes perpendicular to Te−O bonds, similarly to $CdTeO_3$ and $TeO_2$.

Figure 3 shows comparatively the density of states (DOS) in all the compounds, where the zero of energy is aligned with the top of the valence band. A partial DOS analysis indicates that the strongest band in Cd compounds (in the range from $-10$ to $-5$ eV) is due to the Cd 4d electrons. The Cd 4d band is isolated from the upper valence bands in CdTe and CdO, but it is mixed in $CdTeO_3$ and $Cd_3TeO_6$. The upper valence bands (in the range from $-3$ eV to 0 eV) are always dominated by the p levels of the anions valence shells (Te 5p in CdTe, O 2p in the other compounds). The bands between $-15$ and $-20$ eV are dominated by O 2s levels. The rest of the bands are not dominated by any single element level. The most important difference between $CdTeO_3$ and $Cd_3TeO_6$ is the value of the fundamental bandgap (smaller $Cd3TeO_6$). Also, the conduction band edge is smoother in $Cd_3TeO_6$, due to the fact that the lowest conduction band (band diagram in **k**-space) has a low effective mass (0.2 free electron masses) and is isolated from higher bands.

In summary, we have obtained the electronic structure of $\alpha$-$TeO_2$, $CdTeO_3$, and $Cd_3TeO_6$ and have compared them with the known cases of CdTe and CdO. We have found that LDA predicts correctly the insulating character of these compounds, underestimating the optical bandgaps by nearly 1 eV. In the three oxides, as well as in CdO, the top valence bands are formed mainly from the O 2p electrons. In $CdTeO_3$ and $Cd_3TeO_6$, the binding energy of the Cd 4d band, relative to the valence band maximum, is smaller than in CdTe and CdO. We have found that CdTe oxides have a complex spatial structure, where only Cd$-$O and Te$-$O bonds are present. In $TeO_2$ and $CdTeO_3$, there is a localized Te electron lone pair, which is not localized in $Cd_3TeO_6$. However, there is no apparent difference in the DOS that could be related with the differences in the chemical bonds.

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