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Structural, electronic and optical properties of ilmenite and perovskite CdSnO\textsubscript{3} from DFT calculations

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Abstract
CdSnO\textsubscript{3} ilmenite and perovskite crystals were investigated using both the local density and generalized gradient approximations, LDA and GGA, respectively, of the density functional theory (DFT). The electronic band structures, densities of states, dielectric functions, optical absorption and reflectivity spectra related to electronic transitions were obtained, as well as the infrared absorption spectra after computing the vibrational modes of the crystals at \(q = 0\). Dielectric optical permittivities and polarizabilities at \(\omega = 0\) and \(\omega = \infty\) were also calculated. The results show that GGA-optimized geometries are more accurate than LDA ones, and the Kohn–Sham band structures obtained for the CdSnO\textsubscript{3} polymorphs confirm that ilmenite has an indirect band gap, while perovskite has a direct band gap, both being semiconductors. Effective masses for both crystals are obtained for the first time, being highly isotropic for electrons and anisotropic for holes. The optical properties reveal a very small degree of anisotropy of both crystals with respect to different polarization planes of incident light. The phonon calculation at \(q = 0\) for perovskite CdSnO\textsubscript{3} does not show any imaginary frequencies, in contrast to a previous report suggesting the existence of a more stable crystal of perovskite CdSnO\textsubscript{3} with ferroelectric properties.

1. Introduction

New sensing materials and sensor technologies are required to provide control and automation in industrial processes, as well as to manage environmental effects. High sensitivity, stability under adverse conditions and molecular selectivity are essential prerequisites for the development of new sensing materials, as well as reliability, safety, reproducibility and low cost. An interesting material being investigated for gas-sensing applications is cadmium metastannate (CdSnO\textsubscript{3}), a semiconducting transparent oxide which exists in two stable forms: a distorted perovskite crystal (\(\alpha\)) with \(Pnma\) symmetry [1, 2] and a rhombohedral ilmenite structure (\(\beta\)) with \(R\bar{3}\) symmetry [3, 4]. Ilmenite CdSnO\textsubscript{3} crystals are synthesized in a temperature range up to 800 \(^\circ\)C [5–7], while the perovskite structure is synthesized in the 1000–1100 \(^\circ\)C temperature range [1, 5] or under high pressures [3]. A metastable spinel structure can also be obtained through the decomposition of CdSn(OH)\textsubscript{6} [7].

\(\beta\)-CdSnO\textsubscript{3}-based sensors were studied for the first time in the 1990s, showing high sensitivity and selectivity to detect...
In order to perform these computations, the linear muffin-tin orbitals (LMTO) method, together with the Perdew–Wang exchange–correlation functional [21], within the generalized gradient approximation (GGA) was adopted. However, only the electronic band structure of the perovskite phase was presented and discussed in detail in their papers, with only a brief discussion on the ilmenite band structure being put forward.

Lebedev [7], on the other hand, obtained the phonon spectrum of cubic CdSnO3 after optimizing the geometries of several distorted phases through DFT. His calculations were carried out using pseudopotentials and a plane-wave basis set within the local density approximation (LDA) for the exchange–correlation functional. The optimized geometry for perovskite CdSnO3 was presented in detail, as well as the calculated frequencies of the IR and Raman active optical modes for this material. The calculations showed that the ground state of α-CdSnO3 is a ferroelectric Pbn21 phase, with an energy gain from this phase in comparison with the nonpolar phase Pnma of about 30 meV.

The purpose of this paper is to unveil the results of systematic first principles calculations using DFT for ilmenite and perovskite CdSnO3 including optimized geometries, electronic band structures, densities of states, carrier effective masses, optical properties (dielectric function, reflectivity and absorption), infrared absorption spectra, dielectric permittivities and polarizabilities. As we have said, there are no data in the literature depicting the DFT-optimized structure for ilmenite, the optical properties of ilmenite and perovskite, and their infrared spectra (only the phonon optical modes at \( q = 0 \) for perovskite CdSnO3 were computed in [7], without intensities). It is also remarkable that, despite the relevance of the conductivity properties of CdSnO3 for gas sensors, no results on the electron and hole effective masses of CdSnO3 are available, these masses being very useful to model the carrier transport in semiconductor devices [22, 23] and the quantum confinement in semiconductor nanostructures [24].

2. Calculation methodology

Unit cell parameters and internal atomic coordinates for ilmenite and perovskite CdSnO3 were extracted from the x-ray data provided by Mizoguchi et al. [2, 4]. Figure 1 shows some views of both crystals. The CASTEP code [25] was used to carry out the DFT calculations. Two computational runs were performed using the experimental data as input, the first using the Ceperley–Alder–Perdew–Zunger [26, 27] parametrization of the LDA exchange–correlation functional and the second using the Perdew–Burke–Ernzerhof [28] GGA exchange–correlation functional. The interaction of the valence electrons with the ionic cores was modeled by using norm-conserved pseudopotentials, the LDA ones being generated as described in [29], and the GGA ones being generated using the OPIUM code according to the methodology depicted in [30]. The valence electronic configurations were 4d105s2 for Cd, 5s25p2 for Sn, and 2s2p4 for O, with scalar-relativistic corrections taken into account. CASTEP uses a plane-wave basis set to represent the Kohn–Sham electronic wavefunctions, so after checking for self-consistent field (SCF) convergence accuracy, we have adopted (for ilmenite and perovskite) optimal plane-wave energy cutoffs of 800 eV for wavefunctions and 1600 eV for...
ILMENITE

PEROVSKITE

Figure 1. Different views of the ilmenite and perovskite CdSnO₃ crystal structures. Oxygen atoms are shown in light gray, tin atoms in medium gray, and cadmium atoms in dark gray. The a, b, c axes are indicated.

Table 1. Lattice parameters and unit cell volumes for ilmenite and perovskite CdSnO₃ using the LDA and GGA approaches in comparison with experimental data [2, 4].

<table>
<thead>
<tr>
<th></th>
<th>Ilmenite</th>
<th>Perovskite</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.9005 LDA</td>
<td>5.9675 Exp.</td>
</tr>
<tr>
<td></td>
<td>5.6499 GGA</td>
<td>5.2856 Exp.</td>
</tr>
<tr>
<td></td>
<td>5.6098 GGA</td>
<td>5.9675 Exp.</td>
</tr>
<tr>
<td>b (Å)</td>
<td>7.8711</td>
<td>7.4501</td>
</tr>
<tr>
<td></td>
<td>7.4948</td>
<td>7.9488</td>
</tr>
<tr>
<td>c (Å)</td>
<td>5.4588</td>
<td>5.1927</td>
</tr>
<tr>
<td></td>
<td>5.4989</td>
<td>5.4989</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>128.57 Exp.</td>
<td>110.67 Exp.</td>
</tr>
<tr>
<td></td>
<td>239.55 Exp.</td>
<td>204.48 Exp.</td>
</tr>
<tr>
<td></td>
<td>245.07 Exp.</td>
<td>245.07 Exp.</td>
</tr>
<tr>
<td>α (deg)</td>
<td>55.058</td>
<td>90.000</td>
</tr>
<tr>
<td></td>
<td>54.334</td>
<td>90.000</td>
</tr>
<tr>
<td></td>
<td>54.780</td>
<td>90.000</td>
</tr>
</tbody>
</table>

Table 1. Lattice parameters and unit cell volumes for ilmenite and perovskite CdSnO₃ using the LDA and GGA approaches in comparison with experimental data [2, 4].

The optimized lattice parameters obtained after the geometry optimization are presented in table 1. Experimental values are shown as well, for comparison. In the case of ilmenite, the lattice parameter a is about 4% smaller than the experimental data when we look at the LDA result, which was expected as the LDA approach tends to overestimate interatomic forces. On the other hand, the GGA prediction is more accurate, being only slightly larger—about 1.1%—than the x-ray measurement (GGA, contrary to LDA, tends to underestimate the interaction
eigenenergy convergence tolerance of 5.9 × 10⁻⁸ eV, with a tolerance window of three cycles. A Pulay density mixing scheme [33] was also adopted to decrease computation times.

Following geometry optimization, the Kohn–Sham electronic band structures and the partial densities of states per atom and per orbital were calculated. A parabolic fitting of the valence band (VB) and conduction band (CB) curves at their critical points (maxima for VB and minima for CB) allowed us to estimate the effective masses for electrons and holes for both the studied polymorphs of CdSnO₃, as detailed in [34]. Some optical properties related with electronic transitions (dielectric function, reflectivity and absorption) were computed, and a phonon calculation at \( q = 0 \) allowed the determination of the infrared spectra, dielectric permittivities (static and at \( \omega = \infty \)) and polarizabilities within the electric field linear response formalism [35].

3. Geometry optimization
The calculated unit cell volumes are, respectively, 13.9% smaller (LDA) and 2.7% larger (GGA) than experiment. The \( \alpha \) angle, on the other hand, is smaller than experiment for both LDA and GGA, with GGA exhibiting the best accuracy.

The \( a, b, \) and \( c \) unit cell lengths predicted for the perovskite structure have a pattern similar to the one observed for ilmenite; LDA gives a smaller unit cell and GGA a slightly larger unit cell. For the \( a \) parameter, size differences relative to the experimental data are \(-5.2\%\) (LDA) and \(0.6\%\) (GGA). For \( b \) and \( c \) these figures are, respectively, \(-5.3\%\) (LDA) and \(1.0\%\) (LDA), and \(-4.9\%\) (LDA) and \(0.7\%\) (GGA). The LDA unit cell volume is 14.6% smaller than experiment, while the GGA volume is 2.3% larger. The LDA lattice parameter predictions of Lebedev [7], on the other hand, display a somewhat odd behavior if we take into account the binding trend of the LDA exchange–correlation functional, being always larger than the experimental values (except for the \( a \) parameter measured by Smith [1]).

In table 2, the internal atomic coordinates from x-ray data, LDA, and GGA computations are shown. As observed for the lattice parameters, the difference of internal coordinates in comparison with experiment is larger for the LDA exchange–correlation functional. We define here the relative difference of coordinate \( q \) using the functional \( F \) relative to the experimental data (denoted Exp) as:

\[
\Delta q(F) = (100/N) \sum_{i=1}^{N} \frac{|q_i(F) - q_i(\text{Exp})|}{q_i(\text{Exp})}, \tag{1}
\]

where \( q_i \) is the \( q \) coordinate of the \( i \)th atom. If \( q_i(\text{Exp}) = 0 \), the corresponding term in the sum is taken to be zero. Percentage values for these relative differences are also presented in table 2.

A comparison of calculated bond lengths, interatomic distances and angles with experimental data for ilmenite and perovskite CdSnO\(_3\) was also carried out, and is displayed in tables 3 (ilmenite) and 4 (perovskite). In the case of both polymorphs, the bond lengths found experimentally are in general larger (smaller) than the LDA (GGA) values by up to about 11\% (4\%). Nevertheless, GGA values are more accurate in the case of ilmenite for Sn–Sn and Cd–Sn distances, as well as for the Sn–O–Sn, Sn–O–Cd and Cd–O–Cd angles. For perovskite, Sn–O–Sn angles using the GGA approach are more accurate in comparison with the LDA method. In the case of the O–Sn–O angles, however, GGA gives the worst figures in comparison with experimental data. Overall, LDA angles for the perovskite crystal are slightly larger than experimental values, except for O–Sn–O, while the GGA angles do not display a clear pattern.

### 4. Band structure, density of states and effective masses

The Kohn–Sham electronic band structure gives a picture of the electronic eigenenergies \( E \) as a function of a set of quantum numbers which form the components of a wavevector \( \mathbf{k} \) in the

---

**Table 2.** Atomic internal coordinates for ilmenite and perovskite CdSnO\(_3\) obtained from LDA and GGA computations in comparison with experimental data. The labels within parentheses identify the Wyckoff sites of each atom. Percentages for the \( \Delta q(F) \) are shown for each coordinate \( q \) and exchange–correlation functional \( F \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Experimental</th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( x )</td>
<td>( y )</td>
<td>( z )</td>
</tr>
<tr>
<td>Cd(2c)</td>
<td>0.366 01</td>
<td>0.366 01</td>
<td>0.366 01</td>
</tr>
<tr>
<td>Sn(2c)</td>
<td>0.154 41</td>
<td>0.154 41</td>
<td>0.154 41</td>
</tr>
<tr>
<td>O(6f)</td>
<td>0.571 2</td>
<td>0.962 2</td>
<td>0.214 2</td>
</tr>
<tr>
<td>Sn(2c)</td>
<td>0.154 41</td>
<td>0.154 41</td>
<td>0.154 41</td>
</tr>
<tr>
<td>Cd(2c)</td>
<td>0.366 01</td>
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<td>0.214 2</td>
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</tr>
<tr>
<td>Cd(2c)</td>
<td>0.366 01</td>
<td>0.366 01</td>
<td>0.366 01</td>
</tr>
<tr>
<td>O(6f)</td>
<td>0.571 2</td>
<td>0.962 2</td>
<td>0.214 2</td>
</tr>
</tbody>
</table>

**Table 3.** Relevant bond lengths, distances and angles of ilmenite CdSnO\(_3\). The LDA and GGA experimental results are shown for comparison.

<table>
<thead>
<tr>
<th>Bond Lengths/Distances/Angles</th>
<th>Exp</th>
<th>LDA</th>
<th>GGA</th>
<th>LDA-Exp (%)</th>
<th>GGA-Exp (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn–O (( \AA ))</td>
<td>2.061</td>
<td>2.055</td>
<td>2.055</td>
<td>-7.23</td>
<td>-0.29</td>
</tr>
<tr>
<td>Cd–O (( \AA ))</td>
<td>2.191</td>
<td>2.132</td>
<td>2.238</td>
<td>-2.25</td>
<td>2.61</td>
</tr>
<tr>
<td>Sn–Sn (( \AA ))</td>
<td>2.181</td>
<td>2.132</td>
<td>2.238</td>
<td>-2.25</td>
<td>2.61</td>
</tr>
<tr>
<td>Cd–Sn (( \AA ))</td>
<td>3.374</td>
<td>3.061</td>
<td>3.214</td>
<td>-4.97</td>
<td>3.52</td>
</tr>
<tr>
<td>Sn–O–Sn (deg)</td>
<td>101.3</td>
<td>99.9</td>
<td>99.9</td>
<td>2.34</td>
<td>2.34</td>
</tr>
<tr>
<td>Sn–O–Cd (deg)</td>
<td>88.3</td>
<td>87.9</td>
<td>87.9</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>Cd–O–Cd (deg)</td>
<td>91.5</td>
<td>89.7</td>
<td>89.7</td>
<td>1.42</td>
<td>1.42</td>
</tr>
</tbody>
</table>
first Brillouin zone (BZ). For ilmenite and perovskite CdSnO₃, the paths in the BZ used for the DFT computations are formed by straight segments connecting a set of high symmetry points, as shown in Figure 2. For the ilmenite structure, the following high symmetry points were chosen: Γ(0, 0, 0), F(0.5, 0.5, 0), Z(0.5, 0.5, 0.5), and L(0, 0.5, 0). For perovskite, the selected high symmetry points are Γ(0, 0, 0), R(−0.5, 0.5, 0.5), S(−0.5, 0.5, 0), T(−0.5, 0, 0.5), U(0, 0.5, 0.5), X(0, 0.5, 0), Y(−0.5, 0, 0), and Z(0, 0, 0.5). The three primitive vectors of the reciprocal lattice, \( \mathbf{g}_1, \mathbf{g}_2, \) and \( \mathbf{g}_3 \), are also depicted.

Figure 3 presents the electronic band structures obtained for the optimized ilmenite and perovskite CdSnO₃ crystals using the LDA (solid curves) and GGA-PBE (dotted curves) exchange–correlation functionals, together with the respective partial densities of states. The horizontal axis of each band structure plot follows the same scale. Each ilmenite unit cell has two CdSnO₃ units (\( Z = 2 \)), which leads to 68 valence electrons per cell and 34 valence bands, while the corresponding values for perovskite are \( Z = 4 \), 136 valence electrons and 78 valence bands. The partial densities of states per orbital type found after the LDA computations are plotted as well (the per atom contribution will be presented in detail separately). Energy values were gauged to make the highest energy for a valence electron equal to 0 eV.

All in all, the LDA and GGA computations predict ilmenite band structures with curves of similar shape, but shifted relative to one another, the GGA CBs with lower energies in comparison with LDA ones, and the GGA VBs having smaller widths. The same pattern will be observed for the perovskite Kohn–Sham electronic energy bands. The DFT-GGA computations performed by Mizoguchi [2, 4], for perovskite CdSnO₃, notwithstanding the lack of geometry optimization in their calculations and the use of a different exchange–correlation functional, are in agreement with our results.

The contribution of each atomic species to the different electronic energy bands (see Figure 4) following the LDA calculations has many common features as we switch from the ilmenite to the perovskite crystals. The O 2s orbitals dominate the ilmenite (perovskite) bands between −19 and −15.5 eV (−19.4 and −15.5 eV), with smaller contribution from the Sn 5s orbitals. The s bands observed for the perovskite phase in the range between −9.2 and −7.7 eV arise from Sn 5s orbitals also. The LDA (GGA) d bands ranging from −7.7 and −6.3 eV (−6.9 and −5.6 eV) for ilmenite and −7.9 and −6.5 eV (−7.1 and −5.8 eV) for perovskite arise mainly from Cd levels, while the uppermost valence bands have strong O 2p character for both polymorphs. Cd 5s and Sn 5s orbitals dominate the ilmenite CBs up 3.5 eV and the perovskite CBs up to 3.2 eV. Above 4 eV and below 5.2 eV, the CB of perovskite is dominated by Cd 5p contributions, and above 5.2–6.7 eV the Cd 5s contribution rules. From 8.1 eV, the Cd 5p states help to form most of the perovskite PDOS. The same occurs for ilmenite, but for energies above about 7 eV. There are also minor contributions from O 2p levels from 2 up to 12 eV, specially in the 6–8 eV energy range, for perovskite, and from 2 to 17 eV for ilmenite, with significant peaks in the 8–9 eV and 10–13 eV energy ranges.

Figure 5 reveals a close-up of the Kohn–Sham band structures near the main band gaps of both ilmenite and perovskite CdSnO₃. From it one can see that ilmenite has its CB minimum at the Γ point and three very close VB maxima: the one with highest energy occurs at the λ point along the Γ → L segment in VB, the second, only 3 meV lower in energy (LDA, 20 meV lower within the GGA calculation), occurs at the ϕ point along the Γ → F line, and the third highest maximum appears at the ζ point along the Γ → Z segment, being just 14 meV below the λ point energy (LDA, 31 meV below in the GGA case). The main indirect band gap, therefore, is of about 1.91 eV according to the LDA calculation (solid curves) and 1.22 eV according to the GGA approach, while the direct Γ → Γ band gaps are 2.01 eV (LDA) and 1.32 eV (GGA). Such a discrepancy is indicative of the fact that DFT exchange–correlation functionals do not predict accurate band gaps. Indeed, Kohn–Sham eigenvalues do not give the correct excitation energies [36], so in order to estimate energy band gaps one must know the exact form of the exchange–correlation functional [37]. LDA exchange–correlation in general underestimates the main gap of semiconductors and insulators by about 40%, the same happening for GGA
approximations. Notwithstanding that, there are some works suggesting that a rigid shift in the LDA conduction bands is just enough to provide a reasonable agreement with the more sophisticated (and much more computationally expensive) quasi-particle GW approximation [36, 38–40]. One can look, for example, into the work of Migas et al [41], which is similar to ours, on the electronic structure and dielectric functions of CaX (X = Si, Ge, Sn, Pb) compounds. As the GGA band structure presented in this work looks very similar to the LDA one, we are confident that our band gap analysis is meaningful, especially regarding band shapes, if we keep in mind the need to increase the DFT band gaps by a few electronvolts to achieve an agreement with the actual band gaps of ilmenite and perovskite CdSnO₃.

Measurements using diffuse reflectance spectra of the band gap for the CdSnO₃ ilmenite polymorph [18] show that this crystal has an indirect band gap of 3.07 eV and a direct band gap of 3.17 eV which, in comparison with our results, point to a rigid shift energy correction of 1.16 eV upwards for the LDA CB and 1.85 eV upwards for the GGA-PBE CB. The difference between the indirect and direct band gaps, of about 0.1 eV, is the same for our calculations and experiment.

At the bottom of figure 5, the perovskite band structure is displayed. In contrast to the ilmenite, the perovskite polymorph has a direct main energy band gap. The LDA value for the Γ → Γ transition from VB to CB is 1.70 eV, while the GGA-PBE prediction is much smaller, of about 0.94 eV. In comparison, diffuse reflectance spectra of a CdSnO₃ powder, measured by Mizoguchi et al [2], point to a main band gap of 3.0 eV, which means that the LDA CB curves must be shifted upwards by 1.3 eV, while the GGA-DFT CB curves demand a more pronounced shift of about 2.0 eV. One can note that the band gap energy shifts required to make the DFT LDA and GGA-PBE band gaps coincide with experiment are very close for both ilmenite and perovskite CdSnO₃, which indicates that the crystalline structure does not affect the energy gap correction very much. The theoretical band gap predicted by Mizoguchi et al [2] for perovskite CdSnO₃ is identical to the LDA value we calculated here, 1.7 eV, despite the use of a GGA exchange–correlation approximation.
Figure 4. Per atom contributions to the electronic density of states for the ilmenite and perovskite CdSnO\textsubscript{3} polymorphs. Orbital contributions: s (solid curves), p (dashed curves), and d (dotted curves).

In solid state physics, and especially with semiconductor materials, the concept of effective mass is very useful to model the transport of charge carriers [44]. A Newtonian-like approximation in which electrons and holes have a mass which depends on the direction along which an external force (due to an external electric field, for example) can be adopted. These effective masses are estimated by calculating the curvature of the electronic band structure in the wavevector range corresponding to the electron (hole) quantum states disturbed by the external force, a procedure we have detailed in a previous work [34]. The smaller the band curvature, the larger the effective masses will be, and vice versa. An effective mass is obtained for each band curve starting from a given point in the Brillouin zone to another. Effective masses for electrons and holes for ilmenite and perovskite CdSnO\textsubscript{3} are shown in Table 5.

Electron effective masses for ilmenite and perovskite are very close for identical exchange–correlation functionals, being very isotropic. The LDA values are close to 0.26 free
Table 5. Carrier effective masses of ilmenite and perovskite CdSnO3 along a representative set of high symmetry directions. All masses are given in terms of the free electron mass ($m_0$).

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA</th>
<th></th>
<th>LDA</th>
<th>GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ilmenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma \rightarrow F$</td>
<td>0.266</td>
<td>0.205</td>
<td>$\lambda \rightarrow \Gamma$</td>
<td>3.19</td>
<td>3.54</td>
</tr>
<tr>
<td>$\Gamma \rightarrow L$</td>
<td>0.270</td>
<td>0.208</td>
<td>$\lambda \rightarrow L$</td>
<td>5.07</td>
<td>4.34</td>
</tr>
<tr>
<td>$\Gamma \rightarrow Z$</td>
<td>0.262</td>
<td>0.207</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Perovskite | | | | | |
| $\Gamma \rightarrow Z$ | 0.263 | 0.203 | $\Gamma \rightarrow Z$ | 1.01 | 1.07 |
| $\Gamma \rightarrow Y$ | 0.261 | 0.198 | $\Gamma \rightarrow Y$ | 1.71 | 2.44 |
| $\Gamma \rightarrow X$ | 0.257 | 0.189 | $\Gamma \rightarrow X$ | 2.56 | 3.41 |
| $\Gamma \rightarrow U$ | 0.261 | 0.197 | $\Gamma \rightarrow U$ | 1.37 | 1.58 |
| $\Gamma \rightarrow T$ | 0.259 | 0.198 | $\Gamma \rightarrow T$ | 1.27 | 1.51 |
| $\Gamma \rightarrow S$ | 0.258 | 0.193 | $\Gamma \rightarrow S$ | 1.99 | 2.84 |
| $\Gamma \rightarrow R$ | 0.259 | 0.196 | $\Gamma \rightarrow R$ | 1.48 | 1.80 |

Figure 5. Kohn–Sham electronic band structures of ilmenite and perovskite CdSnO3 in the energy range close to the main band gap.

5. Optical properties

Quasi-particle corrections are not necessary to calculate the dielectric constant of a crystal, as this feature is determined by the ground state, which is in general well described when using approximate DFT exchange–correlation energies. The situation is different when one considers the complex dielectric function $\varepsilon(\omega)$, as its value depends on self-energy and local field corrections. Besides, the incorporation of excitonic states in simulations is not feasible due to limitations in the computational tools available nowadays [45]. We must concede, then, that the results we present now for ilmenite and perovskite CdSnO3 must be looked into with some caution. Due to limited computational resources, we have not pursued quasi-particle corrections, our dielectric function curves being only zero-order approximations to the experimental ones.

In this work, we have used the LDA exchange–correlation functional only to compute the optical properties, the real part of the dielectric function being calculated from the imaginary part via the Kramers–Kronig relationship [47, 48]. Even so, the work of Lebègue et al [46] indicates that LDA dielectric functions, in comparison with more sophisticated methods, differ mainly by a scaling factor plus some energy shift. Accordingly, we have also used the difference between the LDA band gaps and the experimental gaps of ilmenite and perovskite CdSnO3 to improve the optical properties calculations by adopting a scissor operator, which rigidly shifts the conduction band with respect to the valence band. Thus we think that the dielectric function results, reflectivity and optical absorption here shown of the two cadmium metastannate polymorphs under study can be helpful assets to interpret experimental data. As a matter of fact, the dielectric function for perovskite CaTiO3 was obtained by an approach similar...
Figure 6. Ilmenite and perovskite CdSnO$_3$: dielectric function real and imaginary parts for distinct incident light polarizations and light irradiated on a polycrystalline sample.

to ours [49], exhibiting good agreement with experiment; we have also published two works reporting the optical properties of triclinic CdSiO$_3$ and perovskite CdGeO$_3$ [50, 51] using the same methodology.

Figure 6 shows the real and imaginary parts of $\varepsilon(\omega)$ for both ilmenite (left) and perovskite (right) CdSnO$_3$. Polarized light was taken into account, with three polarization plane alignments relative to the crystal planes: [100], [010], and [001]. The complex dielectric functions for polycrystalline samples (POLY) were also simulated. From figure 6, one can see that there is no anisotropy of optical properties in ilmenite for the chosen light polarizations, while for perovskite the degree of optical anisotropy is very small. One also can see that the dielectric function of perovskite CdSnO$_3$ shares many features with ilmenite.

From the dielectric functions we have extracted information on the optical reflectivity ($R$) of the CdSnO$_3$ polymorphs, which is shown in figure 7 for the energy interval between 0 and 10 eV. In the visible range, the reflectivity of both crystals is less than 10% at most, with the reflectivity of the perovskite crystal reaching the smallest values, between 9% and 10% for energies between 1.8 and 3.1 eV (which covers the visible spectrum), while ilmenite has $R$ within the 10%–12% interval for the energy limits. For ilmenite, reflectivity maxima occur at the following energies: 4.0, 5.1, 6.2, 7.2, 7.9, 8.8 eV (highest peak, with $R$ about 19%) and 9.7 eV. The perovskite crystal shows a small but noticeable degree of anisotropy in $R$ for energies above 4.7 eV in comparison with ilmenite. For a polycrystalline sample, the main $R$ maxima occur at 4.0, 4.8, 5.3, 6.3, 7.4, and 9.8 eV ($R \approx 23\%$).

Finally, figure 8 depicts the optical absorption spectra of the CdSnO$_3$ crystals. The absorption coefficient measures how much energy is lost when an electromagnetic wave passes through a material, considering that the intensity decays exponentially as a function of the distance from the surface of incidence. The calculated absorption curves of the present work agree well with the experimental data [2, 4] which, however, cover only photon energies between 2 and 4 eV. For ilmenite, the most important absorption peaks are at 4.2, 4.6, and 5.1 eV (related to electronic transitions between the O 2p uppermost valence band and conduction bands originated from Cd 5s and Sn 5s orbitals). There are also peaks at 5.5, 6.1, 6.4, 7.2 and 8 eV with dominant contribution from O 2p (valence band) $\rightarrow$ Cd 5s (conduction band) electronic states.

In the region between about 9 and 10 eV, the optical absorption peaks at 8.9 and 9.9 eV are due to O 2p (valence band) $\rightarrow$
Cd 5s + Sn 5s (conduction band) transitions, and the peaks at 9.1 and 9.5 eV originate from the top of the O 2p valence band and Cd 5s and Sn 5s conduction bands, respectively. For the perovskite crystal, on the other hand, we have important optical absorption peaks at 4.2, 4.9, 5.4, and 8.9 eV being due to O 2p → Cd 5s + Sn 5s (valence to conduction) electronic band transitions. Peaks at 5.9, 6.3, 7.6, and 9.4 eV are mainly originated from O 2p → Cd 5s valence to conduction band excitations. Finally, the peaks at 8.2, 8.7, and 9.7 eV are due to O 2p valence band electrons being optically excited to conduction bands with dominant Sn 5s character. It is easily seen that both polymorphs have very similar absorption curves, with the perovskite reaching higher absorption values than ilmenite only for energies between 8 and 10 eV, where the contribution from O 2p → Sn 5s transitions is more important.

6. Infrared spectra, dielectric permittivities and polarizabilities

The LDA-optimized structures were used to perform density functional perturbation theory (DFPT) calculations [52], which provides an analytical way of obtaining the second derivative of the total energy with respect to some external disturbance, such as an ionic position change, an external electric field or a change in the unit cell vectors, which allows for the determination of properties like the phonon spectra, the dielectric response or elastic constants. The infrared absorption spectrum intensities depend on the dynamical (Hessian) matrix and Born effective charges [53], and can be obtained by calculating the phonons at the Γ point (q = 0). The computed far infrared spectra of ilmenite and perovskite CdSnO3 are shown in figure 9. Tables 6 and 7 present the predicted normal modes with the respective irreducible representations, IR intensities and indicators of Raman activity.

Ilmenite has 27 normal modes at q = 0, with its most pronounced IR absorption peak at about 444 cm⁻¹ (associated with two modes of Eu symmetry), followed in order of intensity by three peaks at 472 cm⁻¹ (A₁u), 322 cm⁻¹ (two E₁g normal modes), and 536 cm⁻¹ (two E₂g normal modes). All these vibrations involve the movement of Sn–O bonds, with no noticeable displacement of the Cd atoms. Besides, all IR inactive modes are Raman active for this crystal. The optical permittivity components for ω = 0 are: ε_xx = 9.451,
The polarizabilities (in $\text{Å}^3$) for $\omega = 0$ ($\infty$) are: $\epsilon_{xx} = 74.452$ (24.841), $\epsilon_{yy} = 76.191$ (24.806), $\epsilon_{zz} = 84.925$ (24.631), $p_{xx} = 2.224$ ($-0.045$), $p_{xy} = 4.266$ ($-0.086$), and $p_{xz} = 6.249$ ($-0.126$).

The infrared spectrum calculated for perovskite CdSnO$_3$ is more structured than that obtained for ilmenite. For example, while the ilmenite crystal has a very small infrared peak at 650 cm$^{-1}$ (Sn–O bond stretching along the $b$ axis), CdSnO$_3$ perovskite exhibits a band of three very close high intensity maxima of absorption between 630 and 690 cm$^{-1}$, the first peak at 638 cm$^{-1}$ (Sn–O bond stretching along the $b$ axis), the second at 661 cm$^{-1}$ (Sn–O bond stretching along the $a$ axis, the 654 cm$^{-1}$ peak is very small), and the third at 687 cm$^{-1}$ (Sn–O bond stretching along the $a + c$ direction). The ilmenite spectrum also has a pronounced peak at 536 cm$^{-1}$ (Sn–O bond stretching along $b$) which in the perovskite polymorph is replaced by a very small peak at 517 cm$^{-1}$ (scissoring movement of Sn–O–Sn bonds along the $b$ axis). Perovskite has two peaks at about 100 cm$^{-1}$ (Cd atoms vibrating along the $b$ axis and Sn–O–Sn chains vibrating parallel to the $a$ axis) which are absent in the ilmenite case, and the two bands of peaks observed for ilmenite between 320 and 480 cm$^{-1}$ (mainly originated from the scissors movement of Sn–O–Sn bonds, with some degree of Sn–O–Sn stretching for the 472 cm$^{-1}$ peak) are replaced by a wide band of peaks between 240 and 440 cm$^{-1}$ in perovskite (Sn–O–Sn scissoring mainly).

Among the 57 normal modes of CdSnO$_3$ perovskite, eight modes have $A_u$ symmetry, being undetectable by both IR and Raman measurements, while all modes in ilmenite are infrared or Raman active. The ilmenite Raman active modes occur in the following wavenumber ranges: 110–141 cm$^{-1}$ (involving the vibration of Cd atoms), 180–290 cm$^{-1}$ (Sn–O–Sn rocking), 340–460 cm$^{-1}$ (Sn–O–Sn scissoring mainly). The Raman active modes for the perovskite crystal appear in the wavenumber ranges 100–200 cm$^{-1}$ (Cd atoms and Sn–O–Sn groups rocking), 213 cm$^{-1}$ and between 280 and 290 cm$^{-1}$ (O–Sn–O twisting), 340 and 500 cm$^{-1}$ (Sn–O–Sn scissoring), 530 and 780 cm$^{-1}$ (Sn–O–Sn bond stretching).

In contrast with the calculations of Lebedev [7], we have not found any normal mode with frequency below 100 cm$^{-1}$ for perovskite CdSnO$_3$ (Lebedev has found four modes below this limit). We have not obtained any sign of structural instability for the optimized crystal as well (Lebedev’s data...
are also indicated.

In summary, we have presented the results of calculations for perovskite CdSnO3 using the local density approximation (LDA) and the generalized gradient approximation (GGA), the last one through the Perdew–Burke–Ernzerhof exchange–correlation functional (PBE). Geometries optimized using the GGA-PBE approach are in general more accurate, with a difference of lattice parameters between experiment and theory of 1.0% at most. The Kohn–Sham band structures of ilmenite and perovskite reveal that the first has an indirect band gap while the second is a direct band gap material, in agreement with previous results published in the literature for non-optimized crystals. The electron effective masses of both polymorphs are isotropic, while the hole effective masses display large anisotropy and are heavier in comparison with electron masses. The optical properties (dielectric function, reflectivity, absorption) of CdSnO3 ilmenite and perovskite are isotropic with respect to the incidence of polarized light. The curves for the real and imaginary parts of the perovskite dielectric function are similar in shape to the ilmenite curves, but rescaled along the energy axis. The optical absorption spectra agree well with experimental data. Finally, the LDA far infrared spectra of CdSnO3 were calculated, the normal modes and main absorption peaks being assigned and Raman active modes indicated. In contrast with previously reported DFT calculations, we have not found any normal mode for perovskite crystals with imaginary frequency.

### 7. Conclusions

In summary, as observed for the ilmenite phase, these vibrations involve mainly the distortion of Sn–O bonds, with practically no movement of Cd. At \( \omega = 0 \), the optical permittivity tensor components are \( \epsilon_{xx} = 12.800, \epsilon_{yy} = 17.337, \epsilon_{zz} = 11.409, \epsilon_{xy} = \epsilon_{xz} = \epsilon_{yz} = 0 \). For \( \omega \) \( \infty \) we have \( \epsilon_{xx} = 3.975, \epsilon_{yy} = 3.963, \epsilon_{zz} = 3.4005, \epsilon_{xy} = \epsilon_{xz} = \epsilon_{yz} = 0 \). The tensor of polarizabilities has the following components at \( \omega = 0 \) (\( \text{all in } \AA^3 \)): \( \rho_{xx} = 192.037 \) (48.414), \( \rho_{yy} = 265.876 \) (48.227), \( \rho_{zz} = 169.408 \) (48.908), \( \rho_{xy} = \rho_{xz} = \rho_{yz} = 0 \) (0).

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