

# First principles study of band structure and density of states of rare earth oxytellurides $R_2O_2Te$ (R=La, Ce, Pr and Nd)

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The electronic structure calculations of the rare earth oxytellurides of formula  $Ln_2O_2Te$  have been investigated by using full potential linearized augmented plane method within Coulomb corrected local spin-density approximation LSDA+U. The LSDA+U calculations yield first time the indirect-gap semiconductors nature ( $E_g \sim 1.82$  eV) for all  $Ln_2O_2Te$ , while no experimental data available. The substantial covalent bonds between Ln and O and less covalent bond between Ln and Te coexist in the materials. These materials have potential application in magneto-optoelectronic industry.

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## 1. Introduction

In the past years lanthanides-containing material received much attention because of their diverse electrical, optical and chemical properties. They can be successfully used in lasers, wide gap electro-luminescent devices, light emitting diodes, scintillator detectors, and as efficient host for the design of phosphorescent materials [1-5]. The rare earth oxytellurides belong to this interesting series of materials. The rare earth oxytellurides have interesting physical properties and are very promising in practical regards [6, 7]. Least studied among these compounds are the REM oxytellurides due to technical difficulties in their preparation [8]. From the pioneering work published by Domange *et. al.* [7] and more recent investigations by Llanos *et. al.* [9], it has been established that the rare earth oxytellurides  $Ln_2O_2Te$  (Ln = La, Ce, Pr, and Nd) crystallize in the tetragonal phase with space group I4/mmm. The crystal structure can be described as an anti-ThCr<sub>2</sub>Si<sub>2</sub>-type structure, where the  $Ln^{+3}$  cations are surrounded by eight anions ( $4O^{2-}$  and  $4Te^{2-}$ ) arranged as a distorted square anti prism.

The polyhedral are connected in a way that maintains the three dimensional coherence of the crystal structure and the charge balance [8]. Recently Llanos *et. al.* [9] reported the synthesis, the optical and magnetic properties and the electronic structure of the rare earths oxytellurides. They have performed the electronic structure calculations within Generalized Gradient approximation (GGA) only for  $La_2O_2Te$  by using the SIESTA code and suggest an indirect band gap. In contrast to the large number of study devoted to the study of rare earth oxysulphide and

oxyselenide, oxytellurides are less explored. In addition, there is no theoretical information about the electronic structure particularly the band structure of the oxytellurides, for example we do not know whether the system has a direct band gap or an indirect one. Furthermore, we do not know any theoretical evidence that could explain the anisotropic refractive indices, though we can expect the property from the anisotropic crystal structure. Knowledge of electronic structure of the rare earth oxytellurides is crucial in order to understand optoelectronic process in the materials. This is why here we carry out the full potential calculations of these materials.

## 2. Computational details

The calculations reported here were performed using the WIEN2k [10] implementation of the full-potential linear augmented plane wave (FLAPW) method in the scalar-relativistic regime. We have found in other theoretical results that LSDA+U approximation is appropriate for calculating the electronic properties of rare earth compounds [11, 12]. To describe the exchange correlation functional we have used rotationally invariant LSDA+U approximation and double counting scheme of Anisimov [13] and collaborators. The standard parameterization of the on-site Coulomb interaction involves two parameters U and J. The role of J reduces to merely re-normalizing the U value. Therefore we can set J=0 and quote just the U value. We have used the U values for  $La_2O_2Te$ ,  $Ce_2O_2Te$ ,

$Pr_2O_2Te$ , and  $Nd_2O_2Te$  from other theoretical work of Singh *et al.* [11] on rare earth sesquioxides. The present calculations were based on spin density functional with the Perdew and Wang parameterization [14] of the exchange-correlation potential. The spin orbit interaction is taken into account in a second variation in each self-consistent loop [15]. In order to calculate the electronic structure and related properties, the following computational parameters were used. The atomic radii were 2.34, 2.08 and 2.5 Bohr for Ln and O, and Te, respectively. The size of the basis was determined by the cut-off = 8. The charge self-consistency was obtained on a grid of 163 irreducible  $k$ -points. The structural parameter for rare earth oxytellurides are taken from the Ref. [8]. This DFT calculation approach is well established and produces number of results with good agreement with experiments [16-23].

### 3. Results and discussion

The band structure (BS) and density of states (DOS) of rare earth oxytellurides have been calculated by means of the LSDA+U approximation. Due to the correlated nature of 4f states, usually, the LSDA calculations yield 4f states close to Fermi energy. To account better for the on-site f electrons correlation, we have adopted the LSDA+U in the present calculations.

The LSDA+U band structures of  $La_2O_2Te$ ,  $Ce_2O_2Te$ ,  $Pr_2O_2Te$ , and  $Nd_2O_2Te$  for spin (solid line) and for spin down (dotted line) are shown in Fig. 1. We find that the top of the valence band is at  $\Gamma$  point and the bottom of the conduction band is at the N point. We thus conclude that these are an indirect-gap semiconductor. There are no experimental data for the direct or indirect-gap structures of these systems. Experimental investigation is thus awaited. In the band structure we also find a very flat band on the top of the valence band. Therefore, we can expect anisotropic behavior from the holes. Moreover, from this anisotropy, we could expect anisotropic physical properties in these systems, for example, anisotropic reflective indices. More experimental data are necessary to confirm these anisotropic properties of rare earth oxytellurides that we found here.

For the sake of simplicity, we have discussed the band structure of  $Nd_2O_2Te$  in detail and later we will do it for other oxytellurides and also made a comparison between them. Considering the LSDA+U band structure for spin up, there are four energy bands close to -20 eV, originating from Nd- $p$  and O- $s$  levels (see Fig. 2), single band near -10 eV comes from Te- $s$  level. The uppermost valence band resulting mostly O- $2p$  orbitals with some amount of Te- $p$  levels. The energy levels in conduction bands, is the mixing contribution from the Nd- $f$ , Nd- $d$  and Te- $d$  states. The band structure of  $Nd_2O_2Te$  for spin down is overlapping with that of spin up except that the unfilled 4f states present in the conduction band for spin down.

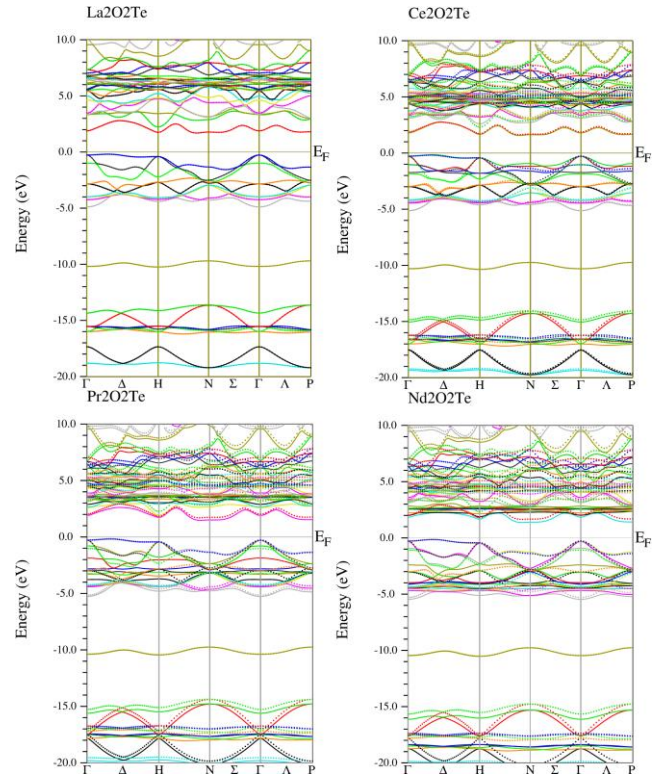


Fig. 1. The calculated band structure of  $Ln_2O_2Te$ .

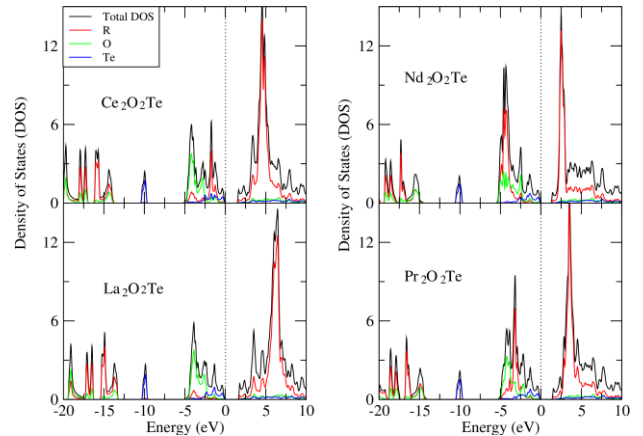


Fig. 2. Total density of states of  $Ln_2O_2Te$ .

The Kohn Sham band gap calculated is indirect, between the valence band maximum at  $\Delta$  and the conduction band minimum at N. The present calculations yield the indirect bandgap  $\sim 1.82$  eV. Which is far smaller as compare to their parent rare earth sesquioxides ( $R_2O_3$ ,  $R = La, Pr, \text{ and } Nd$ ) [11]. This reduction of bandgap is mainly due to Te. From application point of view Te doping could control the bandgap value and can tune to achieve desired optical transitions. The direct bandgap at  $\Gamma$  point is  $\sim 2.12$  eV. We note that due to approximation of Density functional theory (DFT), the theoretically calculated energy gaps are inaccurate and somewhat smaller than the experimental measurements. Therefore,

the smallest actual band gap of rare earth oxytellurides must be larger than calculated one. The band structures of other rare earth oxytellurides are very similar to that of  $\text{Nd}_2\text{O}_2\text{Te}$ , difference come only for the presence of the 4f electrons in conduction bands. This difference can be easily identified in the calculated partial density of states of the rare earth oxytellurides.

The total density of states along with the partial density of states of rare earth oxytellurides are shown in Fig. 2 and Fig. 3. The calculations show that the partial DOS for O and Te are very similar to all rare earth oxytellurides. The difference in the partial DOS is only for rare earth atom. The second row of the Fig. 3 shows the total density of states for spin up and for spin down for the rare earth atom. The electronic optical properties of these materials are under investigation along with magneto-optical study.

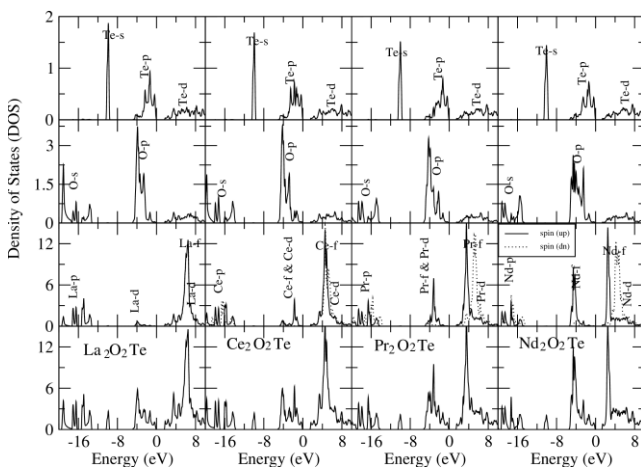


Fig. 3. Partial density of states of  $\text{Ln}_2\text{O}_2\text{Te}$ .

#### 4. Conclusion

First principles calculations of electronic band structure and density of the rare earth oxytellurides of formula  $\text{Ln}_2\text{O}_2\text{Te}$  have been carried out using full potential linearized augmented plane wave plus local orbitals method (FP-LAPW + lo) within Coulomb corrected local spin-density approximation LSDA+U and in the framework of density functional theory (DFT). The LSDA+U calculations yield first time the indirect-gap semiconductors nature ( $E_g \sim 1.82$  eV) for all  $\text{Ln}_2\text{O}_2\text{Te}$ . The substantial covalent bonds between Ln and O and less covalent bond between Ln and Te coexist in the materials. These materials have potential application in optoelectronic industry.

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