INVESTIGATION OF ELECTRONIC AND OPTICAL PROPERTIES OF NOVEL OXYCHALCOGENIDES BY DENSITY FUNCTIONAL THEORY

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Article Info	Abstract
<p><i>Received: 27.07.2020</i> <i>Accepted: 30.11.2020</i></p> <p>Keywords: Oxychalcogen; Density functional theory (DFT); Electronic properties; Optical properties.</p>	<p>The search for a new material with unparalleled properties has attracted the interest of the scientific community due to rapid development of technology and it can be very inspiring to the future experiments. In this paper, electronic structure and optical properties of the new rare earth coinage-metal chalcogenides YCuChO (Ch=S, Se, Te) are investigated in detail using state-of-the art density functional theory (DFT). Both the GGA-PBEsol and TB-mBJ functionals were used to describe the exchange-correlation interactions. These compounds are novel and have not been synthesized before. The optimized structural parameters, viz., lattice parameters and atomic position coordinates, are predicted. The analyses of the electronic properties indicate that the studied compounds are wide direct bandgap semiconductors. The calculated bandgaps varying from 1.69 eV (for the Te compound) to 2.5 eV (for the S compound) with the mBJ approach. Moreover, the optical properties of these compounds were comprehensively studied and discussed in terms of the dielectric function and loss function. The results provide theoretical support for the exploration of YCuChO (Ch=S, Se, Te) materials in potential optoelectronic applications.</p>

1. Introduction

The rare earth coinage-metal chalcogenides are interesting to researchers because of the greater structural complexity due to the additional anion which allows concomitant affect on the electronic structure and their properties [1–4]. These unique physical chemistry properties have driven tremendous applications for diverse areas such as transparent conductors and

materials for rechargeable battery [5] as well as materials for unusual magnetic, chemical and optoelectronic properties [6, 7]. The rare earth coinage-metal chalcogenides, LnMOCh (Ln = rare earth element; $\text{M} = \text{Cu, Ag}$; $\text{Ch} = \text{S, Se, Te}$) are a class of layered materials that consist of alternating $[\text{Ln}_2\text{O}_2]^{2+}$ oxide layers and $[\text{M}_2\text{Ch}_2]^{2-}$ chalcogenide layers stacked perpendicular to the c-axis in a tetragonal unit cell [7–9]. There have been several experimental and theoretical studies reported in the literature on the crystal structures, optoelectronic and thermoelectric properties of the rare earth coinage-metal chalcogenides [10-33].

To the best of our knowledge, there are no experimental or theoretical studies concerning the yttrium copper oxychalcogenides. In this paper, we investigate the structural, electronic and optical properties of YCuChO materials using first principles calculations within density functional theory.

2. Computational methods

Density functional theory (DFT) [34] calculation was carried out based on full potential linearized augmented plane wave (FP-LAPW) [35] method as implemented in WIEN2K [36] package code to calculate structural and optoelectronic properties. The exchange and correlation potentials were treated within the generalized gradient approximation in the form of Perdew Burke-Ernzerhof (PBE-GGA) [37]. It is well known that GGA calculations underestimate the band gap in semiconductors [38, 39]. To ensure the semiconductor behavior we have employed the modified Becke-Johnson (TB-mBJ) semi-local exchange potential [40, 41], which has been known to produce much more accurate band gaps than the standard GGA. The self-consistent energy criterion convergence was set to 10^{-4} eV/cell.

3. Results and discussions

3.1. Structural properties

The crystal structure of YCuChO ($\text{Ch} = \text{S, Se, Te}$) belongs to the ZrSiCuAs -type structure with the tetragonal P4/nmm space group, as shown in Figure 1. The basic atomic positions are the following: Y: $2c(0.25, 0.25, z_Y)$; Cu: $2b(0.75, 0.25, 0.5)$; Ch: $2c(0.25, 0.25, z_{\text{Ch}})$; and O: $2a(0.75, 0.25, 0)$, where z_Y and z_{Ch} are the so-called internal coordinates.

As the first step, the total energy versus cell volume calculations were carried out to determine the optimized geometry for the considered compounds YCuChO ($\text{Ch} = \text{S, Se, Te}$), as shown in Figure 2. The obtained results were fitted using the Murnaghan equation of state [42]. So we just briefly mention its main features here.

The values thus calculated are summarized in Table 1 along with those of the prototype BiCuChO reported in Ref [10]. It is seen from this table that the lattice parameters “ a ” and “ c ” increases from YCuSO to YCuTeO and the results obtained are similar to the values reported in Ref [10]. This result can be attributed to the fact that ionic radii are in the order S (1.04 Å)<Se (1.17 Å)<Te (1.37 Å). In addition, the bulk modulus B decreases from Te to S; this means that YCuTeO a harder material than YCuSeO and YCuSO. The calculated cohesive energy is negative, which indicate that these three compounds are structurally stable and they will not decompose once they have been formed.

Table 1. The calculated lattice parameters, atomic internal coordinates, bulk modulus, derivative of bulk modulus and the cohesive energy of YCuChO.

Compounds	$a(\text{\AA})=b(\text{\AA})$	$c(\text{\AA})$	z_Y	z_{Ch}	B	B'	Ecoh(eV/atom)
YCuSO	3.845	8.318	0.145	0.661	123.426	4.321	-3.337
BiCuSO [10]	3.837	8.416	0.151	0.666			
YCuSeO	3.912	8.667	0.141	0.675	112.693	4.327	-3.199
BiCuSeO[10]	4.004	9.287	0.132	0.679			
YCuTeO	4.014	9.338	0.139	0.688	96.583	4.403	-3.051
BiCuTeO[10]	4.041	9.523	0.126	0.682

Figure 1. The polyhedral view of the layered structure of YCuChO.

3.2. Electronic properties

The knowledge of the electronic properties is essential for a possible application in optoelectronic devices. The band structure and the total density of states (DOS) of YCuChO are shown in Figure 3-4. We start by analyzing the results of our band structure calculations.

Figure 2. Variation of total energy as a function of volume of (a) YCuSO, (b) YCuSeO, (c) YCuTeO, respectively.

Third, YCuSO, YCuSeO and YCuTeO are wide direct bandgap semiconductors, where both the valence band maximum (VBM) and conduction band minimum (CBM) are located at the BZ center, the so-called Γ -point. The TB-mBJ potential improves considerably the bandgaps compared to those yielded by the standard GGA without consuming calculation time. As shown in Figure 3, the TB-mBJ functional significantly opens up the GGA bandgap, but the overall profile of bands is nearly unchanged. The energy gap is equal to 1.55 eV (GGA) and 2.50 eV (mBJ) for YCuSO, 1.34 eV(GGA) and 2.29 eV(mBJ) for YCuSeO, 1.18 eV(GGA) and 1.69 eV (mBJ) for YCuTeO. Our results indicate that the width of the band gap decreases with increasing atomic number of chalcogen atom. The band gap reduction could be attributed to shift of the conduction band towards the Fermi level (E_F) when one move from S

to Te. Unfortunately, there are no theoretical as well as experimental data to compare our calculated band gap results. To describe the behavior of band structure, the electronic distributions are drawn in terms of total and partial density of states (TDOS & PDOS), as shown in Figure 4. The PDOS shows that, the maximum contribution to total density of states (TDOS), above the Fermi level, there is a maximum contribution of *d* states of yttrium. While below the Fermi level, arise mainly from the *p* states of chalcogen and *d* states of Cupper, which confirms the formation of covalent bonds between the copper and chalcogen atoms.

Figure 3. Comparison of GGA and mBJ band structures of (a) YCuTeO, (b) YCuSeO and (c) YCuSO, respectively.

3.3. Optical properties

The optical properties are vital for semiconductor technology and are generated from the linear response of the electrons under an external perturbation. They can be described by the complex dielectric function given by: $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where $\epsilon_1(\omega)$ is the real part of this function which determine the propagation of electromagnetic wave through matter and $\epsilon_2(\omega)$ is the imaginary part and it depends on the electronic transitions due to absorption of photons.

Figure 4. Total and partial density of states for (a) YCuSO, (b) YCuSeO and (c) YCuTeO, using GGA.

Knowing the dielectric function, we can deduce other important optical functions such as reflectivity (R), refractive index (n), absorption coefficient (α) and electron energy loss

spectrum (EELS), and so on. Figure 5, shows the real part and imaginary part of dielectric function. The YCuChO compounds have tetragonal symmetry so they have three main components i.e. $\epsilon_{xx}(\omega)=\epsilon_{yy}(\omega)=\epsilon_{\perp}(\omega)$ and $\epsilon_{zz}(\omega)=\epsilon_{\parallel}(\omega)$, but here we have taken the average of the two former components. From Figure 5a, we have noticed that the static dielectric constant $\epsilon_1(0)$ for YCuSO, YCuSeO and YCuTeO are 7.82, 8.76 and 9.90, respectively. These results reflect the dependency of the optical properties on the electronic band structure for YCuChO compounds. This could be explained following Penn model [43], which describe the relationship between the band gap E_g and $\epsilon_1(0)$. The positive variation ($\epsilon_1(\omega) > 0$) shows a dielectric behavior, while for the negative values ($\epsilon_1(\omega) < 0$) the incident electromagnetic waves are mainly dispersed in this energy zone. Figure 5b, shows the imaginary part (absorptive) of the dielectric function $\epsilon_2(\omega)$ for the oxychalcogenides YCuChO. Our analysis of the $\epsilon_2(\omega)$ curves show that the first critical points of the dielectric function occurs at 1.8 eV, 1.7 eV and 1.5 eV for YCuChO, which also corresponds to the direct interband transition at Γ .

The energy loss spectrum describes the energy loss of a fast electron traversing in the material. The response of energy loss functions to the photon energy of BiOCuCh is shown in Figure. 6. The peak is defined as the bulk plasma frequency, ω_p which occurs where $\epsilon_2 \ll 1$ and ϵ_1 reaches zero. The plasma frequency of BiOCuS, BiOCuSe and BiOCuTe are 18.23, 17.95 and 17.39 eV, respectively.

Figure 5. The calculated real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ parts of dielectric function for YCuChO, using GGA.

Figure 6. Loss functions of YCuChO (Ch=S, Se , Te)

4. Conclusions

In this work, we have used density functional theory to study the structural, electronic and optical properties of the oxychalcogenides YCuChO. We first predicted the structural properties, viz., lattice parameters and atomic position coordinates. We then calculated the electronic properties, which predict a direct band gap for the three compounds at the Γ points. Its energy gap is equal to 1.55 eV (GGA) and 2.50 eV (mBJ) for YCuSO, 1.34 eV(GGA) and 2.29 eV(mBJ) for YCuSeO, 1.18 eV(GGA) and 1.69 eV (mBJ) for YCuTeO. Finally, the optical properties i.e. the real part and the imaginary part of the dielectric function along with the energy-loss function were reported.

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