Journal of Alloys and Compounds 625 (2015) 182–187

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Optoelectronic properties of XIn_2S_4 (X = Cd, Mg) thiospinels through highly accurate all-electron FP-LAPW method coupled with modified approximations

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ARTICLE INFO

Article history:
Received 24 September 2014
Received in revised form 9 November 2014
Accepted 14 November 2014
Available online 23 November 2014

Keywords:
Ab initio calculations
Semiconductors
Band-structure
Optical properties
Thiospinels

ABSTRACT

We report the structural, electronic and optical properties of the thiospinels XIn_2S_4 (X = Cd, Mg), using highly accurate all-electron full potential linearized augmented plane wave plus local orbital method. In order to calculate the exchange and correlation energies, the method is coupled with modified techniques such as GGA+U and mBJ-GGA, which yield improved results as compared to the previous studies. GGA+SOC approximation is also used for the first time on these compounds to examine the spin orbit coupling effect on the band structure. From the analysis of the structural parameters, robust character is predicted for both materials. Energy band structures profiles are fairly the same for GGA, GGA+SOC, GGA+U and mBJ-GGA, confirming the indirect and direct band gap nature of $CdIn_2S_4$ and $MgIn_2S_4$ materials, respectively. We report the trend of band gap results as: (mBJ-GGA) > (GGA+U) > (GGA) > (GGA+SOC). Localized regions appearing in the valence bands for $CdIn_2S_4$ tend to split up nearly by ≈1 eV in the case of GGA+SOC. Many new physical parameters are reported that can be important for the fabrication of optoelectronic devices. Optical spectra namely, dielectric function (DF), refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, optical conductivity $\sigma(\omega)$, absorption coefficient $\alpha(\omega)$ and electron loss function are discussed. Optical's absorption edge is noted to be 1.401 and 1.782 for $CdIn_2S_4$ and $MgIn_2S_4$, respectively. The prominent peaks in the electron energy spectrum situated between 15 eV and 23 eV for the herein studied materials indicate a transition from metallic to the dielectric character.

1. Introduction

The dire requirement for a more efficient optoelectronic devices has led to an increased focus on computationally less studied thiospinels such as XIn_2S_4 (X = Cd, Mg). A study involving a comparative implementation of modern approaches capable of giving results that are in close agreement to experimental values, is elusive. Majority of thiospinels are semiconductors belonging to the space group #227 (Fd-3m), in which S atoms are arranged as a closed packed faced centered structure.

Thiospinels have been the subject of tremendous experimental studies due to their distinguishable physical properties such as nonlinear optical response [1], birefractance character [1], sensitiveness with respect to photo radiations [2] and transparency for high energy photons [2]. These materials show anisotropic pressure dependent properties and therefore have a likely utilization in the field of defect engineering [3]. Recently, Chate et al. studied the electrical, photo-electrochemical and absorption properties of $CdIn_2S_4$ [4]. The authors predicted a high absorption coefficient and measure the optical band gap value of 2.25 eV [4]. The visible region of the solar spectrum is of particular interest for energy conversion applications, which can be found in materials such as $CdIn_2S_4$ having band gap value in the range of 2.1–2.7 eV [5]. $CdIn_2S_4$ can be used in applications such as

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http://dx.doi.org/10.1016/j.jallcom.2014.11.104
0925-8388/

photo-electrochemical solar cells, photoconductors, LEDs and photocatalysis [5–7]. Direct band gap nature for $MgIn_2S_4$ categorizes it as optically active material. The high value of the absorption coefficient (10^4–10^5 cm^{-1}) in the visible light range is of technological interest [8]. The reported experimental band gap range 2.1–2.28 eV [9,10] of $MgIn_2S_4$ matches well with that of intermediated band host (2.0–2.5 eV) [11].

In Density functional theory (DFT), exchange and correlation (XC) energies are critical for overall energy estimation. Localization of *d* electrons in XIn_2S_4 (X = Cd, Mg) makes this task more difficult. Moreover, most of the previous theoretical calculations on these materials using DFT, involved the traditional LDA and GGA approximations for XC energy. The effectiveness of these approximations is compromised as these are based on the mean field potential while, in strongly correlated systems the mean field approximation is badly affected. Both the LDA and GGA approximations generally underrate the band gap value of semiconductors and insulators by roughly 40% [12] and 20–50% in correlated systems [13,14], respectively.

In order to treat the electronic system accurately and to tackle the problem of underestimation of the band gap, two modified approaches called GGA+U [12,15] and mBJ-GGA [16–18] are used, respectively. The first mentioned approach GGA+U considers orbital dependent exchange and Coulomb interactions effectively. While, mBJ-GGA approximation has produced band gap results that are in close agreement with the experimental measurements as well as with the results obtained from expensive GW or hybrid functional methods, for diverse type of materials including thiospinels with strongly localized electrons [19–21]. Calculations are also performed with GGA+SOC approach that involves the spin orbital coupling (SOC) effect that has a profound effect on atomic spectra [22] and energy band structure [23]. All of the mentioned modified tools are used along with the all-electron full potential linearized augmented plane wave plus local orbital (FPLAPW+lo) method [24,25].

The remaining manuscript is divided into three parts. Section 2 describes the computational methodology used in the study. Section 3 involved the discussion over the obtained results for the structural and optoelectronic properties of $CdIn_2S_4$ and $MgIn_2S_4$ compounds. The conclusion of our work is presented in the last section.

2. Computational methodology

Self-consistent calculations of the structural, electronic structure and optical properties based on the full-potential linearized augmented plane wave plus local orbitals (FP-APW+lo) method were carried out using the WIEN2 K package [26]. This is a very precise and efficient approach to solve the Kohn–Sham equations within a framework of the DFT. In this method, the crystal unit cell is partitioned into non-overlapping muffin-tin spheres (MT) surrounding each atomic and interstitial regions. Within this approach, the potential and corresponding charge densities are expanded into radial wave-functions times spherical harmonics inside each muffin-tin sphere and as a Fourier series in the interstitial regions. The wave functions in the interstitial region were expanded in plane waves with a cutoff of $R_{MT} * K_{max} = 7$ (where R_{MT} is the smallest radius of the muffin-tin spheres and K_{max} gives the magnitude of the largest $\boldsymbol{k}$-vector in the plane wave expansion). The muffin-tin sphere radii R_{MT} for Mg, Cd, S and In were chosen to be 2.4, 2.8, 2.18 and 2.5 atomic units (*a.u.*), respectively. The Fourier charge density was expanded up to $G_{max} = 14$ $(Ryd)^{1/2}$. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-3} Ry. To provide a reliable Brillouin zone integration a set of 300 *k*-points in the irreducible wedge of the Brillouin zone was used. In our calculations, the Mg ($2p^6$ $3s^2$), Cd ($4p^6$ $4d^{10}$ $5s^2$), In ($4d^{10}$ $5s^2$ $5p^1$) and S ($3s^2$ $3p^4$) states were considered as valence electrons and Mg ($1s^2$ $2s^2$), Cd ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$), In ($1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$), S ($1s^2$ $2s^2$ $2p^6$) were considered as core electrons. The strong Coulomb repulsion between localized states is treated by adding a Hubbard-like term *U* to the effective potential, leading to an improved description of correlation effects using the approach described by Anisimov et al. [27]. The Hubbard value was taken to be 5.0 eV.

3. Results and discussions

The ternary semiconducting cadmium and magnesium indate sulphides XIn_2S_4 (X = Cd, Mg) crystallize in closed packed face-centered-cubic structure with space group *Fd*-3*m* (#227). The X atom is located at (1/8, 1/8, 1/8), In atom at (1/2, 1/2, 1/2) and the sulphide atom at (*u*, *u*, *u*). The crystalline structure is characterized by two parameters not fixed by the symmetry: the lattice parameter *a* and the internal free parameter *u* defining the position of the S atoms so we should relax both the internal free parameter and lattice parameter for each volume in order to obtain the optimized crystalline structure that minimizes the total energy. In the first step we have optimized the value of the internal parameter *u* by relaxing '*S*' atomic positions inside the unit cell using the experimental lattice parameter. In the second step the optimized values of the sulphide position are used to calculate the total energies for specified sets of lattice constants. The calculated total energies versus unit cell volumes are fitted to the Murnaghan's equation of state (EOS) [28] to determine the ground state properties such as the equilibrium lattice constant a_0, the bulk modulus B_0 and the bulk modulus pressure derivative B'. The computed structural parameters are listed in Table 1 along with the experimental data and theoretical results for comparison. The optimized lattice constants in angstrom units (Å) for $CdIn_2S_4$ and $MgIn_2S_4$ are 10.755(11.021) and 10.657(10.881) within LDA(GGA), respectively. It is found that the obtained lattice constant values with GGA(LDA) are slightly larger (smaller) than the available experimental data. The high values of the bulk moduli reveal the robust character of these compounds. Excellent agreement of the relaxed parameters with other published data sets up the accuracy for the next step for calculating the finding optoelectronic parameters.

A different approximations such as GGA, GGA+SOC, GGA+U and mBJ-GGA are used in order to calculate Kohn–Sham eigenvalues. As a result, the energy band structures of $CdIn_2S_4$ and $MgIn_2S_4$ are obtained along the high symmetry directions in the first Brillouin zone as shown in Fig. 1. The computed direct and indirect band gap values for the herein investigated compounds are given in Table 2 along with previous theoretical and experimental data. From Fig. 1, it is confirmed that the conduction band minimum (CBM) and the valence band maximum (VBM) are along Γ and *K* symmetry points, respectively for $CdIn_2S_4$. Whereas the CBM and the VBM are both along the Γ symmetry point in case of $MgIn_2S_4$. This means $CdIn_2S_4$ and $MgIn_2S_4$ have indirect and direct band gap nature, respectively.

It is seen that the overall shape of the energy band profiles is fairly similar for GGA, GGA+SOC, GGA+U and mBJ-GGA. The band gap values for $CdIn_2S_4$ ($MgIn_2S_4$) are 1.42 eV (1.80 eV), 1.40 eV (1.78 eV), 1.60 eV (1.90 eV) and 2.81 eV (2.83 eV) with GGA, GGA+SOC, GGA+U and mBJ-GGA, respectively. The following trend of band gap is reported as follow: (mBJ-GGA) > (GGA+U) > (GGA) > (GGA+SOC). It is found that the present band gap results with mBJ-GGA are not only improved over previous results but also closer to experimental data results. The bottom of the conduction bands (CBs) is flatter in $MgIn_2S_4$ compared to that in $CdIn_2S_4$. The