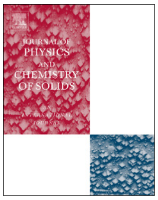
Journal of Physics and Chemistry of Solids 74 (2013) 1363–1368

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

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



Phase transition from BCT to spinel structure in $CdAl_2Se_4$ and its optical properties

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ARTICLE INFO

Article history:
Received 16 October 2012
Received in revised form
6 March 2013
Accepted 12 April 2013
Available online 2 May 2013

Keywords:
A. Semiconductors
C. Ab-initio techniques
D. Electronic properties
D. Phase transition
D. Optical properties

ABSTRACT

We present a detailed first principle investigation on $CdAl_2Se_4$ both at ambient and the high pressure conditions. At ambient condition $CdAl_2Se_4$ exists in body centered tetragonal (BCT) phase and at high pressure in spinel phase. Corresponding to different volume the total energy has been optimized using three functional, viz., the local density approximation (LDA), the generalized gradient approximation (GGA) and the Engel-Vosko generalised gradient approximation (EV-GGA). In all the cases phase transition from the BCT to the spinel phase has been observed. The equilibrium lattice constants, energy band gaps, bulk modulus have been reported at ambient conditions in both the phases. According to our prediction $CdAl_2Se_4$ is a direct band gap material in both the studied phases, contrary to the earlier results reported by Funetes-cabrea and Sankey for spinel phase. Among optical constants index of refraction, absorption coefficient and optical conductivity are calculated and compared with the existing results in both the phases within the energy range of 0–25 eV.

1. Introduction

Wide band gap semiconductors are currently under intense investigation driven by their possible applications in the electronic and optoelectronic devices. In this view the family of Defect chalcopyrite type ternary AB_2C_4 (where A=Zn, Cd, Hg, B=Al, Ga and C=S, Se, Te) compounds have received consideration for their studies [1]. Most of such compounds crystallize either in defect chalcopyrite body centered tetragonal (BCT) or spinel structures [2]. In some cases a pressure induced phase transition from BCT into spinel structure is also reported [3]. $CdAl_2Se_4$ is a potentially attractive material for various optoelectronic applications [4]. Along with extensive experimental studies the structural, electronic and optical properties of this compound have also been studied theoretically by several researchers [5–7].

Knowledge about the electronic and optical properties of a compound is of fundamental scientific interest. An optical spectrum of semiconductor is a rich source of information about their electronic properties. Tuning interactions between light and matter in semiconductors hold great promise for exotic applications. The greater flexibility in designing tailored properties of these ternary semiconductors has stimulated research for building new materials. Dielectric constants, refractive index, absorption coefficient and band gap are the most important designing parameters. Out of these the refractive indices and absorption coefficient are especially important in design and analysis of various optical and optoelectronic devices. Till so far the study of the optical properties for both the phases of $CdAl_2Se_4$ has not been performed.

Range et al. [8] have observed a phase change of $CdAl_2Se_4$ from BCT into spinel structure at 4.5 GPa and 400 °C. The X-ray diffraction study has shown that the BCT phase of $CdAl_2Se_4$ is stable up to a pressure of 9.1 GPa above which a phase transition occurs into disordered Rock salt phase [9]. Funetes-cabrea and Sankey [10] have reported direct to indirect band gap semiconducting crossover using Local density approximation functional at a pressure of 3 GPa.

On the basis of the above facts it is expected that the structural stability and optical behaviour of defect chalcopyrite-type materials at high pressures are also of great utility. In our earlier communication, we have already reported the first principle results of the electronic and thermal properties of $CdAl_2Se_4$ in ground state [11]. Goal of the present paper is to study the pressure induced phase transition and the optical behavior of $CdAl_2Se_4$ for BCT and spinel phase using the first principle methods. The structural and electronic properties for the above two investigated phases shall also be performed using three different exchange correlation potential.

2. Computational details

The considered $CdAl_2Se_4$ compound takes defect chalcopyrite (space group I–4, no. 82) structure at ambient conditions and

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http://dx.doi.org/10.1016/j.jpcs.2013.04.010

spinel (space group Fd-3m, no. 227) structure at high pressures [8]. The total energy has been calculated using the full potential augmented plane wave (FP-LAPW) method as implemented in the WIEN 2k code [12]. Three exchange-correlations functional for energy optimization namely the local density approximation (LDA) [13], the Perdew, Burke and Ernzerhof generalized gradient approximation (PBE-GGA) [14] and the Engel-Vosko generalised gradient approximation (EV-GGA) [15] have been used. In order to see the dependence of the structural properties on the exchange correlation potential different exchange-correlation potential has been considered. For the same kind of atoms in all the calculations similar values of the muffin-tin radius has been taken. The muffin-tin radius is varied to ensure total energy convergence. The final values for muffin-tin radii of Cd, Al, and Se were chosen as 2.38, 2.05 and 2.10 a.u., respectively. In the LAPW calculations, we set the energy threshold between core and valence states at −6.0 Ry. The minimum of the muffin-tin radius multiplied by k_{max} was chosen as 7.0, where k_{max} is the plane wave cut-off wave number. Total 1000 *k*-points were specified in the whole Brillouin zone.

To study the atomic relaxation in both phases, we used the mini routine as implemented in the Wien2K code. For this first, we optimized the c/a ratio for BCT structure and then relaxed all the independent internal atomic coordinates of two structures until the forces on every atom were below the 1 mRy/Bohr. The symmetry around the vacant site is maintained on relaxing the structure.

Optical properties of a solid are usually described in terms of frequency dependent complex dielectric function $\varepsilon(\omega)$, which contains two parts; the real part $\varepsilon_1(\omega)$ and the imaginary part $\varepsilon_2(\omega)$.

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega) \tag{1}$$

Here the real part describes dispersion of electromagnetic wave in the system, and imaginary part shows the dissipation of energy. The first step towards the calculation of optical properties involves computing the eigen-functions and eigen-values corresponding to uniformly distributed k-points. The imaginary part $\varepsilon_2(\omega)$ could be calculated from the momentum matrix elements between the occupied and unoccupied wave functions, ensuring the selection rules. It is given by following equation:

$$\varepsilon_2(\omega)=\frac{e^2\hbar}{\pi m^2\omega^2}\sum_{\nu,c}\int |M_{cv}(k)|^2\delta\left[\omega_{cv}(k)-\omega\right]d^3k. \tag{2}$$

Here the integral is over the first Brillouin zone. The momentum dipole elements M_{cv} and the potential vector defining the electric field δ are the matrix elements for direct transitions between valance $u_{vk}(r)$ and conduction $u_{ck}(r)$ states, and the energy

$$\hbar\omega_{cv}(k)=E_{ck}-E_{vk} \tag{3}$$

is the corresponding transition energy then, the $\varepsilon_2(\omega)$ is regarded as detailing the real transition between the occupied and unoccupied wave functions. The real part of the frequency dependent dielectric function $\varepsilon_1(\omega)$ follows from the Kramers-Kronig relation:

$$\varepsilon_1(\omega)=1+\frac{2}{\pi}p\int\frac{\omega'\varepsilon_2(\omega')}{\omega'^2-\omega^2}d\omega' \tag{4}$$

where, P is the principal integral.

Once the dielectric function is obtained, all of the other optical parameters such as reflectivity, absorption coefficient, refractive index, energy loss function, and optical conductivity can be deduced from it.

3. Result and discussion

From the crystallographic point of view the BCT phase of $CdAl_2Se_4$ has tetragonal unit cell in I–4 space group. The Cd atoms of the unit cell occupy 2a (0, 0, 0), half of the Al atoms 2b (0, 0, 1/2) and other half 2c (0, 1/2, 1/4) and Se occupy 8 g (x_1, y_1, z_1) sites respectively in the tetragonal system, where x_1, y_1 and z_1 are the internal parameters. The spinel type structure crystallises in Fd-3m space group and is ideally described as based on cubic close packed large anions with the smaller cations occupying the tetrahedral and octahedral interstices. The crystallographic unit cell of spinel phase contains 8 formula units depending on distribution of Cd and Al on tetrahedral and octahedral sites. The Cd and Al atoms are located at 8a (1/8, 1/8, 1/8) and 16d (1/2, 1/2, 1/2) Wyckoff sites, while the Se atoms occupy the 32e (x_2, y_2, z_2) sites, where x_2, y_2 and z_2 are internal parameters. The conventional unit cell structures used in calculation, for the BCT and spinel phases are shown in Fig. 1.

3.1. Structural properties

Using the first-principles approach, we have calculated the structural parameters for the BCT and spinel phase of $CdAl_2Se_4$. We calculated the total energy as a function of volume using different exchange-correlation functionals. The sets of energy-volume data were fitted to the Murnaghan equation of state [16]. The obtained equilibrium structural parameters for BCT and spinel phases are listed in Table 1(A) and (B) along with available experimental and earlier reported results. The results indicate that the calculated lattice

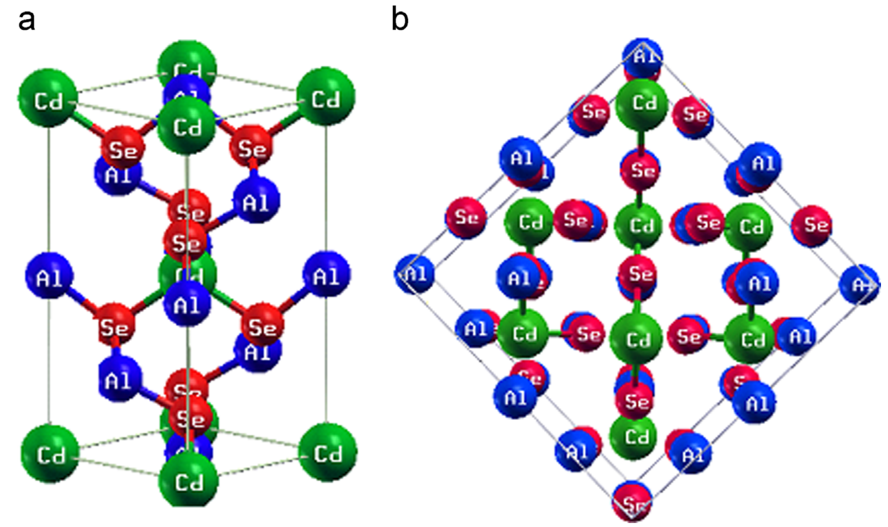

Fig. 1. Conventional unit cell structure for (a) body centred tetragonal phase and (b) spinel phase of $CdAl_2Se_4$.