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First-principles calculations of the structural, electronic and optical properties of $AgGaS_2$ and $AgGaSe_2$

A. Chahed* , O. Benhelal, S. Laksari, B. Abbar, B. Bouhafs, N. Amrane

Computational Materials Science Laboratory, Physics Department, University of Sidi Bel-Abbes, 22000 Sidi Bel-Abbes, Algeria

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Abstract

The structural, electronic and optical properties of two chalcopyrite crystals, $AgGaS_2$ and $AgGaSe_2$, are studied using the full potential linearized augmented plane waves method within the local density approximation. Geometrical optimization of the unit cell (equilibrium volume, c/a ratio, internal parameter u, and bulk modulus) is in good agreement with experimental data. The energy gap is found to be direct for both materials and the nature of the gap crucially depends on the manner in which the Ga 3*d*, and Ag 4*d* electrons are treated as core or valence states. Results on band structures, density of states, and charge-density distributions are presented. We report also our results on optical properties like the complex dielectric functions and the refractive index *n* of the $AgGaS_2$ and $AgGaSe_2$ crystals. We analyze in detail the structures of the dielectric function observed in the studied energy region.

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1. Introduction

Silver gallium sulfide ($AgGaS_2$) and Silver gallium selenite ($AgGaSe_2$) crystals have recently attained special interest for the middle and deep infrared (IR) applications due to their large non-linear optical (NLO) coefficients and high transmission in the IR region [1–6]. $AgGaS_2$ has the advantage of having a wider band gap, but its IR absorption edge/threshold is higher. On the contrary, $AgGaSe_2$ has the advantage of having lower IR absorption edge/threshold than $AgGaS_2$, but its band gap is smaller. The narrow gap of $AgGaSe_2$ like other chalcopyrite compounds makes it suitable as infrared detector including applications in photovoltaic solar cells both as single-crystal materials and as polycrystalline thin films and also light-emitting diodes [7,8].

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*Corresponding author. Tel.: +21 3721 70665; fax: +213048569546.

E-mail address: cha_abbes@yahoo.fr (A. Chahed).

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Furthermore, these materials are uniaxial and therefore birefringent. The magnitude of the birefringence in some ternaries is large enough to permit phase matching in linear and non-linear optical interactions [9–11].

Both $AgGaS_2$ and $AgGaSe_2$ compounds represent part of the $A^{I}B^{III}C_2^{VI}$ family-type compounds which crystallize in the tetragonal space group D_{2d}^{12} with four formula units in each cell, and they have a chalcopyrite structure that is closely related to those of zinc blende and wurtzite structures [12–14]. These materials are isoelectronic with the zinc blende II–VI compound semiconductors. First-principles calculations for phonons in $AgGaX_2$ ($X = \mathrm{Se, Te}$) chalcopyrite crystals have been reported by Lazewski et al. [15]. Cation substitution effects on structural, electronic and optical properties of non-linear optical $AgGa(S_xSe_{1-x})_2$ crystals were investigated theoretically and experimentally by Tang et al. [5].

The most obvious difference between $AgGaS_2$ and $AgGaSe_2$ crystals is their anions. In this paper, we make use of an accurate full-potential density-functional method to study the structural, electronic, and optical properties of $AgGaS_2$ and $AgGaSe_2$ by using a hybrid full-potential (linear) augmented plane-wave plus local orbitals (L/APW + lo) method. The purpose of all of these calculations is to provide a fundamental understanding on how the difference of anion species affects the electronic structure of these two crystals. This paper is organized as follows: Section 2 deals with the chalcopyrite structure. Information on the calculation method is given in Section 3. Section 4 is devoted to the analysis of the structural, electronic, and optical properties. Finally, we summarize the most important results in Section 5.

2. Crystal structure

We have already mentioned that these ternary semiconductors crystallize in the chalcopyrite structure related to the zinc blende structure. It has nearly the same arrangement of anions but differs in the ordered distribution of the cations which makes the unit cell tetragonal with the *c*-axis about twice the *a*-axis of the zinc blende-type unit cell, since each anion is coordinated by two A and B cations, while each anion is tetrahedrally coordinated by four anions [12]. The atomic positions are given as follows: A (0,0,0), (0,1/2,1/2); B $(1/2,1/2,0)$; $(1/2,0,1/4)$, C $(u,1/4,1/8)$; $(-u,3/4,1/8)$; $(3/4,u,7/8)$; $(1/4,-u,7/8)$. In the crystals considered here, the geometrical parameter $\eta = c/2a$ is less than 1, the reason for this distortion is caused by second neighbor interactions, and also the anions are displaced from their ideal tetrahedral sites by an amount u which is a function of the lattice constants given by

$$u = \frac{1}{2} - \left[\frac{c^2}{32a^2} - \frac{1}{16}\right]^{1/2}. \tag{2.1}$$

Third, there are two cations sublattices rather than one, leading to the existence of two basic near-neighbor chemical bonds A–C and B–C, with generally unequal bond lengths $R_{AC} \neq R_{BC}$. Thus, the two near-neighbor distances are given by

$$R_{AC} = a\left[u^2 + \frac{(1+\eta^2)}{16}\right]^{1/2} \tag{2.2}$$

and

$$R_{BC} = a\left[\left(u - \frac{1}{2}\right)^2 + \frac{(1+\eta^2)}{16}\right]^{1/2}. \tag{2.3}$$

Hence, the anion displacement $u - \frac{1}{4} = (R_{AC}^2 - R_{BC}^2)/a^2$ measures the extent of bond alternations in the system. The structural anomalies $((\eta - 1)$ and $(u - \frac{1}{4}))$ relative to the ZB structure ($\eta = 1$ and $u = \frac{1}{4}$) are significant. As a matter of fact, all peculiarities of the chalcopyrite compounds arise from the relative ordering (and the non-equivalence) of these two different bonds. This inequality is the reason for being considered for functional applications in non-linear optics. The 36 known ternary ABC_2 semiconductors exhibit a far richer range of physical and chemical properties which are discussed in several published papers [7–13].

3. Computational details

The electronic configurations for Ag, Ga, S and Se are Ag: $\mathrm{Kr}4d^{10}5s^1$, Ga: $\mathrm{Ar}3d^{10}4s^24p^1$,