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Effect of cation substitution on electronic band structure of $ZnGeAs_2$ pnictides: A mBJLDA approach

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ABSTRACT

The electronic properties of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds have been investigated using WIEN2k implementation of full potential linearized augmented plane wave (FPLAPW) method with an aim to study the effect of changing local environment by substituting cation(s) with corresponding next group element in reference compound ($ZnGeAs_2$) on these properties. The exchange and correlation (XC) effects are taken into account by an orbital independent modified Becke–Johnson (mBJ) potential as coupled with Local Density Approximation (LDA) for these calculations. We predict a direct band gap in all these compounds and observe that the band gap decreases with the change of either one or both cations. The calculated band gaps are in better agreement with corresponding experimental ones as compared to other calculations. The electronic band structure is analyzed in terms of contributions from various electrons and the covalency of two bonds, Zn—As and Ge—As has been discussed with respect to substitutions.

1. Introduction

Ternary $A^{II}B^{IV}C_2^{V}$ semiconductors represent part of pnictides family which crystallize in the chalcopyrite structure and show important optical, electrical and structural properties [1]. These materials have great technological interest to the research community due to their nonlinear optical properties [2,3]. In particular, their narrow band gaps make them suitable in photovoltaic applications such as infrared detectors, light emitting devices, visible light semiconductor lasers and in solar cells [1,4,5]. Recently, some of these compounds show room temperature ferromagnetism (FM) and half metallicity after suitable doping with transition metal ions which is an interesting aspect from spintronics point of view [6,7]. These II–IV–V_2 compounds resemble with the III–V zinc blended binary semiconductors but contain two different cations instead of one in binary. The former structure is logical extension of the latter with some interesting structural anomalies [8,9]. First of all, Goodman [10] investigated the II–IV–V_2 compounds and reported chalcopyrite ($CuFeS_2$) structure for these. A room temperature photoluminescence found in $ZnGeAs_2$ [11] proved its significant device potential and boosted the research activities in this type of compounds. Shay et al. [12] analyzed the electroreflectance spectra of $CdSiAs_2$ and $CdGeAs_2$. They characterized these compounds by large built in compressions and internal displacement of As anions due to difference in the cation covalent radii ($r_{Cd} > r_{Si}, r_{Ge}$) and found a direct band gap for both.

On the theoretical front, Continenza et al. [8] calculated the structural and electronic properties of some II–IV–V_2 type chalcopyrite compounds using the FPLAPW and ab-initio pseudopotential methods and examined the variation of band gap with internal distortion parameter (u). Zopal et al. [13] predicted the structural, thermodynamic and electronic properties of $CdGeAs_2$ using linear combination of atomic orbitals (LCAO) method and studied the effect of pressure on electronic band structure. Limpijumnong and Lambrecht [14] carried out the first principle calculation of $CdGeAs_2$ using linear muffin tin orbital (LMTO) method in full potential (FP) and atomic sphere approximations including spin orbit coupling. The main emphasis of that study was to predict the band gap and energy band splitting near the

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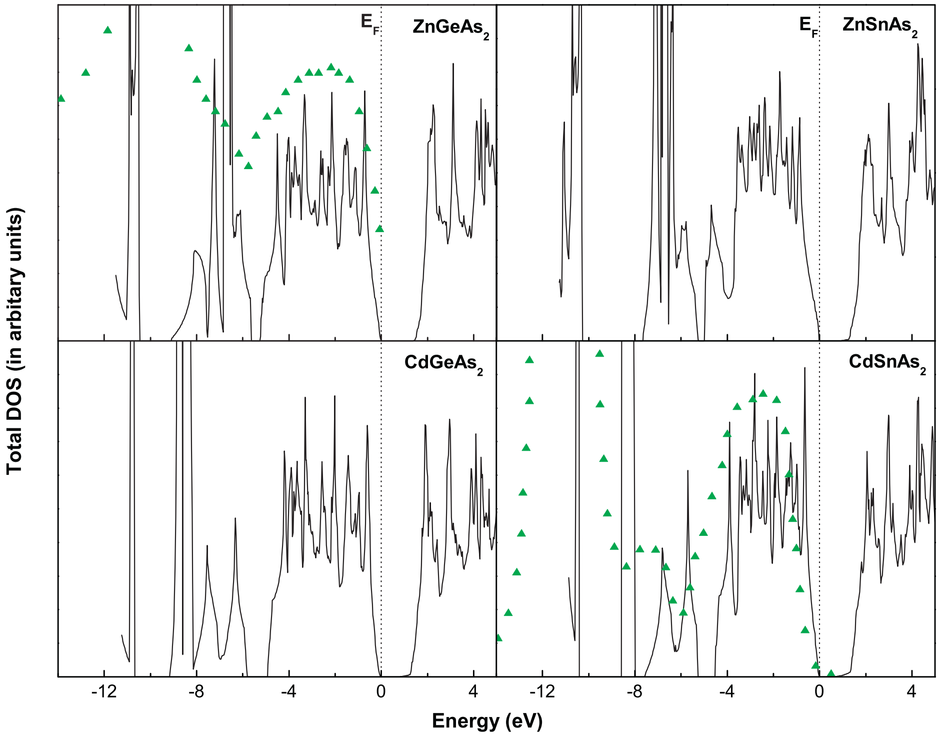

Fig. 1. Calculated total DOS of ABAs$_2$ (A = Zn, Cd; B = Ge, Sn) compounds (solid lines) and comparison with the available experimental XPS data (small triangles).

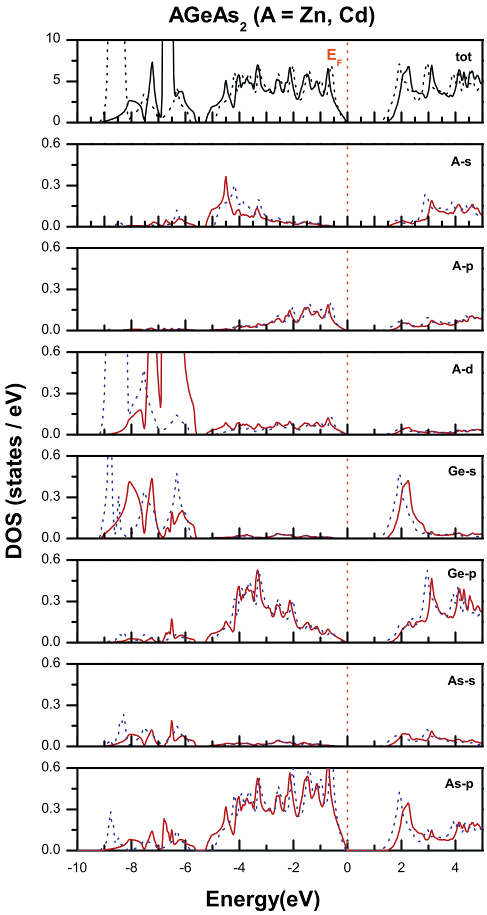

Fig. 2. Calculated partial DOS of AGeAs$_2$ (A = Zn, Cd) compounds. The solid and dotted lines show the contributions of individual states of ZnGeAs$_2$ and CdGeAs$_2$ compounds, respectively.

fundamental gap. The band structure calculation of CdBC$_2$ (B = Si, Ge, Sn; C = P, As) pnictides at ambient pressure and its variation with pressure using LMTO and projector augmented wave (PAW) methods with in LDA and Generalized Gradient Approximation (GGA), respectively, were reported by John [15]. She showed that band gap decreases on increasing pressure which is due to the reduction in p–d interaction between Cd and B atom.

After reviewing the literature, we have observed that the band structure of pnictide compounds is sensitive to the local environment of constituent atoms. Moreover, the band structure parameters may be principle for the prediction of optical and opto-electronic properties of these compounds. Therefore, the aim of present study to investigate the electronic properties of ZnGeAs$_2$ and to access the effect of changing local environment on these properties by substituting cation (Zn or/and Ge) with corresponding next group element. The paper is organized as follows: brief description of computational details is outlined in Section 2. The analysis of electronic properties and band structures is described in Section 3. In the final section, we summarize the results and conclude.

2. Computational details

The unit cell of ternary ABC$_2$ type compounds in chalcopyrite structure (space group, $I\bar{4}2d$) contains two formula units (eight atoms) such that the A atom is present at (0,0,0), B atom is at (1/2,1/2,0) and C atom is situated at $(u,1/4,1/8)$. Here the parameter u represents the displacement of anions from the ideal tetrahedral site. Each cation (A or B) is connected by tetrahedron of anion (C) whereas each anion (C) is also associated to four similarly arranged cations (two A and two B).

In order to compute electronic band structure of these ternary compounds, we have employed FPLAPW method which is based on DFT [16] and is implemented in WIEN2k code [17]. The exchange and correlation (XC) effects were taken into account by using modified Becke–Johnson potential (mBJ) [18] as coupled with Local