Journal of Alloys and Compounds 518 (2012) 74–79

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

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

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ARTICLE INFO

Article history:
Received 21 September 2011
Received in revised form
17 December 2011
Accepted 25 December 2011
Available online 31 December 2011

PACS:
71.15.Mb
71.20.Nr
71.22.+i

Keywords:
Band structure
DFT
FPLAPW method
Chalcopyrite
mBJ

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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doi:10.1016/j.jallcom.2011.12.129

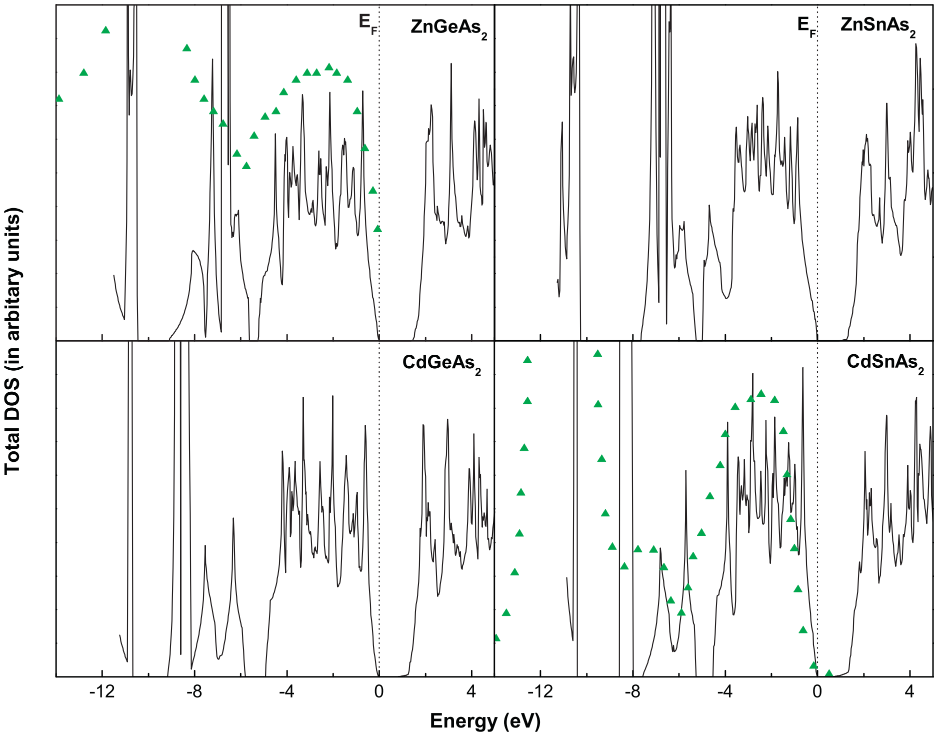

Fig. 1. Calculated total DOS of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds (solid lines) and comparison with the available experimental XPS data (small triangles).

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 optoelectronic 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

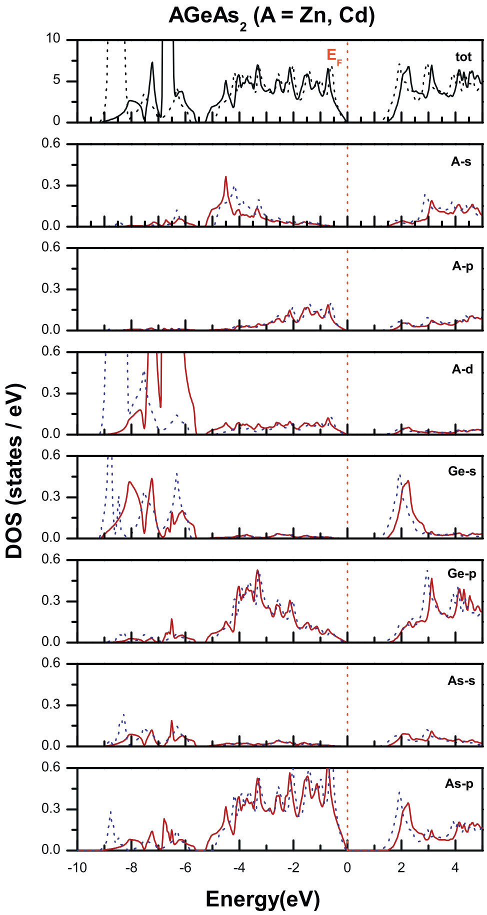

Fig. 2. Calculated partial DOS of $AGeAs_2$ (A = Zn, Cd) compounds. The solid and dotted lines show the contributions of individual states of $ZnGeAs_2$ and $CdGeAs_2$ compounds, respectively.

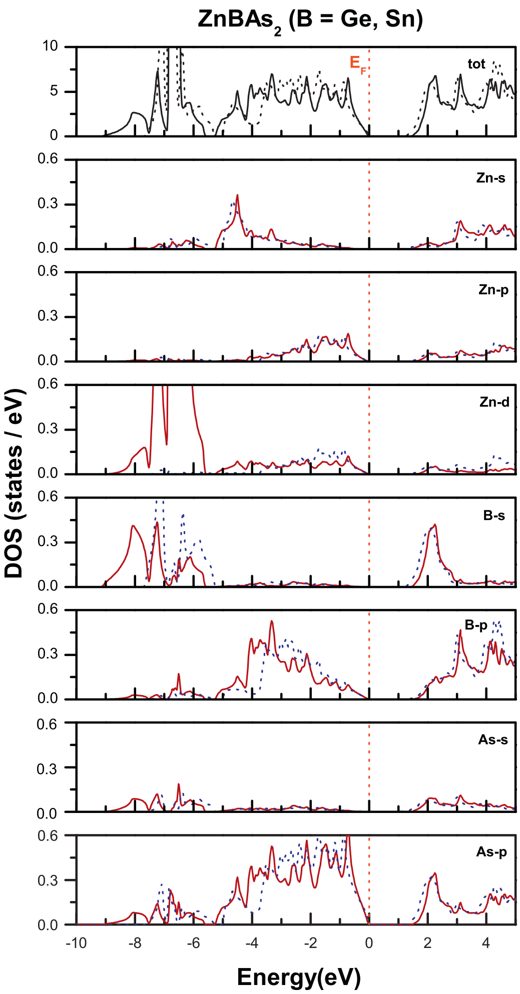

Fig. 3. Calculated partial DOS of $ZnBAs_2$ (B = Ge, Sn) compounds. The solid and dotted lines show the contributions of individual states of $ZnGeAs_2$ and $ZnSnAs_2$ compounds, respectively.

Density Approximation (LDA). In FPLAPW calculations, the core states are treated fully relativistically where as for the valence states, a semirelativistic calculation is performed. The radius of MT spheres (R_{MT}) values for Zn, Cd, Ge, Sn, and As atom were taken to be 2.2, 2.5, 2.3, 2.5 and 2.3 a.u., respectively. The plane wave cut off parameters were decided by $R_{MT}k_{max} = 7$ (where k_{max} is the largest wave vector of the basis set) and $G_{max} = 12$ a.u.$^{-1}$ for Fourier expansion of potential in the interstitial region. The k-space integration has been performed using the modified tetrahedron method [19]. The self consistency is obtained by 405 k-points in the irreducible wedge of the brillouin zone (IBZ) for all compounds where the total energy converges to less than 10^{-4} Ry.

3. Results and discussion

The modified Becke–Johnson potential (mBJ) as proposed by Tran and Blaha [20] reproduces very well the step structure and derivative discontinuity of the exact exchange potential, which is an important result because only the semilocal quantities are used. So this semilocal orbital independent mBJ potential could catch the essentials of orbital dependent potentials (hybrid functionals) and predicts the energy bands more accurately such that calculated band gaps of the materials comes out in good agreement with experiments [21,22]. That is why, the XC potential is selected in such a manner. In order to investigate the effect of

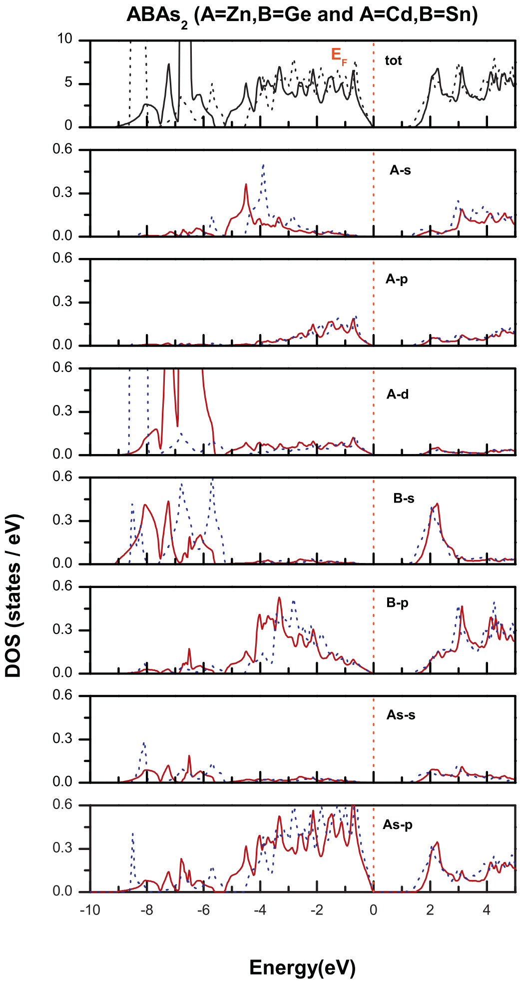

Fig. 4. Calculated partial DOS of $ABAs_2$ (A = Zn, B = Ge and A = Cd, B = Sn) compounds. The solid and dotted lines show the contributions of individual states of $ZnGeAs_2$ and $CdSnAs_2$ compounds, respectively.

Table 1
Experimental lattice constants (a,c) with internal parameter (u) of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds and their band gap using mBJLDA formalism.

Compounds	Lattice const. (Å)	E_g (eV)		
		mBJLDA	Others	Expt.
$ZnGeAs_2$	$a = 5.671^a$ $c = 11.151$ $u = 0.25$	1.27	0.03^b	1.07^d 1.15^e
$CdGeAs_2$	$a = 5.945^a$ $c = 11.212$ $u = 0.28$	0.69	0.32^c 0.12^c	0.66^d 0.57^e
$ZnSnAs_2$	$a = 5.851^a$ $c = 11.702$ $u = 0.232$	0.84	0.18^b	0.76^d 0.75^e
$CdSnAs_2$	$a = 6.10^a$ $c = 11.92$ $u = 0.262$	0.51	0.12^c 0.10^c	0.32^d 0.26^e

[a] Ref. [22].
[b] Ref. [26].
[c] Ref. [15].
[d] Ref. [25].
[e] Ref. [1].

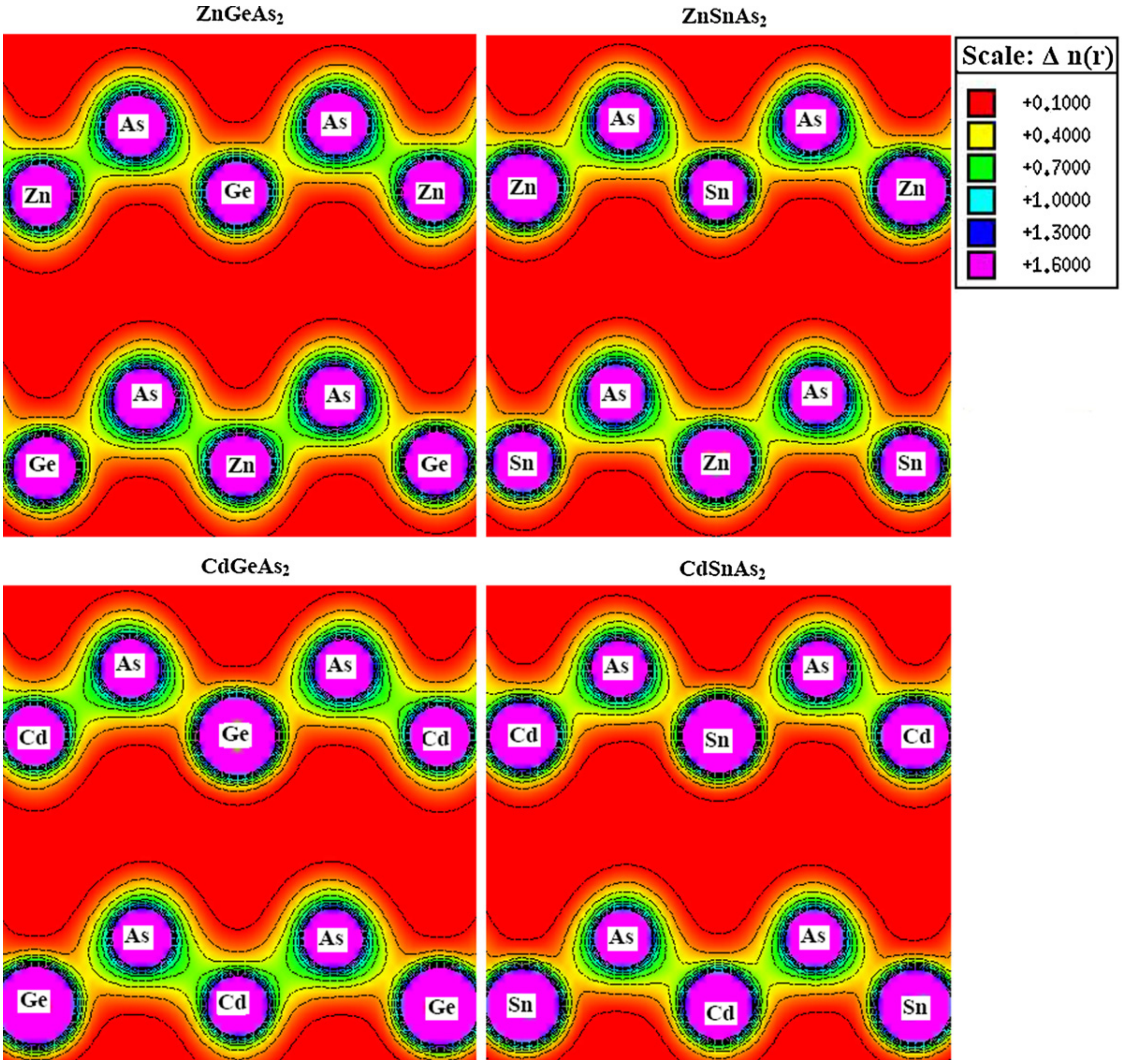

Fig. 5. Total valence electron charge density, $n(r)$ in a (1 1 0) plane in units of $e/Å^3$ for $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds.

changing cation(s) in $ZnGeAs_2$, the first principle calculations of present ternary $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds have been performed at corresponding experimental lattice constants [1,23] as listed in Table 1. First of all, calculated total density of states (DOS) of these compounds with available XPS spectra are presented in Fig. 1. Here, total DOS of $ZnGeAs_2$ and $CdSnAs_2$ compounds are in accordance to the measured XPS data [24,25]. The total DOS of all compounds are generic in nature and show a band gap at Fermi level (E_F). A general observation from the figure is that the band gap decreases with the substitution of either one or both cations (i.e. Zn or/and Ge) in reference compound, $ZnGeAs_2$.

For deep analysis and comparison of the trends observed in DOS by changing cations accordingly, the muffin-tin projected partial DOS for parent ($ZnGeAs_2$) and cation substituted compounds are shown in Figs. 2–4. In $ZnGeAs_2$ (Fig. 2), Zn-d states are localized deeper in valence band along with Ge-s states from −7.5 eV to −5.6 eV, showing no effective role to decide the magnitude of semiconducting band gap. The next manifold band from −5.2 eV to valence band maxima (VBM) is mostly derived from As-p and Ge-p states with a small contribution of Zn-s and -p states. The conduction band minimum mainly contains Ge-s and p states hybridized with As-p states. The Zn-s and As-s states have negligible contribution in both VB and CB. $ZnGeAs_2$ has the strongest overlap of s and p states of cations (Zn and Ge) and anion (As), respectively due to small size of Zn and Ge atoms as compared to cations in other compounds. To access the effect of local environment by substituting cation(s) in $ZnGeAs_2$, we have analyzed the DOS as follows:

(i) *Substitution of cation (Zn) by Cd (next group element)*: This substitution results in $CdGeAs_2$ compound. No significant difference in magnitude of total DOS is observed in the vicinity of E_F by this substitution (Fig. 2). The Cd-d states are shifted lower in energy by ∼2.0 eV than Zn-d states in $ZnGeAs_2$. The width of manifold band in the vicinity of E_F is reduced by 0.3 eV w.r.t. reference compound. Like in $ZnGeAs_2$, the upper VB is mainly dominated by Ge-p and As-p whereas CB is constituted by Ge-s,p and As-p states in $CdGeAs_2$. The CB minimum shows blue shift in energy scale as Ge-s and As-p states lie nearer to E_F in $CdGeAs_2$. Thus, a decrease in band gap of this compound is observed w.r.t. $ZnGeAs_2$.

(ii) *Substitution of cation (Ge) by Sn (next group element)*: The DOS of resultant compound ($ZnSnAs_2$) in VB is energetically favorable and no qualitative changes are exhibited as shown in Fig. 3. But the width of the manifold band in upper VB is 0.2 eV smaller in energy than that in $ZnGeAs_2$.The d-bandwidth remains unaltered as d-states are originated from common Zn atom in both compounds. The contribution of cation, Sn-s states increases

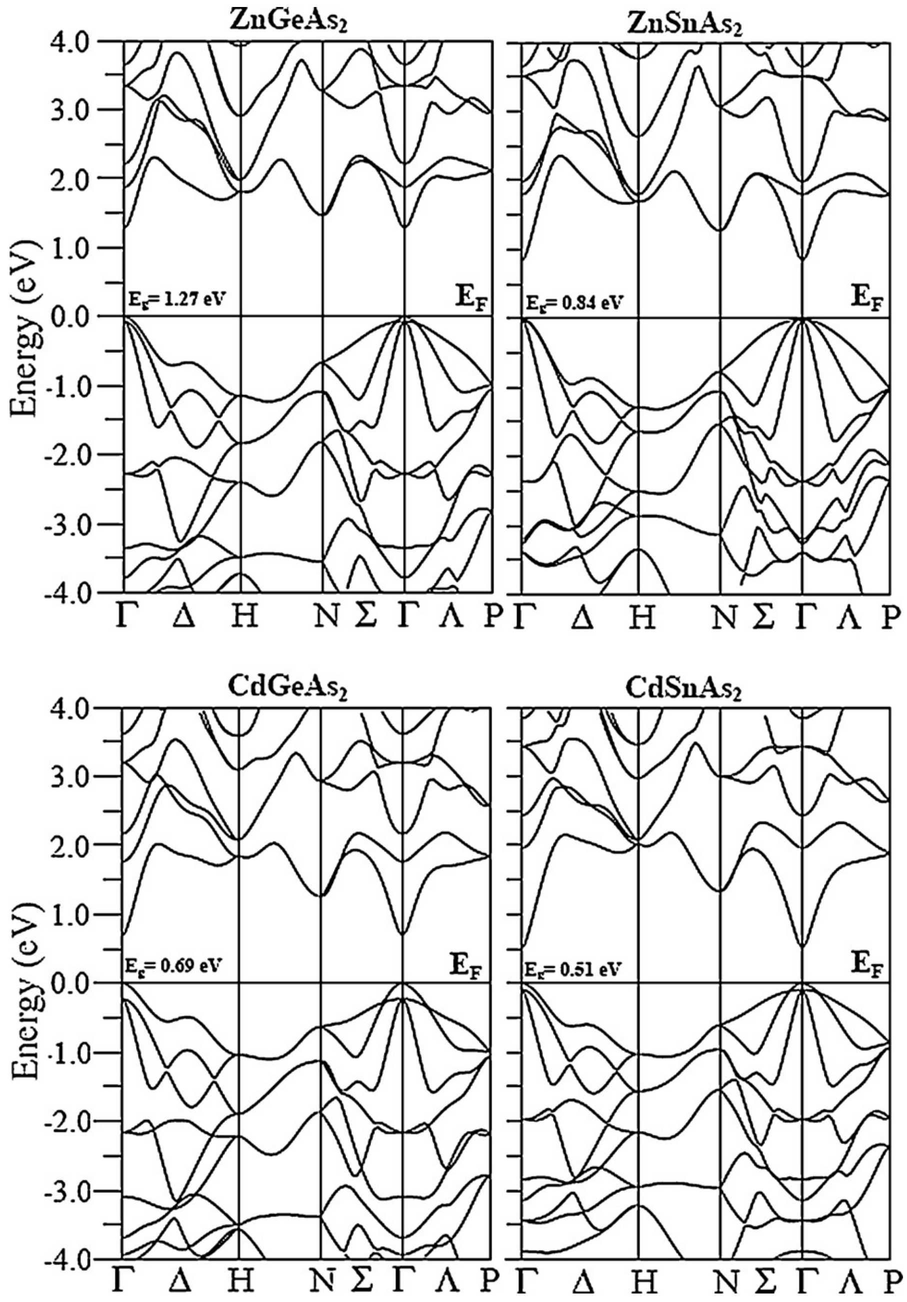

Fig. 6. Calculated band structures of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds. The horizontal line at $E = 0$ eV marks the Fermi level (E_F).

considerably in VB at lower energy than that in $ZnGeAs_2$. The blue shift observed in CB minimum by this substitution is smaller than that in $CdGeAs_2$ (case i). Again, this shifting is due to presence of As-p and Sn-s states in CB at relatively lower energies.

(iii) *Substitution of both cations (Zn and Ge) by Cd and Sn, respectively*: Fig. 4 shows the comparison of total and partial DOS of $ZnGeAs_2$ and $CdSnAs_2$ (resultant compound). In this case, the general shape stays rather unaffected. The width of the manifold band in VB reduces by maximum amount (0.7 eV) in $CdSnAs_2$ as compared to previous two cases. The contribution of Sn-s states becomes more significant. The shifting of d-states towards lower energy is smaller than that in case (i) due to the different local environment established by heavy Sn-atom. Moreover, the blue shift in the CB minimum becomes largest, predicting the lowest band gap for $CdSnAs_2$.

The cations and anions in present compounds are linked with each other by sp^3 hybridization. In these compounds, the characteristics of two bonds, A—As and B—As vary with the change of anyone or both cations (A and B) by their next group element. The electronic charge density contours have been investigated in the (1 1 0) crystallographic plane of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds to analyze the origin of chemical bonds between all atoms as shown in Fig. 5. The contour plot shows tendency of ionic/covalent character for A—As/B—As bond which depends on Pauling electro-negativity difference of the atoms, As (2.18), Ge (2.01), Sn (1.96), Cd (1.69) and Zn (1.65). It is found that majority of charges are accumulated on As-atom and the distribution of electronic charge is spherical which results in the bonding between A—As and B—As atoms. Among the present compounds, Zn—As bond has highest electron negativity difference which governs the strongest ionic tendency for this bond. This ionic character reduces for Cd—As bond slightly. On the other hand, the charge density is largest in between the atoms for Ge—As bond which shows the strong overlap and governs the covalent character. The covalency also decreases by replacing Ge with Sn to form Sn—As bond. Moreover, these plots show that valence electrons from Zn, Ge, Sn and Cd atoms are transferred to As atom.

The calculated band gap for present $ABAs_2$ compounds using mBJLDA are listed in Table 1. Due to the accurate representation of the energy bands, the calculated band gaps of present compounds come out to be in good agreement with corresponding experimental values [1,26]. Even the accuracy of our calculated band gaps w.r.t. experiment is very high as compared to other theoretical results [15,27] for all compounds. The band gaps for studied compounds are found in range 0.51–1.27 eV. Thus, these ternary compounds are characterized as narrow band gap semiconductors and may be very promising for nonlinear optics and optoelectronics particularly up to mid-IR range [28–30]. The band structures of all these compounds are presented in Fig. 6. The common features of these compounds include the observation of direct band gap along the Γ–Γ direction and existence of valence band maximum at E_F. In the band structure of reference compound, $ZnGeAs_2$ (upper left panel of Fig. 6), the manifold-bands ranging from -4 eV to 0 eV in the VB is due to As-p and Ge-p states mainly with a small contribution from Zn-p states. The As-p states are extended up to E_F. Above E_F, the bands at $E > 3$ eV arise from empty As-p and Ge-p states. The overlapping of cations (Zn and Ge)-s and anion (As)-p states, produces the bonding and antibonding states in VB and CB, respectively, resulting the band gap in the compound. $ZnGeAs_2$ has the greatest separation between bonding and antibonding states among present compounds due to the excellent orbital overlap as discussed earlier. Similarly, we can elucidate the semiconducting band structure of other three compounds. Further, the substitution of cation(s) in $ZnGeAs_2$, results in poor overlap of atomic orbitals due to the larger size of substituted cation(s) involved. This leads to smaller separation between bonding and antibonding states which is responsible for lowering the band gap from its initial value in reference compound, $ZnGeAs_2$.

4. Summary and conclusions

To summarize, we have presented a full potential investigation of electronic properties of $ABAs_2$ (A = Zn, Cd; B = Ge, Sn) compounds in chaclopyrite structure from first principles to access the effect of substituting cations in reference compound, $ZnGeAs_2$. The DOS in conduction band (CB) appears to shift towards the E_F with the change of either one or both cations in $ZnGeAs_2$ which accounts for lowering band gaps of resultant compound. The calculated energy band structures show a direct band gap at the Γ point in the brillouin zone for all compounds. These compounds are characterized as narrow band gap semiconductors with a maximum gap (1.27 eV) for $ZnGeAs_2$. The electron density plots show the presence of two bonds, A—As and B—As whose covalent/ionic character depends on Pauling electron-negativity difference of A, B and As atoms. A good agreement of band gaps with experiments indicates that mBJ functional is best suited for calculating electronic structure of semiconductors and insulators.

Acknowledgements

The computation in this work was performed on Kalki server of Inter University Accelerator centre (IUAC), New Delhi, India. One of the authors (M.K. Kashyap) gratefully acknowledges the support from University Grant Commission, New Delhi, India for providing the computational and software facilities under the scheme SAP-I for faculty members. For the author – Ali H. Reshak, the work was supported from the institutional research concept of the project CENAKVA (No. CZ.1.05/2.1.00/01.0024), the grant no. 152/2010/Z of the Grant Agency of the University of South Bohemia. The School of Materials Engineering, University Malaysia Perlis (UniMAP), Perlis, Malaysia.

References

[1] J.L. Shay, J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Pergamon, New York, Electronic Properties and Applications, 1975.

[2] S.N. Rashkeev, S. Limpijumnong, W.R.L. Lambrecht, Phys. Rev. B 59 (1999) 2737.

[3] F.W. Scholl, C.L. Tang, Phys. Rev. B 8 (1973) 4607.

[4] S.C. Abrahams, J.L. Bernstein, J. Chem. Phys. 55 (1971) 796.

[5] A.G. Jackson, M.C. Ohmer, S.R. Leclair, Infrared Phys. Technol. 38 (1997) 233.

[6] M. Novotortsev, S.F. Marenkin, S.A. Varnavskii, L.I. Koroleva, T.A. Kupriyanova, R. Szymczak, L. Kilanski, B. Krzymanska, Russ. J. Inorg. Chem. 53 (2008) 1840.

[7] A. Morozov, L.A. Koroleva, D.M. Zashchirinskii, T.M. Khapaeva, S.F. Marenkin, I.V. Fedorchenko, R.A. Szymczak, B. Krzymanska, Solid State Phenom. 168 (2011) 31.

[8] A. Continenza, S. Massidda, A.J. Freeman, Phys. Rev. B 46 (1992) 10070.

[9] J.E. Jaffe, A. Zunger, Phys. Rev. B 29 (1984) 1882.

[10] C.H.L. Goodman, Nat. Lond. 179 (1957) 828.

[11] F.W. Scholl, E.S. Cory, Mater. Res. Bull. 9 (1974) 1511.

[12] J.L. Shay, E. Buehler, Phys. Rev. B 3 (1971) 2598.

[13] P. Zapol, R. Pandey, M. Seel, J.M. Recio, M.C. Ohme, J. Phys.: Condens. Matter 11 (1999) 4517.

[14] S. Limpijumnong, W.R.L. Lambrecht, Phys. Rev. B 65 (2002) 165204.

[15] R. John, Comp. Mater. Sci. 44 (2008) 106.

[16] M. Weinert, E. Wimmer, A.J. Freeman, Phys. Rev. B 26 (1982) 4571.

[17] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for calculating Crystal Properties, Karlheinz Schwarz, Techn. Universitat Wien, Wien, Austria, 2001, ISBN:3-9501031-1-2.

[18] F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009) 226401.

[19] P.E. Blochl, O. Jepsen, O.K. Andersen, Phys. Rev. B 49 (1994) 16223.

[20] F. Tran, P. Blaha, Phys. Rev. Lett. 102 (2009), 226401(1)–226401(4).

[21] D.J. Singh, Phys. Rev. B 82 (2010) 155145;
D.J. Singh, Phys. Rev. B 82 (2010) 205102.

[22] H. Singh, M. Singh, S. Kumar, M.K. Kashyap, Physica B 406 (2011) 3825.

[23] A.A. Vaipolin, Fiz. Tverd. Tela 15, 1973, 1430 [Sov. Phys. Solid State 15 (1973) 965].

[24] C.V. de Alvarez, M.L. Cohen, L. Ley, S.P. Kowalezyk, F.R. McFeely, D.A. Shirley, R.W. Grant, Phys. Rev. B 10 (1970) 596.

[25] J.C. Rife, R.N. Dexter, P.M. Bridenbaugh, B.W. Veal, Phys. Rev. B 16 (1977) 4491.

[26] V.N. Brudnyi, Semiconductors 43 (2009) 1146.

[27] R. Asokamani, R. Rita, Phys. Stat. Sol. (B) 226 (2001) 375.

[28] Yu. Kogut, A. Fedorchuk, O. Zhbankov, Ya. Romanyuk, I. Kityk, L. Piskach, O. Parasyuk, Alloys Compd. J. 509 (2011) 4264.

[29] Yu. Kogut, A. Fedorchuk, O. Zhbankov, Ya Romanyuk, I. Kityk, L. Piskach, O. Parasyuk, J. Alloys Compd. 509 (2011) 4264.

[30] G.E. Davydyuk, G.L. Myronchuk, I.V. Kityk, S.P. Danylchuk, V.V. Bozhko, O.V. Parasyuk, Opt. Mater. 33 (2011) 1302.