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**Haleem Ud Din, A. H. Reshak,
G. Murtaza, B. Amin, Roshan Ali,
Z. A. Alahmed, J. Chyský, J. Bila &
H. Kamarudin**

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Structural, elastic, thermal and electronic properties of M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds in anti-fluorite structure: first principle calculations

H Ud Din⁴, A H Reshak^{1,2*}, G Murtaza³, B Amin⁴, R Ali⁴, Z A Alahmed⁵, J Chyský⁶, J Bila⁶ and H Kamarudin²

¹New Technologies - Research Center, University of West Bohemia, Univerzitni 8, 306 14 Pilsen, Czech Republic

²Center of Excellence Geopolymer and Green Technology, School of Material Engineering, University Malaysia Perlis, 01007 Kangar, Perlis, Malaysia

³Materials Modeling Lab, Department of Physics, Islamia College University, Peshawar, Pakistan

⁴Materials Modeling Lab, Department of Physics, Hazara University, Mansehra, KPK, Pakistan

⁵Department of Physics and Astronomy, King Saud University, Riyadh 11451, Saudi Arabia

⁶Department of Instrumentation and Control Engineering, Faculty of Mechanical Engineering, CTU in Prague, Technicka 4, 166 07 Prague 6, Czech Republic

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Abstract: First principle calculations of structural, elastic, thermal and electronic properties of M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds in the anti-fluorite type structure are performed within the framework of density functional theory. The lattice constant, bulk modulus, derivative of bulk modulus and ground state energy are calculated. The calculated elastic properties reveal that Sr_2Si , Sr_2Ge , Ba_2Si and Ba_2Ge are classified as brittle, while Sr_2Sn and Ba_2Sn show ductile nature. It is noted that these compounds are elastically stable and the Debye temperature value decreases from Sr to Ba and from top to bottom in group IV-A of periodic table. From electronic charge density plot in the (110) crystallographic plane it is observed that in Sr_2X , Sr shows ionic bond nature with X, while in Ba_2X , Ba forms partially ionic and partially covalent bond with X. The density of states and the electronic band structures are also presented. We have found that these compounds possess narrow and direct band gaps. The values of the energy gaps obtained by using the modified Becke–Johnson approach are better than the values obtained from the generalized gradient approximation.

Keywords: Anti-fluorite; Density functional theory; Modified Becke–Johnson approach; Elastic; Thermal

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1. Introduction

The orthorhombic crystals of Zintl compounds M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) with space group #62-Pnma [1, 2] have been considered as potential candidates due to their several applications and wide use as electronic materials [3] and topological insulator [4]. These materials exhibit semiconducting nature and are frequently used for

optoelectronic and energy-band applications [5]. Some compounds of this group like Be_2C and Mg_2X ($X = \text{Si}$, Ge , Sn) have also been observed in anti-fluorite type structure and significantly used in forming the simplest metal–semiconductor hybrid materials [6]. The narrow band gap of the anti-fluorite materials make them useful for many technological applications such as infrared detectors in the wavelength 1.2–1.8 μm relevant for optical fibers [7, 8]. Hu et al. [1] have reported that the single phase $M_2\text{Si}$ ($M = \text{Mg}$, Ca , Sr) silicides have been grown using Si substrates, by thermal treatment of the substrates in the vapors of the metallic sources. They have investigated the electronic structures and optical properties of the silicides.

*Corresponding author, E-mail: maalidph@yahoo.co.uk

Using the first-principles total-energy calculation program in pseudopotential schemes with plane-wave basis functions, they have calculated the electronic band structures of the silicides.

Like other materials of the same group, M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) semiconductors can have anti-fluorite type structure with space-group #225 (Fm-3 m). This structural transformation changes the crystal structure by changing coordination of the X^{IV} atom from fourfold coordinated in the diamond structure (e.g. Si) to eightfold coordinated in the anti-fluorite structure (e.g. Mg_2Si) [9, 10]. Since the number of valence electrons does not change in both diamond and anti-fluorite structures, the electronic configuration of molecule is not affected by the structural change. Also, the Bravais lattice remains the same and the two structures possess the same Brillouin zone (BZ) resulting in the same electronic structure. In present paper, the main focus is to present first principle calculations of structural, elastic, thermal and electronic properties of M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds in anti-fluorite type structure using the full potential linear augmented plane wave (FP-LAPW) method.

2. Method of calculation

We carried out first principle calculations of the structural, elastic, thermal and electronic properties of anti-fluorite M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds within the framework of the density functional theory (DFT) [11] using the FP-LAPW [12] method as implemented in Wien2k code [13]. The corresponding DFT calculations were performed using generalized gradient approximation (GGA) [14] and the modified Becke–Johnson (mBJ) exchange correlation potential plus Wu–Cohen version of generalized gradient approximation (mBJ–GGA) methods. The mBJ exchange potential [15] was developed from a semi-local exchange potential proposed by Becke and Johnson (BJ-exchange potential). In the GGA, the exchange correlation potential was treated for the self consistent calculations [14]. The modified Becke–Johnson exchange potential (TB-mBJ) yielded very accurate electronic band structure and band gap for various semiconductors and insulators (e.g., *sp* semiconductors, noble-gas solids, and transition-metal oxides) [15–22]. Band structure calculations were presented using GGA and mBJ methods. It was found that the band gaps calculated within mBJ was closer to the experimental value, therefore we focused on mBJ technique.

In the FP-LAPW method, the wave function, charge density and potential were expanded in spherical harmonic functions inside muffin-tin spheres and by a plane-waves basis set in the interstitial region. For anti-fluorite M_2X

Table 1 Calculated lattice constant $a_0(\text{\AA})$, bulk modulus $B_0(\text{GPa})$, its pressure derivatives B' , total ground state energy $E_0(\text{Ry})$ for anti-fluorite M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds

Compounds	$A_0(\text{\AA})$	$B_0(\text{GPa})$	B'	$E_0(\text{Ry})$
Sr_2Si	7.5429	32.89	5.00	-13,296.86
Sr_2Ge	7.5677	27.98	5.00	-16,914.50
Sr_2Sn	7.9666	31.23	5.00	-25,074.06
Ba_2Si	7.8319	23.97	5.00	-33,133.89
Ba_2Ge	7.8685	23.03	5.00	-36,751.53
Ba_2Sn	8.2497	20.99	5.00	-44,911.09

($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds, we chose a plane wave cut-off of $K_{\text{max}} = 7.0/R_{\text{MT}}$. Muffin-tin radii (R_{MT}) values were taken as 2.5 for all compounds. The spherical harmonics in the non-overlapping muffin-tin spheres were expanded up to $l_{\text{max}} = 10$ while charge density was Fourier expanded up to $G_{\text{max}} = 12 (\text{Ryd})^{1/2}$. A mesh of 1,000 k -points in the irreducible Brillouin zone (IBZ) were used. The self consistent calculations were converged since the total energy of the system is stable within 10^{-5} Ry.

3. Results and discussion

3.1. Structural properties

Using the volume optimization method, the structural properties of anti-fluorite M_2X ($M = \text{Sr}$, Ba and $X = \text{Si}$, Ge , Sn) compounds have been computed. To perform volume optimization, the total energy of the unit cell with respect to the volume of unit cell has been minimized and calculated by fitting to the Murnaghan equation of state (EOS) [23]. The lattice constant a_0 , bulk modulus B_0 , its pressure derivatives B' and ground state energies E_0 are evaluated using GGA method. The lattice constant increases from Si to Sn for both Sr_2X and Ba_2X compounds. Moreover, increase in lattice constant from Sr to Ba is also observed for M_2X compounds. As the bulk modulus B_0 gives information about crystal rigidity and the large value of B_0 is responsible for high crystal rigidity. But from Table 1, it is clear that the anti-fluorite M_2X are soft semiconductors.

3.2. Elastic properties

Elastic properties are important in order to study binding characteristics between the adjacent atomic plane, specific heat, Debye temperature, thermal expansion and many other properties. The knowledge of elastic constants C_{ij} is useful and valuable to obtain information about the

Table 2 Predicted elastic constants (C_{11} , C_{12} , C_{44}), Voigt, Reuss and average Shear modulus (G_V , G_R and G), B/G ratio, anisotropy constant (A), Poisson's ratio (ν), Young's modulus (Y), density ρ (g/cm^3), thetransverse, longitudinal and average elastic wave velocities (V_t , V_l and V_m in m/s) and Debye temperature (θ_D in K) for anti-fluorite M_2X ($M = \text{Sr, Ba}$ and $X = \text{Si, Ge, Sn}$) compounds

	Compounds					
	Sr ₂ Si	Sr ₂ Ge	Sr ₂ Sn	Ba ₂ Si	Ba ₂ Ge	Ba ₂ Sn
C_{11}	54.84	59.84	43.24	51.47	42.36	37.46
C_{12}	18.27	21.67	19.73	9.86	13.51	12.89
C_{44}	19.69	19.11	16.57	13.18	13.87	11.09
G_V	19.13	19.10	14.64	16.23	14.09	11.57
G_R	19.10	19.09	14.24	15.44	14.08	11.54
G	19.12	19.095	14.44	15.83	14.085	11.55
B/G	1.72	1.47	2.16	1.51	1.63	1.82
A	1.077	0.99	1.41	0.63	0.96	0.90
V	0.26	0.22	0.299	0.23	0.25	0.27
Y	48.05	46.66	37.53	38.85	35.12	29.32
ρ	1.576	1.902	1.934	2.093	2.368	2.327
V_t	3,483	3,168	2,732	2,750	2,507	2,189
V_l	6,082	5,300	5,109	3,282	3,008	2,796
V_m	3,866	3,506	3,051	2,888	2,636	2,332
θ_D	242	219	181	174	158	134

anisotropic character of the bonding, the structural stability and stiffness of materials. Since anti-fluorite M_2X ($M = \text{Sr, Ba}$ and $X = \text{Si, Ge, Sn}$) compounds have cubic symmetry. To know and explain its mechanical behavior, we have calculated only three independent elastic parameters C_{11} , C_{12} and C_{44} as given in Table 2. Since C_{11} describes unidirectional compression along principal crystallographic direction and its value greater than C_{44} (given in Table 2) predicts that these compounds offer a weak resistance to the pure shear deformation as comparable to resistance to the unidirectional compression. The conventional mechanical stability conditions of elastic constants in cubic crystals are given as:

$$\frac{1}{3}(C_{11} + 2C_{12}) > 0; C_{44} > 0; \frac{1}{2}(C_{11} - C_{12}) > 0; C_{12} < B < C_{11} \quad (1)$$

It is clear from Table 2 that the elastic constants satisfy these stability criteria and are elastically stable. In industrial sciences the elastic anisotropy constant (A) plays vital role for detection of micro cracks in materials, which is defined as

$$A = 2C_{44}/(C_{11} - C_{12}) \quad (2)$$

For $A = 1$, the material is completely isotropic, it is otherwise anisotropic for any value greater or less than unity. From Table 2, it can be seen that all compounds having elastic anisotropy value less or greater than unity show anisotropic behavior.

The Voigt and Reuss [24] shear moduli for the cubic structure are defined as:

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (3)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + (C_{11} - C_{12})} \quad (4)$$

Thus shear modulus G is written as:

$$G = \frac{(G_V + G_R)}{2} \quad (5)$$

The Young's modulus (Y) and Poisson's ratio (ν) related to the bulk modulus B and the shear modulus G can be expressed as:

$$B_V = B_R = \frac{(C_{11} + 2C_{12})}{3} \quad (6)$$

$$Y = \frac{9BG}{(3B + G)} \quad (7)$$

$$\nu = \frac{(3B - 2G)}{2(3B + G)} \quad (8)$$

Young's modulus (Y) is a measure of the stiffness of the material and hence, large value of Y for these compounds is responsible for high stiffness. Also Poisson's ratio (ν) provides information about the bonding forces than any of the other elastic property [25]. The upper and lower limits for central force in solids are 0.5 and 0.25 respectively. In Table 2, the calculated Poisson's ratio (ν) predicts that the force is central for Sr₂Si, Sr₂Sn, Ba₂Ge and Ba₂Sn

Fig. 1 Electron charge density for; (a) Sr_2X ; and (b) Ba_2X ($\text{X} = \text{Si}, \text{Ge}, \text{Sn}$) compounds

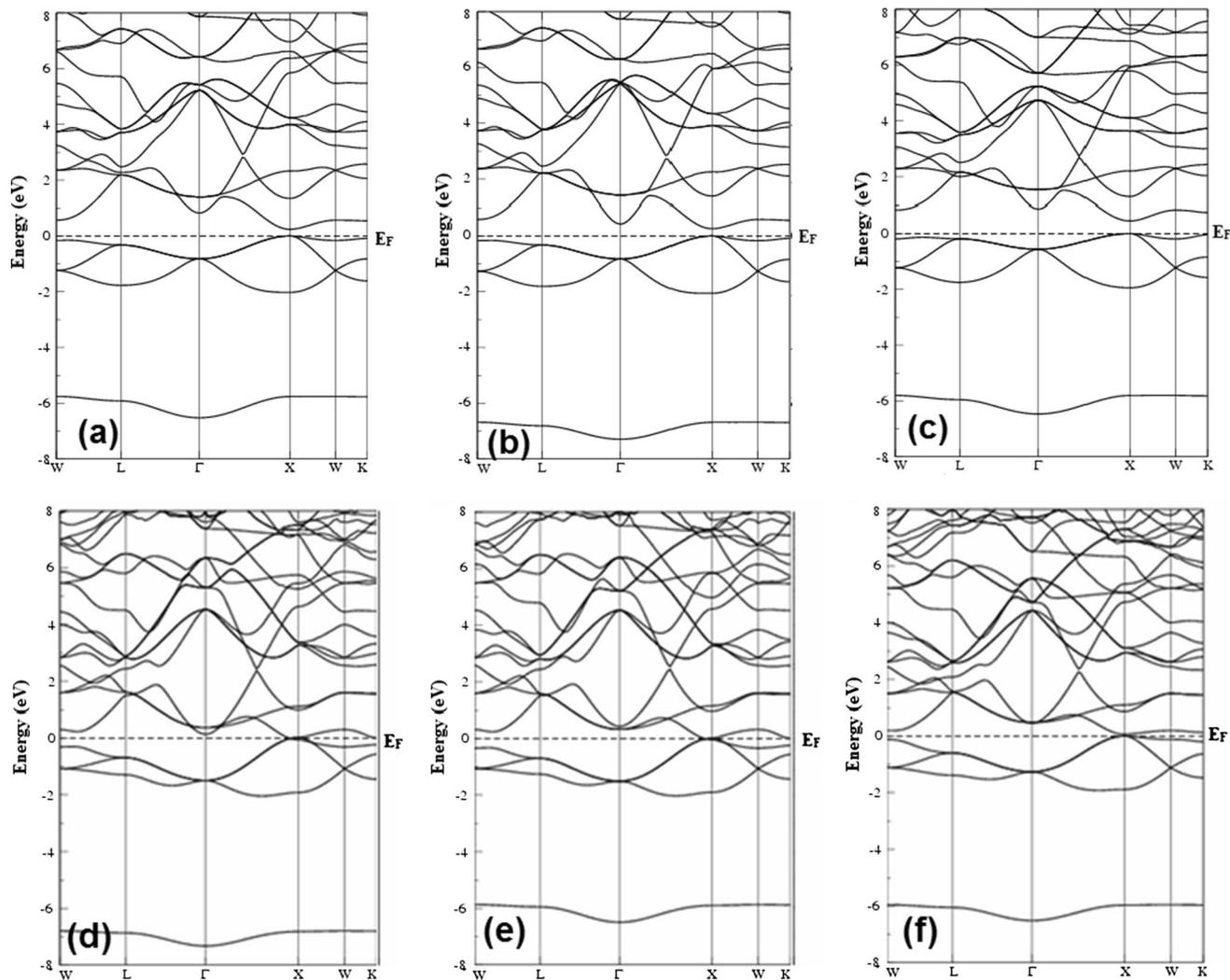
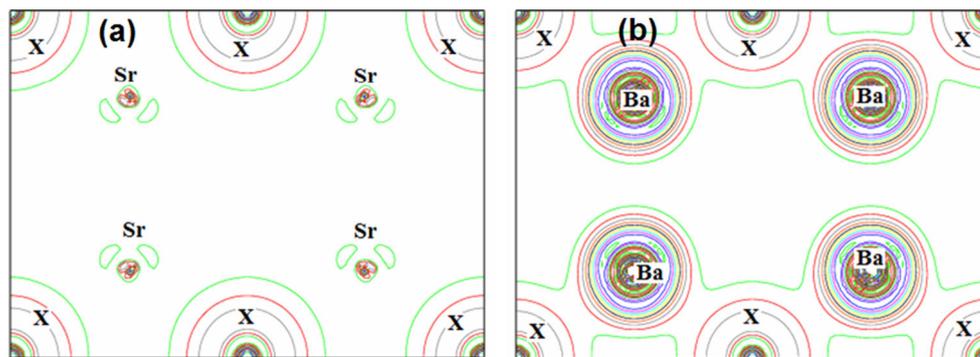


Fig. 2 Calculated band structures using GGA; (a) Sr_2Si ; (b) Sr_2Ge ; (c) Sr_2Sn ; (d) Ba_2Si ; (e) Ba_2Ge ; (f) Ba_2Sn

compounds and non-central for Sr_2Ge and Ba_2Si compounds. According to Pugh's [26] ratio, higher B/G ratio is associated with ductile nature, while smaller B/G ratio corresponds to brittle behavior of the material. The critical number take apart ductile from brittle is 1.75; i.e., material behaves in a ductile behavior for $\text{B/G} > 1.75$,

otherwise it behaves in a brittle manner. Our results show that B/G ratio is 1.72, 1.47, 1.51 and 1.63 for Sr_2Si , Sr_2Ge , Ba_2Si and Ba_2Ge respectively and then classifying these compounds as brittle. On the other hand, B/G ratio for Sr_2Sn and Ba_2Sn are 2.16 and 1.82 respectively, making these compounds ductile.

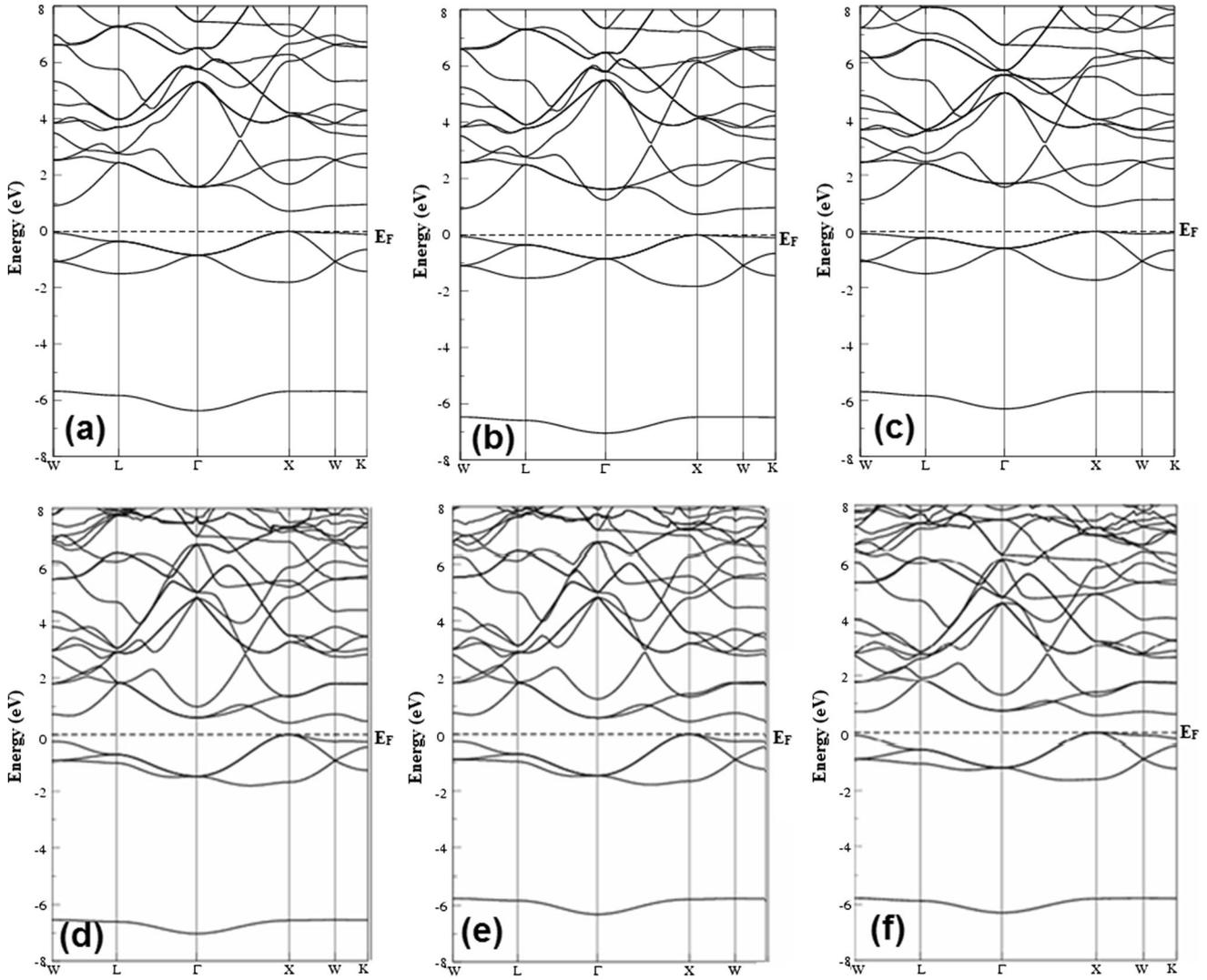


Fig. 3 Calculated band structures using mBJ; (a) Sr_2Si ; (b) Sr_2Ge ; (c) Sr_2Sn ; (d) Ba_2Si ; (e) Ba_2Ge ; (f) Ba_2Sn

3.3. Thermal properties

Debye temperature (θ_D) is associated with upper limit of the phonon frequency in a crystal lattice and can be calculated using following equation [27, 28]:

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{\rho N_A}{M} \right) \right]^{1/3} V_m \quad (9)$$

where h and k are Plank and Boltzmann constants respectively, n is the number of atoms per formula unit, N_A is Avogadro's number, ρ is density of compound, M is molecular mass per formula unit, V_m is average wave velocity [27, 28], which is given by:

$$V_m = \left[\frac{1}{3} \left(\frac{2}{V_t^3} + \frac{1}{V_l^3} \right) \right]^{-1/3} \quad (10)$$

where V_l and V_t , are the longitudinal and transverse elastic wave velocities respectively, which are obtained from Navier's equations [27, 29]:

$$V_l = \left(\frac{3B + 4G}{3\rho} \right)^{1/2} \quad (11)$$

$$V_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (12)$$

The calculated density, average, longitudinal, transverse elastic wave velocities and Debye temperature are given in Table 2. To date, no experimental or theoretical data for the elastic stiffness are available in the literature to be compared with our theoretical results. It can be seen from Table 2, that in M_2X compounds, the value of Debye temperature (θ_D) decreases from Sr to Ba and also from top to bottom of group IV-A of periodic table.

Table 3 Calculated energy gap (E_g at X-symmetry point) for anti-fluorite M_2X ($M = \text{Sr, Ba}$ and $X = \text{Si, Ge, Sn}$) compounds using GGA and mBJ methods

Compounds	GGA	mBJ
Sr_2Si	0.24	0.72
Sr_2Ge	0.26	0.73
Sr_2Sn	0.45	0.89
Ba_2Si	0.002	0.42
Ba_2Ge	0.01	0.45
Ba_2Sn	0.06	0.59

3.4. Electronic properties

We have presented visual contour plot of charge density in (110) crystallographic plane for Sr_2X and Ba_2X ($X = \text{Si, Ge, Sn}$) compounds in Fig. 1(a) and 1(b) respectively. For Sr_2X compounds, Sr and X are cation and anion respectively; hence ionic bond is observed as no sharing of charge occurs between anion and cation. On the other hand, Ba form partially ionic and partially covalent bond with X in Ba_2X , as shown in Fig. 1.

We have performed first principle calculation for the electronic band structure using GGA and mBJ methods for anti-fluorite M_2X ($M = \text{Sr, Ba}$ and $X = \text{Si, Ge, Sn}$) compounds as shown in Fig. 2(a)–2(f) and 3(a)–3(f), respectively. It is clear from Figs. 2(a)–2(f) that the calculated band gaps for Sr_2X compounds are found to be very narrow while it is near to zero for Ba_2X compounds using GGA. On the other hand, slightly large narrow and direct band gaps are obtained at X-symmetry point of the Brillion zone using mBJ method (as shown in Fig. 3). It is observed that the mBJ yields better band gap's value than GGA. For both Sr_2X and Ba_2X , we notice an increase in band gap, when one moves from Si, Ge to Sn. While the band gap decreases with moving from Sr to Ba in M_2X due to larger size of Ba than Sr. In Table 3, we have listed the calculated values of the band gaps.

The calculated total and partial density of states (DOS) plots for anti-fluorite Sr_2X and Ba_2X ($X = \text{Si, Ge, Sn}$) compounds using mBJ method are shown in Figs. 4(a)–4(c) and 5(a)–5(c), respectively. For Sr_2X compounds, the valence bands mainly consist of two regions; the first region is found in the energy range from -5.7 eV to -6.4 eV for both Sr_2Si and Sr_2Sn compounds, which are dominated by Si-3s and Sn-5s states respectively. While for Sr_2Ge compound, the first region occurs in the energy range from -6.4 eV to -7.1 eV and is mainly contributed by Ge-4s state. Second region, located from zero to -1.8 eV is due to Si-3p, Ge-4p and Sn-5p atoms as shown in Fig. 4(a)–4(c).

Similar effect is observed for Ba_2X compounds. It is clear from Fig. 5(a)–5(c) that in the first region (-5.7 eV to -6.4 eV), Si-3s and Sn-5s states are dominant for Ba_2Si

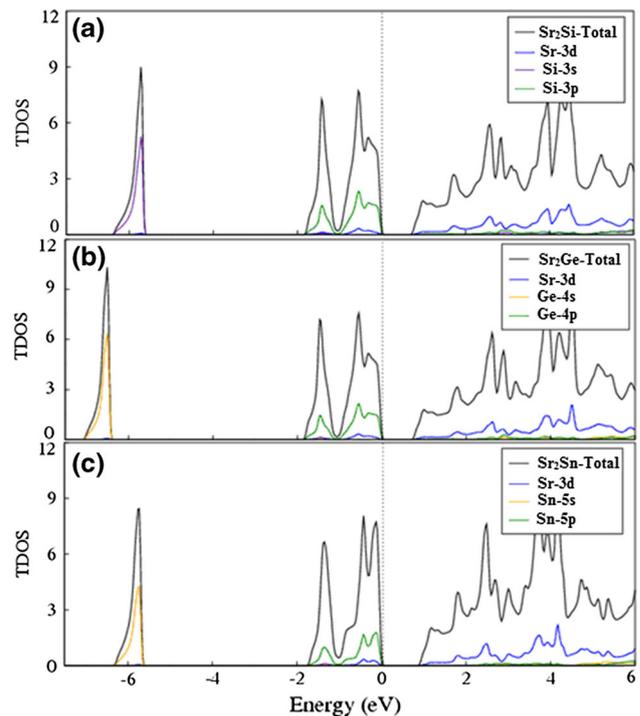


Fig. 4 Calculated mBJ-density of state (DOS) of; (a) Sr_2Si ; (b) Sr_2Ge ; (c) Sr_2Sn

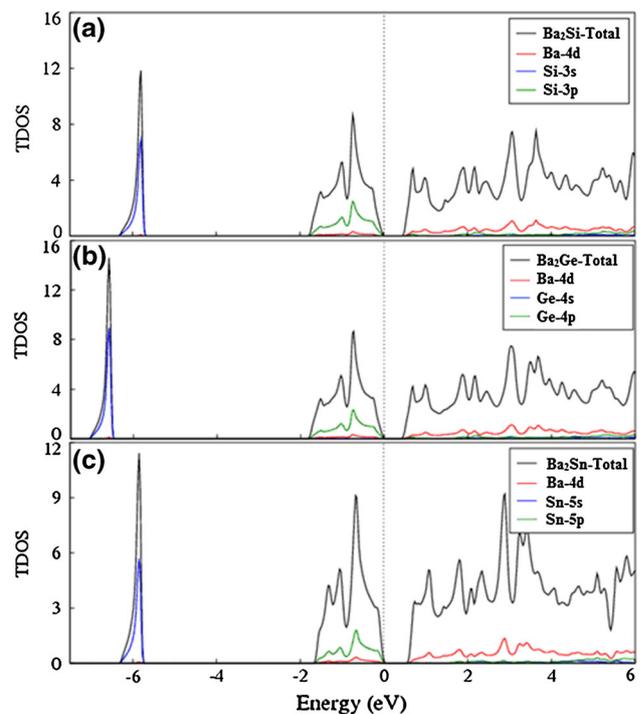


Fig. 5 Calculated mBJ-density of state (DOS) of; (a) Ba_2Si ; (b) Ba_2Ge ; (c) Ba_2Sn

and Ba_2Sn respectively, while Ge-4s state has the main contribution in the energy range -6.5 eV to -7.1 eV. Further, Si-3p and Si-4p states of Ba_2Si and Ba_2Ge

compounds respectively dominate in the second region lying just below the Fermi level from zero to -1.8 eV. Sn- $5p$ state has mainly contributed from zero to -1.6 eV for Ba_2Sn compound. The third region located above Fermi level is dominated by Sr- $3d$ and Ba- $4d$ states as displayed in Figs. 4a–c and 5a–c respectively.

4. Conclusions

In summary, we have performed first principle calculations of structural, elastic, thermal and electronic properties of anti-fluorite M_2X ($M = Sr, Ba$ and $X = Si, Ge, Sn$) compounds by means of DFT. The calculated lattice constant increases with moving from Sr to Ba and also from Si to Sn in M_2X . It is concluded that these compounds are elastically stable. Sr_2Si , Sr_2Ge , Ba_2Si and Ba_2Ge are brittle, while Sr_2Sn and Ba_2Sn are ductile. Also, Debye temperature (θ_D) decreases from top to bottom for M_2X . The electronic charge density contour in the (110) crystallographic plane reveals that Sr form ionic bond with X in Sr_2X while Ba_2X show partially ionic and partially covalent bond nature. The density of states (DOS) and band structure are calculated and discussed in details. The band gap obtained with mBJ is slightly larger than that with GGA, the band gap values increase with moving from Si to Sn for both Sr_2X and Ba_2X , while the values decrease from Sr to Ba for M_2X .

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References

- [1] J Hu, A Kato, T Sadoh, Y Maeda, K N Galkin, T V Turchin and H Tatsuoka *Int. J. Mod. Phys. B.* **24** 3693 (2010)

- [2] B I Sharma, J Maibam, R S Paul, R K Thapa and R K B Singh *Indian J. Phys.* **84** 671 (2010)
- [3] S Brutti, D Nguyen-Manh and D G Pettifor *J. Alloys Compd.* **457** 29 (2008)
- [4] Y Sun, X Q Chen, D Li, C Franchini, S Yunoki, Y Li and Z Fang *Phys. Rev. B* **84** 165127 (2011)
- [5] Y Imai, A Watanabe and M Mukaida *J. Alloy. Compd.* **358** 257 (2003)
- [6] B. Arnaud and M. Alouani *Phys. Rev. B* **64** 033202 (2001)
- [7] A Vantomme et al. *Appl. Phys. Lett.* **70** 1086 (1997)
- [8] F Kalarasse and B Bennecer *J. Phys. Chem. Solids* **69** 1775 (2008)
- [9] D M Wood and A Zunger *Phys. Rev. B* **34** 4105 (1986)
- [10] J Tejada and M Cardona *Phys. Rev. B* **14** 2559 (1976)
- [11] P Hohenberg and W Kohn *Phys. Rev. B* **136** 864 (1964)
- [12] D D Koelling and B N Harmon *J. Phys. C: Solid State Phys.* **10** 3107 (1977)
- [13] P Blaha, K Schwarz, G K H Madsen, D Kvasnicka and J Luitz, *Wien2k, An Augmented Plane Wave Local orbitals program for calculating crystal properties* Karlheinz Schwarz, Techn. Universitat, Wien, Austria, ISBN 3-9501031-1-2(2001)
- [14] J P Perdew, S Burke and M Ernzerhof *Phys. Rev. Lett.* **77** 3865 (1996)
- [15] F Tran and P Blaha *Phys. Rev. Lett.* **102** 226401 (2009)
- [16] G Murtaza and I Ahmad *Phys. B.* **406** 3222 (2011)
- [17] H Ud Din and A H Reshak *Comput. Mater. Sci.* **83** 474 (2014)
- [18] A H Reshak, S Azam, ZA Alahmed and J Chyský *J. Magn. Mater.* **351** 98 (2014)
- [19] B Amin, S Nazir and U Schwingenschlogl *Sci. Rep.* **3** 1705 (2013)
- [20] S A Khan and A H Reshak *Int. J. Electrochem. Sci.* **8** 9459 (2013)
- [21] A H Reshak, H Kamarudin and S Auluk *J. Phys. Chem. B.* **116** 4677 (2012)
- [22] R Ali, S Mohammad, H Ullah, S A Khan, H Ud Din, M Khan and N U Khan *Phys. B* **410** 93 (2013)
- [23] F Birch *J. Geophys. Res.* **83** 1257 (1978)
- [24] M J Mehl, B M Barry and D A Papaconstantopoulos *Intermetallic Compounds: Principle and Practice, Volume 1: Principles* (London: John Wiley and Sons) ed. J H Westbrook and R L Fleischer p 195 (1995)
- [25] B Mayer, H Anton, E Bott, M Methfessel, J Sticht and P C Schmidt *Intermetallics* **11** 23 (2003)
- [26] S F Pugh *Philos. Mag.* **45** 823 (1954)
- [27] Z Sun, S Li, R Ahuja and J M Schneide *Solid. State Commun.* **129** 589 (2004)
- [28] P Wachter, M Filzmoser and J Rebizant *Phys. B.* **293** 199 (2001)
- [29] OL Anderson *J. Phys. Chem. Solids* **24** 909 (1963)