

Structural and electronic properties of $Y_{1-x}Ge_xTe$ ($Y=Sn,Pb$) by DFT

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The structural, electronic, and chemical bonding properties of the Ge doped PbTe and SnTe in the rock salt phase have been calculated by full potential linearized augmented plane wave method within density functional theory. Generalized gradient approximation of Wu and Cohen has been utilized for calculating these properties. With doping of Ge in $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$, the lattice constant reduces linearly as the concentration increases. Also, it is observed that electronic properties of these compounds are affected by varying concentration of doping Ge. The band gap of corresponding compounds varies with respect to the composition, so the electronic properties alter as doping increases. The alloys have direct band gap which varies in the range 0 to 0.19 eV. The alloys $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Sn_xTe$ show covalent bonding nature which enhances by increasing the Ge concentration. As the physical properties vary widely with doping therefore the resulted materials can be used in thermoelectric, optical storage devices, Infrared detectors, Bragg's reflectors and optical devices working in lower frequency regime.

Keywords: Density functional theory, Structural properties, Electronic properties

1 Introduction

IV–VI semiconductors are highly important and promising, when compared with the other family of semiconductors due to their unique and unusual properties. For more than thirty years, these compounds have been the central subject of considerable research work due to the interest in the basic physics of these semiconductors, the technological and commercial applications. IV–VI compounds are successful materials that can be used in thermoelectric, IR radiation, ferroelectric, optical storage devices and other useful applications^{1–3}. Effective thermoelectric semiconductor materials have been developed using small band gap lead chalcogenides. They have complex crystal and electronic structure⁴. The crystalline ternary compounds including $Ge_{1-x}Pb_xTe$, $Ge_{1-x}Sn_xTe$, $PbSrSe$, and $PbEuTe$ are still relatively understood^{5–7}. Now efforts are made to develop efficient semiconductors by annealing new alloys. The efficiency can be increased, by appropriate composition changes e.g., doping, alloying or by engineering techniques. They have been utilized in larger wavelength imaging, diode

lasers. IV–VI semiconductors are also called thermoelectric materials which can also be used for fabricating photovoltaic cells. These can be applied in the direct conversion of thermal energy into electrical energy. Due to this quality these materials have attained high attention for their uses in solid state devices. These devices can be implemented in power generators, heat dissipaters, and thermoelectric coolers⁸. They also applied in pollution control devices and the fields of gas spectroscopy⁹. The doping of Tin (Sn) in PbX ($X= S, Se, Te$) at different concentrations the ternary semiconductors $PbS_{1-x}Se_x$, $Pb_{1-x}Sn_xTe$, $Pb_{1-x}Sn_xSe$, have been experimentally synthesized⁶. These semiconductors have promising applications which are broadly used for photo solar cells and optoelectronic applications, e.g., photovoltaic sensors. These photovoltaic infrared sensors ($Pb_{1-x}Ge_xTe$, $Pb_{1-x}Sn_xSe$, $Sn_xGe_{1-x}Te$, $PbTe$ etc.) are as sensitive as $Hg_{1-x}Cd_xTe$. In this work, we are studying the effect of Ge doping in PbTe and SnTe pure crystals using the first principle technique of density functional theory (DFT). To date, less attention has been paid to investigate the structural and electronic properties of these alloys theoretically.

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Therefore this work will cover the lack of theoretical data on these materials.

2 Computational Details

Present calculations are performed using the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) method¹⁰ as implemented in wien2K package¹¹. The exchange-correlation effects are included by generalized gradient schemes of Wu-Cohen (WC)¹². $R_{MT} * Kmax$ (where R_{MT} is the minimum muffin-tin radii and $Kmax$ gives the magnitude of largest K vector in the plane wave basis) is 7, $Gmax$ (The potential and the charge density Fourier expansion parameter) is taken to be 12, $lmax$ (The valence wave functions inside the atomic muffin-tin-spheres expansion parameter) is 10 and

47 K-points (in the irreducible wedge of the first Brillouin zone (IBZ) has been chosen to obtain self consistent calculations. The self-consistency was achieved up to 0.0001 Ry.

3 Results and Discussion

3.1 Structural properties

The determination of equilibrium structural parameters of $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ was carried out using the total energy calculations as a function of equilibrium volume for binary compounds (at $x = 0, 1$) in the stable rock salt structure. The alloys (at $x = 0.25, 0.50$ and 0.75) have been modeled using the special quasi random structures (SQS)¹³. The calculated total energies as function of volume (shown in Figs 1 and 2) were fitted to the Birch-Murnaghan equation of state¹⁴. The calculated

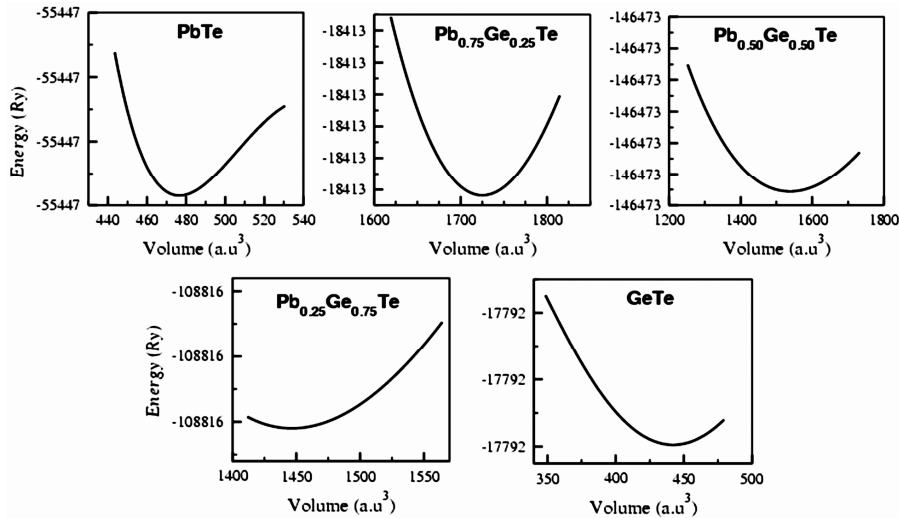


Fig. 1 — Total unit cell energy as function of unit cell volume for $Pb_{1-x}Ge_xTe$

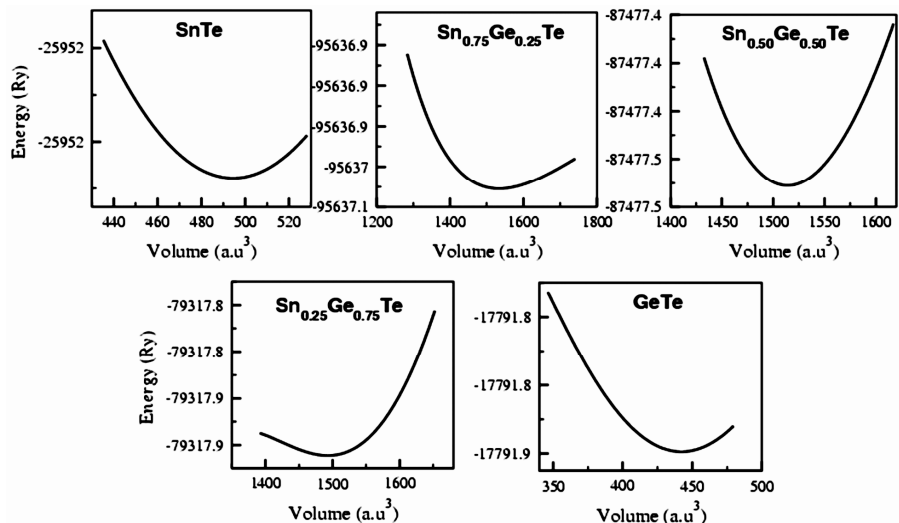


Fig. 2 — Total unit cell energy as function of unit cell volume for $Sn_{1-x}Ge_xTe$

Table 1 — Present calculated structural parameters along with previous experimental and theoretical data

	x	a (Å)			B_o (GPa)		
		Present study	Experimental	Other calculations	Present study	Experimental	Other calculations
$Pb_{1-x}Ge_xTe$	0	6.44	6.47 ^a	6.55 ^c	36.6	39.8 ^c	39.95 ^c
	0.25	6.33			42.27		
	0.50	6.20			48.80		
	0.75	6.06			60.90		
	1	5.925			65.52		
$Sn_{1-x}Ge_xTe$	0	6.43	6.32 ^d	6.31 ^b	52.16		
	0.25	6.214			54.10		
	0.50	6.09			56.86		
	0.75	5.99			67.40		
	1	5.92			65.52		

^aRef. [18], ^bRef. [19], ^cRef. [20], ^dRef. [21]

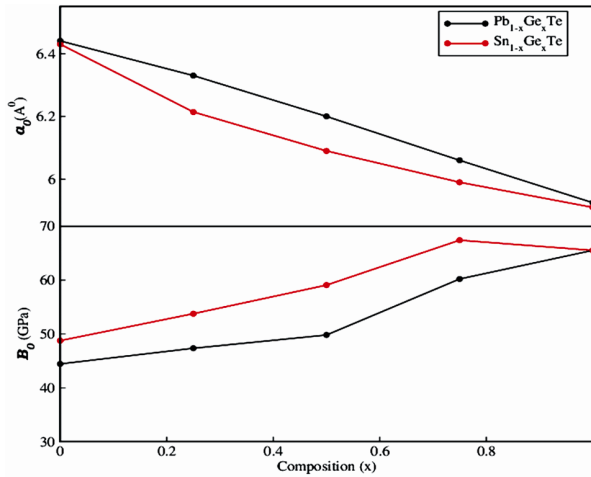


Fig. 3 — Variation of lattice constant (a (Å)) and bulk modulus (B_o (GPa)) as a function of composition for $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$

lattice constants and bulk modulus for binary compounds as well as ternary alloys are given in Table 1 along with the available experimental and theoretical data. The present predicted data shows that the computational results match with the experimental results. In case of alloys, as a rule of thumb, as assumption when atoms are located at ideal sites, the lattice parameters of alloys should have linear relationship with concentration x , which is Vegard's law¹⁵. However, Vegard's law is violated in experimental¹⁶ and theoretical¹⁷ reports for semiconductor alloys. The variation in lattice constant and bulk modulus as function of composition x are plotted and are shown in the Fig. 3. It is seen that lattice constant decreases with increase in concentration x . This is due to the insertion of Germanium-atom with small lattice constant replacing the lead and tin atoms of higher lattice constant. The calculated lattice constants at different compositions x of $Pb_{1-x}Ge_xTe$ alloy show signs of

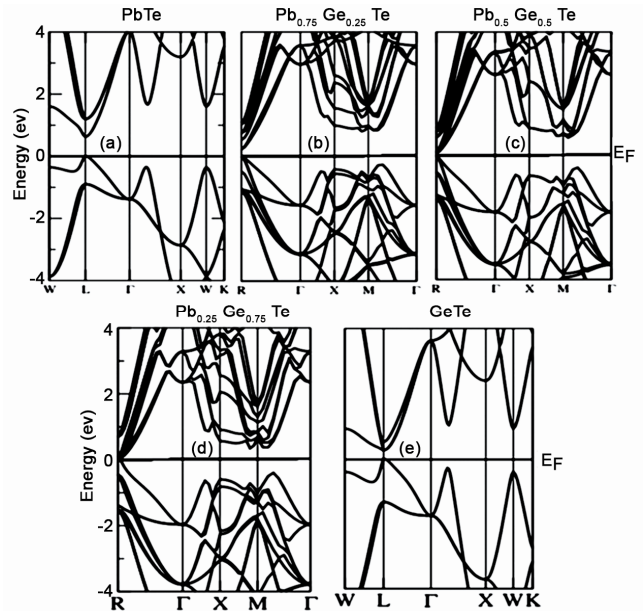


Fig. 4 — Band structures of (a) $PbTe$, (b) $Pb_{0.75}Ge_{0.25}Te$, (c) $Pb_{0.5}Ge_{0.5}Te$, (d) $Pb_{0.25}Ge_{0.75}Te$, and (e) $GeTe$

tendency to Vegard's law with a minor upward bowing parameter of -0.068 Å. In case of $Sn_{1-x}Ge_xTe$, a visible deviation from Vegard's law is predicted with downward bowing parameter of 0.36 Å. In case of bulk modulus, increase is found while increasing the concentration of Ge. Bowing of 1.68 GPa for $Pb_{1-x}Ge_xTe$ and -5.41 GPa for $Sn_{1-x}Ge_xTe$ are predicted. The increase in bulk modulus with increase in concentration is attributed to the hardening of the material while replacing the Pb and Sn atoms by Ge-atom.

3.2 Electronic properties

Band structure of $GeTe$ in the rock salt phase is shown in Fig. 4(a). From figure the minimum value of the conduction band which is represented by CB and

the maximum value of the valance band which is represented by VB, is at L -symmetry point so GeTe is a direct band gap semiconductor of band gap energy 0.2 eV. Similar to GeTe the PbTe also have a direct band gap at L -symmetry point of value 0.8 eV as shown in Fig. 4(b). From Fig. 4(c) it is to be noted that when we doped Ge in $Sn_{1-x}Ge_xTe$ with 25% of the total to have $Pb_{0.25}Ge_{0.75}Te$ the band gap vanishes so that in such case the semiconductor becomes conductor as shown in Fig. 4(d). For $Pb_{0.5}Ge_{0.5}Te$ this band gap is very narrow. It is about 0.05 eV. For $Pb_{0.75}Ge_{0.25}Te$ the band gap becomes a little wide. It is about 0.19 eV. And for PbTe the band gap is 0.8 eV (Fig. 4(e)). So the above semiconductor materials become metallic at doping concentration of $x=0.25, 0.5, 0.75$ and 1 then again there will be different narrow band gap depending upon the doping concentration.

For SnTe the band structure is shown in Fig. 5(a), from figure the minimum value of the CB and the maximum value of the VB is situated at L -symmetry point, so SnTe is a direct band gap semiconductor which has band gap energy 0.07 eV. Similarly GeTe have same L -symmetry point and have direct band gaps of 0.2 eV as shown in Fig. 5(b). From Fig. 5(c) it is to be noted that when we doped Ge in $Sn_{1-x}Ge_xTe$ as 25% of the total that is $Sn_{0.25}Ge_{0.75}Te$ the band gap vanishes so that in this case the semiconductor becomes conductor as shown in Fig. 5(d). For $Sn_{0.5}Ge_{0.5}Te$ this band gap is zero that is why it is still

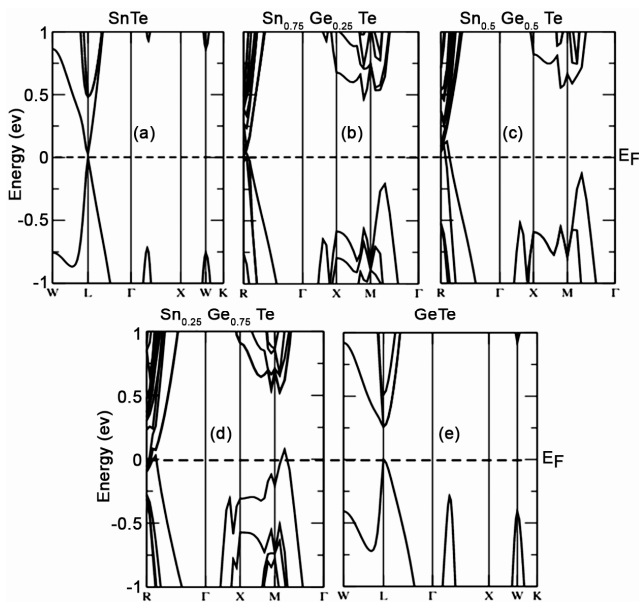


Fig. 5 — Band structures of (a) SnTe, (b) $Sn_{0.75}Ge_{0.25}Te$, (c) $Sn_{0.5}Ge_{0.5}Te$, (d) $Sn_{0.25}Ge_{0.75}Te$ and (e) GeTe

conductor. For $Sn_{0.75}Ge_{0.25}Te$ the energy band gap vanishes and the material becomes conductor, so the above semiconductor materials become metallic at doping concentration of $x=0.25, 0.5$ and 0.75 but at doping concentration of $x=1$ then again there will be narrow band gap depending upon the doping concentration. All the band gap values for different compounds at different doping concentration are mentioned in the Table 2. In the Fig. 6, a graph between energy gap and composition (x) of

Table 2 — Calculated band gap values using GGA, experimental and theoretical values of $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ for concentrations 0, 0.25, 0.50, 0.75 and 1.00. All entities are in eV

Compounds	This work (GGA)	Experimental	Theoretical calculation
PbTe			
E_g	0.8	0.33 ^b , 0.196 ^c	0.649 ^c
$Pb_{0.75}Ge_{0.25}Te$			
E_g	0.19		
$Pb_{0.50}Ge_{0.50}Te$			
E_g	0.05		
$Pb_{0.25}Ge_{0.75}Te$			
E_g	0		
GeTe			
E_g	0.2	0.1 ^d	0.3 ^d
SnTe			
E_g	0.07	0.35 ^a	0.19 ^f
$Sn_{0.750}Ge_{0.250}Te$			
E_g	0		
$Sn_{0.5}Sn_{0.5}Te$			
E_g	0		
$Sn_{0.250}Sn_{0.750}Te$			
E_g	0		

^aRef. [22], ^bRef. [23], ^cRef. [24], ^dRef. [25], ^eRef. [26]

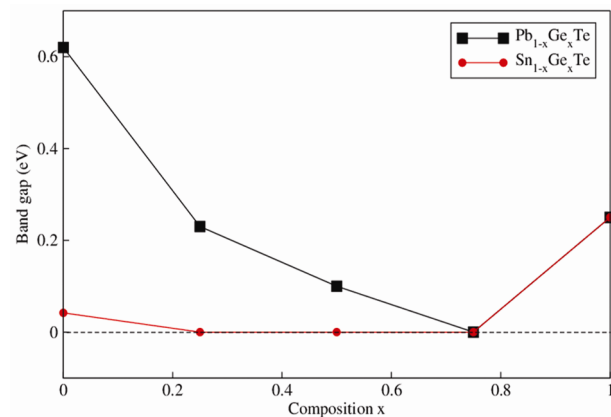


Fig. 6 — Band gap vs composition of $Pb_{1-x}Ge_xTe$ (PbTe, $Pb_{0.75}Ge_{0.25}Te$, $Pb_{0.5}Ge_{0.5}Te$, $Pb_{0.25}Ge_{0.75}Te$, GeTe) and $Sn_{1-x}Ge_xTe$ (SnTe, $Sn_{0.75}Ge_{0.25}Te$, $Sn_{0.5}Ge_{0.5}Te$, $Sn_{0.25}Ge_{0.75}Te$, GeTe)

compounds $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ have been plotted. For compounds $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ as the concentration of doping Ge increases, the energy gap decreases.

Density of states (DOS) defines the number of states of a system per unit energy, which are occupied by the electrons. For the better understanding of the band structure the knowledge of DOS is required. Our calculated DOS of the GeTe which is direct band gap semiconductor, it shows that the major contribution is of Ge-p state that makes the CB shown in Fig. 7 as blue dotted lines, while in VB, the major contribution is due to Te-p and a minor contribution of Ge-p. Now for $Pb_{0.25}Ge_{0.75}Te$ the major contribution in CB is due to Pb-p with minor contribution of Ge-p, while in VB the major contribution comes from Te-d, that is why in this case the semiconductor becomes metal and the valance band and the conduction band overlaps with each other. In the case of $Pb_{0.5}Ge_{0.5}Te$, CB is composed of Pb-p state with very minor contribution of Ge-p, while in VB Te-p state contribute majorly. Now for $Pb_{0.75}Ge_{0.25}Te$, the major contribution in upper CB comes from Pb-p state with no contribution of Ge-p, while in VB the major contribution is due to Te-p with minor contribution of Ge-p, so that in this case the material becomes wide band gap

semiconductor as compared to $Pb_{0.5}Ge_{0.5}Te$. Now for PbTe the major contribution in CB is due to Pb-p state with small contribution of Ge-p state, while in VB the major contribution comes from Te-p with minor contribution of Pb-s, so that in this case the material becomes wide band gap semiconductor as compared to other above cases. The densities of states of $Sn_{1-x}Ge_xTe$ are shown in Fig. 8. The binary compound GeTe which is direct band gap semiconductor, the CB of the compound is due to Ge-p with a small contribution from Ge-d and Te-p states, while in VB the major contribution is due to Te-p with minor contribution of Ge-p and Ge-s states. Now for $Sn_{0.25}Ge_{0.75}Te$, Sn-p and Ge-p contribute majorly in CB, while in VB the major contribution comes from Te-p. Now for $Sn_{0.5}Ge_{0.5}Te$, Sn-p state occupied the CB, while Te-p state contributes in VB with a minor contribution of Ge-s. Now for $Pb_{0.75}Ge_{0.25}Te$ the major contribution in upper band that is conduction band take place by Sn-p with minor contribution of Ge-p, while in VB the major contribution take place by Te-p with minor contribution of Ge-p, In the last for SnTe, the major contribution in upper band that is conduction band take place by Sn-p and with small contribution of Sn-s, while in VB the major contribution comes from Te-p and Sn-s, so that in this

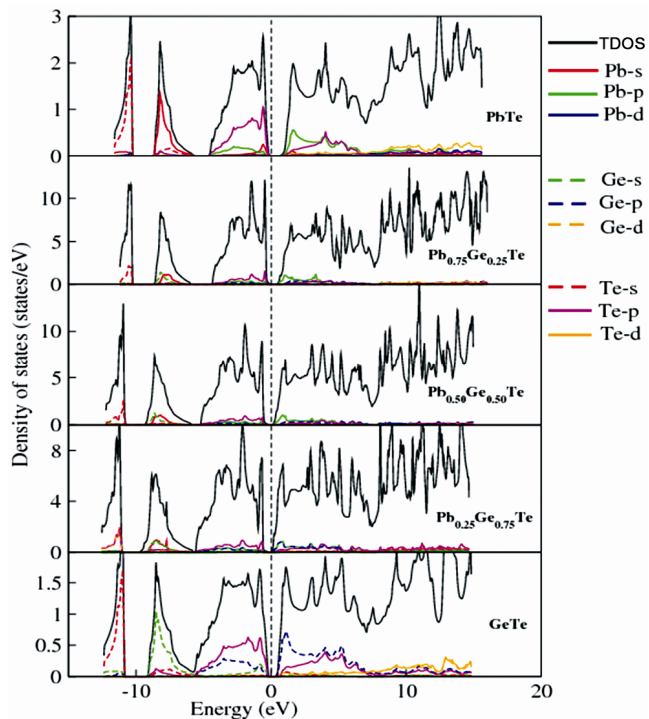


Fig. 7 — Total and partial DOS of PbTe, $Pb_{0.75}Ge_{0.25}Te$, $Pb_{0.5}Ge_{0.5}Te$, $Pb_{0.25}Ge_{0.75}Te$, GeTe

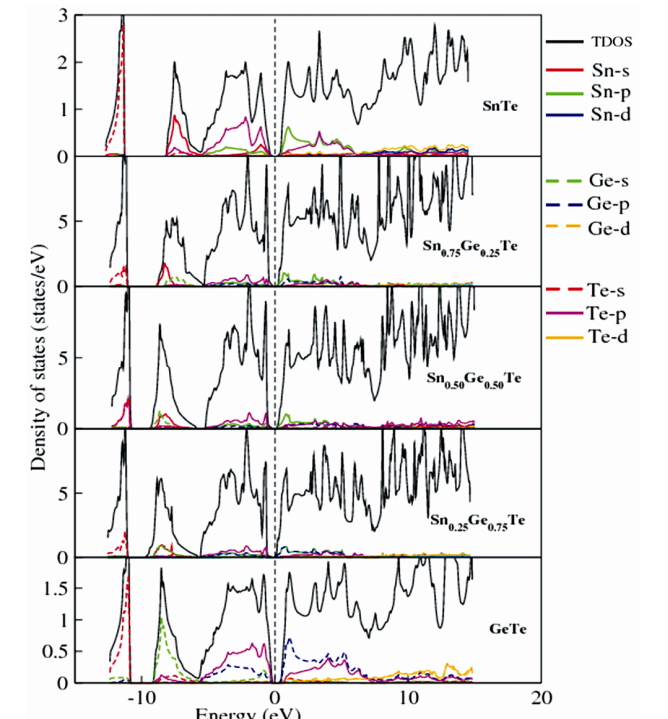


Fig.8 — Total and partial DOS of $Sn_{0.75}Ge_{0.25}Te$, $Sn_{0.5}Ge_{0.5}Te$, $Sn_{0.25}Ge_{0.75}Te$, GeTe

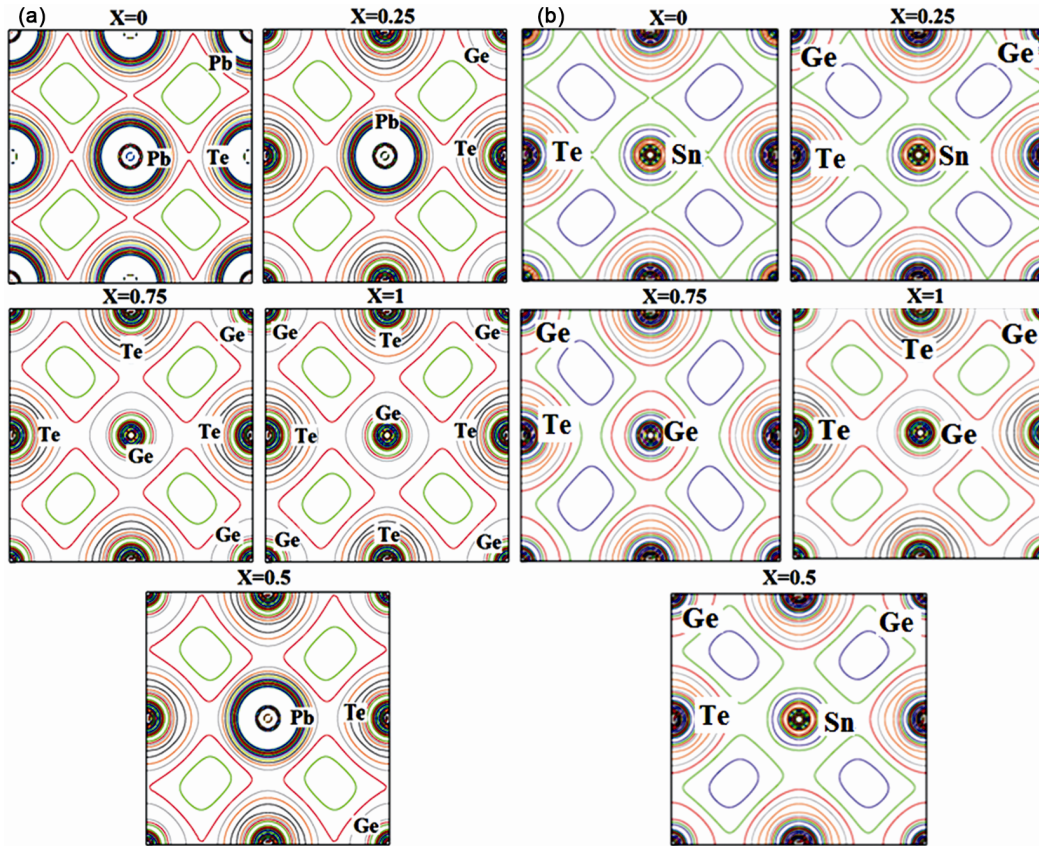


Fig. 9 – (a) Electron charge densities 2D-contour plot of PbTe, Pb_{0.75}Ge_{0.25}Te, Pb_{0.5}Ge_{0.5}Te, Pb_{0.25}Ge_{0.75}Te, and GeTe and (b) Electron charge densities 2D-contour plot of Sn_{0.75}Ge_{0.25}Te, Sn_{0.5}Ge_{0.5}Te, Sn_{0.25}Ge_{0.75}Te, and GeTe

case the material becomes a wide band gap semiconductor as compare to other above cases.

3.3 Electronic charge density and bonding

The chemical bonding properties of the material can be explained by the charge density distribution in a material. The nature of bonding can be explained by electron density, that is ionic or covalent bond between the cation and anion respectively. The electron density plots of adding Ge in the compound $Pb_{1-x}Ge_xTe$ and by adding Ge in the compound $Sn_{1-x}Ge_xTe$ with different concentrations which are shown in Fig. 9(a,b). The electron density plots of these compounds are in rock salt phase along (110) plane. It is clear from figures that the electron density plot of compounds is of covalent nature. By adding Ge in the compounds $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ the nature of covalent bond becomes stronger.

4 Conclusions

The structural, electronic and chemical bonding properties of the Ge doped PbTe and SnTe with concentration $x=0, 0.25, 0.50, 0.75$ and 1.0 in the rock

salt phase are calculated by FP-LAPW method within DFT. Generalized gradient approximation by Wu and Cohen (GGA-WC) is utilized for calculating these properties. With doping Ge in $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$, respectively, the lattice constant reduces linearly as the concentration increases. Also, it is observed that electronic properties of these compounds are affected with varying concentration of doping Ge. The band gap of corresponding compounds varies with respect to the composition of the materials, so the electronic properties alter as doping increases. The plots of $Pb_{1-x}Ge_xTe$ show that it has a direct band gap. So the direct band gap of the ternary alloys varies in the range 0 to 0.19 eV. It has been observed that the *s*, *p*, *d* and *f* states of $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ control their electronic properties. The alloys $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ show covalent bonding nature which enhances by increasing the Ge concentration. From the above discussion it is concluded that the Ge doping of $Pb_{1-x}Ge_xTe$ and $Sn_{1-x}Ge_xTe$ varies the physical properties widely and the resulted materials that can be used in thermoelectric, IR radiation, ferroelectric, optical

storage devices, Infrared detectors, Braggs reflectors and optical devices working in lower frequency regime and other useful applications.

References

- 1 Rogacheva E I, Nashchekina O N, Vekhov Y O, Dresselhaus M S & Dressalhaus G, *Thin Solid Films*, 484 (2005) 433.
- 2 Edwards A H, Pineda A C, Schultz P A, Martin M G, Thompson A P, Hjalmarson H P & Umrigar C J, *Phys Rev B*, 73 (2006) 45210.
- 3 Ciucivara A, Sahu B R & Kleinman L, *Phys Rev B*, 73 (2006) 214105.
- 4 Gautier C, Cambon-Muller M & Averous M, *Appl Surf Sci*, 141 (1999) 1957.
- 5 Clarke R, *Phys Rev B*, 18 (1978) 4920.
- 6 Kumar S, Majeed M A K, Zulfequar M & Husain M, *J Mater Sci*, 42 (2007) 363.
- 7 Khuzhakulov E S, *Semiconductors*, 38 (2004) 742.
- 8 Qadria S B, Singh B A & Yousu M, *Thin Solid Films*, 506 (2003) 431.
- 9 Abbe S, Furukawa Y, Mochizuki K & Masumato K J, *Jpn Inst Metal*, 58 (1994) 346.
- 10 Madsen G K H, Peter B, Karlheinz S, Elisabeth S & Lars N, *Phys Rev B*, 64 (2001) 195134.
- 11 Blaha P, Schwarz K, Madsen G K H, Kvasnicka D & Luitz J, *WIEN2k, An augmented plane wave plus local orbitals program for calculating crystal properties*, Vienna University of Technology, Austria, 2001.
- 12 Wu Z & Cohen R E, *Phys Rev B*, 73 (2006) 235116.
- 13 Perdew J P, Burke K & Ernzerhof M, *Phys Rev Lett*, 77 (1996) 3865.
- 14 Zunger A, Wei S H, Ferreira L G & Bernard J E, *Phys Rev Lett*, 65 (1990) 353.
- 15 Birch F, *Phys Rev*, 71 (1947) 809.
- 16 Vegard L, *Z Phys*, 5 (1921) 17.
- 17 Jobst J, Hommel D, Lunz U, Gerhard T & Landwehr G, *Appl Phys Lett*, 69 (1996) 97.
- 18 El Haj Hassan F, *Phys Stat Sol B*, 242 (2005) 909.
- 19 Aron W & Graeme W W, *J Phys Chem B*, 109 (2005) 18868.
- 20 Nimtz G & Schlicht B, *Narrow-Gap Lead Salts*, (Springer, Berlin), 1983.
- 21 Bencherifa Y, Boukraa A, Zaouic A & Ferhat M, *Mater Chem Phys*, 126 (2011) 707.
- 22 Esaki L, *J Phys Soc Japan*, 21 (1966) 589.
- 23 Saini R, Pallavi, Singh M, Kumar R & Jain G, *Chalcogenide Lett*, 7 (2010) 197.
- 24 Kumar S, Khan M A, Zulfequar M & Husain M, *J Mater Sci*, 42 (2007) 363.
- 25 Rached D, Rabah M, Benkhetto N, Driz M & Soudini B, *Physica B*, 337 (2003) 394.
- 26 Dantas N S, *Electronic structure and optical properties of PbY and SnY (Y = S, Se, and Te)*, Royal Institute of Technology, ISBN 978-91-7178-654-8, 2007.