JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 10, October 2010, p. 2106 - 2112

Structural phase transition and high pressure elastic behavior of BX (X= Sb, Bi) compounds

SADHNA SINGH, MADHU SARWAN*
High Pressure Research Lab, Department of Physics, Barkatullah University
Hoshngabad Road Bhopal - 462026

With the use of three-body potential model, the stability of high pressure structure, the zinc-blend structure, for the BX(X=Sb,Bi) compounds are investigated. We present the calculated pressure for the phase transformation and compare them with other's thereortical data due to the unavaibility of experimental data. The equation of state curves for both B3 (ZB) and B1(RS) structures obtained are in fairly good agreement with the other's results. Also the second order elastic constants (SOEC), thermodynamic properties and sound velocities are obtained. Further, the variation of SOEC, thermodynamic properties and sound velocity with pressures are obtained and compared with others.

(Received April 7, 2010; accepted October 14, 2010)

Keywords: Structural phase transition; Elastic constants; Thermodynamic properties; Boron compounds

---

1. Introduction

The covalent boron compounds have drawn much attention for their structural, electronic and optical applications. In particular, they have potential of application in optoelectronics because of extreme physical properties like low ionicity, small band-gap, short bond length, mechanical strength and melting point [1-2]. At ambient conditions, BX(X=Sb, Bi) compounds crystallize in zinc-blend (ZB) structure having space-group 216/F-43m. Wang et.al [3] used first principle plane-wave pseudopotential calculations and reported that the boron phases have quite different behavior in both their elastic and structural properties from the other III-V compounds. Zaoui et.al [4] have given the possible reason for fundamental differences between Boron compounds and other III-V materials that it can be apparent from the band structures and charge density calculations. H. Meradzi [5] applied a first- principle total energy calculation and studied Boron compounds BX (X=P,As,Sb).There have been a number of efforts by theoretical workers but there is a little work has been done on experimental front. High pressure properties have been discussed by Wentzcouvitch et.al [6-8] by using local density approximation (LDA) within density functional theory and the pseudo potential method. Recently Ferhat et.al [9-11] also reported that the zinc-blend is the ground state of BBi. They have studied structural and electronic properties of BBi.

The elastic constants of Boron compounds have been calculated by Deligoz et.al [1-2], Wang et.al [3], Meradzi et.al [5] and Ferhat et.al [9-11] by using ab initio methods and volume conserving technique. Delogoz et.al [1-2] estimated elastic constants (C_{11}, C_{12} and C_{44}) at high pressure (B1) and low pressure phase (B3). Other elastic properties like Zener anisotropy factor, Pisson ratio and Young's modulus having technological applications have also been calculated by Wang et.al [3] and Delogoz et al [1-2]. Besides these attempes phenomenological models [12-15] have been found successful in similar structures in B3 and B1 structures. But most of the earlier efforts for these properties were based on two body potentials. The limitation of two-body potential model lies in their incapability to justify cauchy violation in ionic crystals. Cauchy violation was explained by Lowdin [12, 13] and Lundquist [14] in terms of three-boy interactions which is originated from the non rigidity of ions resulting in transferred/exchange of charges between adjacent ions [15].

Looking at the interesting properties of BSb and BBi and the fact that no study has been done using three-body interactions potential (TBIP) approach, we thought it pertinent to apply TBIP approach to study BSb and BBi. The importance of this model lies in its simplicity and its applicability becomes more important where a wealth of experimental data is not available. The importance of three-body interactions in potential model to improve result has also been emphasized by others like Sims et al [16], Froyen and Cohen [17], Zhang and Cohen [18] and Chelikowsky [19]. The present model includes the long-range Coulombic, three-body interaction, short range overlap repulsive interaction operative up to second neighbour ions within Hafemeister and Flygare approach [20]. This model has successfully been used in some alkali metal hydrides [21], halides [22-23] and transition metal compounds [24] for their structural stability and electronic properties. The rest of the paper is organized as follows section 2 presents a brief description of the present potential model and method of computation. Section 3 presents the calculated results with discussion, section 4 represents conclusion.

2. Potential model

The application of pressure causes an increase in the overlap of adjacent ions in a crystal and hence charge transfer takes place between the overlapping electron shells. The transferred charges interact with all other ions of the lattice via Coulomb's law and gives rise to many-body interactions. The most significant part of which is three-body interaction [15]. The increased charge-transfer effects, thus obtained, lead to an obvious necessity of their inclusion in the high-pressure study of materials.

In general, the BX compounds transform from B3 to B1 structure under pressure. Thermodynamically, a phase transition is said to occur when the changes in structural details of the phase are caused by the variation of free energy. The stability of particular structure is decided by the minimum of the Gibbs energy, which is given as

$$G=U+PV-TS \tag{1}$$

where U is the lattice energy, which at 0K corresponds to cohesive energy, S is the vibrational entropy at absolute temperature, pressure P and volume V. The Gibbs free energy for the Zinc-blend (B_3, real) and Rack-salt (B_1, hypothetical) structures are given by

$$G_{B3}(r)=U_{B3}(r)+PV_{B3} \tag{2}$$

$$G_{B1}(r')=U_{B1}(r')+PV_{B1} \tag{3}$$

with V_{B3} ($=3.08\ r^3$) and V_{B1} ($= 2.00\ r^3$) as unit cell volumes for B_3 and B_1 phases, respectively. The first term in (2) and (3) are lattice energies for B_3 and B_1 structures and they are expressed as

$$U_{B3}=\frac{-\alpha_M e^2Z^2}{r}-\frac{4\alpha_M e^2Z^2 f(r)}{r}+4b\beta_{ije}[\exp(r_i+r_j-r_{ij})/\rho] \tag{4}$$
$$+6b\beta_{ii}[\exp(2r_{ii}-r_{ij})/\rho]+6b\beta_{jj}[\exp(2r_{jj}-r_{ij})/\rho]$$

$$U_{B1}=\frac{-\alpha_M e^2Z^2}{r'}-\frac{6\alpha'_M e^2Z^2 f'(r)}{r'}+6b\beta_{ij}[\exp(r_i+r_j-r'_{ij})/\rho] \tag{5}$$
$$+6b\beta_{ii}[\exp(2r_i-r'_{ij})/\rho+6b\beta_{jj}[\exp(2r_{jj}-r'_{ij})/\rho]$$

with α_M and α'_M as the Madelung constants for ZB and RS structures, respectively. β_{ij} (i,j = 1,2) are the pauling coefficients defined as $\beta_{ij} = 1 + (Z_i/n_i) +(Z_j/n_j)$ with Z_i (Z_j) and n_i (n_j) are the valence and the number of electrons in the outermost orbit. Ze is the ionic charge, k(k') the structural factor for B3(B1) structure, b (ρ) are the hardness (range) parameters, r(r') are the nearest neighbour separation for ZB (RS) structure, f(r) is the three-body force parameter expressed as $f(r) = f_0\exp(-r/\rho)$ and r_i (r_j) are the ionic radii of ions i (j). These lattice energies consist of long range Coulomb energy (first term), three-body interactions corresponding to the nearest neighbour separation r (r') (second term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (third, fourth and fifth terms).

3. Results and discussion

The TBP described above for the ZB and RS phases contains three model parameters namely the range, hardness and three body force parameters (ρ, b, f(r)). Their values have been calculated from the equilibrium condition, first and second space derivatives of cohesive energy U such as,

$$B_1 + B_2 = -1.261Z[Z + 8f(r)] \tag{6}$$

$$\left|\frac{dU}{dr}\right|_{r=r0} = 0 \tag{7}$$

and

$$\frac{d^2U}{dr} = 9kr_0B \tag{8}$$

The input data and the model parameters are given in Table 1. The stable phase is always associated with minimum energy. While estimating the structural phase transition of BX compounds, we have followed the technique of minimization of U_{B3} (r) and U_{B1} (r') at different pressure in order to obtain inter ionic separation r and r' for B_3 and B_1 phases respectively associated with minimum energies.

Table 1

Solids →	BSb	BBi
Input data		
a (Å)	5.21[21]	5.415[18]
B_0 (Å)	110[2]	99.30[1]
Model parameters		
b (10^{-19} J.)	2.12	7.0684
ρ(Å)	0.360	0.480
f(r)	-0.0152	0.0422

We have evaluated the corresponding G_{B3} (r) and G_{B1}(r') and their respective differences $\Delta G=G_{B3}(r)–G_{B1}(r')$.The factor ΔG is important- as it varies with pressure. The pressure corresponding to ΔG approaching zero is the phase transition pressure (P_t). At zero pressure, the B_3

crystal phase is thermodynamically and mechanically stable, while the B_1 is not.

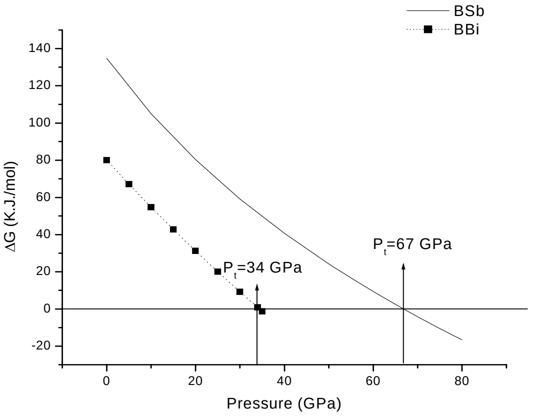

Fig. 1. Phase transition from ZB to RS structure

Beyond phase transition pressure ΔG becomes negative as the phase B_1 become thermodynamically and mechanically stable.

Eventually, at a pressure higher than phase transition pressure, the B_3 phase becomes thermodynamically unstable while the B_1 phase remains stable up to the greatest pressure studied.

Fig.1 shows the Gibbs free energy difference (ΔG) for the B_3 and B_1 phases plotted as function of pressure (P).

Table 2

Solids	Phase transition Pressure (GPa)	Volume collapse
BSb		
Present	67	0.0415
Theory[1]	59	0.0983
Theory[25]		53
Theory[26]	68	
Theory[27]	216	
BBi		
Present	34	0.112
Theory[1]	31.74	0.066

The phase transition pressure so obtained is presented in Table 2 and compared with the other theoretical results [1, 25-27]. Fig1 shows the phase transition from ZB to Rack-salt structure in BSb and BBi at 67 and 34 GPa, this is closed to the other theoretical results [1, 26]. The values of relative volume change associated with various compressions have been computed by using the TBI potential model. Deduced the pressure dependent radii r for both the structures (B_3 and B_1) have been used to compute the relative volume change and are plotted against the pressure (P) as shown in Fig. 2(a) and 2(b) for BSb and BBi. Relative volumes plotted against pressure for BX compounds have been compared with other's results [1, 26] in Fig. 2(a) and 2(b). Present results are shown by thick solid lines for B_3 and B_1 phases with earlier theoretical data [1-2] (thick and thin broken lines for B_3 and B_1 phases). The magnitudes of the discontinuity in volume collapse at the transition pressure have been obtained from the phase diagram and the values are listed in Table 2 and compared with only the earlier theoretical results due to the unavaibility of experimental results.

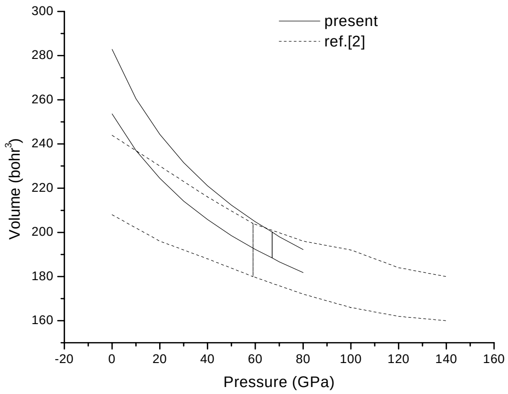

Fig. 2(a). Volume collapse of BSb compound

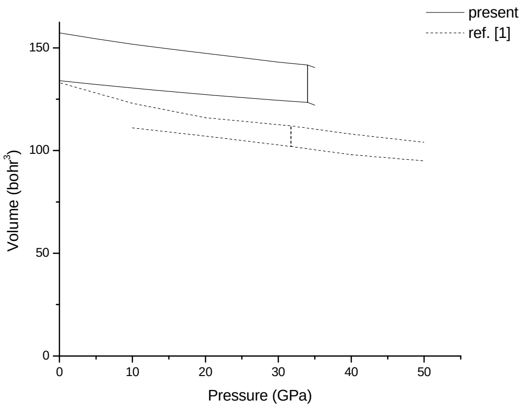

Fig. 2(b). Volume collapse of BBi compound

Elastic constants define the properties of material that undergo stress, deform and then recover after the returns to its original shape. These constants are important in solids because they are related to various fundamental solid-state phenomena such as interatomic bonding, equation of state and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, Debye temperature, thermal expansion and Gruneisen parameter. The important knowledge of elastic constants is essential for many applications related to the mechanical properties such as load deflection, sound velocities, and thermo elastic stress. The expressions for the second order elastic constants are as follows: [28]

$$C_{11} = (e^2/4a^4)\begin{bmatrix} 0.2477\ Z(Z+8f(r)) + \frac{A_1+2B_1}{3} \\ + \frac{A_2+B_2}{2} + 5.8243\ aZf'(r) \end{bmatrix} \tag{9}$$

$$C_{12} = (e^2/4a^4)\begin{bmatrix} -2.6458\ Z(Z+8f(r)) + \frac{A_1-4B_1}{3} \\ + \frac{A_2-5B_2}{4} + 5.8243\ aZf'(r) \end{bmatrix} \tag{10}$$

$$C_{44} = (e^2/4a^4)\begin{bmatrix} -0.123\ Z(Z+8f(r)) + \frac{A_1+2B_1}{3} + \\ \frac{A_2+3B_2}{4} - \nabla/3(-7.53912\ Z(Z+8f(r)) \\ + A_1 - B_1 \\ \end{bmatrix} \tag{11}$$

Where

$$\nabla/3 = \frac{-7.53912Z(Z+8f(r)) + A_1 - B_1}{-3.141Z(Z+8f(r)) + A_1 + 2B_1 + 21.765aZf'(r)}$$

The calculated elastic constants (C_{11}, C_{12}, and C44), bulk modulus (B) in ZB phase for BX compounds are reported in Table 3. These values are comparable with those obtained by Delogoz et al [1-2] and others [3, 5 and 26]. We notice that our calculated C_{11} and C_{44} values are in reasonable agreement with those of other works and C_{12} is in better agreement with others [3, 26, and 5].

Table 3.

Ref.	C_{11}(GPa)	C_{12}(GPa)	C_{44}(GPa)
BSb (pres.)	218.25	60.35	88.0
Theo.[2]	193.53	68.42	104.12
Theo.[3]	205.0	62.5	112.10
Theo.[26]	192	58.5	105
Theo.[5]	223	62.0	140
Theo.[5]	207(GGA)	47	105
BBi (pres.)	197.78	85.87	105.9
Theo.[3]	160.2	51.5	87.4
Theo.[10]	163.8	28.3	86.3

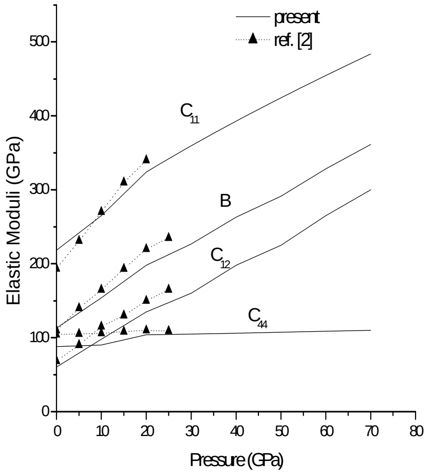

Fig. 3(a). Variation of elastic moduli with pressure for BSb

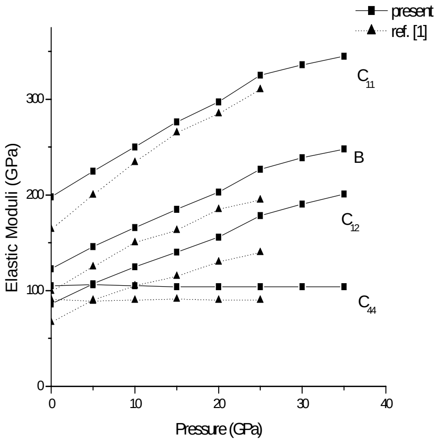

Fig. 3(b). Variation of elastic moduli with pressure for BBi

Also we have studied the effect of pressure on the elastic properties. In Fig. 3(a) and 3(b), we present the variation of the elastic constants and bulk modulus of BX compounds with respect to the variation of pressure (P). It is clearly seen that the elastic constants C_{11}, C_{12}, C_{44} and bulk modulus increase when the pressure is increased and we can notice a linear dependence in all curves in the considered range of pressures. Our results in variation of elastic constants and bulk modulus with pressure are agreed well with the others result [1-2]. It is found that C_{11} varies largely under the effect of pressure as compared with the variation in the C_{12} and C_{44}.The elastic constant C_{11} represents elasticity in length and C_{12} and C_{44} are related to the elasticity in shape. A transverse strain causes a change in shape without a change in volume. Therefore, C_{12} and C_{44} are less sensitive of pressure as compared with C_{11}.

Through the elastic constants, we can obtained the Zener anisotropy parameter (A), young modulus(Y), and poisson ratio (ν) and shear modulus (S) which are most interesting for applications and they are calculated by using the following equations. [1]

$$A=\frac{2C_{44}}{C_{11}-C_{12}} \tag{12}$$

$$Y=\frac{9GB}{G+3B} \tag{13}$$

$$\nu=\frac{1}{2}\left[\frac{\left(B-\frac{2}{3}G\right)}{\left(B+\frac{1}{3}G\right)}\right] \tag{14}$$

$$S=\frac{C_{11}-C_{12}}{2} \tag{15}$$

where $G=(G_V+G_R)/2$ is the isotropic shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values and G_R is Reuss's shear modulus corresponding to the lower bound of G values. These shear modulus are written as

$$G_V=(C_{11}-C_{12}+3C_{44})/5 \tag{16}$$

$$5/G_R=4/(C_{11}-C_{12})+3/C_{44} \tag{17}$$

Table 4 summarizes all numerical values of the Zener anisotropy factor (A), young modulus(Y) and poisson ratio (ν) and shear modulus (S) obtained from the above Equation (12-17). After this, we have been obtained the Zener anisotropy factor (A) young modulus(Y), poisson ratio (ν) and shear modulus (S) at various pressures for the BX compounds. Fig. 4(a) and 4(b) shows the variation of anisotropy factor (A) and poisson ratio (ν) for the BSb and BBi compounds and fig. 5(a) and 5(b) represents the variation of young modulus(Y) and shear modulus (S) with pressures. These are compared with the Deligoz's results [1, 2]. There is some deviation in variation of anisotropy factor for BX compounds with others [1, 2]. We have also calculated the longitudinal (v_l), transverse (v_t) and average wave velocities (v_m) and compared them with others [2, 24, 1]. Fig. 6(a) shows behavior of pressure dependence of these calculated velocities up to 70 GPa for BSb along with other's results [2]. For BBi fig.6 (b) shows the pressure dependence of these calculated sound velocities up to 35 GPa and the trend in BBi is same as BSb.

Table 4

Solids	A	ν	Y(GPa)	S(GPa)
BSb				
pres.	1.11	0.20	202.622	78.95
theo.[2]	1.664	0.163	221.81	62.55
theo.[3]	1.573	0.234	175.8	71.3
BBi				
pres.	1.87	0.22	201.37	55
theo.[1]	1.840	0.211	171.99	48.57
theo.[3]	1.608	0.243	135.10	54.30

Table 5

Solids	v_l (m. /s.)	v_t (m. /s.)	v_m (m. /s.)
BSb			
pres.	7068.60	4323.68	4777.60
theo.[2]	6170.5	3911.22	4302.35
BBi			
pres.	6187.6	3676.5990	4015.912
theo. [1]	4563.58	2841.25	3131.204

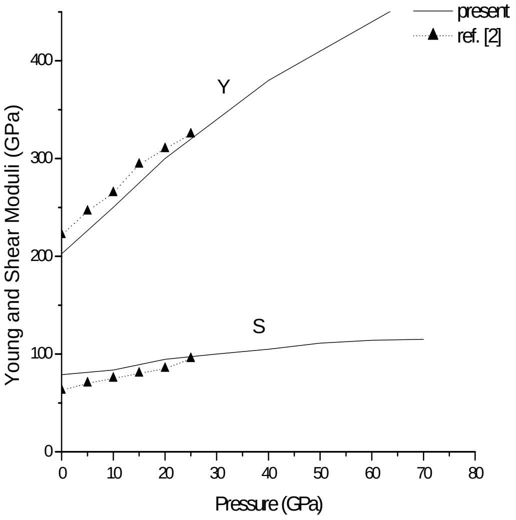

Fig 4 (a). Young and Shear modulus of BSb.

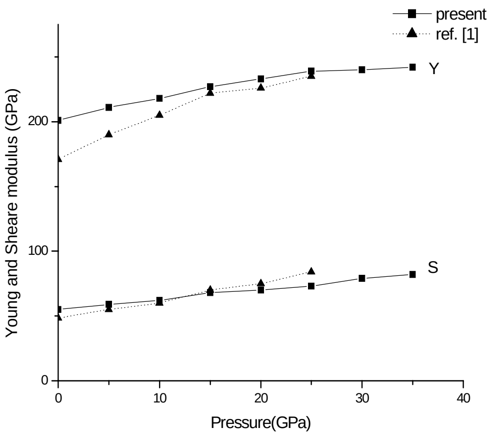

Fig. 4(b). Young and Shear modulus of BBi

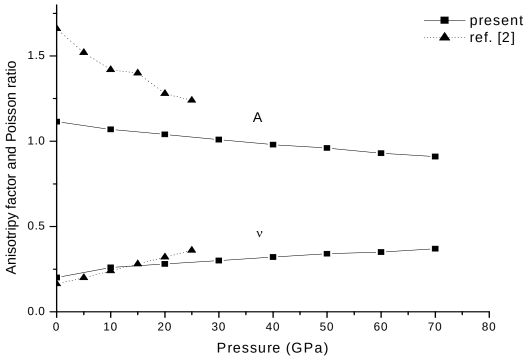

Fig. 5(a). Anisotropy factor and Poisson ratio of BSb.

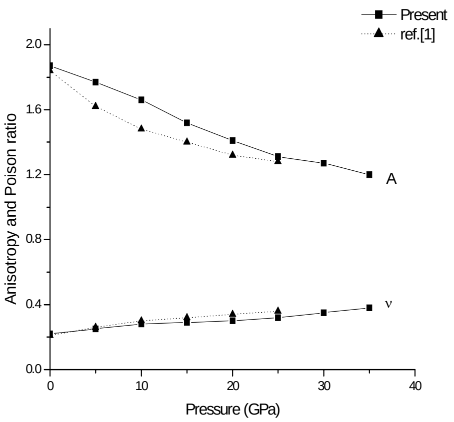

Fig. 5 (b). Anisotropy factor and Poisson ratio of BBi.

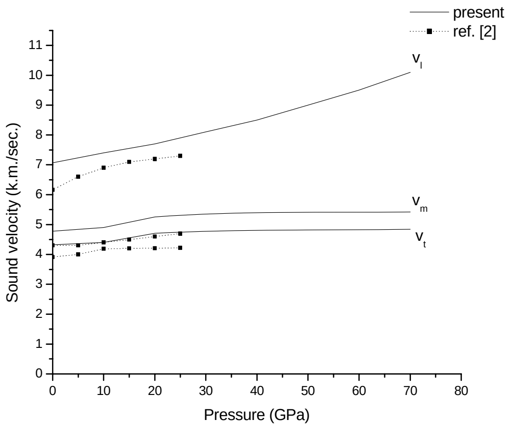

Fig 6(a). Sound velocities of BSb.

The calculated sound velocities having the same trend with others. The upper thick square (near to v_t) is the value of average elastic waves and lower thick square (near to vt) is the value of transverse elastic waves

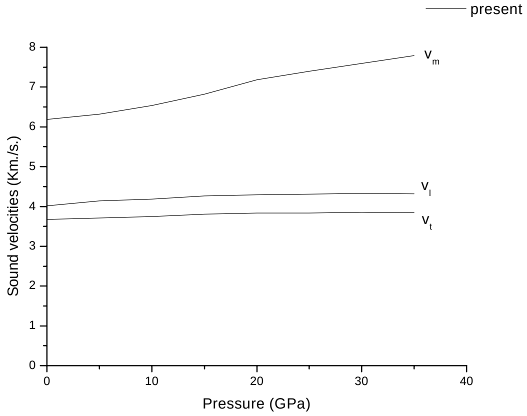

Fig. 6 (b). Sound velocities of BBi.

4. Conclusions

Our work gives a comprehensive study of structural, elastic and thermodynamic properties of BX compounds. To our knowledge, there is no study available with TBIP model for these properties for BX compounds. It is evident from Fig. 1 and Table 2 that our computed phase transition pressure for BSb and BBi are 67 and 34 GPa which are in comparable range with others reported data (53-216 GPa) and (31-34GPa). Also from Fig. 2 and Table 1, we find that there is a volume discontinuity at phase transition pressure showing the occurrence of first order phase transition in there compounds. Looking at the Table 3 and Fig. 3(a, b), we find that the trend of elastic constants follow the same as reported by others. Here, we can see that C_{11} is most affected by pressure and C_{44} is least affected by pressure. C_{11} is affected more with increasing pressure as compared to C_{12} and $C_{44.}$ As we know that C_{11} represents elasticity in length and longitudinal strain causes a change in $C_{11.}$ However remaining two elastic constants C_{12} and C_{44} are related to shape. The values of Young modulus and shear modulus have also been computed at zero pressure as well as with different pressure and they are presented in Table 4 and Fig. 4(a, b) and they are compared with Deligoz et al [1,2].The results of phase transition pressure, elastic constants and thermodynamic properties are compared with Deligoz et al [1,2], where we find a good agreement. The calculated values of C_{11}, C_{12} ,C_{44} and B are in agreement with other theoretical values. The sound velocities v_l, v_t and v_m are also obtained, first time by this model and compared with Deligoz et al [1, 2]. Looking at the overall results we can say that the present results are in comparable range with available theoretical results. Finally, we have found that the TBIP model used in present work describes well the Phase transition, elastic properties and thermodynamic properties of BX compounds. This led us to state that it is also suitable to new properties in several different experimental conditions.

Acknowledgement

The authors are thankful to UGC New Delhi for financial support

References

[1] E. Deligoz, K. Colakoglu, Y.O. Ciftci, H. Ozisik, Comput. Mater. Sci. **39**, 533 (2007).
[2] E. Deligoz, K. Colakoglu, Y.O. Ciftci, Jour.of Phys. and Chem. of Sol. **68**, 482 (2007).
[3] S.Q. Wang, H.Q. Ye, Phys. Stat. Sol. (b) **240**, 45 (2003).
[4] A. Zaoui, M. Ferhat, Phys. Stat. Sol. (b) **225**, 15 (2001).
[5] H. Meradji, S.Drablia, S.Ghemid, H. Belkhir, B. Bouhafs and A.Tadjer, Phys. Stat. Sol.(b) **241**, 2881 (2004).
[6] R. M. Wentzcovitch, M. L. Cohen, J. Phys. C: Solid State Phys. **19**, 6791 (1986).
[7] R .M. Wentzcovitch, K. J. Chang, M. L. Cohen, Phys. Rev. B **34**, 1071 (1986).
[8] R. M. Wentzcovitch and M.L. Cohen, P.K. Lam, Phys. Rev. B **36**, 6058 (1987).
[9] D. Madouri, M. Ferhat, Phys. Stat. Sol. (b) **242**, 285 (2005).
[10] M. Ferhat, A. Zaoui, Phys. Rev. B **73**, 115107 (2006).
[11] M. Ferhat, A. Zaoui, Appl. Phys. Lett. **88**, 161902 (2006).
[12] P.O. Lowdin Adv. Phys. **5**, 1 (1956).
[13] P.O. Lowdin, Ark. Mat. Astr, Fys (Sweden) **35** A, 30 (1947).
[14] S.O. Lundquist Ark. Fys. (Sweden) **12**,365 (1957).
[15] R.K. Singh, Phys. Rep. (Netherlands) **85**,259 (1982).
[16] C.E. Sims, G.D. Barrera, N.L. Allan, Phys. Rev. B **57**, 11164 (1998).
[17] S. Froyen, M.L. Cohen, Phys. Rev. B **28**, 3258 (1983).
[18] S.B. Zhang, M.L. Cohen, Phys. Rev. B **35**, 7604 (1987).
[19] J. R. Chelikowsky, Phys. Rev. B **35**, 1174 (1987).
[20] D. W. Hafemeister, W.H. Flygare, J. Chem. Phys. **43**,795 (1992).
[21] S. Singh, R.K. Singh, High Press. Res. **21**, 105 (2001).
[22] S. Singh, R.K. Singh, R. Rai and B.P. Singh, Jour. Phys. Soc. Jpn. **68**, 1269 (1999).
[23] S. Singh, R.K. Singh, B.P. Singh, R. Chopra, Phys. Stat. Sol. (a) **180**, 459(2000).
[24] R. Chauhan, S. Singh, R. K. Singh, Cent. Eur. J. Phys**.** **6**(2), 277 (2008).
[25] A. Zaoui, F. El Haj Hassan, J. Phys. Condens. Matter **13**, 253 (2001).
[26] F. El Haj Hassan, H. Akbarzade, M. Zoaeter, J. Phys. Condense Matter **16**, 293(2004).
[27] G. K. H. Madsen, P.Blaha, K. Schwarz, E. Sjostedt, L. Nordstrom, Phys. Rev. B **64,** 195134 (2001).
[28] R. K. Singh, S. Singh, Phys. Stat. Sol. (b) **140**, 407 (1987).

---

[*] Corresponding author: drsadhna_in@rediffmail.com