

# ***Ab initio* calculation of thermal and mechanical properties of BeX (X=S, Se, Te): An application of density functional theory**

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## -----ABSTRACT-----

*We calculated the electronic, structural, mechanical, and thermal properties of cubic structured binary compounds of Beryllium chalcogenides (BeS, BeSe and BeTe) belonging to group II–VI compounds. We implemented established model of the full-potential linear-augmented plane wave (FP-LAPW) method based on the density functional theory (DFT) for the study of structural, elastic, electronic, and thermal properties of Be-chalcogenides. The standard generalised gradient approximation (GGA) has been exploited to model the exchange-correlation (Exc) interaction in Kohn–Sham calculations. Murnaghan’s equation of state (EOS) has performed the volume optimization with the process of minimizing the total energy considered as a function of the unit cell volume. With the knowledge of electronic density of states (DOS) and band structures, mechanical and thermal properties of Be-chalcogenides have been estimated.*

**Keywords** - Be-Chalcogenides, electronic properties, mechanical properties, DFT, FP-LAPW..

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## I. INTRODUCTION

They having higher bonding energy and hardness, exhibit unusual electronic, mechanical, thermal, optical properties. These exclusive properties create them very useful for various technological applications including laser diodes, high efficiency photo-detectors. The II–VI group beryllium chalcogenides (BeS, BeSe and BeTe) crystallizing in the four-fold coordinated zinc-blende structure have received a considerable attention in the recent years [1–5]. A typical characteristic of these compounds is that the mass and ionic radius of Be atom is much smaller than the chalcogen (S, Se, and Te) atoms. Unlike other II–VI compounds having partially ionic bond, Be-chalcogenides exhibit a high degree of covalent bond [5–8]. Due to higher bonding energy, Be-chalcogenides exhibit unusual electronic properties characterized by a large band gap and offer potential device applications in technology of green semiconductor lasers. These materials are very promising for the possibility of the application in low dimensional (quantum-well and superlattices) device production [5,8]. The optoelectronic devices based on beryllium chalcogenides have advantage over other II–VI semiconductors due to their high p type doping concentrations and long lifetimes. Incorporation of transition metal ions into beryllium chalcogenide crystal creates dilute magnetic semiconductors commonly used in spintronics applications [9]. A great deal of extensive theoretical studies of the structural, electronic, optical and lattice dynamics for Zn chalcogenides exist in wide span of literatures [10–14]. For instance an ab initio calculation helped a lot for the investigation of the lattice dynamics for ZnO [10]. Linear muffin tin orbital model [11] applied in the determination of density functional of electronic charge for analysing the electronic structures of ZnX compounds. Some

report can be found on the application of the empirical pseudopotential method to examine the band structure and on the density of states for ZnX binary compound [13].

On the other hand less research has been reported on the electronic properties study of Be-chalcogenides. The present work is aimed on the applying the full-potential linear-augmented plane wave (FP-LAPW) method within the application of the density functional theory (DFT) for the determination of structural, electronic, and optical properties of BeX materials. The standard method of generalised gradient approximation (GGA) performed the computation for the solution of Kohn–Sham equation to determine the exchange-correlation energy (Exc). Murnaghan’s equation of state (EOS) has made a proper fitting of volume optimization with the total energy to calculate the equilibrium unit cell volume. Further the calculated electronic properties were used to determine elastic, mechanical and thermal properties of binary Be chalcogenide .

## II. METHOD OF CALCULATION

The structural, electronic and thermal properties of the compound BeX have been studied in the frame work of the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) with Wien2k code [15]. The generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) [16] has been used. By optimization of the total energy with respect to the unit cell volume using Murnaghan’s equation of state [17], equilibrium structural parameters are estimated. The calculations were performed with  $RMT_{kmax} = 7$ , to accomplish energy eigen value convergence, where RMT is the smallest radius of the muffin-tin (MT) spheres and  $k_{max}$  is the maximum value of the wave vector. The maximum value of the angular momentum  $l_{max}$  is taken as 10 for the wave function expansion inside the atomic spheres. Irreducible Brillouin zone (BZ) of the zinc-blende structure comprises  $k$ -points as designed based on Monkhorst–Pack model with a grid of  $10 \times 10 \times 10$  matrix for the computational work. Iteration on the convergence for the total energy and charge continues up to 0.0001Ry and 0.001e, respectively.

## III. RESULT AND DISCUSSIONS

### A. Structural properties

The zinc-blende structured BeX compound has the cubic symmetry as displayed in Figure 1. The Zn atom is positioned at the origin and the X atom is placed at (1/4, 1/4, 1/4). The configuration has the space group of F-43M. The unit cell volume at ground-state is obtained by Murnaghan’s equation. The calculated total energy as a function of the unit-cell volume is minimized by fitting the quadratic curve according to the Murnaghan’s equation of state [17]:

$$E_T(V) = \left[ \frac{B_0 V (V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] + E_0 - \frac{V_0 B_0}{B_0' - 1} \quad (1)$$

The variation of the total energy with volume of the unit-cell for BeS is shown in Figure 2. We have considered BeS as prototype binary compound of the Be-chalcogenides.

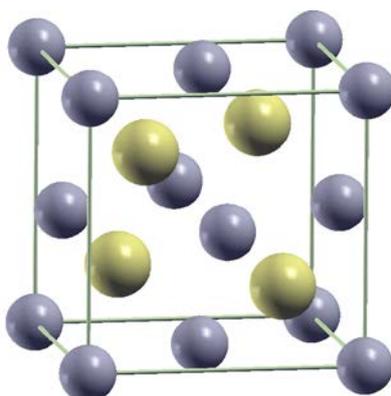


Figure 1. Crystal structure of the zinc-blende BeX (X = S, Se, Te). The violet ball is Be atom and the yellow ball is X atom.

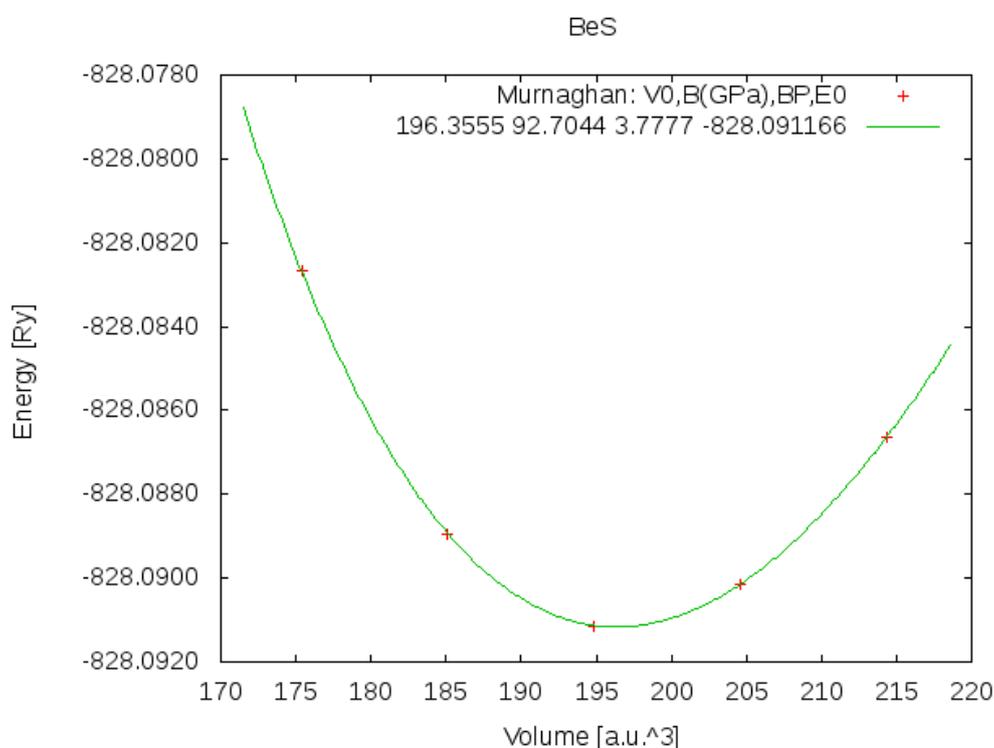


Figure 2. Configuration energy with unit-cell volume variation for BeS. For simulation Murnaghan's equation of state has been considered. Different fitting parameters are shown in Table 1

By the fitting of Murnaghan's equation of state, we estimate the bulk modulus  $B_0$ , its pressure derivative  $B_0'$  and the equilibrium lattice constant  $a_0$ , for the ZB structure of the binary BeX at zero pressure as presented in Table 1. We compare the estimated lattice parameters with further theoretical and experimental data. For BeS, BeSe and BeTe, the energy minimisation occurs for  $a_0 = 4.882, 5.183,$  and  $5.668 \text{ \AA}$ , which is in good agreement with the experimental values of  $4.87, 5.14,$  and  $5.62 \text{ \AA}$ . Hence well-defined structural properties are adequate for more study on electronic and optical properties.

Table 1. Calculated bulk modulus  $B_0$  (GPa), its pressure derivative  $B_0'$  and lattice constant  $a_0$  (Å) of BeX along with the available theoretical and experimental data.

Compound	Fitting Parameters		Lattice Constant $a_0$ (Å)		
	$B_0$ (GPa)	$B_0'$	Present	Others	
				Exp.	Theo.
BeS	92.99	3.82	4.882	4.87 [c]	4.82 [Ref. 17] 4.75 [Ref. 18] 4.83 [Ref. 20]
BeSe	75.62	3.78	5.183	5.14 [d]	5.12 [Ref. 17] 5.04 [Ref. 18] 5.13 [Ref. 20]
BeTe	56.36	3.74	5.668	5.62 [e]	5.57 [Ref. 17] 5.53 [Ref. 17] 5.58 [Ref. 18]

### B. Electronic properties

The calculated band structure at equilibrium for BeS is shown in Figure 3. BeS is considered as a prototype since the band profiles are quit similar for all three compounds, with little differentiation. The overall bands are in quite good agreement with other theoretical results [19-24]. Maxima of the valence band and the minima of conduction band in each member of BeX appears at different q point.

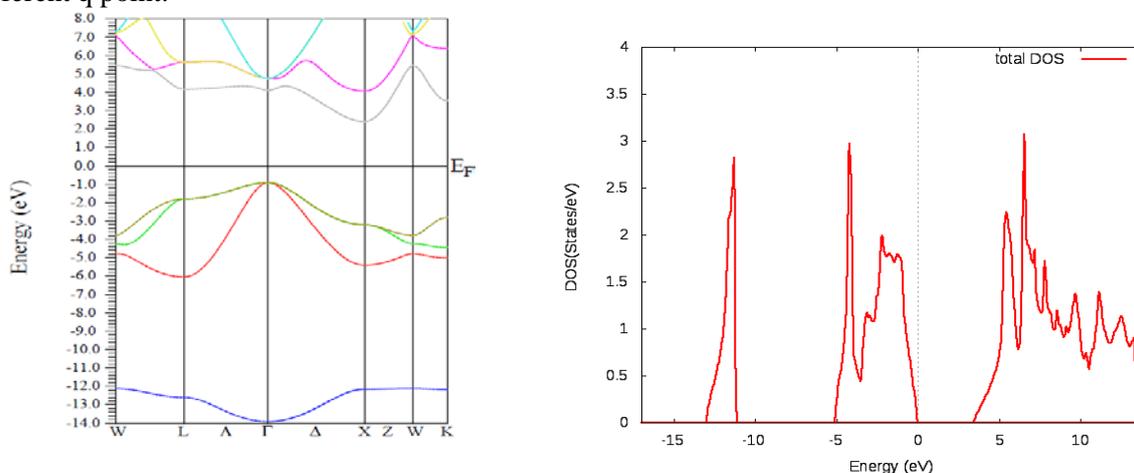


Figure 3. (Left): Electron energy band of BeS. (Right): electron density of states of BeS.

It means that the maxima and minima are not lying in the same value of q point. So the energy difference between the valence band maxima and the conduction band minima is indirect. It is observed that the chalcogen p bands move up in energy with the increase of atomic number starting from the sulphide to the telluride. It is a concern of increase of the lattice parameters, as perceived in other II–VI compounds also [25]. From band structure one can see that the obtained band gap is always underestimated in comparison to experiments results. It is due to fact that the simple form of GGA is not sufficient to account for the quasiparticle nature in the self-energy determination [26]. Figure 3 displays the density of states (DOS) for BeS. DOS in the other member of BeX is very similar with small difference. The first structure in the total DOS is concentrated around -12.52 eV, -

12.47 eV and -11.38 eV for BeS, BeSe and BeTe respectively. This structure originates from the chalcogen s states and is related to the lowest lying band with the spreading in the section around the  $\Gamma$  point in the Brillouin zone. The next structures exist in between -5 eV and 0 eV in all BeX compounds. It can be described as a feature of Be d states and chalcogen p states. They occupy the major states. Also it is well observed that the structures in the energy range of -5 eV and zero pay much contribution to the upper Valence Band. The DOS appearing above the Fermi level are created mostly from the s and p states of Be and in conjunction with partially mixed chalcogen d states. We estimated the band width of valence band as determined from the width of the peaks in DOS spreading below Fermi level. They are equal to 14.02 eV, 14.34 eV, 12.73 eV for BeS, BeSe and BeTe, respectively. The spreading of DOS can be considered as a measure of the localization of the wave function. BeTe possesses the minimum valence band width; evidently show that the wave function in BeTe is the most localized than that in other BeX compound.

### **C. Mechanical properties**

The The present work is on the determination of the elastic constants of BeX compounds, the calculation is performed using the method which is established by Charpin in the combination with WIEN2k code [27]. For the determination of three independent elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$  of zinc blende cubic structure we apply the principle of distorting the lattice with different deformation, which in turn help calculating the elastic constants. In such case one can consider the following three equations:

$$B_0 = (C_{11} + 2C_{12})/3, \Delta E_{rhomb} = \frac{1}{6}(C_{11} + 2C_{12} + 4C_{44})V_0\delta^2, \Delta E_{tetra} = 6(C_{11} - C_{12})V_0\delta^2 \quad (2)$$

If a rhombohedral strain ( $\delta$ ) is applied on the lattice the second equation expresses the variation of strain energy ( $\Delta E_{rhomb}$ ) with volume-conserving rhombohedral strain ( $\delta$ ). Similarly applying tetragonal strain ( $\delta$ ) on the lattice the third equation finds the variation of strain energy ( $\Delta E_{tetra}$ ) with volume conserving tetragonal strain ( $\delta$ ). After such calculation we found the values of elastic constants for the zinc-blende BeX, as displayed in Table 2 .

Table-2: Calculated values of elastic constants ( $C_{ij}$  in GPa) at equilibrium for BeX compound.

	$C_{11}$	$C_{12}$	$C_{44}$
BeS	111	71	69
BeSe	91	63	59
BeTe	79	48	41

Starting from S to Te, generally cohesive energy decreases through the nearest-neighbour distance [28] and hence diminishing spring constant makes influence on the elastic constants. In such case they decrease in magnitude, even though one can expect the increase in lattice dimension from S to Te. Now the mechanical stability in a cubic crystal demands the elastic constants supporting the conditions as,  $C_{11} - C_{12} > 0$ ,  $C_{44} > 0$ ,  $C_{11} + 2C_{12} > 0$ ,  $C_{12} < B_0 < C_{11}$ . The elastic constants displayed in Table 2 follow these conditions. After obtaining the values of elastic constants they are used to define Bulk modulus,  $B_0$ , Young's modulus,  $Y$ , Isotropic shear modulus,  $G$  and Poisson ratio,  $\sigma$  in accordance with the following explicit expressions [29, 30],

$$G = (G_V + G_R)/2, \quad G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (3)$$

Also the Young's modulus and Poisson's ratio can be expressed in terms of Bulk modulus and shear modulus as given by,

$$Y = \frac{9GB}{G + 3B}, \quad \sigma = \frac{3B - 2G}{6B + 2G} \quad (4)$$

Based on equation 3 and 4 the calculated values of elastic modulus are estimated and are included in table 3. It is worthy to be noted that the ductility of the material can be evaluated by B0/G ratio [31].

Table – 3: Calculated values of elastic modulus (in GPa) for BeX

	G (GPa)	B <sub>0</sub> /G	C <sub>12</sub> -C <sub>44</sub> (GPa)	Y (GPa)	σ
BeS	41.88662	2.15152	1.88	108.8	0.299
BeSe	33.41409	2.16735	3.93	86.88	0.3
BeTe	27.48057	2.19755	7.57	71.584	0.302

Because The ratio B0/G is always greater than 1.75 for all BeX as noted in table 3. It confirms the ductile nature of the compounds of all Be-chalcogenides in our work. The highest value of B0/G ratio is found to be 2.19 for BeTe. It indicates that BeTe is the most ductile in comparison to other BeX compounds. With increase in positive Cauchy pressure (C12–C44) is an indicator of the metallic bond, character of the compound is likely to form metallic bond. Tab 3 shows the increasing values of Cauchy pressure starting from S to Te. The BeTe possesses the highest positive Cauchy pressure indicating that it has the strongest metallic bonding (ductility) as compared to other compounds. Also one can find that the value of Y occurs in decreasing order from BeS to BeTe. The highest value of Y is found to exist in BeS. It suggests that BeS is more covalent in nature in comparison to other BeX compounds. Poisson's ratio (σ) is the degree of compressibility of solids. Values of Poisson's ratio for all BeX compounds in the present study are lying between 0.29 and 0.30, hence the result predict the compressibility of all the BeX compounds.

#### D. Calculation of Debye temperature

The Debye temperature (θD) is very important parameter for various physical properties of solids, which includes specific heat, elastic constants, melting temperature, etc. The Debye temperature (θD) is related to the average sound velocity Vm by the equation, [32, 33]

$$\theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} V_m \quad (5)$$

Where NA is Avogadro's number, M is the molecular weight, ρ is the density. Once we can know the elastic constants, we may get the average sound velocity (Vm) as given by [29, 31]

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}, \quad v_t = \sqrt{\frac{C_{44} - \frac{1}{5}(2C_{44} + C_{12} - C_{11})}{\rho}}, \quad v_l = \sqrt{\frac{C_{11} + \frac{2}{5}(2C_{44} + C_{12} - C_{11})}{\rho}} \quad (6)$$

Where  $v_t$  and  $v_l$  are the transverse and longitudinal sound velocities. Based on equation 5 and 6, we have calculated the sound velocities and Debye temperatures with the help of the calculated elastic constants (Table 4).

Table 4: Calculated sound velocities and Debye temperatures for BeX compounds

	$\rho$ (Kg/m <sup>3</sup> )	$V_t$ (m/s)	$V_l$ (m/s)	$V_m$ (m/s)	$\theta_D$ (K)
BeS	4109	3459	6038	3846	423
BeSe	5251	2779	4892	3098	324
BeTe	5643	2322	4167	2578	249

#### IV. CONCLUSION

We have worked on the electronic, elastic and thermal properties of Be-chalcogenides (BeTe, BeSe and BeS) based on FP-LAPW + lo method in the outline of density functional theory. We have calculated the band structure, elastic constant, and Debye temperature based on the structural electronic properties. The generalized gradient approximation (GGA) was taken care for the exchange and correlation effects calculations. The elastic constants maintain all conditions to be satisfied for mechanical stability of the compound. The profound ductility in BeX compound was observed with the increase in chalcogen atomic number. From the band structure of Be-chalcogenides it was confirmed that there is the existence of the indirect energy gap between the valence band maxima and the conduction band minima.

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