

Sound velocities and Debye temperature of BeSe under high pressure up to 50 GPa

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Abstract

The mechanical behavior, sound velocities and Debye temperature of beryllium-selenide (BeSe) semiconductor under pressure up to 50 GPa have been estimated using the structural parameters and elastic constants of Fanjie Kong and Gang Jiang (Physica B 404 (2009) 3935-3940). The Pugh ratio, the directional dependence of elastic wave velocity, the longitudinal, transverse and average sound velocities, and the Debye temperature are successfully predicted and analyzed in comparison with the available theoretical data. The analysis of the Pugh ratio indicates that this compound is prone to brittle behavior. Our obtained results of the longitudinal, transverse and average sound velocities at high pressure indicate that these of Kong and Jiang (Physica B 404 (2009) 3935-3940) are not correctly predicted.

Keywords: Elastic Wave Velocity; Thermal Properties; Beryllium-Selenide (BeSe) Material.

1. Introduction

The beryllium monochalcogenides BeX (X=S, Se and Te) are II-VI compounds. Except to some other group-II A chalcogenides materials, at low pressure the BeX (X=S, Se and Te) materials crystallize in the cubic zincblende structure [1]. They are characterized by their small ionic radius ratio and by the high degree of covalent binding [1].

Using the first principles full-potential linearized augmented plane wave calculations (FP-LAPW) with density functional theory in local density approximations (LDA), Khenata et al. [1] have investigated the pressure dependence of structural parameters, elastic constants and optical properties of cubic zincblende BeS, BeSe and BeTe materials. They found that the elastic constants and the Valence band width of all compounds increase monotonically with increasing pressure, while the transverse (v_t) and average (v_m) wave velocities become almost constants with increasing pressure. The effect of high pressure on the phase transition and the variation of some other physical properties of BeS compound under pressure have been investigated by Ji et al. [2]. They found that the longitudinal wave velocity (v_l) of BeS compound in its cubic zincblende structure increases with pressure, while the transverse (v_t) and average (v_m) wave velocities become almost constants with increasing pressure.

El Haj Hassan and Akbarzadeh [3] have used an Ab initio calculation to study, the ground state properties, the structural phase transformation, elastic constants and the electronic properties of BeX (X=S, Se and Te) materials. Their results on the cohesive energy and bulk modulus suggest that BeTe is more compressible compared to BeS and BeSe materials.

Rai et al. [4] have investigated the electronic, optical, elastic and some thermal properties of BeX (X=S, Se and Te) materials by using FP-LAPW method with both the generalized gradient approximation (GGA) and the modified Becke Johnson (TB-mBJ) potential for the exchange correlation approximation.

The sound velocity, the thermal properties and other physical quantities under pressure and at equilibrium conditions of BeX (X=S, Se and Te) binary compounds [5-12] and ternary alloys [13] are the subject of several studies.

In the present work, we have predicted the directional dependence of elastic wave velocity, the longitudinal, transverse and average sound velocities, and the Debye temperature up to 50 GPa of BeSe semiconductor. The structural parameters and elastic constants are taken from the work of Kong and Jiang [5]. Our results are discussed and compared with the results of the original paper [5], and other theoretical and experimental data of the literature.

2. Theory, calculations and results

2. 1. Crystal density and sound velocities

The solving of the Christoffel equation which relates the sound-wave velocity and the elastic constants C_{ij} was usually used to predict the directional dependence in crystal of elastic wave velocities. For cubic crystals, 3 elastic constants (C_{11} , C_{12} and C_{44}) were used to predict the directional dependence in crystal of elastic wave velocities [14], [15]. The different formulas used here to obtain the directional dependence of the elastic wave velocities are cited in the Refs [14], [15]. The numerical values of the elastic constants C_{ij} and the lattice parameter a (Å) (which are estimated approximately from V/V_0 curve of Fig.2 in Ref [5]) of BeSe semiconductor are taken from the Ref [5], and they are reported in Table. 1. It is very important to note that the values of the bulk modulus B calculated in Ref [5] are not correct, so the correct values of B are recalculated here, and they are reported in Table. 1. The numerical values of the shear modulus G are also recalculated here, and they are also reported in Table. 1.

Table 1: Elastic Constants C_{ij} (GPa) and the Lattice Parameter a Calculated By Kong and Jiang [5]. Bulk Modulus B (GPa), Shear Modulus G in GPa Up to 50 GPa of BeSe Materials are Recalculated Here.

Pressure (GPa)	C_{11}	C_{12}	C_{44}	a (Å)	B	G
0	125.46	45.51	73.40	5.180	72.16	57.51
10	156.45	69.55	103.80	4.983	98.51	73.19
20	182.68	91.48	131.16	4.856	121.88	85.93
30	206.44	112.28	156.86	4.756	143.67	97.05
40	229.00	132.29	181.39	4.673	164.53	107.27
50	250.30	151.63	204.97	4.601	184.52	116.67

The numerical values of the crystal density ρ recalculated here are also reported in Table. 2. The spacing between nearest-neighbors atoms (bond length) is equal to: $d_1 = \sqrt{3} a/4$, and the spacing between the near-neighbor atoms is equal to: $d_2 = a/\sqrt{2}$ [15]. For (B3) BeSe compound, the calculated nearest-neighbor and near-neighbor distances up to 50 GPa are also reported in Table. 2. We profit the existence of the bulk modulus B and the shear modulus G results to analyze the mechanical behavior (the ductility and the brittleness) of BeSe semiconductor up to 50 GPa. Pugh [16] proposed a ratio (B/G) to study the ductility and the brittleness in solid. The value 1.75 is considered as limit to separate the ductile and the brittle domains. A high value of B/G indicates tendency of material for ductility, while a low value of B/G indicates its tendency for brittleness behavior. The calculated values of the ratio (B/G) up to 50 GPa are reported in Table. 2. From 0 to 50 GPa, the values of the ratio (B/G) of BeSe are inferior to 1.75; which suggest that this compound is prone to brittle behavior.

Table 2: Nearest-Neighbors d_1 , Near-Neighbor d_2 , Crystal Density ρ , and Pugh Ratio (B/G) Up to 50 GPa of BeSe Materials are Recalculated Here.

Pressure (GPa)	d_1 (Å)	d_2 (Å)	ρ (g/cm ³)	B/G
0	2.243	3.663	4.204	1.25
10	2.158	3.524	4.723	1.35
20	2.103	3.433	5.104	1.42
30	2.059	3.363	5.433	1.48
40	2.023	3.304	5.728	1.53
50	1.992	3.253	6.000	1.58

At zero-pressure, our calculated value of B/G of BeSe material is relatively lower from the value 1.37 obtained by Ji et al. [2] for BeS compound, indicating a brittle nature of beryllium-chalcogenides (BeS and BeSe) at low pressure. The crystal density ρ reported in Table. 2 is also plotted in Figure.1. An analytical relation for the pressure (in GPa) dependence of the crystal density ρ (in g/cm³) of BeSe material is given by the following a quadratic fit: $\rho = 4.224 + 4.93 \times 10^{-2} p - 2.82 \times 10^{-4} p^2$. The data reported in Table. 2 and in Figure.1, show that the crystal density ρ increases gradually with increasing of hydrostatic pressure, where it takes the value about 4.204 g/cm³ at zero-pressure, and it reaches the value 6 g/cm³ at $P = 50$ GPa. At zero pressure, our obtained value (4.204 g/cm³) of the crystal density ρ is in good agreement compared to the value (4.31 g/cm³) cited by Adachi [15], the deviation between these two values is only about 2.46 %. It is noted that the value of the ideal crystal density ρ is not considerably affected by the presence of a small number of defects (Frenkel defects), so it is almost equal to the bulk density ρ_m ($\rho_m = \rho$), but it is well known that the formation of vacancies in metals or Schottky defects in ionic crystals with big quantity leads to an increase in bulk volume as new atomic layers are formed on the crystal surface. This means that the bulk density (ρ_m) decreases ($\rho_m < \rho$) [17]. On other hand, the existence of pure interstitials results in an increase in bulk density ($\rho_m > \rho$) [17]. So the crystal density ρ can play a very important role on the identification of defects in crystals, and with consequence in solid state physics.

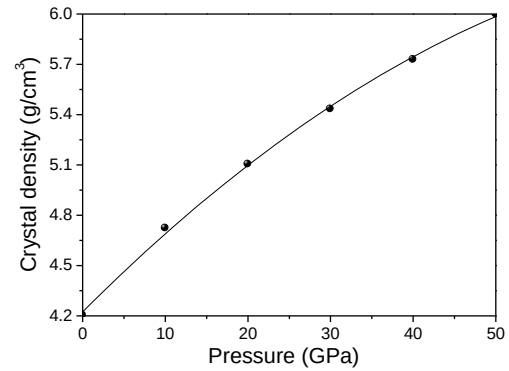


Fig. 1: Crystal Density of BeSe Semiconductor in Cubic Zincblende Type Structure versus Pressure Up to 50 GPa.

Using the previous numerical values of the elastic constants C_{ij} and the crystal density g , the numerical values obtained of the sound velocities for major directions in BeSe semiconductor up to 50 GPa are reported in Table. 3. The obtained values at zero-pressure are compared to the data obtained in our previous work [12]. To the best of our knowledge, there are no data available in the literature on the sound velocities for major directions in BeSe material at high pressure.

Table 3: Sound Velocities in (km/s) for Major Directions in BeSe Material Up to 50 GPa. ^a Longitudinal Waves, ^b Shear Waves. Results with * Are Calculated in Our Previous Work [12]

Propagation (Direction)	Plane of Polarization	Pressure (GPa)		
		0	10	20
[100]	[100] ^a	5.463	5.051*	5.756
	(100) ^b	4.178	3.416*	4.688
[110]	[100] ^a	6.148	5.670*	6.775
	[001] ^b	3.084	2.244*	3.033
[111]	[111] ^a	6.359	5.862*	7.083
	[100] ^a	3.487	2.692*	3.669

Propagation (Direction)	Plane of Polarization	Pressure (GPa)		
		30	40	50
[100]	[100] ^a	6.164	6.323	6.459
	(100) ^b	5.373	5.628	5.845
[110]	[100] ^a	7.629	7.950	8.225
	[001] ^b	2.944	2.906	2.868
[111]	[111] ^a	8.059	8.423	8.735
	[100] ^a	3.924	4.023	4.107

It is important to note also that in single crystal, the Young's modulus E and the Poisson's ratio ν are also change with the crystallographic directions (for more detail on this subject see for example S. Adachi, Properties of Group-IV, III-V and II-VI Semiconductors, John Wiley & Sons, England, (2005)). But, usually the thin films and bulk materials are used in the fabrication of the electronic and optoelectronic devices, so with consequence, the average values of different quantities are used. The average sound velocity (v_m) is determined from the longitudinal (v_l) and transverse (v_t) wave velocities by using the following formula [12], [14]

$$v_m = \left[(1/3) \left((2/v_t^3) + (1/v_l^3) \right) \right]^{-1/3} \quad (1)$$

The longitudinal and transverse wave velocities may be calculated using the following expressions [12], [14]:

$$v_l = \sqrt{(3B+4G)/3\rho}, \text{ and } v_t = \sqrt{G/\rho} \quad (2)$$

Where: B is the bulk modulus, G is the isotropic shear modulus, and g is the crystal density.

The calculated values of the longitudinal (v_l), transverse (v_t) and average (v_m) elastic wave velocities of BeSe semiconductor are

presented in Figure.2. From this figure we observe clearly that all sound velocities increase with increasing pressure up to 50 GPa. Three analytical relations for the pressure (in GPa) dependence of v_l , v_t and v_m (in km/s) of (B3) BeSe semiconductor which are given by the following a quadratic fits:

$$v_l = 5.968 + 4.84 \times 10^{-2} p - 3.50 \times 10^{-4} p^2 \quad (3-a)$$

$$v_t = 3.709 + 2.32 \times 10^{-2} p - 1.86 \times 10^{-4} p^2 \quad (3-b)$$

$$v_m = 4.088 + 2.63 \times 10^{-2} p - 2.09 \times 10^{-4} p^2 \quad (3-c)$$

It is noted that the average (v_m) elastic wave velocity of (B3) BeSe semiconductor tend to increases with increasing hydrostatic pressure to reach a value 4.889 km/s at pressure of 50 GPa.

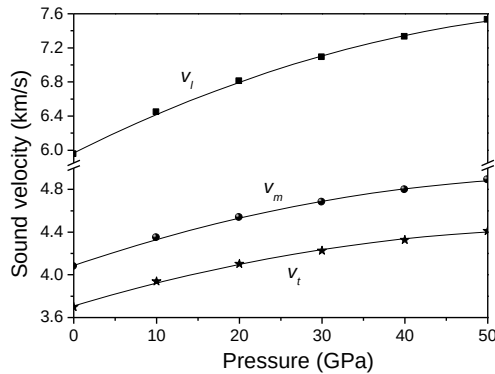


Fig. 2: Elastic Wave Velocities of BeSe Semiconductor in Cubic Zincblende Type Structure versus Pressure Up to 50 GPa.

Despite, Kong and Jiang [5] did not give the exact numerical values of v_l , v_t and v_m at high pressure (because their results are given as a curves and not as tables data); it is very clear from the Figure.9 of the Ref. [5], that the longitudinal, transverse and average sound velocities decrease with increasing pressure, and with consequence the numerical values of v_l , v_t and v_m at no-null pressure obtained by Kong and Jiang [5] are not correctly predicted. Perhaps, the cause of this mistake is the incorrect values of the bulk modulus B calculated by Kong and Jiang [5]. The behavior of the sound velocity under pressure observed here concord well with that obtained by Ji et al. [2] for BeS compound, where the longitudinal wave velocity increase monotony with increasing pressure.

2. 2. Debye temperature

The Debye temperature θ_D is a fundamental thermophysical property; it is used to distinguish between high and low temperature regions for a solid [4], [5]. At low temperature ($T < \theta_D$) one expects high-frequency modes to be frozen, the vibrational excitations arise solely from acoustic vibrations and with consequence the Debye temperature calculated from elastic constants is same as that determined from specific heat measurement [4]. At high temperature ($T > \theta_D$) one expects all modes to have energy $k_B T$ [4], [5]. There are several empirical formulas related the Debye temperature θ_D and other physical quantities (elastic constants, thermal conductivity, sound velocity,...etc). For materials with cubic zincblende and cubic rock-salt structures, the Debye temperature θ_D can be obtained from the average sound velocity v_m (given in km/s) and the lattice parameter a (given in Å) by means of the following simple formula [12], [14]:

$$\theta_D \approx (595.467) v_m / a \quad (4)$$

In cubic system, the Debye temperature and the elastic constants C_{ij} are related also by the following formula [12], [14].

$$\theta_D^3 = \frac{3.15}{8\pi} \left(\frac{h}{k} \right)^3 \left(\frac{n}{g^{3/2} v_a} \right) (C_{11} - C_{12})^{1/2} (C_{11} + C_{12} + 2C_{44})^{1/2} (C_{44})^{1/2} \quad (5)$$

Where: h is the Planck's constant, k is the Boltzmann constant, n is the number of atoms in unit cell of volume v_a , and g is the crystal density.

Another simple formula is also used to predict the Debye temperature θ_D of cubic CsCl (B2) TlSb and TlBi compounds [18], it is given as function of the Wigner radius r , the bulk modulus B , and the average atomic weight M .

Using the values reported in Table1 of the elastic constants C_{ij} and the crystal density g , our calculated values of the Debye temperature of BeSe compound at zero-pressure obtained by using the formula of Eq. (4) and Eq. (5) are: 469 K, and 502 K respectively. These two values are relatively higher than the value (407.93 K) of Kong and Jiang [5] obtained from the quasi-harmonic Debye model approximation [19]. At zero-pressure, our calculated value (469 K) of the Debye temperature of BeSe compound is agree very well with other data of the literature [7], [8], it is deviates from the value (456 K) of Dabhi et al. [7], and the (459 K) of Laref et al. [8] by only about 2.85 % and 2.18 % respectively.

At zero-pressure, our calculated value (502 K) of the Debye temperature obtained from Eq. (5) of BeSe material is also agree very good agreement with the value (502.47 K) in our previous work [20], the deviation is only about 0.09 %.

Using the formula of Eq. (4) and Eq. (5), and also the average value of two results, the Debye temperatures of BeSe semiconductor are presented in Figure.3. From this figure we observe clearly that Debye temperature increase also with increasing pressure up to 50 GPa. Three analytical relations for the pressure dependence of the Debye temperature of (B3) BeSe semiconductor which are given by the following a quadratic fits respectively:

$$\theta_{D(Eq.4)} = 470.61 + 4.93 p - 3.43 \times 10^{-2} p^2 \quad (6-a)$$

$$\theta_{D(Eq.5)} = 503.84 + 5.35 p - 3.74 \times 10^{-2} p^2 \quad (6-b)$$

$$\theta_{D \text{ average}} = 487.22 + 5.14 p - 3.59 \times 10^{-2} p^2 \quad (6-c)$$

It is observed that the values of θ_D of (B3) BeSe material obtained from Eq. (4) and Eq. (5) trend to increase with increasing pressure, where the first one begins with a value of about 470 K at zero-pressure and reaches a value 633 K at pressure of 50 GPa, while the second one begins with a value of about 503 K at zero-pressure and reaches a value 680 K at pressure of 50 GPa. The average value of θ_D increases also with increasing pressure, where it takes a value of 487 K at zero-pressure, and it reaches a value 656 K at 50 GPa.

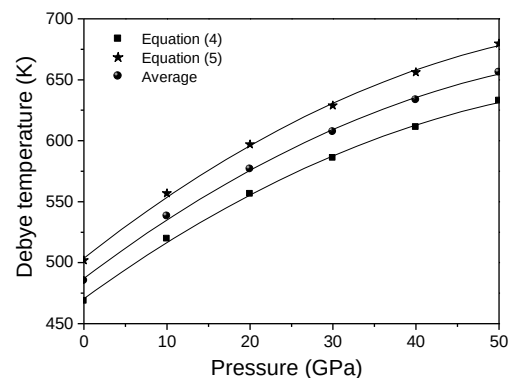


Fig. 3: Debye Temperature of BeSe Semiconductor in Cubic Zincblende Type Structure versus Pressure Up to 50 GPa.

It is very important to note that θ_D of materials obtained from Eq. (5) are always superior to those obtained from Eq. (4); this important observation is confirmed recently in our previous works on some Beryllium-monochalcogenides semiconductors BeX (X=S, Se and Te) [12], and on BX (X=As, Sb) compounds [14].

3. Conclusion

Using the elastic constants and the lattice parameters of Ref. [5]; the sound velocities and Debye temperature of BeSe semiconductor under compression have been predicted and analyzed. The crystal density, the directional dependence of the elastic wave velocity, the longitudinal, transverse and average elastic wave velocities, and the Debye temperature up pressure of 50 GPa are calculated and compared with the available theoretical data of the literature. At zero-pressure, our obtained results are in general in agreement with other theoretical data of the literature.

Contrary to the results of the longitudinal, transverse and average sound velocities obtained by Kong and Jiang [5] at high pressure, our results of all these quantities increase gradually with increasing of pressure which indicates that all these of Kong and Jiang [5] (which decrease with increasing of pressure) are not correctly predicted.

The variation of the Debye temperature of under pressure up to 50 GPa is determined using two different formulas. The average value is also calculated.

To the best of our knowledge, our calculated values of the directional dependence of the elastic wave velocity, the longitudinal, transverse and average sound velocities, and the Debye temperature of BeSe semiconductor under pressure are new (except the results of the original paper [5]), so future experimental and other theoretical results are needed for the validating of our finding data.

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