Crystal density of CaS under pressure up to 40 GPa

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Abstract

Based on the experimental ground state parameters reported in the literature (Luo et al., Phys. Rev. B 50 (1994)16232-16237); in the present work we reproduce the variation in the volume with the pressure up to 40 GPa for calcium sulfide (CaS) compound, which criticized in cubic rock-salt structure. We used two different models of equation of state (EOS); the fist is the model of Vinet, while the second one is the EOS Murnaghan's model. We studied also the effect of the pressure on the crystal density. We established some analytical models relating the volume with the pressure, as well as the crystal density with the pressure.
Finally, we predicted the melting point, the Debye temperature and the sound velocity of CaS material, which are 1202.2 K, 423.7 K, and 4049.5 m/s, respectively.

Keywords:*Equation of State (EOS); Calcium Sulfide; Hydrostatic Pressure; Crystal Density.*

1. Introduction

II–VI semiconducting materials have recently attracted great attention [1-3]. These binary compounds are made from group II and VI elements of the Periodic Table. II–VI semiconductors are used as host material for various applications ranging from photo and electroluminescent thin films to magneto-optical devices [4]. At room temperature and ambient pressure, several IIB–VIB binary compounds (ZnS, ZnSe, CdS, CdTe,…..etc) crystallize in zincblende (B3) or/and wurtzite (B4) phases [5, 6], while the majority of IIA–VIB group (MgS, MgSe, CaTe, …..etc) crystallize in rock-salt (B1) or/and zincblende (B3) phases [1, 7, 8].
Using the energy-dispersive x-ray-diffraction techniques, Luo et al. [1] have investigated the crystal structures of three calcium chalcogenides CaS, CaSe, and CaTe compounds. They found that first-order phase transformation from the NaC1 phase to the CsCl phase was observed at 40 GPa for CaS semiconducting compound.
Using the FP-LAPW method, Amari [7] has studied the structural, electronic magnetic and elastic properties of $Ca_{0.75}Mn_{0.25}S$ and $Ca_{0.75}Fe_{0.25}S$ semiconductors, while Ali et al. [8] have investigated the structural parameters, electronic properties and optical response of II–VI compounds through the modified Becke–Johnson (mBJ) potential. They found that mBJ is an efficient theoretical technique for the calculation of the band structures of II–VI chalcogenides compared to other theoretical approaches (LDA, GGA, and EV-GGA).
In the present work, we reproduce the variation in the volume with the pressure for CaS semiconductor. In order to show how the variation in the volume $-\Delta V/V_0$ of the unit cell and the crystal density in CaS compound behave under applied hydrostatic pressure p, we used the experimental ground state parameters (a= 5.689 Å, B = 64 GPa, and B'_0 = 4.2) reported by Luo et al. [1]. Additionally, we expected the melting point and the Debye temperature of CaS at ambient conditions.

2. Theory, results and discussion

The study of equation of state means the investigation of pressure, volume and temperature (P–V–T) relation. By assuming that the bulk modulus B has a linear dependence on the applied pressure to the crystal (i.e., B (p) = B_0 + B'_0 p), it can be deduced as [9]:

$$V = V_0\left[1 + (B_0' p / B_0)^{-1/B_0'}\right] \tag{1}$$

Where B_0 and V_0 represent the bulk modulus and unit cell volume at ambient pressure, respectively, while B'_0 is the first-order pressure derivative of the bulk modulus evaluated at ambient pressure (the derivative of B with respect to pressure).
It should be noted that the Murnaghan EOS is based on the empirical data, and it does not include non-linear pressure contributions.
The investigation of the pressure dependence with the volume can be also expressed with a universal equation of state, called Vinet model, given as follow [10], [11]:

$$P(V) = 3B_0 \left[\frac{1 - (V/V_0)^{1/3}}{(V/V_0)^{2/3}} \right] \exp \left\{ \frac{3}{2} (B_0' - 1) \left[1 - \left(\frac{V}{V_0} \right)^{1/3} \right] \right\} \tag{2}$$

Fig. 1 shows the variation in the unit cell volume $-\Delta V/V_0$ of CaS compound as a function of pressure p. The fits of our data on ($-\Delta V/V_0$) as a function of p (where p is expressed in GPa) obey these 2nd order polynomial expressions: $-\Delta V/V_0 = 0.65 \times 10^{-2} + 1.15 \times 10^{-2}$ p -1.20 x 10^{-4} p^2 (from Vinet EOS), and $-\Delta V/V_0 = 0.69 \times 10^{-2} + 1.13 \times 10^{-2}$ p -1.25 x 10^{-4} p^2 (from Murnaghan EOS), respectively.
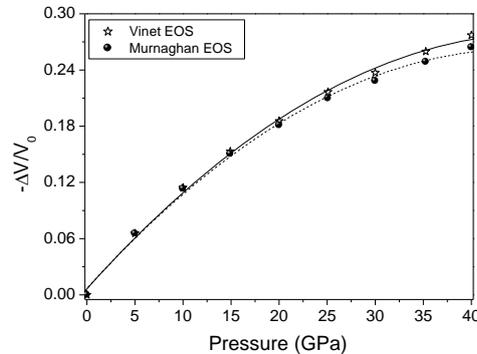
Fig. 1: Variation in the Unit Cell Volume $-\Delta V/V_0$ Versus Pressure for Cubic Rock-Salt (B1) CaS Compound.

Afterwards, the pressure effects on the crystal density ρ for CaS compound were studied. In a conventional unit cell of cubic zinc-blende (B3) and cubic rock-salt (B1) lattices, there are four molecules [12-17]; while these having cubic CsCl-type (B2) structure, there is only one molecule [18-21]. The pressure dependence of the crystal density ρ for CaS semiconducting compound was offered in Fig. 2. It is conventional to fit the crystal density ρ vs pressure to the form: $\rho(p) = \rho_0 + \alpha\, p + \beta\, p^2$ [11, 22]. The best fits of our data regarding the crystal density ρ (expressed in g/cm^3) as a function of pressure p (expressed in GPa) obey the following polynomial expressions: $\rho = 2.61 + 3.44 \times 10^{-2}$ p -2.46 x 10^{-4} p^2 (from Vinet EOS), and $\rho = 2.61 + 3.41 \times 10^{-2}$ p -2.80 x 10^{-4} p^2 (from Murnaghan EOS), respectively.
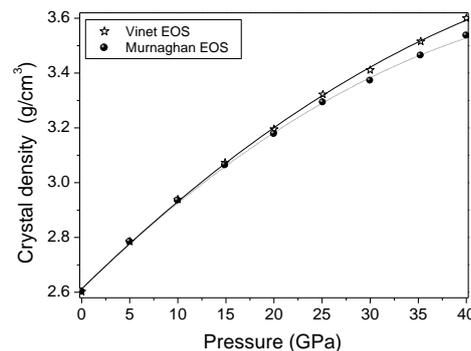
Fig. 2: Crystal Density ρ Versus Pressure for Cubic Rock-Salt (B1) CaS Compound.

As the pressure varied from 0 to 40 GPa, the crystal density ρ values of CaS change from 2.603 to 3.536 g/cm^3 usingMurnaghan's model, and from 2.603 to 3.601 g/cm^3 using Vinet's model, respectively. At zero-pressure, our value (2.603 g/cm3) of ρ for CaS compound is slightly higher than that(2.316 g/cm^3) of AlP semiconducting compound[11].

Under consideration of the scarce data on the thermophysical properties of CaS material, next we discuss the melting point T_m and the Debye temperature θ_D of CaS material. The melting point T_m of several cubic crystals correlates with the bulk modulus B as follow $T_m = 9.3B + 607$ [23], [24], where T_m is expressed in K, and B is expressed in GPa. Replacing in this expression the experimental bulk modulus B (64 GPa) reported by Luo et al. [1], the predicted value of the melting point T_m for CaS semiconducting compound was found to be 1202.2 K. To the best of authors' knowledge, there are no experimental and other theoretical data available in literature on the melting point T_m for CaS material to make comparison.

In the case of ionic binary compounds, the Debye temperature θ_D can be calculated as follow $\theta_D = (\hbar/k_B)(5r_0 B/\mu)^{1/2}$ [25, 26], here $\hbar = h/2\pi$, h is the Planck constant, k_B is the Boltzmann constant, r_0 is the distance between nearest neigh-bours (the inter-ionic distance), B is the bulk modulus, and μ is the reduced mass. The number 5 applies only to crystals with NaCl (B1) structure; it has a different value for other structures [25], [26]. By substituting the experimental values reported by Luoet al. [1] of r_0 and B into previous equation, the value of θ_D was found to be 423.7 K, which is in good agreement with the theoretical ones (458 K, 418 K and 556 K) reported by Narain [15], and $\theta_D = \sim 450$ K reported by Varshney et al.[27], respectively. To the best of our knowledge, there is no experimental data available in literature on θ_D for CaS compound.

In the Debye model, the sound velocity $V_s$may be calculated from the Debye temperature$\theta_D$using the following formula[28]:

$$V_S = k_B\, \theta_D \left/ \sqrt[3]{6\pi^2 \hbar^3\, N/V} \right. \tag{3}$$

Where N/V represents the concentration of atoms in solid.
Replacing our value (423.7 K) of θ_D into equation (3), the sound velocity of CaS compound was found equal to 4049.5 m/s.

3. Conclusion

Using the experimental ground state parameters reported by Luo et al. [1],we investigate the effect of the hydrostatic pressure up to 40 GPa on the variation in the unit cell volume $-\Delta V/V_0$ and the crystal density ρ for cubic rock-salt calcium sulfide (CaS) compound, using two models of equation of state (EOS). We established different analytical expressions relating $-\Delta V/V_0$ with the pressure, which are: $-\Delta V/V_0 = 0.65 \times 10^{-2} +1.15 \times 10^{-2}$ p -1.20×10^{-4} p^2 using Vinet EOS model, and $-\Delta V/V_0 = 0.69 \times 10^{-2} +1.13 \times 10^{-2}$ p -1.25×10^{-4} p^2 using Murnaghan's EOS model, respectively. The crystal density ρ and the pressure p are related by: $\rho = 2.61 + 3.44 \times 10^{-2}$ p -2.46×10^{-4} p^2 (from Vinet EOS model), and $\rho = 2.61 + 3.41 \times 10^{-2}$ p -2.80×10^{-4} p^2 (from Murnaghan EOS model).

Furthermore, we expected the melting point, the Debye temperature and the sound velocity of CaS material, which are 1202.2 K, and 423.7 K and4049.5 m/s, respectively.

References

[1] H. Luo, R. G. Greene, K. G. Handehari, T. Li and A. L. Ruoff, "Structural phase transformations and the equations of state of calcium chalcogenides at high pressure", Physical Review B, Vol. 50, No.22, (1994), pp. 16232-16237. https://doi.org/10.1103/PhysRevB.50.16232.

[2] S. Daoud,"Simplified expressions for calculating Debye temperature andmelting point of II-VI and III-V semiconductors", International Journal of Scientific World, Vol. 3, No.2, (2015), pp. 275-279. https://doi.org/10.14419/ijsw.v3i2.5314.

[3] S. Daoud,"Linear correlation between Debye temperature and lattice thermal conductivity in II-VI and III-V semiconductors", International Journal of Scientific World, Vol. 3, No.2, (2015), pp. 216-220. https://doi.org/10.14419/ijsw.v3i2.4793.

[4] S. Boucenna, Y. Medkour, L. Louail, M. Boucenna, A. Hachemi, A. Roumili, "High pressure induced structural, elastic and electronic properties of Calcium Chalcogenides CaX (X = S, Se and Te) via first-principles calculations", Computational Materials Science, Vol. 68, No. 2, (2013), pp. 325–334. https://doi.org/10.1016/j.commatsci.2012.11.004.

[5] H. Wu, X. Cheng, H. Zhang, and Z. Liu, "Elastic properties of the high-pressure rock-salt phase of ZnO", Philosophical Magazine Letters, Vol. 88, No. 3, (2008), pp. 181–190. https://doi.org/10.1080/09500830701846186.

[6] S. Adachi, "Properties of group-IV, III-V and II-VI semiconductors", John Wiley & Sons Ltd, England, (2005). ISBN 0-470-09032-4. https://doi.org/10.1002/0470090340.

[7] S. Amari," Physical properties of Mn- and Fe-doped CaS: A DFT insights", Computational Condensed Matter, Vol. 27, No. 6, (2021), pp. e00559. https://doi.org/10.1016/j.cocom.2021.e00559

[8] R. Ali, S. Mohammad, Hamid Ullah, S.A. Khan, H. Uddin, M. Khan, and N.U. Khan, "The structural, electronic and optical response of IIA–VIA compounds through the modified Becke–Johnson potential", Physica B, Vol. 410, No. 2 (2013), pp. 93–98. . https://doi.org/10.1016/j.physb.2012.09.050.

[9] F. Murnaghan, "The compressibility of media under extreme pressures", Proceedings of the National Academy of Sciences of the United States of America , Vol. 30, No. 9,(1944), pp. 244–247.https://doi.org/10.1073/pnas.30.9.244.

[10] A.R. Oganov, J.P. Brodholt, G.D. Price, "*Ab initio* theory of phase transitions and thermoelasticity of minerals", Vol. 4, Chapter 5, pp. 83-170. In "Energy Modeling in Minerals", edited by C.M. Gramaccioli, *Eötvös* University Press, Budapest, 2002.https://doi.org/10.1180/EMU-notes.4.

[11] S. Daoud, R. Mezouar, and A. Benmakhlouf, " Structural and piezoelectric coefficients of AlP under pressure ", International Journal of Physical Research, Vol. 6, No. 2, (2018), pp. 53-55. https://doi.org/10.14419/ijpr.v6i2.11020.

[12] W. J. Tropf, M. F. Thomas & T. J. Harris, "Properties of crystals and glasses", Handbook of Optics, Vol. IV, McGraw-Hill, New York, (2004).http://photonics.intec.ugent.be/education/IVPV/res_handbook/v2ch33.pdf.

[13] S. Daoud, and N. Bioud, "Structural properties of (B3) TlP under pressure", International Journal of Physical Research, Vol. 2, No. 2, (2014), pp. 50-55. https://doi.org/10.14419/ijpr.v2i2.3100.

[14] S. Daoud, N. Bioud, and N. Lebga, " Elastic, optoelectronic and thermal properties of boron phosphide ", Journal of Nano- and Electronic Physics,Vol. 5, No. 4, (2013), pp. 04061 (6 pages). https://jnep.sumdu.edu.ua/download/numbers/2013/4/articles/jnep_2013_V5_04061.pdf

[15] S. Narain, "Analysis of the Debye temperature for $A^N B^{8-N}$ type crystals", Physica Status Solidi B, Vol. 182, No. 2, (1994), pp. 273-278. https://doi.org/10.1002/pssb.2221820203.

[16] S. Daoud, "Sound velocities and thermal properties of BX (X=As, Sb) compounds", International Journal of Scientific World: Vol. 3, No.1, (2015), pp. 43-48. https://doi.org/10.14419/ijsw.v3i1.4039.

[17] S. Daoud, A. Bencheikh, and L. Belagraa, "Quasi-linear correlation between high-frequency and static dielectric constants in II-VI and III-V semiconductors ", International Journal of Physical Research, Vol. 5, No.1, (2017), pp. 4-6. https://doi.org/10.14419/ijpr.v5i1.6961.

[18] S. Daoud, N. Bouarissa, A. Benmakhlouf, and O. Allaoui, "High-pressure effect on elastic constants and their related properties of MgCa intermetallic compound", Physica Status Solidi B, Vol. 257,No. 6, (2020), pp. 1900537 (10 pages). https://doi.org/10.1002/pssb.201900537.

[19] A. Benmakhlouf, A. Benmakhlouf, O. Allaoui, and S. Daoud, "Theoretical study of elastic and thermodynamic properties of CuSc intermetallic compound under high pressure", Chinese Journal of Physics, Vol. 57, No. 2, (2019), pp. 179-188. https://doi.org/10.1016/j.cjph.2018.11.017.

[20] A. Benmakhlouf, A. Benmakhlouf, O. Allaoui, and S. Daoud, "Corrigendum to Theoretical study of elastic and thermodynamic properties of CuSc intermetallic compound under high pressure [Chin. J. Phys. 57 (2019) 179–188]", Chinese Journal of Physics: Vol. 59, No. 6, (2019), pp. 656. https://doi.org/10.1016/j.cjph.2019.04.010.

[21] S. Daoud, N. Bioud, and P. K. Saini, "Finite temperature thermophysical properties of MgCu intermetallic compound from quasi-harmonic Debye model", Journal of Magnesium and Alloys, Vol. 7, No. 2, (2019), pp. 335-344. https://doi.org/10.1016/j.jma.2019.01.006.

[22] A. Benamrani, S. Daoud, Manal M. Abdus Salam, and H. Rekab-Djabri, " Structural, elastic and thermodynamic properties of YRh: DFT study ", Materials Today Communications, Vol. 28, No. 9, (2021), pp. 102529 (8 pages). https://doi.org/10.1016/j.mtcomm.2021.102529.

[23] M. E. Fine, L. D. Brown, and H. L. Marcus, "Elastic constants versus melting temperature in metals", Scripta Metallurgica, Vol. 18, No. 9, (1984), pp. 951–956. https://doi.org/10.1016/0036-9748(84)90267-9.

[24] S. Daoud, P. K. Saini, and H. Rekab-Djabri, "Theoretical prediction of some physical properties of $B_x Al_{1-x} Sb$ ternary alloys", Journal of Nano- and Electronic Physics, Vol. 12, No 6, (2020), pp. 06008(5pp). https://doi.org/10.21272/jnep.12(6).06008.

[25] M. Blackman, "On the relation of Debye theory and the lattice theory of specific heats", Proceedings of the Royal Society of London. Series A, Vol. 181, No. 984, (1942), pp. 58-67. https://doi.org/10.1098/rspa.1942.0058.

[26] A. Benamrani, S. Daoud, and P. K. Saini, " Structural, elastic and thermodynamic properties of ScP compound: DFT study ", Journal of Nano- and Electronic Physics, Vol. 13, No 1, (2021), pp. 01008(5pp). https://doi.org/10.21272/jnep.13(1).01008.

[27] D. Varshney, V. Rathore, R. Kinge, R. K. Singh, "High-pressure induced structural phase transition in alkaline earth CaX (X=S, Se and Te) semiconductors: NaCl-type (B1) to CsCl-type (B2)",Journal of Alloys and Compounds, Vol. 484, No 1-2,(2009), pp. 239–245. https://doi.org/10.1016/j.jallcom.2009.04.022.

[28] K. W. Böer, U. W. Pohl, "Semiconductor Physics", Springer International Publishing AG, Switzerland, (2018).ISBN 978-3-319-69149-7 https://doi.org/10.1007/978-3-319-69150-3.