Mass density, sound velocity and Debye temperature of CaTe semiconductor under high compression

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Abstract

Using the structural parameters and the elastic stiffness constants reported in the literature (by Guo et al. in Solid State Commun., 340, 114488 (2021)) as well as different appropriate analytical and semi-empirical expressions, we reported the high compression effect up to pressure of 27.8 GPa on the average sound velocity and Debye temperature θ_D of cubic rocksalt calcium telluride (CaTe) semiconducting compound. The pressure dependence of the Debye temperature θ_D for CaTe compound was obtained using two different approaches. We found that both the average sound velocity and Debye temperature of CaTe compound increase monotonously and non-linearly with enhanced pressure up to 27.8 GPa. We note that similar behavior on the average sound velocity and Debye temperature θ_D was also observed in the literature for the same compound and for other materials with different crystallographic structures. The deviations on θ_D between the two different approaches and to those of the literature are quite large at high pressures.

Keywords: *Calcium-based chalcogenides; High pressure; Sound velocity; Debye temperature.*

1. Introduction

It is known that alkaline earth chalcogenides (AECs) just like calcium sulfide (CaS), calcium selenide (CaSe) and calcium telluride (CaTe) semiconductors have great importance in many technological applications including catalysis, microelectronics, etc [1].

Using density functional theory (DFT) calculations, Guo et al. [1] have studied the structural phase transition of crystalline CaTe in pressure ranging from 0 to 60 GPa. They found that under high compression the cubic rocksalt (B1) phase of CaTe compound transforms to an intermediate tetragonal structure of P4/nmm at pressure of 27.8 GPa. Guo et al. [1] have studied also the pressure dependence of mechanical properties of CaTe with five different forms, and the change of the elastic constants.

Luo et al. [2] have investigated experimentally the structural phase transition of calcium (Ca) based chalcogenides CaX (X = S, Se, Te) compounds up to 52 GPa using energy-dispersive x-ray-diffraction techniques with a synchrotron source. They found that under high compression the B1 phase of CaS transforms from B1 phase to CsCl-type phase (B2) at pressure of 40 GPa [2]; the CaSe transformed from B1 to B2 at 38 GPa [2], while for the CaTe, the transformation of B1 phase to the manganese phosphide structure (MnP-type) is at around 25 GPa [2].

Okba and Mezouar [3] have studied the effect of high compression up to phase transition pressure on the unit cell volume, bulk modulus, and Grüneisen parameter for CaX (X = S, Se, Te) materials using only the experimental parameters of equations of state reported in the literature. They found that as the pressure increases, both the mass density and the bulk modulus increase, while both the first order pressure derivative of the bulk modulus and the Grüneisen parameter decrease.

Varshney et al. [4] have investigated the effect of high pressure on unit cell volume, Gibbs free energy, elastic constants, and the Debye temperature of CaX (X = S, Se, Te) materials in both NaCl-type (B1) and CsCl-type phase (B2) structures using a theoretical approach based on the effective inter-ionic potential. They found that the Debye temperature of all these compounds increases monotonously with enhanced pressure.

Khaldi et al. [5] have investigated the effect of high compression up to 30 GPa on the structural and elastic properties of CaX (X = S, Se, Te) semiconducting materials in B1 phase using an ab-initio calculations. For all these compounds, they found that the elastic constant C_{11} increases monotonously with enhanced pressure up to 30 GPa, while both the elastic constants C_{12} and C_{44} remain almost unchanged with increasing pressure from 0 up to 30 GPa.

Using first principles calculations, Labidi et al. [6] have studied the structural parameters, elastic constants and the thermodynamic properties of CaS, CaSe, and CaTe compounds in the temperature ranging from 0 to 100 K, while in the same context, Maizi et al. [7] have studied the same properties in the pressure ranging from 0 to 30 GPa and temperature ranging from 0 to 1200 K.

In the present contribution, we studied the high hydrostatic compression effect up to 27.8 GPa on the variation of the mass density,sound velocity and Debye temperature of CaTe compound using the structural parameters and the elastic constants reported by Guo et al. [1].

2. Theory, results, and discussion

2.1. Mass density

If accurate lattice parameters or unit cell volume are available, the calculation of the mass density ρ gives in principle a good and reliable value [8-11]. The so-called X-ray crystal density ρ of any crystal can be written in term of the molecular density d_M as follows: $\rho = M d_M/N_A$ [12], where M is the molecular weight, and $N_A = 6.022 \times 10^{23}$ mol^{-1} is the Avogadro constant.

There are four molecules in a unit cell of both cubic zincblende (B3) and cubic rocksalt (B1) lattices. So for both B3 and B1 phases, the molecular density: $d_M = 4/V = 4/a^3$, where V is the unit cell volume and a is the lattice constant [12]. To simplify the previous formula, the X-ray crystal density ρ of both B3 and B1 phases can be expressed as [12]:

$$\rho = 4M/N_A V = 4M/N_A a^3 \tag{1}$$

for CaTe, the molecular weight: M = 167.678 g/mol.

Fig. 1 illustrates the pressure dependence of the crystal density ρ for CaTe compound, along the results of Okba and Mezouar [3]. Fig. 1 indicates that the mass density ρ of CaTe material increases non-linearly with increasing in pressure up to 27.8 GPa. An analytical relationship for the pressure (in GPa) dependence of the mass density ρ (in g/cm^3) of CaTe semiconducting material is given by the following a quadratic fit: $\rho = 4.2813 + 9.29 \times 10^{-2}$ p - 0.10 x10^{-2} p^2.

We note that a similar behavior was observed for wide range of materials such calcium-based chalcogenides CaX (X = S, Se, Te) semiconductor materials [3], copper nitride (Cu$_3$N) compound in its phase cubic anti-ReO$_3$-type up to 30 GPa [8], cubic zincblende (B3) boron nitride material in the pressure ranging from 0 to 4 Mbar [13], and beryllium-selenide (BeSe) compound up to 50 GPa [14].
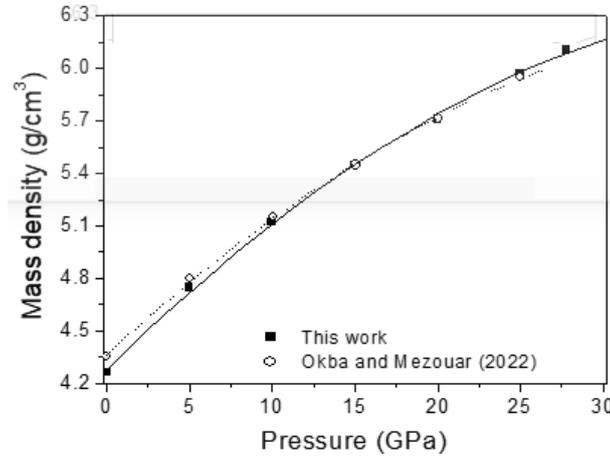
Fig. 1: Mass Density P Versus Pressure for CaTe Compound, Along the Theoretical Results of Okba and Mezouar [3].

2.2. Sound velocity and Debye temperature

The Debye temperature θ_D is an important fundamental thermophysical parameter closely related to several other physical properties such as melting temperature and specific heat capacity [15 - 21]. At low temperatures, the Debye temperature calculated from the elastic constants is the same as that determined from the specific heat measurements [15], [16]. One of the standard methods to calculate θ_D is from elastic constants measurements, since θ_D may be estimated from the average sound velocity v_m by the following equation [15]:

$$\theta_D = \frac{h}{k_B}\left(\frac{3n}{4\pi}(N_A\rho/M)\right)^{1/3} v_m \tag{2}$$

where h is the Plank's constant (h= 6.6262.10^{-34} J.s), k_B is the Boltzmann's constant (k_B = 1.38062.10^{23} J.deg^{-1}), N_A is the Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, ρ is the mass density. The average sound velocity v_m is given by [22-25]:

$$v_m = \left(\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right)^{-1/3} \tag{3}$$

where v_l and v_t are the longitudinal and transverse sound velocity obtained using the shear modulus G, the bulk modulus B and the density g from Navier's equations: $v_l = [(3B+4G)/3\rho]^{1/2}$, and $v_t = (G/\rho)^{1/2}$ [13], [16]. Using the elastic constants $C_{ij}(p)$ and the lattice parameter a (p) calculated by Guo et al. [1], the compression effects on the longitudinal v_l, transverse v_t and average v_m sound velocity for CaTe compound are illustrated in Fig. 2. Fig. 2 indicates that v_m of CaTe material increases non-linearly with increasing in pressure up to 27.8 GPa. The best fits of the longitudinal v_l, transverse v_t and average v_m sound velocity (expressed in km/s) against pressure p (expressed in GPa) for CaTe material may be written as: $v_l = 4.04 + 9.09 \times 10^{-2}$ p-1.24×10^{-3} p^2, $v_t = 2.37 + 2.60 \times 10^{-2}$ p$- 4.45 \times 10^{-4}$ p^2, and $v_m = 2.52 + 3.8 \times 10^{-2}$ p$- 1.2 \times 10^{-3}$ p$^2 + 1.6 \times 10^{-5}$ p^3, respectively. We note that a similar behavior is shown for copper nitride (Cu$_3$N) in its phase cubic anti-ReO$_3$-type up to 30 GPa [8], for cubic zinc blende (B3) boron nitride compound up to 4 Mbar [13], for beryllium-selenide (BeSe) semiconducting compound up to 50 GPa [14], and for compressed rock salt (B1) CuCl and CuBr binary compounds in the pressure ranging from 10 to 20 GPa [26].
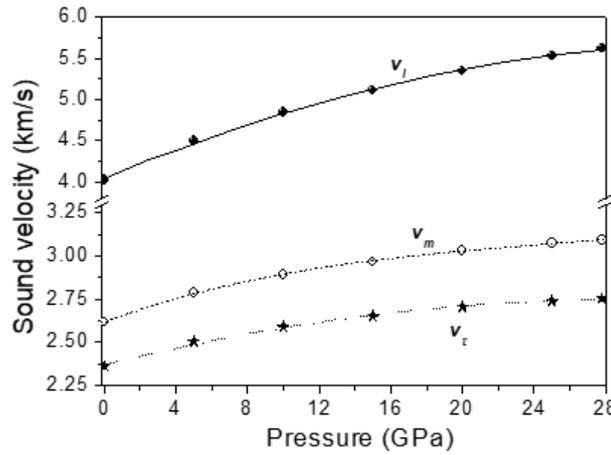
Fig. 2: Longitudinal v_l, Transverse v_t and Average v_m Sound Velocity Versus Pressure for CaTe Material.

Using the formula of equation (2), the obtained values of θ_D for CaTe material are reported in table 1 and presented in Fig. 3. At zero-pressure, our obtained value (244 K) of θ_D is relatively lower than the theoretical value (~ 257K) obtained by Varshney et al.[4], the deviation being ~ 5%. The available data on θ_D for CaTe can thus only be considered as a rough indication of its order of magnitude.

Table 1: Debye Temperature Θ_D Obtained from Eq. (2) Versus Pressure P for CaTe Material, * from Ref [4]

p (GPa)	0	5	10	15	20	25	27.8
θ_D (K)	244, ~257*	269	287	300	311	321	325

For materials with cubic structures, the Debye temperature θ_D could be calculated using the following semi-empirical formula [27]:

$$\theta_D = C_c s^{-1/6}\left(a\,G_c/M\right)^{1/2} \tag{4}$$

Where, $C_c = (26.05 \pm 0.81)$ K (m kg N^{-1})$^{1/2}$ (it is important to note that the numerical value 26.05 ± 0.81 K (m kg N^{-1})$^{1/2}$ is valuable only for crystals with cubic structures), s is the number of atoms in the unit cell of our structure of interest, a is the lattice parameter expressed in m, and M is the atomic weight (arithmetical average of the masses of the species), respectively, and.

$$G_c = \left[C_{44}\left[C_{44}(C_{11}-C_{12})/2\right]^{1/2}(C_{11}-C_{12}+C_{44})/3\right]^{1/3} \tag{5}$$

Using the calculated elastic constants $C_{ij}(p)$ and the lattice parameter a (p) reported by Guo et al. [1] with the formula of equation (4), the obtained values of θ_D for CaTe material are reported in table 2 and presented also in Fig. 3 (left). At zero-pressure, the value (239 K) of θ_D obtained from equation (4) is in good agreement with the value (244 K) obtained from equation (2), the deviation being only ~ 2%.

Table 2: Debye Temperature Θ_D of CaTe Material Obtained from Eq. (4) Versus Pressure

p (GPa)	0	5	10	15	20	25	27.8
θ_D (K)	239	263	278	288	296	300	301

It is inferred from tables 1 and 2 and Fig. 3 that the Debye temperature θ_D of CaTe compound increases non-linearly with increasing in pressure up to 27.8 GPa. We note that a similar behavior and good agreement was observed in comparison to data obtained for CaX (X = S, Se, Te) materials [4]. The same behavior is shown for Cu_3N up to 30 GPa [8], for cubic zincblende boron nitride [13], for BeSe compound up to 50 GPa [14], and for compressed rock salt (B1) CuCl and CuBr compounds in the pressure ranging from 10 to 20 GPa [26].
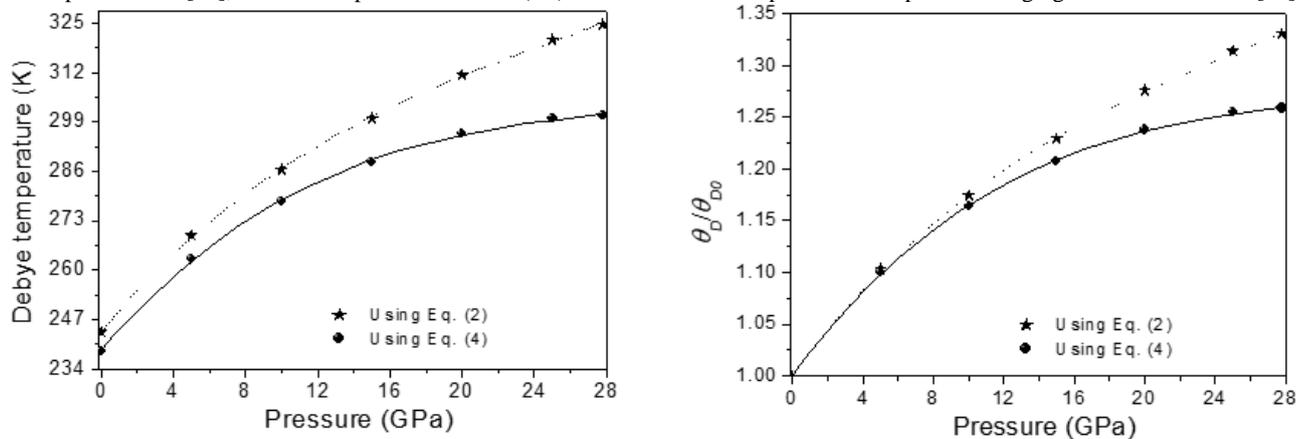
Fig. 3: Debye Temperature Θ_D (left) and Normalized Debye Temperature Θ_D/Θ_{D0} (right) Versus Pressure for CaTe Compound.

The fits of the Debye temperature θ_D (expressed in K) versus pressure p (expressed in GPa) for CaTe compound are given as follows: $\theta_D = 239 + 5.45\,p - 0.17\,p^2 + 0.002\,p^3$ using Eq. (2), and $\theta_D = 244 + 5.62\,p - 0.153\,p^2 + 0.002\,p^3$ using Eq. (4), respectively. Except the theoretical data reported in Refs [4], to the best of our knowledge, no experimental or other calculations have been reported to date on the pressure dependence of θ_D for CaTe compound. Another form to compare our data on θ_D for CaTe compound is by using the normalized De-

bye temperature θ_D/θ_{D0} curves, the results obtained are presented in Fig. 3 (right). Unfortunately, the scarcity of experimental data from different sources of the literature on the Debye temperature θ_D for CaTe compound prevents reaching definite conclusions regarding the exact and true values of this property under high pressures.

3. Conclusion

The study of the effect of high compression up to 27.8 GPa on the average sound velocity and Debye temperature of CaTe shows that:
Both the mass density and average acoustic wave speed of CaTe increase monotonously and non-linearly with increasing pressure and a similar behavior was observed in the literature for other materials with different crystallographic natures.
The Debye temperature θ_D of our material of interest increases also non-linearly and monotonously with enhanced pressure up to 27.8 GPa. We note that similar behavior on θ_D was observed in the literature for CaX (X = S, Se, Te) compounds, Cu_3N material, cubic zincblende boron nitride, beryllium-selenide (BeSe), compressed rocksalt CuCl and CuBr compounds and for other materials.
To the best of our knowledge, no experimental data has been reported to date on the pressure dependence of θ_D for CaTe compound. The combined results on CaTe semiconductor represent considerable data with the potential to provide more consistency at high pressure.

References

[1] Y. Guo, D. Xia, Q. Liu, X. Zhao and J. Li, "Phase transition of CaTe induced by high-pressure: Structural and elastic DFT study of five structures", *Solid State Communications*, Vol. 340, No.12, (2021), pp. 114488 (6 pages). https://doi.org/10.1016/j.ssc.2021.114488.

[2] 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.

[3] F. Okba and R. Mezouar, " Some physical parameters of calcium chalcogenides at high pressures: Semi-empirical approach", *Journal of Nano- and Electronic Physics*, Vol. 14, No 4, (2022) pp. 04004 (4 pages). https://doi.org/10.21272/jnep.14(4).04004.

[4] D. Varshney, V. Rathore, R. Kinge and 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.

[5] A. Khaldi, N. Bouarissa and L. Tabourot, "The pressure influence on structural parameters and elastic properties of rock-salt CaX (X=S, Se and Te) materials", *Chemical Physics Impact,* Vol. 6, No 1 (2023), pp. 100237 (9 pages). https://doi.org/10.1016/j.chphi.2023.100237.

[6] S. Labidi, M. Boudjendlia, M. Labidi, and R. Bensalem, "First principles calculations of the structural, elastic, and thermal properties of the rock-salt CaX (X = S, Se, Te) ", *Chinese Journal of Physics*, Vol. 52, No 3, (2014), pp. 1081 –1090.

[7] R. Maizi, A. Boudjahem and M. Boulbazine, "First-principles investigations on structural, elastic, and thermodynamic properties of CaX (X = S, Se, and Te) under pressure", *Russian Journal of Physical Chemistry A,* Vol. 93, No 13, (2019), pp. 2726–2734. https://doi.org/10.1134/S0036024419130181.

[8] S. Daoud, "Comment on the effect of pressure on the physical properties of Cu_3N ", *Physica Scripta*, Vol. 91, No. 5, (2016), pp. 057001 (2 pages). https://doi.org/10.1088/0031-8949/91/5/057001.

[9] S. Daoud," Comment on Ab initio calculations of B2 type RHg (R = Ce, Pr, Eu and Gd) intermetallic compounds", *The European Physical Journal B*, Vol. 89,(2016), pp. 47 (2 pages). https://doi.org/10.1140/epjb/e2016-60844-9.

[10] K.B. Modi, "Elastic moduli determination through IR spectroscopy for zinc substituted copper ferri chromates", *Journal of Materials Science*, Vol. 39, No 4, (2004), pp. 2887–2890.https://doi.org/10.1023/B:JMSC.0000021472.00590.9b.

[11] S. Daoud, "Comment on ab initio study of the structural, elastic, electronic and optical properties of Cu_3N ", *Materials Research*, Vol. 19, No. 2, (2016) pp. 314-315. https://doi.org/10.1590/1980-5373-MR-2015-0602.

[12] S. Adachi, *Properties of Group-IV, III-V and II-VI Semiconductors*, John Wiley & Sons Ltd, USA, (2005)https://doi.org/10.1002/0470090340.

[13] S. Daoud and N. Bioud, "Anisotropy and pressure effect on the elastic and mechanical properties of (B3) BN", *Ukrainian Journal of Physics*, Vol. 59, No. 4, (2014), pp. 418 – 425. https://doi.org/10.15407/ujpe59.04.0418.

[14] S. Daoud, "Sound velocities and Debye temperature of BeSe under high pressure up to 50 GPa", *International Journal of Physical Research*, Vol. 5, No. 1, (2017), pp. 7-10. https://doi.org/10.14419/ijpr.v5i1.7013.

[15] O.L. Anderson, "A simplified method for calculating the Debye temperature from elastic constants", *Journal of Physics and Chemistry of Solids*, Vol. 24, No. 7, (1963), pp. 909-917. https://doi.org/10.1016/0022-3697(63)90067-2.

[16] S. Daoud, K. Loucif, N. Bioud and N. Lebga, "First-principles study of structural, elastic and mechanical properties of zinc-blende boron nitride (B3-BN) ", *Acta Physica Polonica A*, Vol. 122, No. 1, (2012), pp.109-115. https://doi.org/10.12693/APhysPolA.122.109.

[17] 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.

[18] 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.

[19] S. Daoud and A. Latreche, "Comment on density functional investigation on electronic structure and elastic properties of BeX at high pressure ", *Indian Journal of Physics*, Vol. 90, No 11, (2016), pp. 1243-1244. https://doi.org/10.1007/s12648-016-0863-4.

[20] 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.

[21] S. Daoud, "Thermal properties of cubic zincblende thallium-phosphide from quasi-harmonic Debye model approximation", International Journal of Physical Research: Vol. 5, No. 1, (2017), pp. 14-16. https://doi.org/10.14419/ijpr.v5i1.7093.

[22] S. Amari, H. Rekab-Djabri and S. Daoud, "Mechanical, thermal, electronic, and magnetic properties of $Ca_{0.75}Er_{0.25}S$ alloy from a DFT approach: a promising material for spintronic applications", *Materials Today Communications*, Vol. 33, (2022), pp. 104237 (9 pages). https://doi.org/10.1016/j.mtcomm.2022.104237.

[23] H. Rekab-Djabri, M. Drief, Manel. M. Abdus Salam, S. Daoud, F. El Haj Hassan and S. Louhibi-Fasla, " Full-potential linear muffin-tin orbital investigation of the structural, electronic, elastic and optical properties of semiconducting $AgBr_{1-x}I_x$ ($0 \leq x \leq 1$) ternary alloys", *Canadian Journal of Physics*, Vol. 98, No. 9, (2020), pp. 834-848.https://doi.org/10.1139/cjp-2019-0357.

[24] S. Benyettou, S. Saib and N. Bouarissa,"Materials properties, lattice dynamics and polaron characteristics in $InSb_xP_{1-x}$ ternary alloys", Materials Science in Semiconductor Processing, Vol. 125, No. 4, (2021), pp. 105640 (9 pages).https://doi.org/10.1016/j.mssp.2020.105640.

[25] S. Daoud and H. Rekab-Djabri, "Bulk modulus of CaO under high pressure up to 65 GPa ", *International Journal of Advanced Chemistry*, Vol. 10, No. 2, (2022), pp. 135-137. https://doi.org/10.14419/ijac.v10i2.32191.

[26] N. Bioud, X-W. Sun, N. Bouarissa and S. Daoud,"Elastic constants and related properties of compressed rocksalt CuX (X =Cl, Br): Ab initio study", *Zeitschrift Für Naturforschung A*, Vol. 73, No. 8, (2018), pp.767–773. https://doi.org/10.1515/zna-2018-0120.

[27] H. Siethoff, "Debye temperature, self-diffusion and elastic constants of intermetallic compounds", *Intermetallics*, Vol. 5, No. 8, (1997), pp. 625-632. https://doi.org/10.1016/S0966-9795(97)00037-X.