Journal of Nano- and Electronic Physics
Vol. **14** No 2, 02020(4pp) (2022)

Журнал нано- та електронної фізики
Том **14** № 2, 02020(4cc) (2022)

Study of the Grüneisen Parameter of ZnO at High Pressures

Binita Shah*

Department of Physics, Electronics and Space Sciences, University School of Sciences, Gujarat University, Navrangpura, Ahmedabad-38009, India

(Received 28 February 2022; revised manuscript received 16 April 2022; published online 29 April 2022)

Investigations of thermoelastic properties for several types of solids is very important for researchers to understand the earth's lower mantle structure and core at high pressure range. The Grüneisen parameter (γ) plays a very important role in the study of thermoelastic properties as it provides the fundamental basis regarding the frequency distribution of phonon spectrum in solids. In the present study, an attempt has been made to theoretically compute the pressure dependent Grüneisen parameter for wurtzite (B4) and rock salt (B1) phases of bulk and nano zinc oxide (ZnO) up to about 200 GPa. The free volume expression for the Grüneisen parameter derived by Vaschenko and Zubarev and isothermal equations of state (EOS) are used to numerate the values. We have found that the trend of variation of the Grüneisen parameter against pressure obtained for ZnO is similar to the trend obtained for other metals as per literature.

Keywords: ZnO, EOS, Grüneisen parameter, Wurtzite and rock salt phase, Thermoelastic properties.

DOI: 10.21272/jnep.14(2).02020 PACS numbers: 64.30. – t, 65.40. – b, 63.20.Ry

1. INTRODUCTION

Among all semiconductor metal oxides, zinc oxide (ZnO) is known to be one of the most widely studied materials because of its unique structural, mechanical, electronic and thermal properties. It is highly functional, versatile, favorable, inorganic, white solid powder which shows a wide range of industrial and technological applications in various fields. In the present paper,the Grüneisen parameter (γ) of ZnO is analyzed. The Grüneisen parameter is the most valuable thermodynamic quantity in geophysics, condensed matter physics and solid-state physics as it is approximately constant and dimensionless with a value close to unity which varies slowly with pressure and temperature [1, 2]. It has both microscopic and macroscopic definition. The microscopic definition relates the vibrational frequencies of atoms in a material, whereas the macroscopic definition requires experimental measurements of thermodynamic properties such as heat capacities, bulk modulus and thermal expansion coefficient at high pressure and high temperature [2]. The study of the Grüneisen parameter (γ) is very essential in modern technology for better applications of semiconductor materials. It provides information about the lattice anharmonicity of the forces acting in a crystal needed for a fundamental understanding of the elastic constants and the frequency distribution of the phonon spectrum at high pressure and high temperatures [3]. The Grüneisen parameter can be considered as the ratio of change in pressure to the corresponding increase in energy density [1]. The study of the Grüneisen parameter plays a very important role in the exploration of theoretical equations of state (EOS), geophysical models, ultrasonic measurements and melting of solids. The knowledge of the pressure dependent Grüneisen parameter is very useful in the diminution of shock-wave data to isothermal data [4]. Due to the lack of proper theory and the difficulties associated with experimental evidence, there has been a long-standing interest in the behavior of the Grüneisen parameter at high pressure or compression, which provides a fundamental basis for studying thermoelastic properties of solids [5]. The logarithmic pressure derivative of the diffusion coefficient can also be determined by the Grüneisen parameter [6]. In the present study, an attempt was made to theoretically predict the pressure dependent Grüneisen parameter for wurtzite (B4) and rock salt (B1) phases of bulk and nano ZnO at high pressure range.

2. METHOD OF ANALYSIS

The vibrational Grüneisen ratio (γ_i), according to the microscopic definition of the Grüneisen parameter, can be defined as the logarithmic volume derivative of the lattice phonon frequency ω_i [1] given as

$$\gamma_i = -\frac{\partial \ln w_i}{\partial \ln V}. \quad (1)$$

According to the macroscopic definition, Grüneisen parameter related to the thermoelastic properties can be defined as [1],

$$\gamma_{th} = \frac{\alpha B V}{C_V}, \quad (2)$$

where α is thermal expansion co-efficient, B is isothermal bulk modulus, V represents volume of the unit cell, C_V is heat capacity (per mass) at constant volume.

Using different approaches, many researchers have derived various approximate expressions to study the variation of Grüneisen parameter theoretically with high pressure and volume [7].

Vaschenko and Zubarev [3] proposed the free volume formula which relates Grüneisen parameter with the isothermal bulk modulus along with its pressure derivative given by,

$$\gamma_{ba-s} = \frac{\frac{1}{2}B' - \frac{5}{6} + \frac{2}{9}\left(\frac{P}{B}\right)}{\left(1 - \frac{4P}{3B}\right)}, \quad (3)$$

* binitashah100@gmail.com

where P is the pressure, B_0 is the isothermal bulk modulus at zero pressure and B'_0 is the first order pressure derivative of the isothermal bulk modulus.

An effort was made to compute the Grüneisen parameter of ZnO using the Tait's [8] and Vinet's [3] EOS.

The Tait's EOS, representing the relationship between pressure and volume at a fixed temperature, is given by:

$$P = \frac{B_o}{B_0^{'}+1}\left[\exp\left\{\left(B_0^{'}+1\right)\left(1-\frac{V}{V_0}\right)\right\}-1\right]. \quad (4)$$

Based on the Einstein model, the universal EOS proposed by Vinet, which shows the relationship between binding energy and interatomic distance in solids, is as follows:

$$P = 3B_0 x^{-2}\left(1-x\right)\exp[\eta(1-x)], \quad (5)$$

where $x = \left(\frac{V}{V_o}\right)^{\frac{1}{3}}$, $\eta = \frac{3}{2}\left(B_o^{'}-1\right)$.

Here, V is the volume of the solid at pressure P and V_0 is the volume of the solid at zero pressure.

The isothermal bulk modulus derived from equations (4) and (5) is given as:

$$B = B_o\left(\frac{V}{V_o}\right)\left[\exp\left\{\left(B_o^{'}+1\right)\left(1-\frac{V}{V_o}\right)\right\}\right], \quad (6)$$

$$B = B_o x^{-2}\left[1+\left(\eta x+1\right)\left(1-x\right)\right]\exp\left\{\eta\left(1-x\right)\right\}. \quad (7)$$

The corresponding zero pressure derivatives are derived as follows:

$$B' = \left(\frac{V}{V_o}\right)\left(B_o^{'}+1\right)-1, \quad (8)$$

$$B' = \frac{1}{3}\left[\frac{x\left(1-\eta\right)+2\eta x^2}{1+\left(\eta x+1\right)\left(1-x\right)}+\eta x+2\right]. \quad (9)$$

3. RESULTS AND DISCUSSION

In the present work, the computation of the Grüneisen parameter as a function of pressure is carried out for wurtzite (B4) and rock salt (B1) phases of bulk and nano ZnO using Tait's and Vinet's EOS. The input parameters required to compute the Grüneisen parameter for both phases of bulk ZnO are tabulated in Table 1 [9].

Table 1 – The input parameters used for the determination of the Grüneisen parameter for B4 and B1 phases of bulk ZnO

Material	B_0 [9] (GPa)	B'_0 [9]
ZnO (B4)	181	4
ZnO (B1)	194	4.8

Using equation (3), we have computed the Grüneisen parameter for both phases of ZnO. Fig. 1 shows our predicted results for the pressure dependent Grüneisen parameter for wurtzite (B4) and rock salt (B1) phases of bulk ZnO using Tait's and Vinet's EOS, respectively. Numerical values were found with an error within the permissible range.

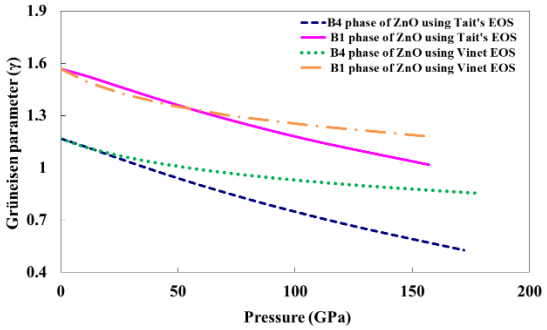

Fig. 1 – Grüneisen parameter against pressure for both phases of bulk ZnO using Tait's and Vinet's EOS

It is found from Fig. 1 that variation of the Grüneisen parameter against pressure reported for ZnO material is almost identical to that of the Grüneisen parameter observed for other metals as a function of pressure as per literature [4, 10]. It is also concluded that at zero pressure, the Grüneisen parameter of rock salt (B1) phase is greater than the Grüneisen parameter of wurtzite (B4) phase, so we can say that the ZnO material for B1 phase is harder than for B4 phase.

It is observed that the trend of the Grüneisen parameter as a function of pressure using universal Vinet's EOS is similar to the variation predicted using Tait's EOS. The Grüneisen parameter of rock salt (B1) phase is greater than the Grüneisen parameter of wurtzite (B4) phase. It is found that, as the pressure increases, the Grüneisen parameter reduces for Tait's EOS as well as for Vinet's EOS. The reason for this phenomenon is that, as we increase the pressure, the internuclear separation between atoms of the material (bond length) becomes shorter. The shortening bond lengths benefits higher vibration constants which leads to higher phonon frequency of the optical branch of the material. As the Grüneisen parameter is associated with the phonon frequency distribution (Eq. (1)), it reduces as the pressure increases.

The study of the Grüneisen parameter as a function of pressure for nano ZnO having two different particle sizes (10 nm and 65 nm) using Tait's and Vinet's EOS for both wurtzite and rock salt phases was also carried out. The results for Tait's EOS are reported in Fig. 2. The input parameters used for the determination of the Grüneisen parameter for nano ZnO are listed in Table 2 [11, 12].

Table 2 – The input parameters used in the determination of the Grüneisen parameter for nano ZnO for two different particle sizes for B4 and B1 phases

Material	Particle size (nm)	B_0 [10, 11] (GPa)	B'_0 [10, 11]
ZnO (B4)	10	294	4
	65	184	4
ZnO (B1)	10	264	4
	65	260	3.5

From Fig. 2, it is clear that the Grüneisen parameter at zero pressure for both particle sizes of ZnO in wurtzite (B4) phase is found to be the same, but that is

not true for rock salt phase. We can also conclude that as the pressure increases, the Grüneisen parameter reduces for both particle sizes and for both phases.

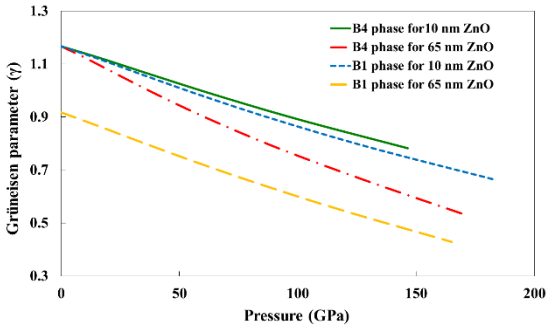

Fig. 2 – Grüneisen parameter against pressure for both phases of ZnO for two different particle sizes (10 nm and 65 nm) using Tait's EOS

As we increase the particle size, the surface to volume ratio of the material increases, which gives rise to an increase in the number of interior atoms of the material. Therefore, this results in the increment of the lattice energy of the cell, which leads to the decrement of the Grüneisen parameter. The predicted results of the Grüneisen parameter as a function of pressure using Vinet's EOS for both particle sizes and for both phases are shown below in Fig. 3.

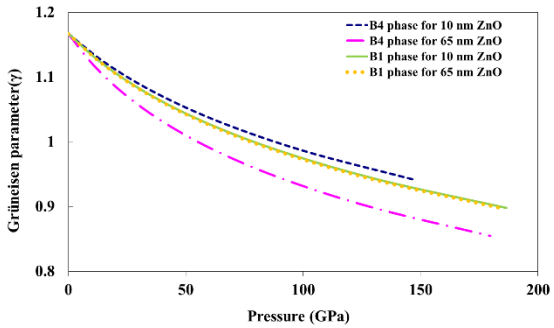

Fig. 3 – Grüneisen parameter against pressure for wurtzite (B4) phase of ZnO for two different particle sizes (10 nm and 65 nm) using Vinet's EOS

From Fig. 3, it is predicted that the Grüneisen parameter at zero pressure is the same for both particle sizes of ZnO for both phases using Vinet's EOS. Also, for both phases, as the pressure increases, the Grüneisen parameter reduces. From Fig. 3, it is also reported that for the wurtzite phase of ZnO, as the particle size increases, the Grüneisen parameter reduces, whereas for the rock salt phase, the Grüneisen parameter is almost the same for both particle sizes of ZnO as seen from the above Fig. 3.

4. CONCLUSIONS

The study of the Grüneisen parameter as a function of pressure says that, as the pressure increases, the Grüneisen parameter reduces using Tait's EOS as well as for Vinet's EOS for both bulk and nano ZnO materials for both B4 and B1 phases. It is realized that the variation of the Grüneisen parameter versus pressure reported for ZnO material is almost similar to that of the Grüneisen parameter against pressure observed for other metals as per the literature. At zero pressure, the Grüneisen parameter of rock salt (B1) phase is greater than the Grüneisen parameter of wurtzite (B4) phase. Hence, we can conclude that ZnO material in B1 phase is harder than that in B4 phase. It is also observed that the Grüneisen parameter decreases as the particle size increases for both phases of ZnO using Tait's EOS. At zero pressure, the Grüneisen parameters are same in the case of wurtzite (B4) phase, but this is not observed for rock salt (B1) phase for nano ZnO using Tait's EOS. It is observed that the Grüneisen parameter is the same at zero pressure for both particle sizes and both phases of ZnO using Vinet's EOS. It is predicted that for the wurtzite phase of ZnO, as the size of the particle increases, the Grüneisen parameter decreases, whereas for the rock salt phase, the Grüneisen parameter is almost the same for both particle sizes of nano ZnO using Vinet's EOS.

ACKNOWLEDGEMENTS

I would like to express my special thanks of gratitude to my guide, late Prof. Tushar Pandya, Associate Professor, Department of Physics and Electronics, St. Xavier's College, Ahmedabad, for his expert advice and guidance throughout the research project. I would also like to extend my heartfelt gratitude to Prof. P.N. Gajjar, Professor and Head, Department of Physics, Electronics and Space Sciences, University School of Sciences, Gujarat University, Ahmedabad, for his fruitful comments and discussions.

REFERENCES

1. M. Panwar, S.K. Sharma, S. Panwar, *Indian J. Pure Appl. Phys.* **55**, 203 (2017).
2. H.K. Rai, S.P. Shukla, A.K. Mishra, et al, *J. Chem. Pharmaceut. Res.* **2** No 4, 343 (2010).
3. Brijesh K. Pande, Anjani K. Pandey, Chandra K. Singh, *AIP Conf. Proc.* **120004**, 1 (2008).
4. C.V. Pandya, P.R. Vyas, T.C. Pandya, et al, *Bull. Mater. Sci.* **25**, 63 (2002).
5. Sanjay Kumar, S.K. Sharma, O.P. Pandey, *Indian J. Pure Appl. Phys.* **52**, 541 (2014).
6. R.V. Gopala Rao, R. Venkatesh, *Indian J. Pure Appl. Phys.* **38**, 313 (2000).
7. Quan Liu, Li Rong Chen, *Indian J. Pure Appl. Phys.* **55**, 368 (2017).
8. Nilesh A. Thakar, Apoorva D. Bhatt, Tushar C. Pandya, *AIP Conf. Proc.* **1591**, 88 (2014).
9. Uma D. Sharma, M. Kumar, *Indian J. Pure Appl. Phys.* **53**, 304 (2015).
10. J. Ramakrishnan, George C. Kennedy, *Phys. Chem. Solid.* **41**, 301 (1980).
11. Archana Bhatt, Geeta Sharma, Munish Kumar, *Indian J. Pure Appl. Phys.* **51**, 642 (2013).
12. H. Teisseyre, Duzynska, R. Hrubiak, et al, *High Pressure Res.* **32** No 3 (2012).

Дослідження параметра Грюнайзена ZnO при високих тисках

Binita Shah

Department of Physics, Electronics and Space Sciences, University School of Sciences, Gujarat University, Navrangpura, Ahmedabad-38009, India

Дослідження термопружних властивостей кількох типів твердих тіл дуже важливо для дослідників, щоб зрозуміти структуру нижньої мантії Землі та ядра в діапазоні високих тисків. Параметр Грюнайзена відіграє дуже важливу роль у вивченні термопружних властивостей, оскільки забезпечує фундаментальну основу щодо частотного розподілу фононного спектру в твердих тілах. У дослідженні була зроблена спроба теоретично обчислити залежний від тиску параметр Грюнайзена для фаз вюрциту (B4) та кам'яної солі (B1) об'ємного та нанооксиду цинку (ZnO) приблизно до 200 ГПа. Вираз вільного об'єму для параметра Грюнайзена, отриманий Ващенком і Зубаревим, та ізотермічні рівняння стану (EOS) використовуються для обчислення його значень. Ми виявили, що тенденція зміни параметра Грюнайзена від тиску, отримана для ZnO, подібна до тенденції, отриманої для металів згідно літературних джерел.

Ключові слова: ZnO, EOS, Параметр Грюнайзена, Фази вюрциту та кам'яної солі, Термопружні властивості.