

The Effects of High-Pressure Compression on Bulk Modulus and its Pressure Derivatives for Nanomaterials

¹Rajendra K. Mishra, ²Om Prakash Gupta

^{1,2}Department of Physics, D.B.S. College Govind Nagar, CSJM University Kanpur, Uttar Pradesh, India

Corresponding Author: [Rajendra K.Mishra](#)

Abstract: This study compares the effects of high pressure on the bulk modulus and pressure derivatives of a few nanomaterials, including Ge(13 nm), TiO₂, Ni(20 nm), CuO, and Si(4.1 nm), which have better uses in contemporary technology. The pressure dependence of bulk modulus was assessed using the EOS of Vinet and Birch-Murnaghan. It was found that the high-pressure effect is highly dependent on the considered particle size. The current study aims to theoretically predict the bulk modulus of nanomaterials of varying sizes in relation to pressure at a standard temperature. The bulk modulus and pressure derivative of the bulk modulus's trend of change against volume compressions, as we have discovered.

Key words: Compression , Bulk Modulus, Nanomaterials, Pressure derivative, Equation of states.

1.0 Introduction

Materials with distinctive properties at the nanoscale, typically between 1 and 100 nanometers in size, are referred to as nanomaterials. In comparison to their bulk counterparts, materials frequently display different physical, chemical, and biological characteristics at this scale. Nanomaterials, which can be created artificially or organically, are used in a wide range of industries, including electronics, health, energy, and environmental science. Due to their high surface area to volume ratio, quantum effects, and elevated reactivity, nanomaterials have special features. Some of their notable characteristics include enhanced strength, improved electrical conductivity, altered optical properties, increased catalytic activity, and enhanced biological interactions. Nanomaterials are used in electronics to make transistors, memory chips, and sensors, which are smaller and faster. They can be used in tissue engineering, diagnostic imaging, and drug administration in medicine. In energy storage and conversion devices like batteries and solar cells, nanomaterials are also essential. They can be used in

environmental science for water filtration, pollution detection, and clean up. The use of nanomaterials, however, also raises questions about their possible environmental impact, health dangers, and ethical implications, much like any new technology does.

Due to the fact that it offers useful information on the thermodynamic and thermoelastic properties of solids at high pressures and temperatures, the equation-of-state (EOS) has played a crucial role in the fields of high pressure physics and geophysics [1,2].

Now, high-pressure studies of nanomaterials are being conducted in tandem with the advancement of nano sciences to either better understand the characteristics of nanomaterials or to create other means of creating new nanomaterials[3].

There are relationships between bulk modulus, transition pressure, and crystal size, according to earlier high-pressure investigations. However, depending on the system under study, the grain-size effect on the transition pressure can be of either sign [4].

X-ray diffraction and synchrotron radiation have been used to investigate the equation of state for the transition of nanocrystalline Ge. Values of the bulk modulus and the transition pressure rise with decreasing particle size, however the percentage volume collapse at the transition remains constant. The interface structure significantly influences the physical properties of nanocrystalline Ge because a considerable portion of the atoms reside in the grain borders[5].

TiO₂ is an essential substance with various known and potential commercial applications in both macrocrystalline and nanocrystalline forms. This material's principal technological applications include pigments, polymers, cosmetics, electronics, and catalysts [6].

Recently, nanocrystalline TiO₂ has been employed as a model system to examine the size-dependent phase transition behavior of nanoscale oxides in terrestrial environments[7].

The strength of materials with micrometer or nanoscale dimensions can be significantly higher than that of macroscopic objects, this strength rarely reaches the material's maximal theoretical strength. Researchers show that faceted single-crystalline nickel (Ni) nanoparticles have a compressive strength that is extremely high (up to 34 GPa) and unheard of in metallic materials. This value is consistent with the theoretical strength predictions for Ni. This record-breaking strength is the result of three distinct factors: a substantial Ni shear modulus, rounded nanoparticle corners, and a thin oxide coating covering the particle surface[8].

Based on published research, the compressive strength, thermal characteristics, and microstructure of self-compacting concrete containing various quantities of CuO nanoparticles have been examined. Various characteristics of the specimens were tested when self-compacting concrete was mixed with CuO nanoparticles, with an average particle size of 15 nm. The findings show that CuO nanoparticles can counteract the

detrimental effects of the superplasticizer on specimens' compressive strength and enhance the compressive strength of self-compacting concrete[9].

Raman spectroscopy methods and high energy Synchrotron radiation have been used to study the EOS of nanocrystallineCuO. The bulk modulus and the first order pressure derivative of the bulk modulus, particularly for nanomaterials, are two input parameters in addition to the models that are now available for the investigation of the high pressure compression behaviour. Therefore, it is appropriate and potentially helpful to propose a straightforward theoretical method for studying the high pressure compression behaviour of nanomaterials that only requires a zero pressure value of the bulk modulus at zero pressure[10].

Amorphous Si nanoclusters upon release of pressure from the high-pressure form of silicon (the β -Sn phase) was obtained. This behaviour differs from bulk silicon, which following the same thermodynamic path transforms commonly to a slightly distorted tetrahedral phase known as BC8. Amorphization was also observed in silicon upon compression on films of porous Si, which contains nanometre-sized domains of diamond-structured material. The high density amorphous phase was shown to transform to low density amorphous silicon upon decompression..

After releasing pressure from the high-pressure form of silicon (the β -Sn phase), amorphous Si nanoclusters were formed. This behaviour contrasts from that of bulk silicon, which, when subjected to the same thermodynamic conditions, often changes to a slightly deformed tetrahedral phase known as BC8. Amorphization was also seen in silicon after compression on porous Si sheets with nanometre-sized diamond-structured domains. On decompression, the high density amorphous phase was demonstrated to convert into low density amorphous silicon[11].

Researchers concentrate on the behaviors of NPs under pressure at the atomic and mesoscales, the structural and property transitions of perovskite NPs under pressure, and changes in the properties of inorganic NPs following compression [12].

2.0Method of analysis

The link between a material's state variables (such as pressure, volume, and temperature) is described by the equation of state (EOS). The type of EOS used is determined on the properties of the material being examined. Several commonly used EOS models for solid materials utilised for nanomaterial compression include.

Vinet equation of state[13] based on interatomic potentials of solids and takes in accounts the exponential compression of solids at high pressure.

$$P = 3B_0 \left(\frac{V}{V_0}\right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right] \exp \left[\frac{3}{2} (B'_0 - 1) \left(1 - \left(\frac{V}{V_0}\right)^{\frac{1}{3}}\right) \right] \quad (1)$$

The isothermal bulk modulus B is assumed to vary linearly with pressure in both the Murnaghan[14] and Birch[15] first order equations.

$$B = B_0 + B'_0 P \quad (2)$$

The Murnaghan equation has the form

$$P = (B_0/B'_0)[(V_0/V)^{B'_0} - 1] \quad (3)$$

A frequently used equation to describe the pressure-volume connection of materials, including nanomaterials, is the Birch-Murnaghan equation of state[16]. The original Birch equation, which was created for bulk materials, is expanded upon in this formula.

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left[1 + \frac{3}{4} (B'_0 - 4) \left(\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right) \right] \quad (4)$$

Where V is the volume of solid at pressure P and V₀ is the volume of solid at zero pressure.

Expression for isothermal Bulk modulus corresponding to equation (1) and (4) is obtained by using the relationship

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (5)$$

Given as by Vinet,

$$B = B_0 \left[2 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{1}{3}} + \frac{3}{2} (B'_0 - 1) \left[\left(\frac{V}{V_0} \right)^{-\frac{1}{3}} - 1 \right] \right] \exp \left[\frac{3}{2} (B'_0 - 1) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right] \quad (6)$$

By Birch-Murnaghan

$$B = \frac{B_0}{2} \left(7 \left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - 5 \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right) + \frac{3}{8} B_0 (B'_0 - 4) \left(9 \left(\frac{V}{V_0} \right)^{-\frac{9}{3}} - 14 \left(\frac{V}{V_0} \right)^{-\frac{7}{3}} + 5 \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right) \quad (7)$$

Corresponding Isothermal Pressure derivative of Bulk modulus

$$B' = \left(\frac{\partial B}{\partial P} \right)_T = \left(\frac{\partial B}{\partial V} \frac{\partial V}{\partial P} \right)_T = -\frac{V}{B} \left(\frac{\partial B}{\partial V} \right)_T \quad (8)$$

Thus by use of eq.(6)

$$B' =$$

$$\frac{B_0}{12B} \left[16 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 4 \left(\frac{V}{V_0} \right)^{-\frac{1}{3}} + 6(B'_0 - 1) \left[3 \left(\frac{V}{V_0} \right)^{-\frac{1}{3}} - 1 \right] + 9(B'_0 - 1)^2 \left[1 - \left(\frac{V}{V_0} \right)^{-\frac{1}{3}} \right] \right] \exp \left[\frac{3}{2} (B'_0 - 1) \left(1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right) \right] \quad (9)$$

By use of eq.(9)

$$B' = \frac{B_0}{8B} (B'_0 - 4) \left[81 \left(\frac{V}{V_0} \right)^{-9/3} - 98 \left(\frac{V}{V_0} \right)^{-7/3} + 25 \left(\frac{V}{V_0} \right)^{-5/3} \right] + \frac{B_0}{6B} \left[49 \left(\frac{V}{V_0} \right)^{-7/3} - 25 \left(\frac{V}{V_0} \right)^{-5/3} \right]$$

(10)

3.0 Result and discussion

Table 1 Input parameters utilized in this research

Nanomaterials	B_0 (Gpa)	B_0' (Gpa)	Ref.
Ge(13nm)	112	4	[17]
TiO ₂	211	8	[18]
Ni (20nm)	185	4	[19]
CuO	81	4	[10]
Si(4.1nm)	67	4.1	[20]

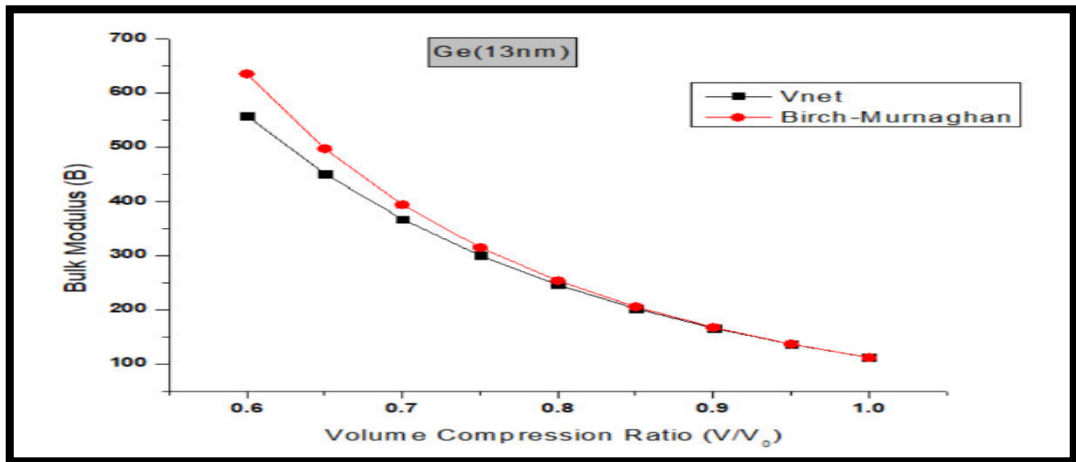


Fig1 Shows the values of Bulk Modulus(B) with different compression for Ge(13nm)

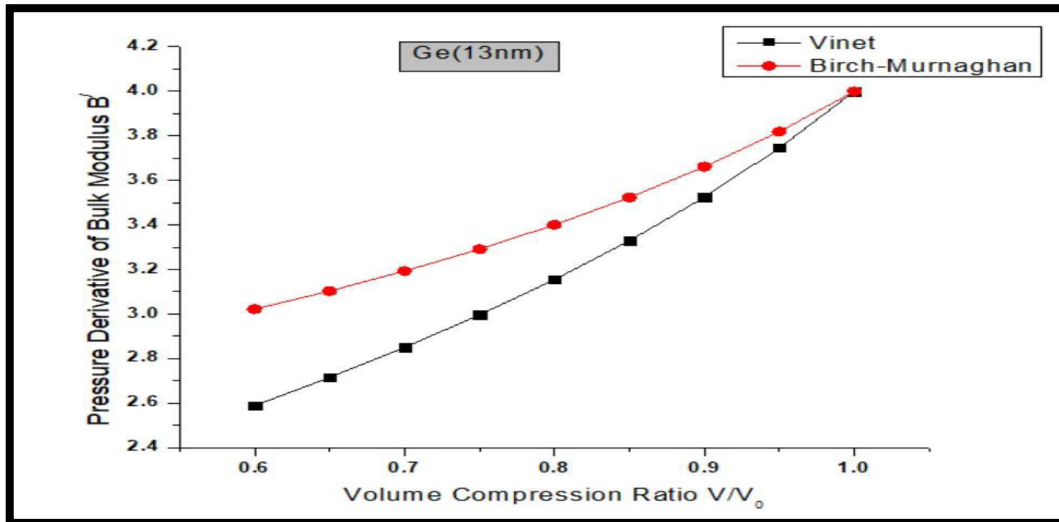


Fig2 Values of pressure derivative of bulk modulus with different compression B' for Ge(13nm)

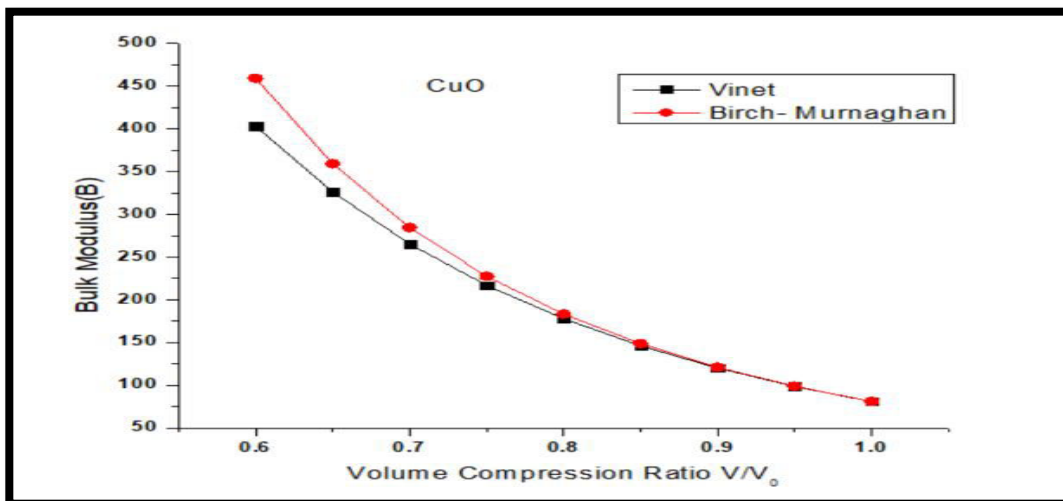


Fig3 Values of Bulk Modulus with different compression (B) for CuO .

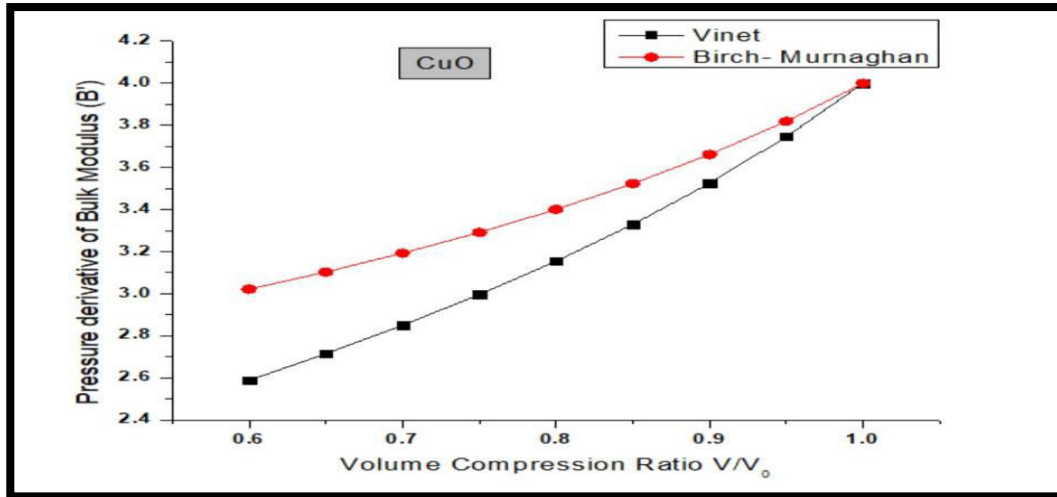


Fig4 Values of pressure derivative of bulk modulus with different compression B' for CuO.

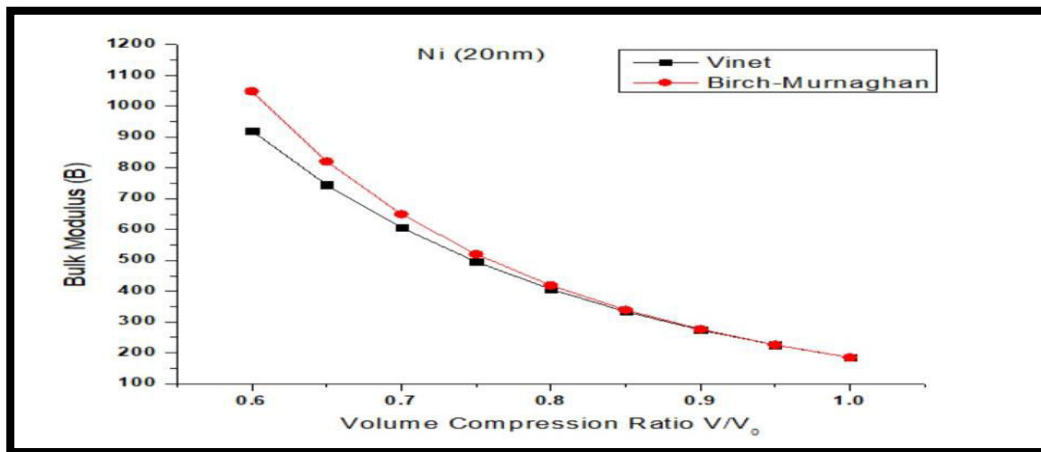


Fig5 Values of Bulk Modulus with different compression (B) for Ni(20nm)

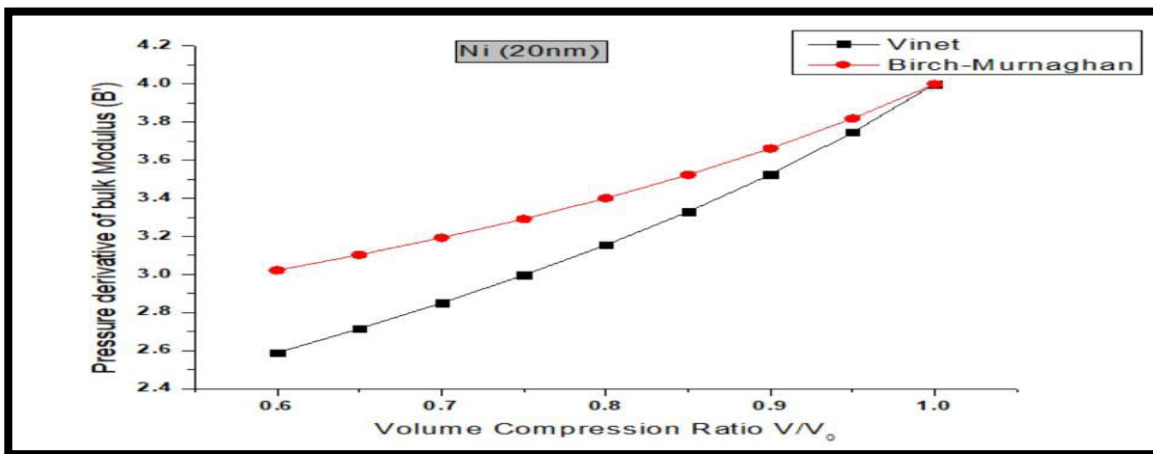


Fig6 Values of pressure derivative of bulk modulus with different Compression (B') for Ni(20nm).

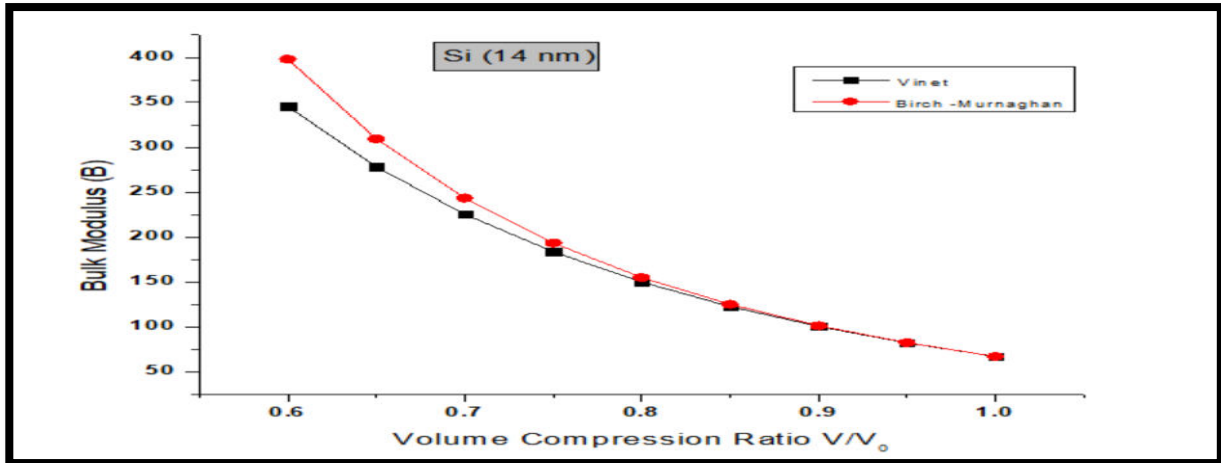


Fig7 Values of Bulk Modulus with different compression (B) for Si (14nm)

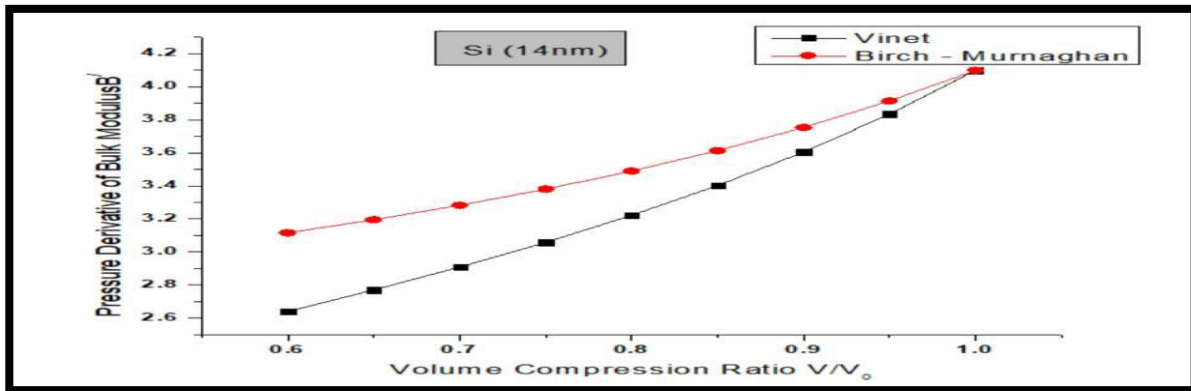


Fig 8 Values of pressure derivative of bulk modulus with different compression (B') for Si(14nm).

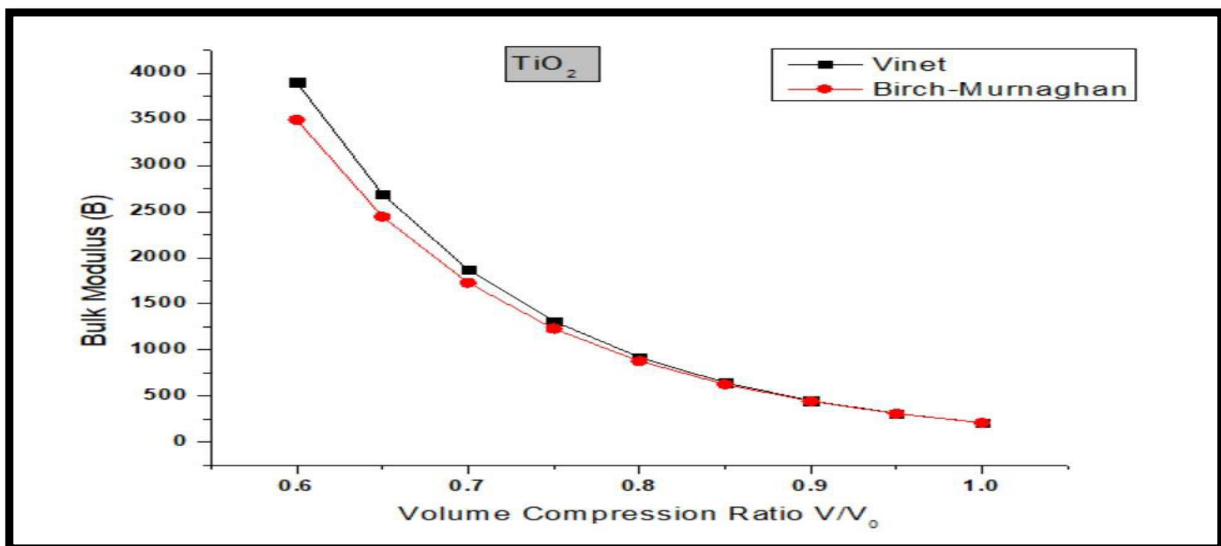


Fig 9 Values of bulk Modulus with different compression (B) for TiO₂ .

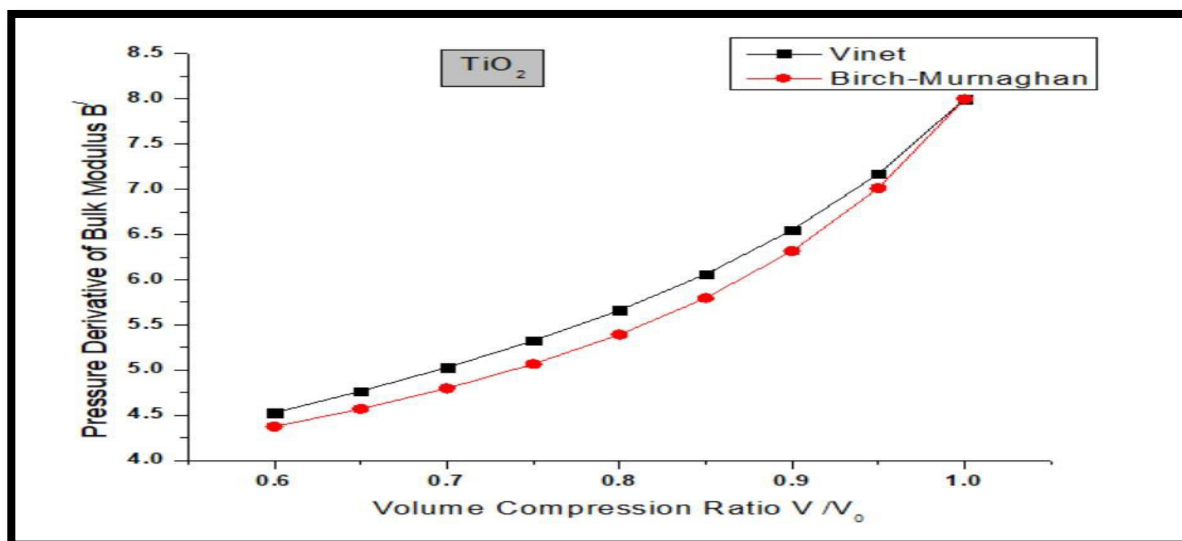


Fig 10 Values of Pressure derivative of bulk modulus with different compression (B') for TiO_2 .

In the present work we have described two different forms of EOS; equations (1) and (4). Equation (1) corresponds to Vinet EOS, equation (4) corresponds to Birch-Murnaghan EOS. All the two EOS contains only two parameters B_0 and B_0' both at zero pressure. These values of B_0 and B_0' have been recommended by [17,18,19,10,20]. The values of pressure P for nanomaterials Ge(13nm), TiO_2 , Ni(20nm), CuO, Si(4.1nm) were computed for given increments of V/V_0 by using equation (1) and (4). The value of input parameter, B_0 and B_0' are taken from literature displayed in table-1. Using the value of pressure P computed from equations (1) and (4) for nanomaterials, Isothermal Bulk Modulus (B) and first pressure derivative of bulk modulus (B') at constant temperature has computed by using equations (6), (7), (9), and (10). The dependency of B and B' with compression displayed in Fig-1 to Fig-10.

In all Figures It is found that the volume of the nanoparticle decreases with the increase in pressure and bulk modulus increases with increase of compression but pressure derivative of bulk modulus decreases with increase of compression. At low pressure value, all curves with the two EOSs are relatively close to each other. The result of both EOSs for bulk modulus B are significantly close up to relative compression of .85 for all nanoparticle. Increasing compression values beyond .85 causes the curves of both EOSs to exhibit more divergence. The variation in bulk modulus with relative volume of TiO_2 greatly differ with B-M EOS and vinet EOS comparison to other nanomaterials. Thus, the trend of variation of pressure derivative of bulk modulus with relative volume with B-M EOS differs from that of Vinet EOS are similar to all compression and reaches to

minimum value at compression $V/V_0 = .6$, at this compression Si (14nm) shows more deviation compare to other taken nanomaterials in this research.

4.0 Conclusions

The rise in the repulsive force in the short distance between two nanoparticle atoms is related to the change in bulk modulus and pressure derivative with compression; the repulsive force is noticed between two neighboring atoms, whereas the attractive force is detected between all of the particle's atoms. Since the new study provides results that are fairly close to the experimental data for nanomaterials, it may be especially helpful for analyzing the high-pressure compression behavior of solids, particularly nanomaterials. Therefore, the present formulation could be helpful in developing high-pressure experiments on the compression behavior of nanomaterials in the future.

5.0 References:

1. J. Hama and K. Suito, "The search for a universal equation of state correct up to very high pressures," *Journal of Physics: Condensed Matter*, vol. 8, no. 1, p. 67, 1996.
2. A. San-Miguel, "Nanomaterials under high-pressure," 2006, *Royal Society of Chemistry*.
3. J. Z. Jiang, "Mechanochemistry And Mechanical Alloying 2003 Phase transformations in nanocrystals," *Journal of Material Science*, vol. 39, 2004.
4. H. Wang *et al.*, "High-pressure structural behavior of nanocrystalline germanium,"
5. V. Swamy *et al.*, "Compression behavior of nanocrystalline anatase TiO₂," *solid state electronics*, vol. 125, pp. 111–115, 2003, [Online]. Available: www.altairtechnologies.com.
6. J. F. Banfield and H. Zhang, "Nanoparticles in the environment," *Rev Mineral Geochem*, vol. 44, pp. 1–58, 2001.
7. A. Sharma, J. Hickman, N. Gazit, E. Rabkin, and Y. Mishin, "Nickel nanoparticles set a new record of strength," *Nat Commun*, vol. 9, no. 1, Dec. 2018.
8. A. Nazari and S. Riahi, "Effects of CuO nanoparticles on compressive strength of self-compacting concrete," *Indian Academy of Sciences*, vol. 36, pp. 371–391, 2011.
9. Z. Wang, V. Pishedda, S. K. Saxena, and P. Lazor, "X-ray diffraction and Raman spectroscopic study of nanocrystalline CuO under pressures," *solid state communication*, vol. 121, pp. 275–279, 2002, [Online].
10. A. San-Miguel, "Nanomaterials under high-pressure," 2006, *Royal Society of Chemistry*.
11. L. Meng, T. V Vu, L. J. Criscenti, T. A. Ho, Y. Qin, and H. Fan, "Theoretical and Experimental Advances in High-Pressure Behaviors of Nanoparticles," *Chem Rev*, vol. 123, no. 16, pp. 10206–10257, Aug. 2023.
12. P. Vinet, J. Ferrant, J. R. Smith, and J. H. Rose, "A universal equation of state for solids," 1986.
13. F. D. Murnaghan, "The compressibility of media under extreme pressures," *Proc Natl Acad Sci U S A*, vol. 30, no. 9, p. 244, 1944.

14. F. Birch, "Equation of state and thermodynamic parameters of NaCl to 300 kbar in the high-temperature domain," *J Geophys Res*, vol. 91, no.B5, p. 4949, 1986.
15. T. C. Pandya, A. I. Shaikh, and A. D. Bhatt, "Particle-size effect on the compressibility of nanocrystalline germanium," in *AIP Conference Proceedings*, 2011, pp. 413-414.
16. K. Kholiya and J. Chandra, "Equation of state model for studying high-pressure compression behaviour of nanomaterials," *Journal of Taibah University for Science*, vol. 8, no. 2, pp. 137-141, 2014.
17. B. Chen, D. Penwell, and M. B. Kruger, "The compressibility of nanocrystalline nickel," *Solid State Commun*, vol. 115, pp. 191-194, 2000.
18. Suleiman A K, "Optical and Acoustic Grüneisen Parameter of Nano-sized Particles," *Eurasian Journal of Science and Engineering*, vol. 4, no. 3, 2019.