

**INVESTIGATING THE BULK MODULUS AND ELASTIC PROPERTIES OF NANOMATERIALS UNDER PRESSURE****Varsha Ghosh and Dr. Ritesh Yadav**

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**ABSTRACT**

*Because of quantum confinement and surface effects, nanomaterials have distinct mechanical characteristics compared to their bulk equivalents. Based on the assumption that the product of the thermal expansion coefficient ( $\alpha$ ) and bulk modulus ( $BT$ ) stays constant under pressure, the quasi-harmonic approximation is used as the research approach in this work. Different nanomaterials, such as  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, CuO, AlN, TiO<sub>2</sub> (in the anatase phase), Ni (20nm), Ge (49nm), CNT (single-walled carbon nanotube), and CdSe (in the rock salt phase), were subjected to pressure analysis using this method for varying compression ratios ( $V/V_0$ ). This proves that the present approach is valid; the findings are found to align perfectly with the existing experimental data, confirming that the formulation utilized in this work is accurate.*

**Keywords:** Nanomaterial, Pressure, Bulk modulus, Elastic properties, Quasi

**I. INTRODUCTION**

Because of their striking differences in physicochemical characteristics between bulk materials and nanomaterials, the latter have attracted a great deal of interest in the last few decades. Amazing mechanical strength, electrical conductivity, optical behavior, and chemical reactivity are hallmarks of these materials, which often have nanoscale dimensions (1-100 nm). Electronics, medicine, energy storage, and catalysis are just a few areas that have benefited greatly from the capacity to control materials at the atomic or molecular level. Pressure is one of the many environmental factors that affect nanomaterials, changing their mechanical, electrical, and structural characteristics. Exciting new phenomena including phase transitions, improved mechanical stability, bandgap tuning, and altered surface interactions have been uncovered via high-pressure studies of nanomaterials.

One of the most basic thermodynamic parameters, pressure, may alter the electrical and structural configurations of materials by drastically changing their interatomic spacing. The existence of quantum confinement effects and the higher surface-to-volume ratio at the nanoscale may make pressure-induced alterations more noticeable. In order to probe the structural alterations of nanomaterials with atomic accuracy, methods including high-pressure X-ray diffraction, diamond anvil cells (DAC), and shock compression are used in the research of nanomaterials under pressure. Nanomaterials including carbon-based nanostructures, metal oxides, metal nanoparticles, and two-dimensional (2D) materials like graphene and transition metal dichalcogenides (TMDs) have all been the subject of new phases, metastable states, and improved mechanical properties as a result of these investigations.

Under pressure, carbon-based nanostructures including graphene, carbon nanotubes, and nanodiamonds have been among the most researched nanomaterials. Because of their high heat conductivity and remarkable mechanical strength, these materials are great options for a wide range of technical and industrial uses. The structural distortions that graphene experiences when heated to high pressure cause it to lose some of its electrical characteristics. Researchers have shown that graphene may change its hardness and conductivity into a diamond-like phase when subjected to very high pressures. In a similar vein, the mechanical and electrical characteristics of carbon nanotubes may be affected by radial deformation and possible phase transitions. The capacity to manipulate these changes by applying pressure has consequences for the development of superhard materials and high-performance electrical gadgets.

Under high-pressure circumstances, metal nanoparticles also exhibit fascinating behavior. Nanoparticles often undergo pressure-induced phase transitions at lower thresholds than bulk materials because of their smaller size, which makes them more compressible. The optical characteristics and catalytic activity of gold nanoparticles may be changed by structural alterations that occur at lower pressures compared to bulk gold. The biological, sensory,

and nano-catalytic fields stand to benefit greatly from these pressure-dependent metal nanoparticle modifications. Moreover, nanoparticles of noble metals, such as palladium and platinum, exhibit pressure effects that vary with particle size; these factors impact their electrical and mechanical characteristics in ways that might be used in energy conversion and storage devices.

Photocatalysis, semiconductors, and biomedical applications all make extensive use of metal oxides, such as zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>). The structural phase transitions that these materials exhibit, as shown by high-pressure investigations, have the potential to alter or improve their useful characteristics. As an example, the efficiency of TiO<sub>2</sub> in solar energy applications is affected by phase changes, which change its bandgap and, in turn, its photocatalytic efficiency. Also, electrical gadgets and pressure sensors may benefit from ZnO's piezoelectric capabilities, which are very sensitive to changes in pressure. Understanding how to pressurize these materials provides important information for optimising their characteristics for use in targeted technological contexts.

Graphene, molybdenum disulfide (MoS<sub>2</sub>), and black phosphorus are only a few examples of the two-dimensional (2D) materials that have recently gained attention as possible components of next-generation optoelectronic and electrical devices. Because of their very thin atomic layers and extremely strong in-plane bonds, these materials display exceptional mechanical and electrical characteristics. 2D materials may undergo electronic band structure modifications, semiconductor-to-metal transitions, improved superconductivity, and changing interlayer interactions when heated to high pressure. As an example, MoS<sub>2</sub> is ideal for optoelectronic applications because to its strong tunability, which is caused by its pressure-induced bandgap lowering. Similarly, the transport characteristics of black phosphorus are affected by band structure alterations caused by anisotropic compression. Developing performance-optimal adjustable nanoscale devices requires a thorough understanding of these effects caused by pressure.

Research into nanomaterials subjected to pressure has important practical ramifications outside the realm of basic science. To create new nanomaterials with better characteristics, materials scientists use pressure-assisted synthesis methods. Advanced materials for aerospace, military, and industrial uses may be developed by subjecting them to high-pressure conditions, which can increase mechanical strength, thermal stability, and the formation of metastable phases. Because many nanomaterials exist naturally in the Earth's mantle and space, studying them under tremendous pressure helps us comprehend planetary and geological processes. To better understand how minerals and other nanostructures react in harsh settings, scientists have begun to mimic similar circumstances in the lab.

Research on nanomaterials under high pressure has many applications, one of which is in biomedicine. Many nanomaterial-based imaging agents, drug delivery devices, and biosensors encounter a wide range of pressure conditions in their natural habitats. If we want these materials to be stable, effective, and safe for medical uses, we need to know how they react to changes in pressure. In addition, sterilizing procedures for nanomaterials having a biological application involve high-pressure methods to guarantee that they are safe for human health.

### **Bulk Modulus Properties of Nanomaterials under Pressure**

One basic mechanical parameter that measures the resistance of a material to homogeneous compression is its bulk modulus. The mechanical resilience, structural stability, and high-pressure behavior of materials are all affected by it. Nanomaterials' smaller dimensions, high surface-to-volume ratio, and quantum confinement effects cause their bulk modulus to differ from traditional bulk material behavior. These distinct nanoscale features impact the mechanical properties of nanomaterials, which in turn affect how these materials react to external pressure, and these adjustments are size dependent. For nanotechnology, aerospace, energy storage, high-pressure physics, and materials science applications of nanomaterials to be optimized, it is crucial to understand their bulk modulus qualities under pressure.

Surface effect is one of the main causes of these differences. Atomic coordination is weaker on the surface of nanomaterials than in their bulk core, where the majority of atoms are concentrated. This causes stress and surface

energy to rise, which, depending on the kind of atomic interactions, might cause the material to become stiffer or softer. The bulk modulus of metallic nanoparticles is often higher than that of semiconductor and oxide nanomaterials because of the stronger bonding between their surfaces, while the reverse is true for these materials.

The bulk modulus of nanoparticles is also greatly affected by size-dependent behavior. According to both theoretical and experimental research, the bulk modulus of nanoparticles may go up or down as their size goes down, material dependent. Materials like silica and ceria display decreased bulk moduli owing to changes in atomic packing, whereas gold and silver nanoparticles usually show a greater bulk modulus at smaller sizes because of enhanced surface electron density. A number of variables, including crystallinity, flaws, and surface passivation, affect the nanomaterials' unique critical size thresholds, beyond which these effects start to dominate.

Phase transitions generated by pressure are another important element that influences the bulk modulus of nanomaterials when subjected to pressure. As a result of structural changes that occur under high pressures, the bulk modulus of nanomaterials may change. Because of nanoscale influences, these phase transitions could not be the same as in bulk materials. For instance, when carbon-based nanomaterials like graphene and nanodiamonds are heated to very high pressures, their bulk modulus changes dramatically, and in rare cases, they form superhard phases that have improved mechanical characteristics. Pressure also causes phase transitions in metal oxides and transition metal dichalcogenides (TMDs), which drastically changes their compressibility and mechanical behavior.

Nanomaterials' bulk modulus characteristics are also affected by their morphology and form. As a result of differences in atomic arrangement and deformation processes, spherical nanoparticles, nanowires, and nanoplates react differently to compression. For instance, the bulk modulus of anisotropic mechanically behaving nanowires and nanotubes may change in response to pressure applied in different directions. To create nanomaterials with specialized mechanical characteristics for particular applications, this directional dependency is critical.

Experimental methods and computer modeling are used to investigate the bulk modulus characteristics of nanomaterials subjected to pressure. Precise measurements of volume changes and compressibility under severe circumstances are made possible by high-pressure experimental methods including diamond anvil cells (DAC), high-pressure X-ray diffraction (HPXRD), and Brillouin spectroscopy. These techniques allow for the real-time observation of structural rearrangements, bulk modulus fluctuations, phase transitions, and other similar phenomena. Nanoindentation methods also allow for localized mechanical property measurements, which provide light on how nanostructured materials' stiffness and hardness vary with size. At the same time, computational methods like molecular dynamics (MD) simulations and density functional theory (DFT) reveal the pressure-dependent behavior of nanomaterials at the atomic level. The impact of surface stress, interactions between defects, and changes to the electronic structure on the bulk modulus may be better anticipated with the use of these models. Researchers may use theoretical models to investigate circumstances of very high pressure that can be difficult to accomplish in experiments. As an example, the study of pressure-induced stiffening or softening in nanoscale metals, ceramics, and semiconductors has been conducted using first-principles calculations, which have provided significant suggestions for material design.

Multiple scientific and industrial domains are affected by the implications of bulk modulus characteristics under pressure. The field of materials science makes use of high-pressure methods to create nanoparticles that are very hard and have improved mechanical characteristics. A few examples of materials that have been developed by pressure tuning of bulk modulus are nanodiamonds, superhard carbides, and boron nitride nanoparticles. You won't find cutting tools, protective coatings, or wear-resistant components without these materials.

For the development of state-of-the-art battery electrodes, supercapacitors, and materials for hydrogen storage, it is essential to comprehend the bulk modulus changes in nanomaterials. For example, maximizing the bulk modulus of electrode materials in lithium-ion batteries guarantees mechanical stability and performance over the long term, as these materials experience frequent volume changes during charge-discharge cycles. The efficiency of next-generation energy storage devices is affected by pressure-induced changes in bulk modulus, which in turn

affect the ion transport pathways in solid electrolytes. Aerospace and military industries use bulk-modulus nanomaterials to create spacecraft, armor, and high-strength structural components that are both lightweight and mechanically strong. Nanocomposites with enhanced impact resistance and durability may be created by manipulating the bulk modulus via pressure engineering. The mechanical behavior of minerals found deep under the Earth's mantle and in alien settings may be better understood via the study of nanomaterials under severe pressure circumstances, which is beneficial to geophysics and planetary science. Material stability in high-pressure situations, such the cores of massive planets, earthquakes, and planetary interiors may be better predicted by studying the pressure response of nanophases.

### **Elastic Properties of Nanomaterials under Pressure**

Nanomaterials are mechanically distinct from bulk materials because of their small size and high surface-to-volume ratio. In particular, when subjected to high pressure, their elastic qualities are critical in defining how they react to outside pressures. The bulk modulus, Young's modulus, shear modulus, and Poisson's ratio are important mechanical characteristics that measure a material's elasticity, which is defined as its capacity to return to its original shape after deformation. The material's mechanical stability and performance in various applications are affected by these factors, which describe its resistance to compression, tension, and shear forces. The elastic behavior of nanomaterials may be changed by applying pressure because this force changes their atomic structure, bonding connections, and deformation processes.

Size, shape, content, and structural organization have a significant impact on the elastic characteristics of nanomaterials. Due to their microscopic size, nanomaterials are subject to surface and interface effects rather than the long-range atomic interactions that determine the elasticity of bulk materials. Since surface atoms are now more important in deciding the material's stress response, this causes departures from traditional mechanical behavior. To illustrate the point, metallic nanoparticles often show size-dependent elastic moduli, meaning that smaller particles are stiffer than larger ones because surface stress is higher. Graphene, carbon nanotubes, and nanodiamonds are carbon-based nanomaterials that are among the stiffest known due to their very high Young's moduli. Carbon nanotube chirality and graphene's number of atomic layers are two structural characteristics that affect how these materials react to pressure.

Changes in the interatomic spacing of nanomaterials cause differences in their elastic constants when subjected to external pressure. Pressure fluctuations have a disproportionate impact on nanomaterials' bulk modulus, a measure of a material's resistance to uniform compression. The compression of bulk materials mostly causes homogeneous atomic rearrangements, however the quantum confinement effects and increased surface energy of nanomaterials cause them to undergo complicated structural alterations. One example is the size-dependent bulk modulus variation in metal nanoparticles like gold and silver. As the surface electron density increases, the resistance to compression is stronger for smaller particles. However, surface-induced bond weakening may cause the bulk modulus of semiconductor nanoparticles and transition metal oxides to drop as their size decreases. Nanoscale mechanics is crucial for the creation of materials with adjustable elastic characteristics, as these effects of size and pressure demonstrate.

Nanomaterials also display unusual pressure-dependent behavior of Young's modulus, which characterizes a material's rigidity under uniaxial stress. As an example, graphene's strong  $sp^2$  carbon-carbon bonds cause it to have a very high Young's modulus ( $\sim 1$  TPa). But graphene may change its elastic behavior when subjected to extreme pressure, when its structure distorts. Under strain, the interlayer interactions in graphene oxide and multi-layer graphene become noticeable, impacting the mechanical resilience and overall stiffness of the material. Another kind of nanostructured material, carbon nanotubes exhibit anisotropic elasticity, which means that the direction of stress application determines the elastic response. The very directed character of nanostructured materials' elasticity is shown by the fact that axial compression of carbon nanotubes yields a much higher modulus than radial compression.



Nanoscale pressure also affects another important elastic parameter, the shear modulus, which quantifies the resistance of a material to shape change under shear stress. Boron nitride nanotubes, metal nanowires, and other nanomaterials with strong metallic or covalent bonds are notoriously resistant to deformation due to their large shear moduli. Shear modulus values may change, nevertheless, because to structural changes such phase transitions, sliding grain boundaries, and defect rearrangement when subjected to pressure. For instance, MoS<sub>2</sub> and other transition metal dichalcogenides (TMDs) undergo pressure-induced layer rearrangements, which alter their shear response and, in turn, their electrical and mechanical characteristics. To improve the mechanical robustness and flexibility of nanomaterials for use in flexible devices and nanoelectronics, it is crucial to understand these shear effects.

Another important measure for describing the elastic response of nanomaterials when subjected to pressure is Poisson's ratio, which is the ratio of transverse strain to axial strain when stress is applied. When compressing a material in one direction, its Poisson's ratio is usually positive in bulk materials, indicating that the material expands in the opposite direction. Unusual elastic behavior, such as a negative Poisson's ratio (auxetic behavior), may be caused by pressure-induced changes in some nanomaterials. Some graphene-based structures and polymer nanocomposites are auxetic nanomaterials; they show paradoxical expansion under compression, which makes them useful for energy-absorbing and impact-resistant applications. Pressure engineering's capacity to modify Poisson's ratio opens the door to the construction of next-gen nanomaterials with tunable mechanical characteristics.

## II. REVIEW OF LITERATURE

Mishra, R K et al., (2022) A basic thermodynamic study has been conducted on a number of nanomaterials. Several equations of states (EOS) proposed by Tait, Shanker, and Suzuki were tested and compared with experimental data. Several nanomaterials, such as TiO<sub>2</sub>(rutile phase), MgO, CuO, 3C-SiC, Zr<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>2</sub>, e-Fe, Rb<sub>3</sub>C<sub>60</sub>, and Ge (13 nm), are studied in relation to their bulk modulus under isothermal compression and how it depends on pressure using an equation developed from thermodynamic approximation. The acquired results are in good agreement with the available experimental data, demonstrating the validity of the formulation utilized in this work.

Gupta, Rohit et al., (2021) The behavior of nanomaterials made of titanium dioxide (TiO<sub>2</sub>) (Rutile phase), iron oxide ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), magnesium oxide (MgO), and copper oxide (CuO) under high-pressure compression is examined using many theoretical equation of state (EOS) models, which are tested against experimental data. Theoretical EOS models take pressure into account as a relative change in volume and as pressure-based experimental data. Additionally, the current EOS model dictates that the experimental data be closely followed.

Alsheikh, A. et al., (2020) For Ni, Cu, and Ag, EOSs from Vinet and Birch-Marnghan, as well as Nano EOSs, have been used to assess the change of V/V<sub>0</sub> in bulk and Nano forms subjected to high pressure. Experimental data and the solutions to several equations were compared. Since the various EOSs produced consistent findings, it's possible to use the EOSs of bulk materials to compute nanomaterials. Completed calculations of bulk modulus fluctuations with high pressure for the identical materials in both bulk and nanomaterial scenarios further demonstrated the feasibility of applying EOSs of bulk materials to nanoparticles.

Kholiya, Kuldeep et al., (2019) This research presents the results of an elementary theoretical investigation into the shape of the pressure dependence of the compressibility of bulk and nano crystalline SnO<sub>2</sub> with three distinct sizes (3, 8, and 14 nm) using the Equation of state model. In this study, we find that nano-crystals' compressibility is size dependent, proving that size and pressure have an impact on compression. The current model is valid at both the bulk and nano scales, as shown by comparing the findings to the existing experimental data. Consistent with previous experimental and theoretical evidence, this research also finds that compressibility rises with decreasing particle size.

Bhatt, Jeewan et al., (2015) To forecast how nanomaterials would react when compressed at high pressure, an equation of state (EOS) model is suggested. The essential premise of the model is that, when subjected to

pressure, the product of the thermal expansion coefficient ( $\alpha$ ) and the bulk modulus ( $BT$ ), denoted as  $\alpha BT$ , does not change. For the purpose of studying the compression behavior of various nanomaterials, such as CuO, TiO<sub>2</sub> (Anatase),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, n-ZnO, n-CeO<sub>2</sub>, n-PbS, Carbon nanotube (individual), Ni-filled multi-wall carbon nano tube (MWCNT), Fe-filled MWCNT, AlN (hexagonal),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (67 nm), Ni (20 nm), and CdSe (rocksalt phase). The model used in this work is rather attractive as it requires only a single input parameter, which is the bulk modulus at zero pressure. It is clear from the findings that the current formulation is in excellent agreement with the available experimental evidence. The current technique is validated by this.

Kholiya, Kuldeep et al., (2014) We used two theoretical equation of state (EOS) models to examine the high-pressure compression behavior of the following nanomaterials: 3C-SiC, Zr<sub>0.1</sub>Ti<sub>0.9</sub>O<sub>2</sub>, CuO, AlN, TiO<sub>2</sub> (anatase), TiO<sub>2</sub> (rutile),  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\epsilon$ -Fe, and Rb<sub>3</sub>C<sub>60</sub>. First, we assumed that pressure was quadratic with respect to the change in relative volume; second, we assumed that pressure was quadratic with respect to density. Both models provide superior outcomes, according to the experimental data. We also looked at how well the two models performed when subjected to very high compression.

Singh, Madan et al., (2013) In order to analyze the impact of pressure on the growth of nanomaterials' volumes, a straightforward hypothesis is put up. We go over the many equations of state and how they relate to one another. The computations only need two input parameters, the bulk modulus and its first pressure derivative. In order to examine the impact of pressure on various nanomaterials, we have taken into account a broad range of sizes, including CdSe (4.2 nm), Fe-Cu (14 nm),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (67 nm),  $\epsilon$ -Al<sub>2</sub>O<sub>3</sub> (37 nm), Ni (20 nm), Fe (10 nm), CeO<sub>2</sub> (cubic Fluorite phase) (15 nm), CeO<sub>2</sub> (Orthorhombic Phase) (15 nm), CuO (24 nm), and TiO<sub>2</sub> (rutile phase) (10 nm). The experimental findings and other theoretical models are in agreement with the theoretical predictions for the specified nanomaterials.

### III. RESEARCH METHODOLOGY

Under pressure, the product of the thermal expansion coefficient  $\alpha$  and the bulk modulus  $BT$  stays constant, according to the present method for studying how pressure affects nanomaterials. Various nanomaterials, including  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, CuO, AlN, TiO<sub>2</sub> (anatase phase), Ni(20nm), Ge(49nm), CNT (single walled Corban Nanotube), and CdSe (rock salt phase), were studied for the necessary pressure using the same approach for the needed compression ratios ( $V/V_0$ ). Use the values of  $B_0$  and  $B'_0$ , as well as the constant  $A$ , from Table 1. Using the same parameters, the Birch-Murnaghan equation, Vinet EOS, and Shanker EOS have all been used to determine pressure for various volume ratios ( $V/V_0$ ).

**Table 1: Input Parameters**

Nanomaterials	$B_0$	$B'_0$	$A = B'_0 + 1$
$\gamma$ - Fe <sub>2</sub> O <sub>3</sub>	374	4	5
CuO	81	4	5
AlN	321	4	5
TiO <sub>2</sub> (anatase)	243	4	5
Ni(20nm)	185	4	5
Ge(13nm)	92	4	5
CNT	230	4	5
CdSe(Rock salt phase)	74	4	5

### IV. RESULTS AND DISCUSSION

Information gathered from experiments, as shown in the figures (1-8). Our findings show that the theoretical and experimental frameworks are very congruent. Given the aforementioned, it is worth mentioning that the present approach can accurately characterize the compressional and elastic properties of nanomaterials subjected to high pressure. Scientists investigating the elastic properties of nanomaterials subjected to high pressure may find this appealing because to its practicality and ease of usage.

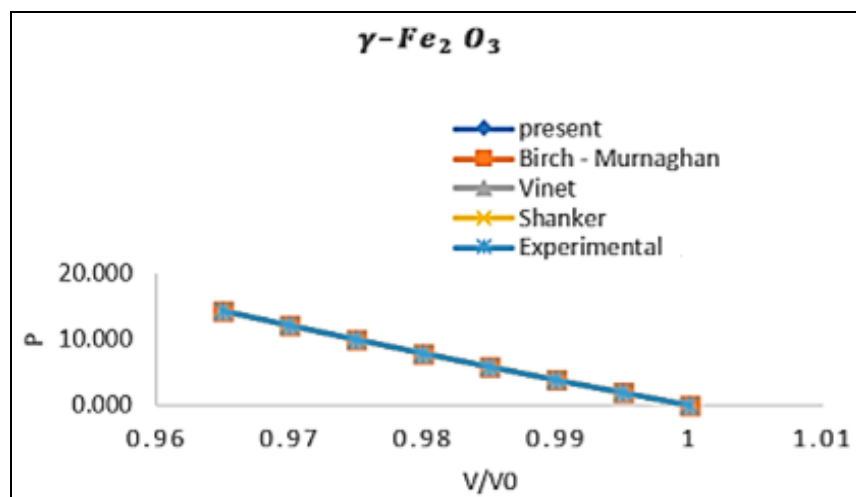


Figure 1: Variation of pressure with required  $V/V_0$  for  $\gamma - Fe_2O_3$

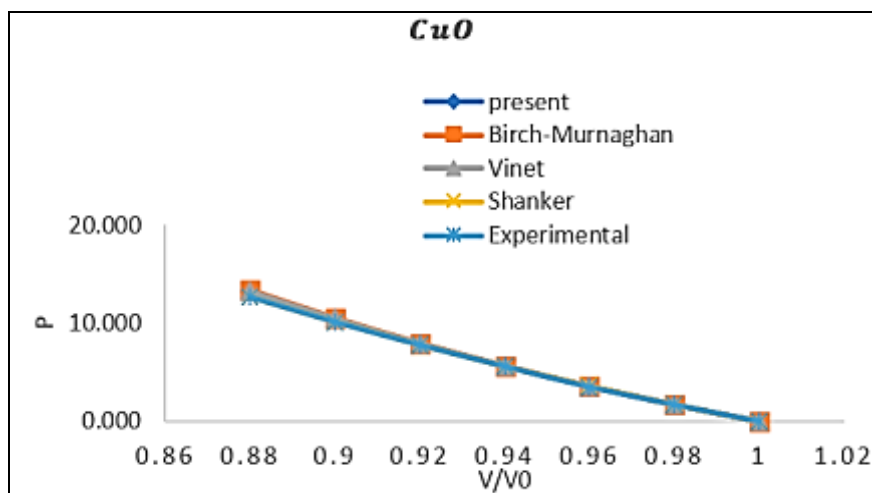


Figure 2: Variation of pressure with required  $V/V_0$  for CuO

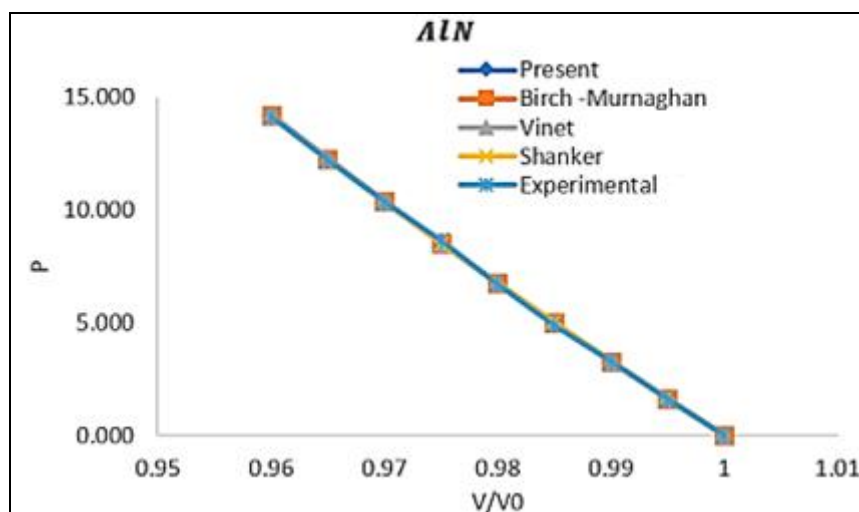
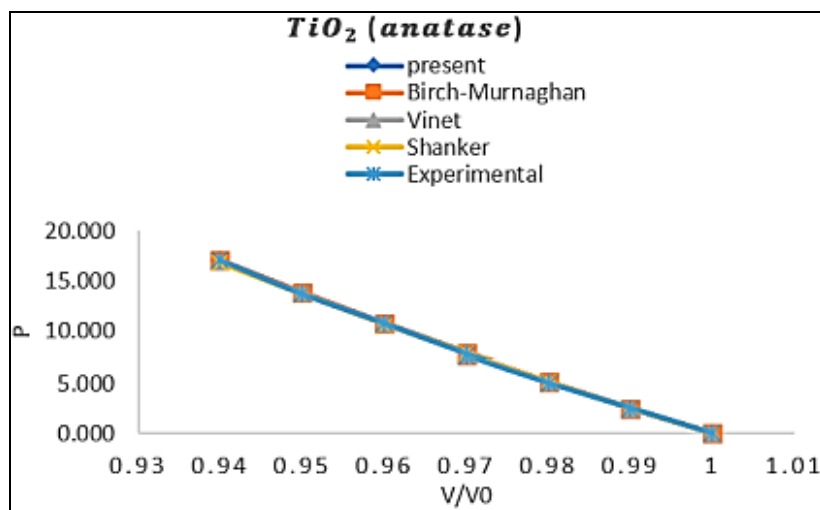
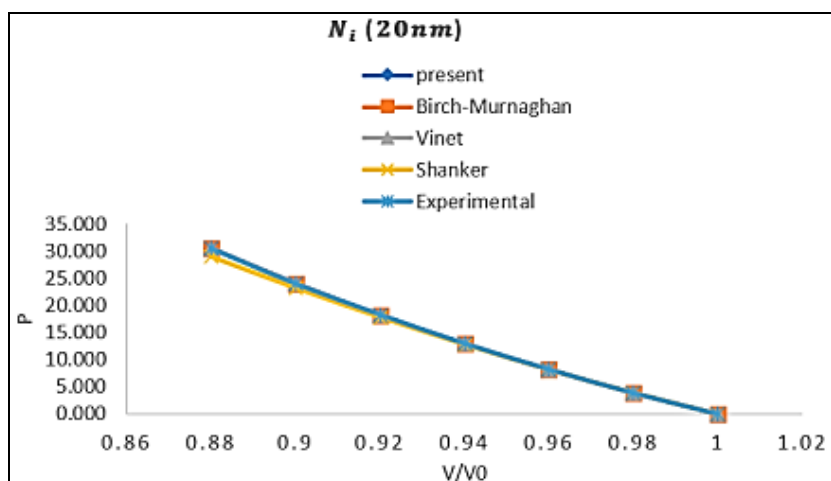
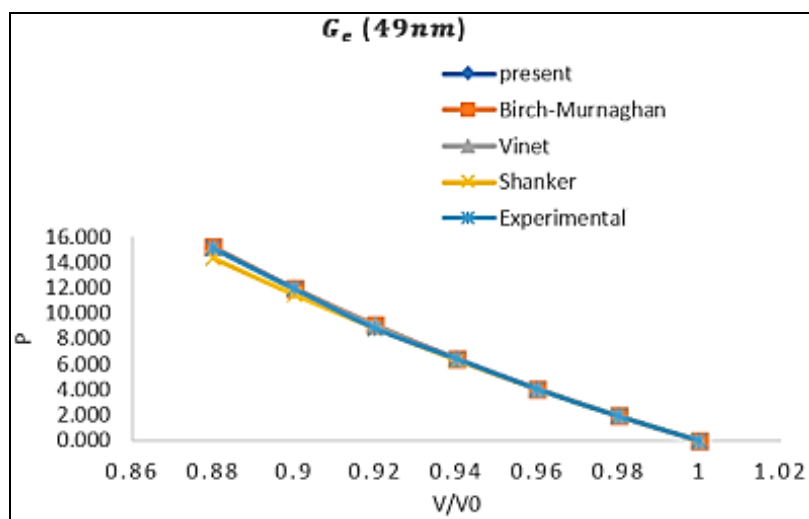


Figure 3: Variation of pressure with required  $V/V_0$  for AlN

Figure 4: Variation of pressure with required V/V0 for  $TiO_2$ (anatase)Figure 5: Variation of pressure With required V/V0 for  $Ni(20nm)$ Figure 6: Variation of pressure With required V/V0 for  $Ge(49nm)$



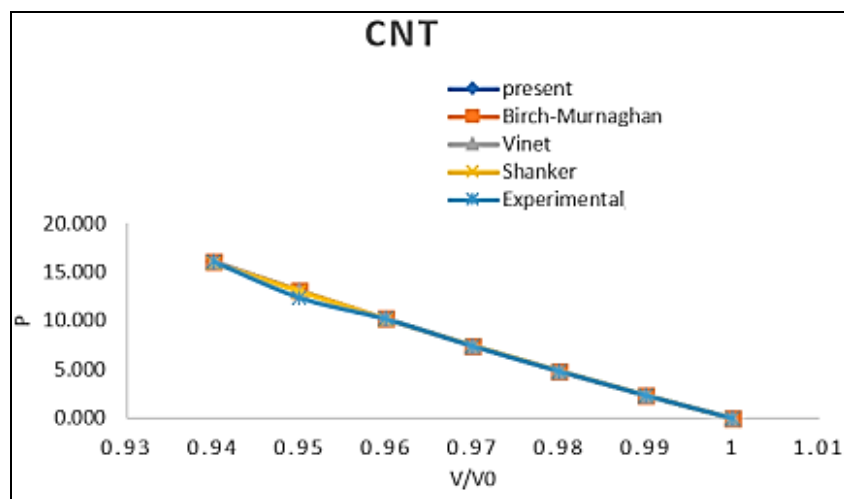


Figure 7: Variation of pressure With required V/V0 for CNT

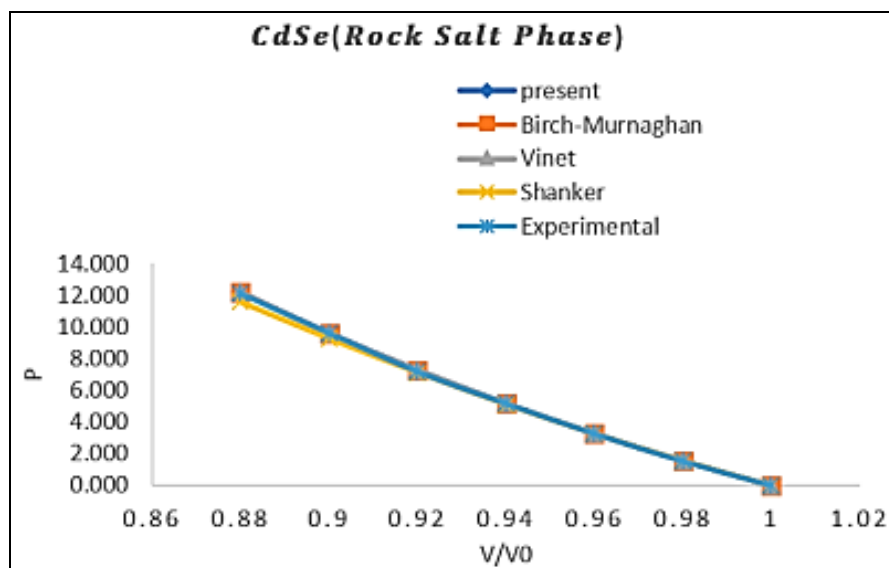


Figure 8: Variation of pressure with required V/V0 for CNT CdSe (Rock salt phase)

## V. CONCLUSION

We confirm the validity and usefulness of the selected models by discovering that there is a significant connection between theoretical predictions and experimental data when we look at the link between pressure and compression ratio ( $V/V_0$ ). This method successfully describes the compressional and elastic properties of nanomaterials under high-pressure circumstances, as shown by the findings. This approach provides useful information for studying the mechanical stability and structural development of nanomaterials in harsh settings since it is simple and reliable. This research adds to our knowledge of high-pressure materials and might be useful in fields including nanotechnology, engineering materials, and smart manufacturing.

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