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RESEARCH ARTICLE

RELATIVE STUDY OF COMPRESSION RATIO VARIATION WITH PRESSURE FOR NANOMATERIALS USING EOS

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Abstract

A basic thermodynamical study of various nanomaterials has been done. Different Equation of states [EOS] (Tait, Shanker & Suzuki) have been applied and compared with the experimental result. An derived equation using thermodynamical approximation is used to investigate the isothermal compression and pressure dependency of bulk modulus of nanomaterials i.e. TiO_2(rutile phase), MgO, CuO, 3C-SiC, $Zr_{0.1}Ti_{0.9}O_2$, ε-Fe, Rb_3C_{60}, Ge(13 nm).The acquired results are found to be in excellent accord with known experimental data, demonstrating the validity of the formulation utilized in this work.

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Introduction:-

Nanomaterials are projected to represent the tipping point in the next technological revolution in solid-state electronics, emerging as novel structural materials, serving as medication delivery systems, and having a significant influence across virtually all fields of research. External elements like as pressure and temperature are extremely sensitive to nanoparticles. The study of nanoparticles under high pressure is being examined as a way to broaden the spectrum of solid-state materials accessible. High pressure applications offer the potential to explore an infinite number of avenues for nano-assembling or phase change in a regulated manner, and they represent a one-of-a-kind route for the development of novel materials. Pressure application, similar to that used on bulk materials, allows for continual alteration of the nano-interatomic object's interactions and is a useful tool for studying physico-chemical interactions at the nanoscale and their relationship to physical attributes of interest.

The structure and interatomic spacing of materials have a substantial impact on their physical characteristics. High pressure can change these distances, allowing us to investigate correlations between material structure and attributes[1].

Many mechanical characteristics, such as hardness, elastic modulus, fracture, toughness, scratch resistance, and fatigue strength, are changed and varied at the nanoscale compared to their bulk counterparts. Many nanomaterial systems have been found to have high value of hardness. Recently, it was discovered that nano semiconductors with decreased dimensions have electrical and optical characteristics that change with particle size, making them attractive candidates for applications requiring tenability of optical and/or electronic properties [2].

At ambient temperature, XRD examinations of baddeleyite structures under high-pressure (20–30 GPa) behaviors of nanocrystalline rutile TiO2 was studied and found excellent results[3].

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Investigation of the compressibility in MgO with particle size 100 nm has been extensively researched since it is a well-known refractory oxide with a wide range of industrial uses, including the production of high-temperature rebrick, insulating materials, and so on. It has a basic rock salt structure and is a known substantial constituent of the Earth's mantle, making it geo-physically significant. The elastic characteristics of MgO have been evaluated by a series of static, ultrasonic, and shock compression studies[4]. Some researchers have analysed the high-energy synchrotron radiation and Raman spectroscopy of copper oxide (CuO) at 24 nm[5]. SiC has sparked a lot of attention since it is a highly hard and robust ceramic with applications in things like automotive brakes and clutches, as well as ceramic plates in bulletproof vests. This material has remarkable thermal shock resistance due to its strong thermal conductivity, minimal thermal expansion, and high strength. SiC ceramics with few or no grain boundary imperfections retain strength at extremely high temperatures with minimal loss of strength [6].

Compression behavior and mechanical properties such as stress and strain of Zr doped nano anatase were studied. This study investigated that the bulk modulus of anatase increases as the crystallite size decreases [7].

The synchrotron x-ray diffraction on nanocrystalline α and ε-Fe was performed through a diamond-anvil cell to pressures of 46 GPa. There was no significant grain growth when they were put under pressure. Using XRD characterized images, they have discovered that the one phase lasted at 46 GPa, which was the highest pressure in this investigation. At the lowest pressure i.e. 7.6 GPa, through the in situ method it has been observed that α-Fe did not transition back to the phase upon decompression. However, transmission electron microscopy (TEM) images revealed that no ε-Fe exist at 0 GPa. These images also revealed that via compression the crystallite size did not change appreciably.

Research was conducted for the Rb_3C_{60} and other nanomaterials, which utilized different equation of state (Tait, shanker &suzuki) models for the high-pressure compression behavior study [8].

X-ray diffraction and synchrotron radiation techniques were used to investigate the equation of state and the I–II transition of nanocrystalline Ge with crystallite sizes of 13, 49, and 100 nm. Whereas, with the reduction of the nanomaterial particle size, the percentage volume collapse during the transition, and the bulk modulus and transition pressure rise. However, the enhanced bulk modulus is due to compression forces induced by the amorphous grain boundary zones in the nanophase material[9].

In this article, we present a simple theoretical approach to study the compression behaviour of nano systems under pressure. An EOS has been developed and after examining its validity, it has been used to calculate the change in volume of some nanomaterials under high pressure. Moreover, the results calculated from our EOS have been compared with those obtained through other methods.

Method:-

According to property of Solid, material contract while cooling and expands on heating for a particular temperature. It was determined by thermal expansion coefficient which is generally a function of volume and temperature at constant pressure. And it is known as:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (1)$$

Where V is volume, P is pressure and T is temperature

Utilizing simulations of single-walled Carbon nanotubes in molecular dynamics, the thermal expansion coefficient was calculated [10] . During such study [10] used the temperature dependence of $\propto$ as given below;

$$\propto = a + b\,T + c\,T^2 \qquad (2)$$

Where a, b, c are constants. It should be noted that the aforementioned equation does not match the initial boundary conditions ,$\propto = \propto_0\ at T = T_0$, In order to satisfy this condition eq. (2)can be write as follows

$$\propto = a + b\,(T-T_0) + c\,(T-T_0)^2 \qquad (3)$$

or

$$\alpha = \alpha_0 + \alpha_0'(T - T_0) + (\tfrac{1}{2})\alpha_0''(T - T_0)^2 \qquad (4)$$

Where $\propto_0$, α_0' and α_0'' are the zero, first and second order derivatives of α with temperature at T_0 .

The Anderson -Gruneisen parameter δ_T which plays an important role in understanding the harmonic properties of ionic solid is defined as [11]

$\delta_T = -\frac{1}{\propto B_T}\left(\frac{\partial B_T}{\partial T}\right)_P$ (5)

Where $\propto$ and B_T are the volume thermal expansion and bulk modulus, respectively,
Using thermodynamical approximation [12]:
$\alpha B_T = constant$ (6)
We have [13]
$\delta_T = \frac{1}{\propto^2}\left(\frac{\partial \propto}{\partial T}\right)_P$ (7)
From this relationship , we will get results as follows:[14]
$\propto_0^{'} = \left(\frac{\partial \propto}{\partial T}\right)_P = \delta_T {\alpha_0}^2$ (8)
$\propto_0^{''} = \left(\frac{\partial^2 \propto}{\partial T^2}\right)_P = 2\delta_T^2 {\alpha_0}^3$ (9)
In which we additionally use the assumption that δ_T is independent of temperature (T).
$\alpha = \alpha_0 + \alpha_0^2\delta_T(T - T_0) + \alpha_0^3\delta_T^2(T - T_0)^2$ (10)
Eq. (10) has shown that α depends on T quadratically. Moreover, considering the temperature dependence of α given by Eq. (10) neglects the higher order terms, which may introduce the error on temperature dependence of α, therefore, it is necessary to consider the complete from which we write as follows:

$$\alpha = \alpha_0 + \alpha_0^2\delta_T(T - T_0) + \alpha_0^3\delta_T^2(T - T_0)^2 + \cdots \ldots \ldots \ldots \ldots \ldots \infty$$

Or

$$\alpha = \alpha_0[1 - \alpha_0\delta_T(T - T_0)]^{-1}$$

$\frac{\alpha}{\alpha_0} = [1 - \alpha_0\delta_T(T - T_0)]^{-1}$ (11)

By taking the value of α from equation (11) and replacing it in the equation (1) gives a new equation which was then integrated to derive the standard equation of our study as given below:
$\int \frac{dV}{V} = \alpha_0 \int [1 - \alpha_0\delta_T(T - T_0)]^{-1}\, dT$ (12)
And boundary conditions for the initial stage are denoted as follows:
At T $= T_0$ V $= V_0$

Solving equation (12) with the above boundary condition results in the following form:
$\log\frac{V}{V_0} = \log[1 - \alpha_0\delta_T(T - T_0)]^{-\frac{1}{\delta_T}}$ (13)
$\frac{V}{V_0} = [1 - \alpha_0\delta_T(T - T_0)]^{-\frac{1}{\delta_T}}$ (14)
Where V_0 and α_0 are the reference values of volume expansion and coefficient of thermal expansion, respectively.

Thermal pressure (P_{Th}) which is relative pressure variation of a solid or a fluid as a result to a temperature variation at constant volume. This is taken from the literature as mentioned below[14]:
$P_{Th} = \int_{T_0}^{T} \alpha B dT$ (15)
In accordance with quasi-harmonic approximation [14, 15]:
$P_{Th} = \alpha_0 B_0 (T - T_0)$ (16)
Where α_0 is the coefficient of thermal expansion at temperature T_0&T_0 is the reference temperature &T is elevated temperature in kelvin.Taking$(T - T_0)$value from equation (16) placing into equation (14) becomes equation (17):
$\frac{V}{V_0} = \left[1 - \frac{\delta_T}{B_0}P_{Th}\right]^{-\frac{1}{\delta_T}}$ (17)
$P_{Th} = \frac{B_0}{\delta_T}\left[1 - \left(\frac{V}{V_0}\right)^{-\delta_T}\right]$ (18)
If applied pressure is P then total pressure including thermal pressure and applied pressure can be rewritten as given in the below terms:
$P_{Th} - P = \frac{B_0}{\delta_T}\left[1 - \left(\frac{V}{V_0}\right)^{-\delta_T}\right]$ (19)
Considering $P_{Th} = 0$ as given in literature[14] equation (19) becomes:
$P = -\frac{B_0}{\delta_T}\left[1 - \left(\frac{V}{V_0}\right)^{-\delta_T}\right]$(20)

However, the approximation δ_T equal to $B_0^{'}$ as discussed by Anderson[14].Where, $B_0^{'}$ is the first order pressure derivation of B. Eq. (20) takes the following from:

$$P = -\frac{B_0}{B_0^{'}}\left[1-\left(\frac{V}{V_0}\right)^{-B_0^{'}}\right] \qquad (21)$$

Or $$\frac{V}{V_0} = \left[1+\frac{B_0^{'}}{B_0}P\right]^{-\frac{1}{B_0^{'}}} \qquad (22)$$

Or $$\frac{V}{V_0} = \exp\left[-\frac{1}{B_0^{'}}\ln\left\{1+\left(\frac{B_0^{'}}{B_0}\right)P\right\}\right] \qquad (23)$$

Thus, we get Eq. (23), which is same as given by Murnaghan in a different way.

As our result has been shown in comparison with these standard EOS given in literature [16][17][18] in the following form:

Tait EOS reads as [16]

$$\frac{V}{V_0} = 1-\frac{1}{\left(B_0^{/}+1\right)}\left[ln\left\{1+\frac{P\left(B_0^{/}+1\right)}{B_0}\right\}\right] (24)$$

Shanker EOS reads as [17]

$$\frac{V}{V_0} = 1+\frac{\left[1-\left[1+2\left\{\frac{B_0^{'}+1}{B_0}\right\}P\right]^{\frac{1}{2}}\right]}{B_0^{'}+1} \qquad (25)$$

Suzuki EOS reads as [18]

$$\frac{V}{V_0} = 1+\frac{\left[1-\left[1+2\left\{\frac{B_0^{'}-1}{B_0}\right\}P\right]^{\frac{1}{2}}\right]}{B_0^{'}-1} \qquad (26)$$

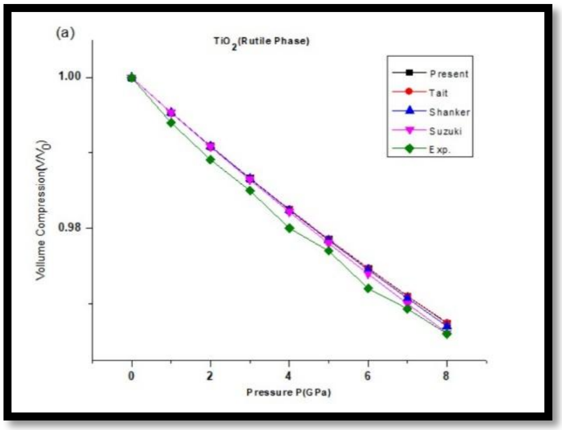
Result and Discussion:-

The current approach for analyzing the effect of pressure on Nanomaterials is based on the quasi-harmonic approximation that the product of the thermal expansion coefficient $\propto$and Bulk modulus B_T remains constant under pressure [15]. Using the same approximation, in this study we have investigated the effect of change of pressure on different nanomaterials such that TiO_2(rutile phase), MgO, CuO, 3C-SiC, $Zr_{0.1}Ti_{0.9}O_2$, ε-Fe, Rb_3C_{60}, Ge(13 nm). From the equation (22), the volume ratio (V/V_0) at different pressure have been calculated. Input parameters B_0& $B_0^{/}$ as listed in Table 1 was taken from literature. The results obtained are shown in Figures. 1-2. Similarly, with the same input parameters, volume ratio (V/V0) have been calculated using equation (24) also known as Tait equation and equation (25) called Shanker equation and equation (26) Suzuki EOS . Experimental data as referenced in the figures (1-2) was taken from the various literature and compared with the result obtained by our derived equation and different EOS. We found that there is very good agreement between theory and experiment.

On the basis of the above, it should be noted that the current method is capable of properly describing the compressional and elastic characteristics of nanomaterials under high pressure. This may be of current interest to researchers studying the elastic characteristics of nanomaterials under high pressure because of its simplicity and applicability.

Table 1:- Input parameters utilized in this research.

Materials	**B_0**	**$B_0^{¢}$**	**Ref.**
TiO_2(Rutile phase)	**211**	**8**	[19]
MgO	**179**	**1.5**	[20]
CuO	**81**	**4**	[5]
3C-SiC	**245**	**2.9**	[6]
$Z_{r0.1}Ti_{0.9}O_2$	**213**	**17.9**	[7]
ε-Fe	**179**	**3.6**	[21]
Rb_3 C_{60}	**17.35**	**3.9**	[5]
Ge(13nm)	**92**	**4**	[9]



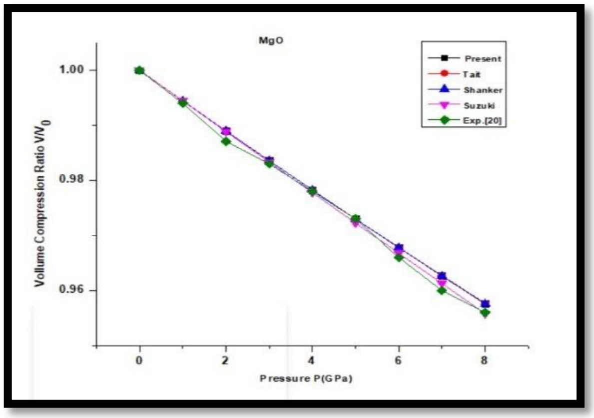
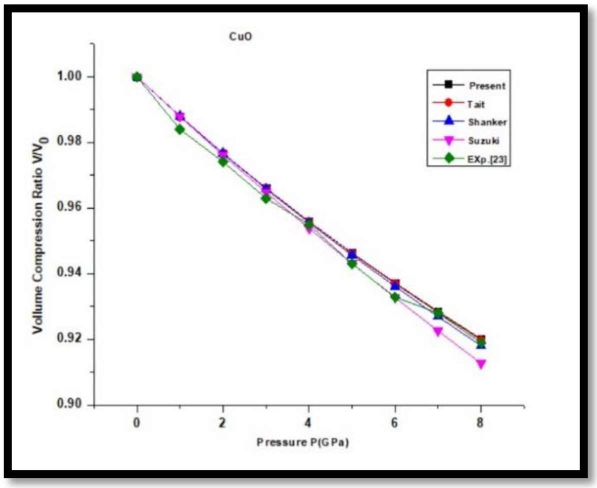


Fig. 1:- Compression Behaviour of **TiO_2(Rutile Phase)** **Fig. 2**:- Compression Behaviour of **MgO**
with Exp. from Ref.[22] with Exp. from Ref.[20]



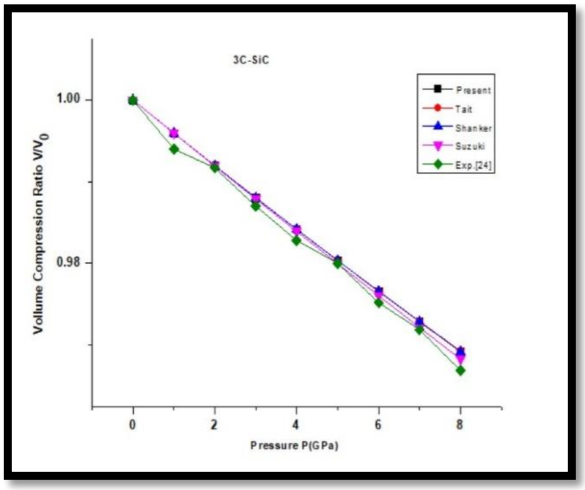
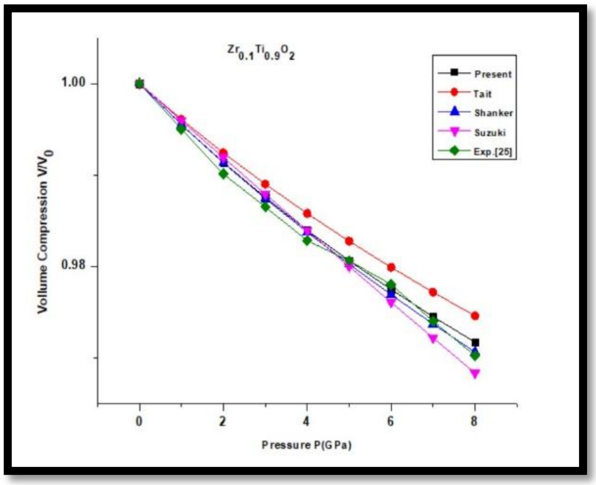
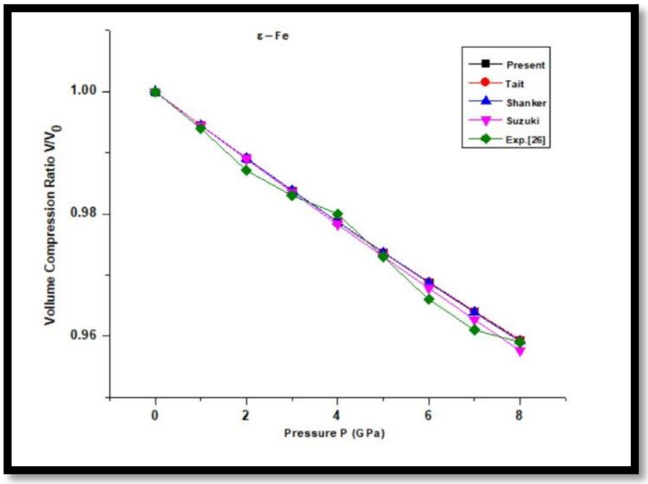


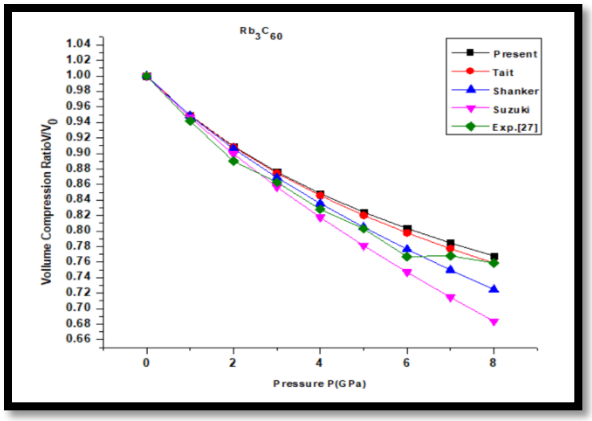
Fig. 3:- Compression Behaviour of **CuO** with

Fig. 4:- Compression Behaviour of **3C-SiC**
Exp. from Ref.[23]with Exp. from Ref.[24]

Fig. 5:- Compression Behaviour of **$Zr_{0.1}Ti_{0.9}O_2$** **Fig. 6** :- Compression Behaviour of $\epsilon - F_e$
with Exp. from Ref.[25] with Exp. from Ref.[26]







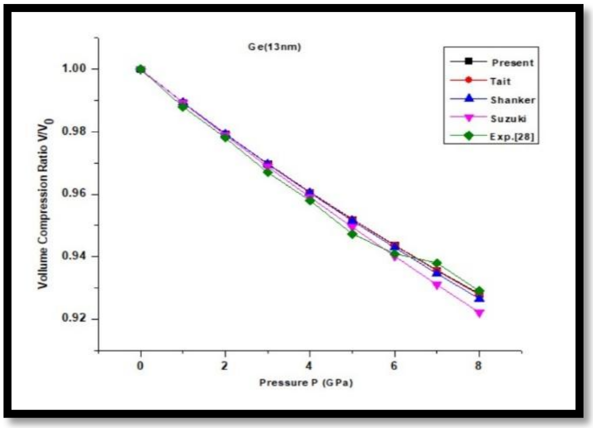


Fig. 7:- Compression Behaviour of Rb_3C_{60}**Fig. 8**:- Compression Behaviour of **Ge (13nm)**with Exp. from Ref.[27]with Exp. from Ref.[28]

Conclusions:-

The current formulation may be particularly useful for analyzing the high-pressure compression behavior of solids, especially nanomaterials, since it offers findings that are pretty near to the experimental data for nanomaterials. However, the main benefit of this formulation is that it follows the basic thermodynamic laws at high pressure, allowing extrapolation into realms where experimental data is not accessible.

As a result, the current formulation might be useful in designing future high-pressure tests on nanomaterial compression behavior.

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