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Size dependent compressibility of nano crystalline materials

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ABSTRACT

Present paper reports a simple theoretical study to investigate the compressional behavior of some nanomaterial using Equation of state. The pressure dependence of compressibility of nanocrystalline PbS of three different sizes (2.6nm, 5.4nm & 8.8nm), nanocrystalline Ni of two different sizes (62nm & 20nm), and nanocrystalline SnO₂ of three different sizes (3 nm, 8 nm & 14 nm) have been analyzed by using Usual Tait's Equation of state (UTE). The compressional behavior of these nanocrystals is compared with available experimental data. This proves the validity of Usual Tait's Equation of State (UTE) at nano scale. This study shows that the compressibility of nano-crystals depends upon size. It is found in this study that compressibility increases with decreasing particle size.

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KEYWORDS

Equation of state;
Compressibility;
Bulk modulus.

INTRODUCTION

Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small size, have the potential for wide-ranging industrial, biomedical, and electronic applications. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Nanocrystalline materials with particle size of 1-100 nm are of current interest because they show noble physical and chemical properties that may differ from those of the corresponding bulk materials^[1]. The chemical preparation method used plays a significant role in controlling the size distribution, structure and crystallinity of these particles. In nanocrystals, approximately half the atoms are on the surface. It is important to understand the surface struc-

ture, so that it can be modified at will, if one has to develop any device using these materials. The surface structure of a nanoparticle, hence its shape, is determined by minimization of the surface energy. This is accomplished by maximizing the amount of low-energy, low-index facets of the crystals. One way of inducing changes in the shape and structure of nanoparticles is to apply high pressure. The size of the nanocrystalline material plays important role in explaining the various physical properties such as melting temperature, hardness, sintering ability and electronic structure^[2,3] Phase transition pressure also depend upon particle size. Some nanomaterials have elevated phase transition pressures with decreasing particle size^[4,5] while some have reduced phase transition pressures with decreasing particle size^[6] During recent past years investigations about

nanocrystalline ceramics, metals and semiconductors have been done^[7,8] on large scale. The important physical properties of nanocrystalline Ni such as magnetic, mechanical, electrical behaviour, diffusion coefficient, vibrational modes and compression behaviour have been widely studied experimentally and theoretically^[9]. Recent investigations show that the compressibility of Nanocrystalline Ni with a large stability range of pressures (i.e. they do not undergo first order transformations) do not change with particle size^[10]. The extraordinary behavior of n-Fe, its magnetic, thermal and electrical properties, surface passivation, and mechanical properties such as ductility, hardness, phonon density of states and compressibility have been investigated^[11,12].

The size of the Nano crystalline material plays important role in explaining the various physical properties such as melting temperature, hardness, sintering ability and electronic structure^[13,14]. Investigation on melting temperature shows that it decreases with decreasing particle size^[14]. Phase transition pressure also depend upon particle size. Some nanomaterials have elevated phase transition pressures with decreasing particle size^[15,16] while some have reduced phase transition pressures with decreasing particle size^[17]. An en-

hancement of transition pressure in nanocrystals ZnO, ZnS, and PbS^[18-20] as compared with their corresponding bulk material is also observed. The high pressure X-ray diffraction investigation by Haines and Legar^[21] indicates three phase transition in nature for SnO₂. With application of high pressure, SnO₂ can transform to the fluorite- type cubic phase. The transition is rather sluggish, and both the low-pressure and cubic phases coexist up to a pressure of 40 Gpa.

In the present work we are analyzing the mechanical properties especially the volume compression (V/V_0) and bulk modulus of n-PbS (for three sizes, 2.6nm, 5.4nm and 8.8nm), nanocrystalline n-Ni of two different sizes (62nm, 20nm n-SnO₂ of three different sizes (3 nm, 8 nm, and 14 nm) using the usual Tait2 s equation of State (EOS). Although, the Tait2 s equation has been widely used in most of the bulk materials^[22,23] however, this equation has not been used so far to study the compression behaviour and the variation of bulk modulus with pressure in nanomaterials. We have therefore, predicted the pressure dependence of unit cell volume and bulk modulus of nanomaterials in the present study for the first time by applying the usual Tait equation of state.

TABLE 1 : The equation of state parameters, K_0 (Gpa) and K'_0 for PbS^[24], Ni (62nm, 20nm and bulk)^[25], and SnO₂^[26]

	PbS (2.6nm)	PbS (5.4nm)	PbS (8.8nm)	Ni (62nm)	Ni (20nm)	Ni (bulk)	SnO ₂ (3nm)	SnO ₂ (8nm)	SnO ₂ (14nm)	SnO ₂ (Bulk)
K_0	33.50	46.51	75	216	228	180	228	225	277	328
K'_0	4.0	4.0	4.0	4	4.02	4	5.6	6.0	2.0	3.28

METHOD OF ANALYSIS

The usual Tait equation of state is obtained by assuming the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (K_T) is constant under the effect of pressure^[27] i.e.

$$\alpha K = \text{constant.} \quad (1)$$

Differentiation of equation 1 with respect to volume at constant temperature, gives

$$\alpha \left(\frac{dK}{dV} \right)_T + K \left(\frac{d\alpha}{dV} \right)_T = 0 \quad (2)$$

Anderson-Gruneisen parameter is defined as

$$\delta_T \frac{V}{\alpha} \left(\frac{d\alpha}{dV} \right)_T \quad (3)$$

where δ_T is Anderson-Gruneisen parameter at constant temperature.

From equations 2 and 3, we get

$$\delta_T \frac{V}{\alpha} \left(\frac{d\alpha}{dV} \right)_T = - \frac{V}{K} \left(\frac{dK}{dV} \right)_T \quad (4)$$

Assuming δ_T to be independent of V ,

$$\delta_T \left(\frac{dK}{dP} \right)_T = K_0^1 \quad (5)$$

Anderson-Gruneisen parameter δ_T and $\eta = V/V_0$ (where V_0 is the initial volume) are related by the following relation^[28]

$$\frac{(\delta_T + 1)}{\eta} = A \quad (6)$$

where, A is a constant for a given solid. In view of equa-

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tion 6, equation 4 can be written as

$$\frac{dK}{K} = \left[-\frac{A}{V_0} + \frac{1}{V} \right] dV \quad (7)$$

Integrating above equation, we get

$$\frac{K}{K_0} = \frac{V}{V_0} \exp A \left[1 - \frac{V}{V_0} \right] \quad (8)$$

$$\text{where } K = -V \left(\frac{dP}{dV} \right)_T \quad (9)$$

In view of equation 9, equation 8 is written as

$$\frac{K}{K_0} \exp A \left[1 - \frac{V}{V_0} \right] dV = -dP \quad (10)$$

The integration of equation 10 gives

$$P = \frac{K_0}{A} \left[\exp A \left(1 - \frac{V}{V_0} \right) - 1 \right] \quad (11)$$

Here, K_0 is the bulk modulus at the zero pressure and the constant A is determined from the initial conditions, viz. at $V=V_0$, $A = \delta_T^0 + 1$.

On substitution of A in equation 11 and taking the natural log, we get the following final form of usual Tait equation of state.

$$\frac{V(P, T_0)}{V(0, T_0)} = 1 - \frac{1}{K_0^1 + 1} \ln \left\{ 1 + \left(\frac{K_0^1 + 1}{K_0} \right) P \right\} \quad (12)$$

where $V(P, T_0)$ is the volume of the solid at pressure required to compress it, keeping the temperature constant. V_0 is the initial volume at $P=0$ at room temperature T_0 . K_0 and K_0^1 are the isothermal bulk modulus and its first pressure derivative at $T=T_0$.

The beauty of this equation of state is that it requires less number of input parameters and provides a simple and straight forward approach to predict the relative compression in solids at high pressure. To test the validity of this equation of state in nanomaterials, (as in bulk materials), we have, therefore, employed Tait's equation of state to predict the compressional behaviour of nanomaterials.

RESULT AND DISCUSSION

The values of volume compression (V/V_0) at different pressure have been calculated from Equation 12

for nanomaterial's considered. Input parameters viz. bulk modulus and its pressure derivative at zero pressure and room temperature, are given in the TABLE 1. Calculated results are shown in Figure 1-9. Figure 1-3 shows the variation of V/V_0 with pressure for n-PbS (2.6nm, 5.4nm & 8.8nm) respectively using UTE along with experimental data. Figure 4 shows the comparative curve of V/V_0 with pressure for these three n-PbS using UTE. Figure 1-4 shows an excellent agreement with the experimental data for the nanomaterials considered. On considering Figure 4, we can say that the compressibility increases with decreases particle size. Figure 5 shows the variation of V/V_0 vs. pressure for Ni (20nm, 62nm & bulk and we concludes from Figure 5 that compressibility increases with decreasing particle size also the nanomaterial Ni is more compressible than bulk Ni. Figure 6, 7&8 shows the variation of relative volume change with pressure for n-SnO₂ (3nm, 8nm & 14nm) along with available experi-

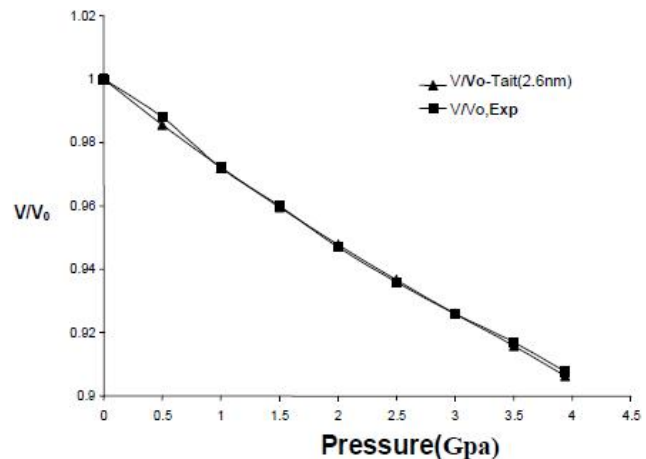


Figure 1 : V/V_0 Vs Pressure (Gpa) for PbS (2.6nm)

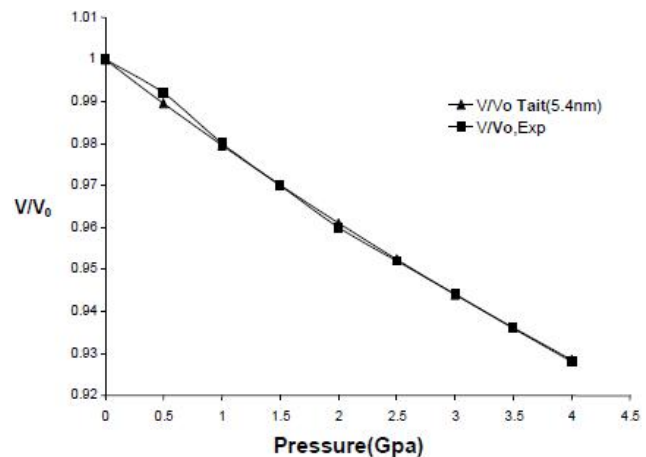
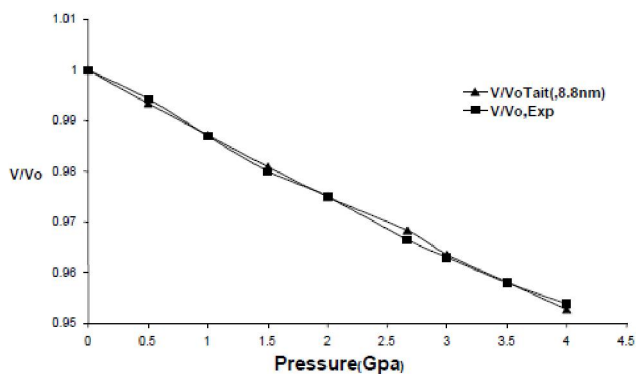
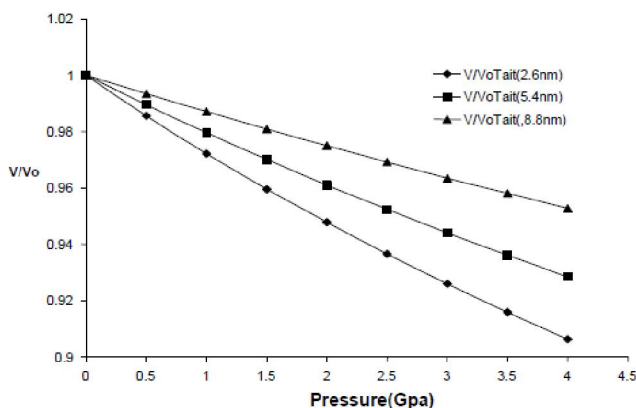
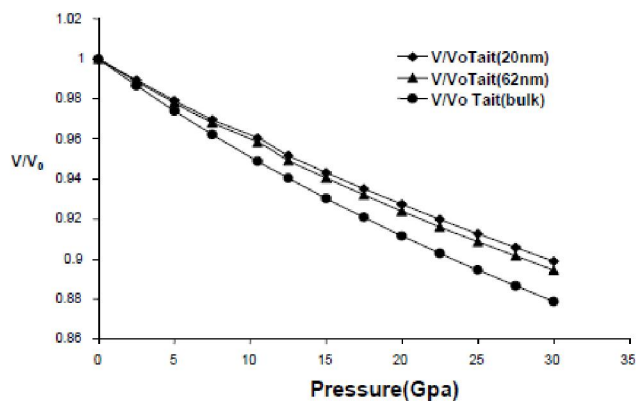
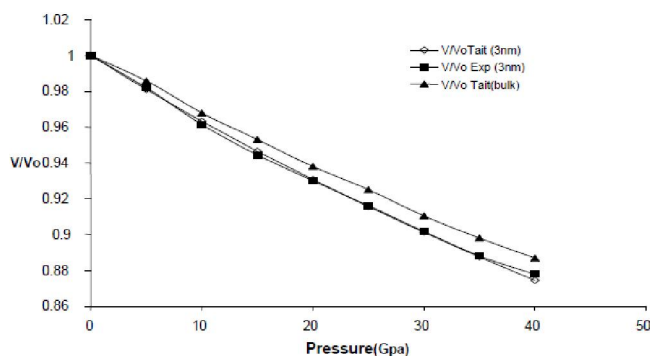
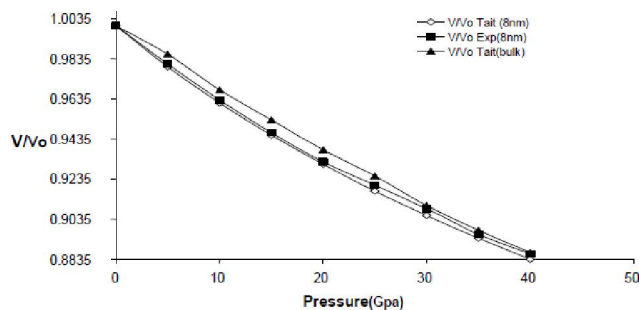
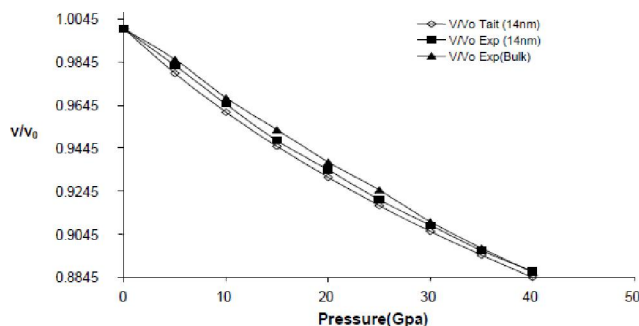
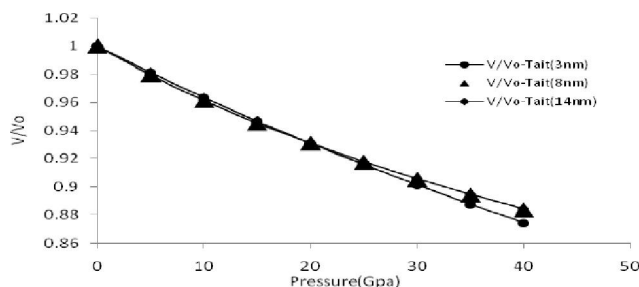


Figure 2 : V/V_0 Vs Pressure (Gpa) for PbS (5.4nm)

Figure 3 : V/V_0 Vs pressure (Gpa) for PbS (8.8nm)Figure 4 : V/V_0 Vs pressure (Gpa) for three PbS nanocrystalsFigure 5 : V/V_0 Vs pressure (Gpa) for Ni (20nm, 62nm & bulk)Figure 6 : V/V_0 Vs pressure (Gpa) for 3nm-SnO₂Figure 7 : V/V_0 Vs pressure (Gpa) for 8nm-SnO₂Figure 8 : V/V_0 Vs pressure (Gpa) for 14nm-SnO₂Figure 9 : V/V_0 Vs pressure (Gpa) for SnO₂ (3nm, 8nm & 14nm)

mental data. We are also using the experimental data for bulk SnO₂ for comparison purpose. Figure 9 shows the comparison of relative change of volume for three different n-SnO₂ (3nm, 8nm & 14nm) using UTE. It is concluded from Figure 9 that the compressibility of the nanocrystals increases with decreasing particle size i.e. lower size nanomaterial is more compressible.

CONCLUSION

Thus it is emphasized here that the Tait's equation of state (UTE) successfully explain the compression properties of nanomaterial's. A single equation of state based on any two parameters can thus explain the mechanical properties of bulk materials and its nanomaterials with same potential. The reason for its success can be traced in fact that the compression

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behaviour of bulk material and nano material is nearly same which is clear from the Figure 1-9. Thus on the overall discussion, it may be concluded that UTE successfully explain the compressibility of nanomaterials and compressibility increases with decreasing particle size or it is also concluded that the nanomaterials are more compressible than its bulk counterparts.

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