Annexure I
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High pressure and high temperature study of nanocrystalline forsterite

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In the present study we have analysed elastic properties of nanocrystalline forsterite under high pressure and high temperature using equation of state model. Relative volume change (V/Vo), bulk modulus and coefficient of volume thermal expansion under temperature range 300–1573 K and pressure range 0–9.6 GPa are studied for nanocrystalline forsterite. Our calculated results of Volume change under different pressure and temperature are compared with available experimental data. An excellent agreement is found between our calculated values and experimental data. We also extended our approach to study the variation of bulk modulus and volume thermal expansion with pressure under different temperature range for nanocrystalline forsterite. Our calculated results for high-pressure high-temperature behaviour of bulk modulus and the coefficient of volume thermal expansion are consistent with the general trend.

Keywords: Equation of state, Volume change, bulk modulus, thermal expansion

1 Introduction
The behaviour of minerals under extreme conditions of pressure and temperature plays an important role in understanding the dynamics and evolution of the lower mantle of the earth. Forsterite and Faylite are two minerals that
are simply known as olivine. Faylite (Fe$_2$SiO$_4$) is the iron rich member while Foresterite (Mg$_2$SiO$_4$) is the magnesium rich member. The two minerals form a series where Fe and Mg are substitutable for each other without much effect to the crystal structure. It is the most abundant mineral in the Earth upper mantle [1]. Foresterite is found in ultramafic igneous rocks (rocks with a high iron and magnesium content) or in marbles made from the metamorphism of dolomitic limestones. Foresterite is also found in many iron-nickel meteorites. Not just as small grains but as significantly sized crystal sometimes occupying over 50% of the meteorites volume.

Foresterite is an ideal substrate material for electronics and suitable material for engineers and designers, especially as an active medium for tunable laser [2,3]. Nanocrystalline materials can possess good biocompatibility and might be suitable for biomedical application [4]. Recent investigations suggest that forsterite ceramics possess good biocompatibility and mechanical properties and might be suitable for potential application, like bone implant materials [5]. So it is of great interest to study its behaviour under high pressure and high temperature conditions.

The characterization of minerals at high pressures and temperatures is an essential part of the earth sciences. Many physical properties of minerals including compressibility, thermal expansivity, and electrical conductivity are functions of temperature and pressure. Since a solid's physical properties are a direct consequence of its atomic arrangement, the continuous variation of atomic positions resulting from changes in T and P may thus be used to understand more fully the variation of physical properties with these intensive parameters.

The high-pressure behaviour of ortho silicates at geologically relevant pressures has been the focus of much recent experimental and theoretical investigation. Grain-size and grain-shape parameters have a great influence on the physical properties of minerals and on geophysical processes. Rheological properties of minerals are strongly dependent on grain size [6]. With the decrease of grain size, the deformation mechanism passes from dislocation-controlled creep to diffusion-controlled creep. Physical properties of Earth minerals are usually studied at micro- or millimetric scales but not at nanometric scale. Even though nanocrystalline minerals might have an important influence on geological processes [7], they are very poorly studied. Despite their limited occurrences in the crust and the mantle, studies show their importance in geophysics.

The behaviour of thermo-elastic constants under the effect of temperature has attracted the attention of theoretical as well as experimental workers [8-11] because of their essential need in the study of technological problems.

Various experimental studies [12-16] and theoretical simulations [17,19] on nanocrystalline metal, alloys, ceramic, and oxides have demonstrated the influence of grain size on their elastic properties. In numerous cases, elastic moduli of nanomaterial are lower than their bulk counterpart and decreases
with the decreasing of grain size within a range of 2 nm to a few tens of nanometers, although their plastic behaviours may sometimes show an opposite trend [20,21].

In the literature a lot of study has been done on the high pressure and high-temperature behavior of olivine group minerals [22–30]. But the investigation on the study of their nano counterparts under high pressure and high temperature are still lacking. Though theoretical attempts based on interionic potential models [31,32] have been carried out by various workers, but these models involve heavy computational work in order to get the results.

Recently Chandra et al. [33,34] have used a temperature-dependent Integral form of equation of state (IFEOS) to study the high-temperature elastic properties of n-ZnO, n-NiO, n-TiO₂, a-(Ni+Fe) n-Ni and fullerene. While, Kholiya [35] has applied an isothermal EOS to study the high-pressure elastic properties of single wall carbon nanotubes.

The purpose of the present study is to formulate a simple and straightforward EOS that can be comfortably used to study the $P\Psi-V\Psi-T\Psi$ variation in nanomaterials and apply it to study the high-pressure and high-temperature elastic behavior of nanocrystalline Foresterite. The theoretical model is presented in Section 2 and the results and discussion in Section 3.

2 METHOD OF ANALYSIS

Assuming the fact that product of the thermal expansion coefficient ($\alpha$) and the bulk modulus ($B_t$) is constant under the effect of pressure [36] i.e.

$$\alpha B_t = \text{constant}$$  (1)

Differentiation of Eq. (1) with respect to volume at constant temperature, gives

$$\alpha \left( \frac{dB}{dV} \right)_T + B \left( \frac{d\alpha}{dV} \right)_T = 0.$$  (2)

Anderson-Grüneisen parameter is defined as

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

where, $\delta_T$ is Anderson-Grüneisen parameter at constant temperature.

From Eq. (2) and Eq. (3) we get

$$\delta_T = \frac{V}{\alpha} \left( \frac{d\alpha}{dV} \right)_T = -\frac{V}{B} \left( \frac{dB}{dV} \right)_T$$  (4)
Assuming $\delta_r$ to be independent of $V_r$,

$$\delta_r = \frac{dB}{dP} B_0 \cdot \left( \frac{dV}{dP} \right)_r. \quad (5)$$

Anderson-Grüneisen parameter $\delta_r$ and $\eta = V/V_0$ (where $V_0$ is the initial volume) are related by the following relation [37]

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

where, $A$ is a constant for a given solid. In view of Eq. (6), Eq. (4) can be written as

$$\frac{dB}{B} = \left( -\frac{A}{V_0} + \frac{1}{V} \right) dV. \quad (7)$$

Integrating above equation, we get

$$\frac{B}{B_0} = \frac{V}{V_0} \exp A \left| 1 - \frac{V}{V_0} \right| \cdot \quad (8)$$

Where

$$B = -V \left( \frac{dP}{dV} \right)_r. \quad (9)$$

Using Eq. (9), Eq. (8) may be written as

$$\frac{B}{B_0} \exp A \left| 1 - \frac{V}{V_0} \right| dV = -dP. \quad (10)$$

The integration of Eq. (10) gives

$$P = \frac{B_0}{A} \exp A \left( 1 - \frac{V}{V_0} \right) - 1. \quad (11)$$

Here, $B_0$ is the bulk modulus at the zero pressure and the constant $A$ is determined from the initial conditions, viz at $V = V_0, A = \delta_r^0 + 1$, or $\Delta^0 = B_0$.

Equation (11) is the Usual Tait's Equation (UTE) and it can be written as follows

$$\frac{V}{V_0} = \left| 1 - \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} P \right] \right| \quad (12)$$

Where $A = B_0 + 1$.
To make Eq. (12) temperature dependent, we have used the basic EOS, which is in terms of thermal pressure, as [38]

\[ P(V, T) = P(V, T_0) + P_{TH} \]  

(13)

Where thermal pressure \( P_{TH} \) may be written as

\[ P_{TH} = \int_{T_0}^T \alpha B_T dT \]  

(14)

In the quasi harmonic approximation considering \( \alpha B_T = \alpha_0 B_0 = \text{constant} \), for nanocrystalline forsterite, Eq (14) gives

\[ P_{TH} = \alpha_0 B_0 (T - T_0) \]  

(15)

Hence temperature dependent form of Eq. (12) may be written as

\[ \frac{V}{V_0} = 1 - \frac{1}{A} \ln \left[ 1 + \frac{A}{B_0} \left( P - \alpha_0 B_0 (T - T_0) \right) \right] \]  

(16)

Using Eq. (9) and Eq. (16), the expression for bulk modulus may be written as

\[ B_T = B_0 \left[ 1 - \frac{1}{A} \ln \left[ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right] \right] \left[ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right]^{-1} \]  

(17)

Or

\[ B_T = B_0 \left[ 1 - \frac{1}{A} \ln[X] \right] X^{-1} \]  

(18)

Where \( X = 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \) and \( A = B_0 + 1 \)

The coefficients of volume thermal expansion is defined as

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]  

(19)

Therefore using Eq. (16) the coefficients of volume thermal expansion may be written as:

\[ \frac{\alpha}{\alpha_0} = \left[ 1 - \frac{1}{A} \ln \left[ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right] \right]^{-1} \times \left[ 1 + \frac{AP}{B_0} - A\alpha_0 (T - T_0) \right]^{-1} \]  

(20)

Or

\[ \frac{\alpha}{\alpha_0} = \left[ 1 - \frac{1}{A} \ln[X] \right]^{-1} \times X^{-1} \]  

(21)
3 RESULTS AND DISCUSSIONS

To study high pressure and high temperature variation of volume change, bulk modulus and thermal expansion coefficient present model requires three input parameters i.e., $B_0$, $B'_0$ and $\alpha_0$ which are 123.3 GPa, 3.88, and $2.471 \times 10^{-4}$ K$^{-1}$ respectively [39]. We have calculated Variation of volume change at constant temperature and pressure, from Eq. (16) and calculated values along with experimental results are shown in Figs. 1–5. Present calculated values (Eq.16) of $V/V_0$ at constant temperature and varying pressure

**FIGURE 1**
$V/V_0$ Versus Pressure at $T = 300$ K for n-Forsterite.

**FIGURE 2**
$V/V_0$ Versus Pressure at $T = 473$ K for n-Forsterite.
FIGURE 3
V/\(V_0\) Versus Pressure at \(T = 673\, \text{K}\) for n-Forsterite.

FIGURE 4
V/\(V_0\) Versus Pressure at \(T = 873\, \text{K}\) for n-Forsterite.

FIGURE 5
V/\(V_0\) Versus Pressure at \(T = 1073\, \text{K}\) for n-Forsterite.
along with corresponding experimental values are also shown in table-I. A close agreement between the calculated and the experimental results shows the validity of present approach (Eq. (16)). It is found that compression under pressure i.e., $V/V_0$ decreases with pressure, occurs in nanocrystalline forsterite which is a general trend in bulk forsterite, also. Recently compression behaviour of nanocrystalline forsterite is studied by Chandra et al [40]. They mentioned that equation of state is equally applicable for bulk as well as nano counterpart of forsterite and nano forsterite is more compressible than bulk forsterite.
TABLE 1
Pressure(Gpa) Vs. V/V₀ (Eq. 16) & V/V₀ (Exp. 39) at various temperature for α-Foresiterite:

<table>
<thead>
<tr>
<th>Pressure(GPa)</th>
<th>Eq. (16)</th>
<th>Exp [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2.3</td>
<td>0.982147</td>
<td>0.9824</td>
</tr>
<tr>
<td>3.7</td>
<td>0.971996</td>
<td>0.9717</td>
</tr>
<tr>
<td>5.1</td>
<td>0.962323</td>
<td>0.9624</td>
</tr>
<tr>
<td>6.5</td>
<td>0.953087</td>
<td>0.9562</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure(GPa)</th>
<th>Eq. (16)</th>
<th>Exp [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>0.982349</td>
<td>0.9824</td>
</tr>
<tr>
<td>4.2</td>
<td>0.972187</td>
<td>0.9724</td>
</tr>
<tr>
<td>5.5</td>
<td>0.963183</td>
<td>0.9652</td>
</tr>
<tr>
<td>6.2</td>
<td>0.958493</td>
<td>0.958</td>
</tr>
<tr>
<td>6.9</td>
<td>0.953909</td>
<td>0.9535</td>
</tr>
<tr>
<td>7.4</td>
<td>0.950696</td>
<td>0.9528</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pressure(GPa)</th>
<th>Eq. (16)</th>
<th>Exp [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>0.983164</td>
<td>0.9831</td>
</tr>
<tr>
<td>4.8</td>
<td>0.972254</td>
<td>0.9738</td>
</tr>
<tr>
<td>6.1</td>
<td>0.963246</td>
<td>0.9662</td>
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<tr>
<td>6.9</td>
<td>0.957894</td>
<td>0.9614</td>
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<tr>
<td>7.6</td>
<td>0.953323</td>
<td>0.9531</td>
</tr>
<tr>
<td>8</td>
<td>0.950755</td>
<td>0.9542</td>
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<table>
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<th>Pressure(GPa)</th>
<th>Eq. (16)</th>
<th>Exp [39]</th>
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</thead>
<tbody>
<tr>
<td>3.7</td>
<td>0.984734</td>
<td>0.9855</td>
</tr>
<tr>
<td>5.3</td>
<td>0.97303</td>
<td>0.9745</td>
</tr>
<tr>
<td>6.6</td>
<td>0.963989</td>
<td>0.9673</td>
</tr>
<tr>
<td>7.4</td>
<td>0.958617</td>
<td>0.9597</td>
</tr>
<tr>
<td>8.1</td>
<td>0.95403</td>
<td>0.9549</td>
</tr>
<tr>
<td>8.6</td>
<td>0.950815</td>
<td>0.9545</td>
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<table>
<thead>
<tr>
<th>Pressure(GPa)</th>
<th>Eq. (16)</th>
<th>Exp [39]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.6</td>
<td>0.975241</td>
<td>0.9755</td>
</tr>
<tr>
<td>6.8</td>
<td>0.966793</td>
<td>0.9676</td>
</tr>
<tr>
<td>7.8</td>
<td>0.960009</td>
<td>0.9611</td>
</tr>
<tr>
<td>8.5</td>
<td>0.955391</td>
<td>0.9552</td>
</tr>
<tr>
<td>9</td>
<td>0.952155</td>
<td>0.9559</td>
</tr>
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</table>

(To be continued)
This encouraged us to extend present approach to calculate high pressure and high temperature behaviour of bulk modulus and coefficient of thermal expansion. We have used Eq. (18) to calculate bulk modulus under different pressure and temperature. The result regarding the high pressure high temperature dependence of bulk modulus is shown in Fig. 8. From this figure we may conclude that bulk modulus increases with pressure and decreases with increases in temperature. Eq. (21) is used here to compute coefficient of volume thermal expansion for nanocrystalline forsterite under different pressure and different temperature. The result of coefficient of volume thermal expansion is shown in Fig. 9 and demonstrates the inverted results in comparison to the bulk modulus due to the fact that the coefficient of volume thermal expansion and bulk modulus are reciprocal to each other. Our calculated results for high-pressure high-temperature behaviour of bulk modulus and the coefficient of volume thermal expansion are consistent with the general trend and may stimulate some experimental or theoretical research regarding this as, in the best of our knowledge, high-pressure high-temperature behaviour of bulk modulus and the coefficient of volume thermal expansion for nanocrystalline forsterite has not yet been reported in the literature.

Thus our present approach which is based on the fact that the product of coefficient of volume thermal expansion coefficient and bulk modulus is constant and valid for nanocrystalline forsterite under the given temperature ranges. Due to simple approach and applicability of the model, it may be the current interest of the researchers engaged in the study of high pressure and
high temperature elastic properties of nonmaterials and may be extended for the variety of nanomaterials.

At last it is pertinent to mention here that the present model is derived in such a way that it is structure independent. For the nanomaterials the zero pressure bulk modulus \( (B_0) \) differs significantly from their counter bulk-sized materials and the present model require \( B_0 \) as input parameter. Therefore, taking \( B_0 \) corresponding to the bulk material, present model work for bulk material while taking \( B_0 \) corresponding to their counter nano-sized material model work for nanomaterial.
REFERENCES

INTRODUCTION

Graphene is a two dimensional crystalline material and discovered in 2004. It has exceptional mechanical properties investigated by the different researchers during recent past years. It has been found that electronic structure of graphene depends on the strain produced at different temperatures in it. Graphene band structure can be changed by applying strains larger than 15%7. In addition to that it is noted that a compressed monolayer of graphene with size 30×100 µm² is fastened with 0.7% strain approximately8. There are two widely used theoretical approaches available to study the various mechanical properties. These theories are based on elastic continuum and the interatomic potentials (EP)4,9,10 such as the Brenner potential (REBO)11,12 and the LCBOPII potential13.

Due to instability coupled with stretching modes, the graphene is expected to be strongly anharmonic. This coupling plays an important role to prevent the cracking in crystal and stabilize the flat phase14 as confirmed by atomistic simulations for graphene15 at room temperature. This is well established that anharmonicity is of general importance in condensed matter in relation to structural phase transitions16,17,18, soft modes in ferroelectrics18, melting19, and other related phenomena. Since the anharmonicity in crystals is very weak, it can be explained within the framework of quantum theory of perturbation16,20–.
However, this is not true for graphene which is a strongly anharmonic crystal. Therefore, the atomistic simulations offer the possibility to study anharmonic effects for a specific material without the need of perturbation theory. A very accurate description of thermodynamic properties of different allotropes of carbon including graphene\textsuperscript{15, 23} is provided by the empirical bond order potential LCBOPI\textsuperscript{24, 25, 26}.

Many interatomic potentials have been used to calculate the thermal and bending modulus properties of graphene at zero temperature\textsuperscript{11,12, 13, 18}. In the present study we have applied for the first time, the potential free model to analyze the thermal expansion behavior of graphene with varying temperature from room temperature to higher temperature range. The mathematical formulation is described in section 2 and the results are discussed in section 3.

**Mathematical formulation**

Considering the product of thermal expansion coefficient \( \alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_p \) and bulk modulus (\( K_T \)) remains constant\textsuperscript{27, 28} under the effect of temperature i.e.

\[
\alpha K_T = \text{Constant} \quad \ldots (1)
\]

On the basis of equation (1) Singh and Gupta \[29\] derived the equation of state to determine the values of \( \alpha_T \) and \( V/V_0 \). These expressions are given below:

\[
\alpha_T = a_0 \frac{\delta T^0 \alpha_0}{T_0^k} T^{k-1} \quad \ldots (2)
\]

and

\[
\frac{V}{V_0} = \exp \left[ \int_{T_0}^{T} \frac{a_0 \delta T^0}{T_0^k (k+1)} \left( T^{k+1} - T_0^{k+1} \right) \right] 
\quad \ldots (3)
\]

Or

\[
\frac{V}{V_0} = \exp \left[ \int_{T_0}^{T} \frac{a_0}{1 - A \left( T^{k+1} - T_0^{k+1} \right)} \right] dT 
\quad \ldots (4)
\]

Where

\( \delta T^0 \) is the value of Anderson Gruneisen parameter (\( \delta_g \)) and \( \alpha_0 \) is the thermal expansion coefficient at \( T_0 \), \( K_0 \) is the bulk modulus and \( k \) is the dimensionless thermoelastic parameter. The derivations for them are not derived here as they are already given elsewhere\textsuperscript{29}. The equation (4) known as the integral form of equation of state has been used to calculate the nature of volume thermal expansion in graphene as shown in fig.1.

**RESULTS AND DISCUSSIONS**

In the present paper we have determined the value of volume thermal expansion \( (V/V_0) \), using the integral form of equation of state (Eq. 4) and the thermal expansion coefficient (TEC) of graphene from equation (2) with varying temperature from room temperature to 1000K. The calculated values are shown in table 2 along with the available experimental data. The input data used in the present work are given in table 1 with appropriate references. The results on thermal expansion and thermal expansion coefficient of graphene achieved in the present work are also shown in figures 1 and 2 and compared with the experimental values. It is clear from figs. 1 and 2 that the results achieved in the present study are in close agreement with the experimental data. The negative values of thermal expansion coefficient (TEC) of graphene are

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \alpha_T ) (10(^{-6})K(^{-1}))</th>
<th>( \frac{V}{V_0} )</th>
<th>( K_0 ) (eV Å(^{-2}))</th>
<th>( \alpha_T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-4.6</td>
<td>0.9973</td>
<td>12.7</td>
<td>0.9840</td>
</tr>
<tr>
<td>400</td>
<td>-3.45</td>
<td>0.9969</td>
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<td>500</td>
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<td>600</td>
<td>-2.5</td>
<td>0.9947</td>
<td>12.7</td>
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<td>700</td>
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<td>0.9945</td>
<td>12.7</td>
<td>0.9832</td>
</tr>
<tr>
<td>800</td>
<td>-2.08</td>
<td>0.9943</td>
<td>12.7</td>
<td>0.9830</td>
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</table>

Table 1: Input data used in present work for Graphene at room temperature

Table 2: Calculated values of thermal expansion coefficient (\( \alpha_T \)), volume thermal expansion (\( V/V_0 \)) and bulk modulus (\( K_T \)) with varying temperature
conformed with the temperature dependent Raman spectroscopy26 and in good agreement with those values obtained from QHA-GGA ab-initio study25. This confirms the validity of the equation of state used in the present investigation to analyze the thermal expansion behavior of graphene at high temperature.

On the basis of overall descriptions it is emphasized that a simple and straightforward method used in the present study is capable of explaining the temperature dependent properties of graphene successfully. The methodology adopted in the present work may be of current interest to those researchers engaged in the study of mechanical properties of nanomaterials and alike materials.

REFERENCES

Behaviour of nanomaterials under pressure

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ABSTRACT

Equation of state model is used to study the compression behaviour of nanomaterials. The well known Suzuki’s EOS is shown to be mathematically inconsistent and hence modified by applying the initial boundary conditions. Thermodynamically and mathematically consistent, modified Suzuki’s EOS is applied to study the compression behaviour of various nanomaterials (Zr0.1Ti0.9O2, 3C-SiC, ε-Fe, CuO). The results obtained using the thermodynamically consistent formulation (modified Suzuki’s EOS) are found to be in better agreement with the experimental data in comparison to the Suzuki EOS.

INTRODUCTION

It is evident from the exiting literature that during past years several experimental studies have been performed to understand the high pressure behaviour of nanomaterials. Studies of compressibility and pressure induced phase transitions for nanocrystalline materials can improve our understanding of the stable state of materials down to nanometer scale. Most high pressure research on nanocrystalline materials has been on semiconductor, although some work on insulators and metals has been reported recently. On applying the high pressure on nanomaterial, many effects may occur, such as (i) transformation of nano-constitutive elements (ii) transformation of the interaction between nano objects (iii) modification of interactions between the nano-objects and pressure transmitting medium. Due to such applications, the effects of pressure on nanomaterials have attracted the attention of the researchers.

The compression behaviour of Zr-doped nanocrystalline Zr0.1Ti0.9O2 synthesized by the sol gel method was studied by Holbig et al.[1] using a diamond anvil cell (DAC) and found no evidence of phase transition up to a pressure of 13 GPa. Lie et al.[2] have synthesized the nanocrystalline 3C-SiC (30 nm) by laser induced vapour phase reactions and performed the energy dispersive X-ray diffraction (EDXRD) experiment at room temperature using silicon oil as a pressure transmitting medium to obtain quasi hydrostatic condition. They observed a decrease of the Born’s transverse effective charge of these nanocrystals with increasing pressure, in contrast to its bulk counterpart. Chen et al.[3] have performed X-ray diffraction measurements on nanocrystalline ε-Fe up to 46 GPa and determined the value of bulk modulus and its pressure derivative from the analysis of lattice parameter data. The EOS of nanocrystalline CuO (24 nm) has been studied by Wang et al.[4], using high energy Syncrotron...
radiation and Raman spectroscopic techniques. The study based on the equation of states at high-pressure permits interpolation and extrapolation in to the regions in which the experimental data is not available adequately and hence may be helpful in planning future high pressure experiments\[^5\text{-}^{12}\]. In the present paper our aim is to develop a simple theoretical model to study the high pressure elastic properties of nanomaterials. To develop the theoretical model we have chosen the well known Suzuki’s EOS\[^13\text{-}^{14}\] as a base. It is shown that the Suzuki EOS is mathematically inconsistent and does not follow the basic thermodynamic conditions. Therefore, to make Suzuki’s EOS mathematically consistent some modifications are required and in the present paper it is modified by using the basic thermodynamic relations and initial boundary conditions as mentioned in method of analysis section. The obtained results with the Suzuki and the modified Suzuki EOS along with the experimentally obtained data are given and discussed in results and discussion section.

**Method of analysis**

In the literature Mie-Gruneisen Debye theory is being widely used. Using Mie-Gruneisen Debye theory Suzuki\[^13\] reported what became known as the Suzuki relation for thermal expansivity. This reads as follows\[^13\text{-}^{14}\].

\[
\frac{V}{V_0} = \frac{1 + 2k - \left(1 - \frac{4k E_{Th}}{Q}\right)^{1/2}}{2k}
\]  

(1)

Where \(k = \frac{(B'_0 - 1)}{2}\), \(Q = \frac{B_0 V_0}{\gamma_0}\), \(\gamma_0\) is the Gruneisen ratio and \(E_{Th}\) is the thermal energy.

Shanker\[^15\] used \(P_{Th} = \frac{\gamma_0 E_{Th}}{V_0}\) and rearranged Eq. (1) as follows

\[
\frac{V}{V_0} - 1 = \frac{1 - 1 - \left(\frac{B'_0 - 1}{B_0}\right)P_{Th}}{(B'_0 - 1)}^{1/2}
\]

(2)

Where \(P_{Th}\) is the thermal pressure. Eq (2) is valid at \(P=0\). Following the arguments of Kushwaha and Shanker\[^16\] when \(P\) is not equal to zero, Eq. (2) may be rewritten as follows

\[
\frac{V}{V_0} - 1 = \frac{1 - 1 - \left(\frac{B'_0 - 1}{B_0}\right)(P_{Th} - P)}{(B'_0 - 1)}^{1/2}
\]

(3)

Now, when thermal pressure is zero \((P_{Th}=0)\), Eq. (3) gives the following simple relation.

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

Or

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

(4)

Eq. (5) is widely used Suzuki’s EOS, which gives the compression curve quite close to the experimental values, but Suzuki’s EOS given by Eq. (5) is found to be mathematically inconsistent and does not follow the basic thermodynamic conditions. Mathematical inconsistency in the Suzuki EOS may be shown as follows:

The expression for bulk modulus, i.e. \(B = -V\left(\frac{dP}{dV}\right)\), obtained from Eq. (5) comes out as:

\[
B = \left(\frac{V}{V_0}\right)B_0 \left[1 + 2\left(\frac{B'_0 - 1}{2}\right)\left(1 - \frac{V}{V_0}\right)\right]
\]

(6)

From Eq. (6), the first order pressure derivative of bulk modulus, \(B' = \frac{dB}{dP}\) comes out to be:

\[
B' = -\left[\frac{1 + \left(\frac{B'_0 - 1}{2}\right)\left(1 - \frac{2V}{V_0}\right)}{1 + \left(\frac{B'_0 - 1}{2}\right)\left(1 - \frac{V}{V_0}\right)}\right]
\]

(7)

Now, from the thermodynamic boundary condition at \(P=0;\ V=V_0\) and one should have \(B=B_0\), but at \(P=0;\ V=V_0\), Eq. (7), gives \(B' = B'_0 - 2\), therefore, the Suzuki EOS is mathematically and thermodynamically inconsistent. So we have to modify Suzuki’s EOS...
in such a way that it follows the basic thermodynamic relations. Therefore, the aim of the present paper is to redefine the Suzuki EOS and formulate an EOS which is mathematically consistent and explains the compression behaviour of different solids. In the present paper, to modify the Suzuki EOS, the expansion method, have been considered and the product $PV$ is expended in powers of $1-(V/V_0)$ up to the quadratic term, as:

$$P \left( \frac{V}{V_0} \right) = A_0 + A_1 \left( 1 - \frac{V}{V_0} \right) + A_2 \left( 1 - \frac{V}{V_0} \right)^2$$  \hspace{1cm} (8)

where $A_0, A_1$ and $A_2$ are constants and may be determined from the initial boundary conditions as used by Shanker and Kushwah\[4\] i.e. at initial pressure $P=0$; $V=V_0$ and therefore, from Eq. (8), we have $A_0=0$. The expression for bulk modulus, i.e. , obtained from Eq. (8) comes out as:

$$B = \left( \frac{V_0}{V} \right) \left[ A_1 + A_2 \left( 1 - \left( \frac{V}{V_0} \right)^2 \right) \right]$$  \hspace{1cm} (9)

The expression for first order pressure derivative of bulk modulus, i.e. $B' = \frac{dB}{dP}$ by differentiating Eq. (9) with respect to pressure is as follows:

$$B' = \frac{A_1 + A_2 \left( 1 + \left( \frac{V}{V_0} \right)^2 \right)}{A_1 + A_2 \left( 1 - \left( \frac{V}{V_0} \right)^2 \right)}$$  \hspace{1cm} (10)

At $P=0$; $V=V_0$; Eqs. (9) and (10) give $A_1=B_0$ and,

$$A_2 = B_0 \left( \frac{B_0' - 1}{2} \right)$$

where $B_0$ and $B_0'$ are the values of bulk modulus and first order pressure derivative of bulk modulus at zero pressure, respectively.

Substituting the values of $A_0, A_1$ and $A_2$ in Eq. (8) becomes:

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

$$+ \left( \frac{B_0' - 1}{2} \right) \left( \frac{V_0}{V} \right) \left( 1 - \frac{V}{V_0} \right)^2$$

$$+ \left( \frac{B_0' - 1}{2} \right) \left( 1 - \frac{V}{V_0} \right)^4$$  \hspace{1cm} (11)

Eq. (11) can be regarded as the modified Suzuki EOS and is thermodynamically and mathematically consistent.

### RESULTS AND DISCUSSION

To study the high pressure behaviour using equation of states, we requires two input parameters ‘$B_0$’ and ‘$B_0’$, these parameters are given in TABLE 1 along with corresponding references. The results obtained for the pressure dependence of the volume compression for 4 nanomaterials (Zr0.1Ti0.9O2, 3C-SiC, ε-Fe, CuO, using Suzuki’s EOS [Eq. (5)] and modified Suzuki’s EOS [Eq. (11)] are shown in Figures (1 to 4) along with the experimental data. From these figures, it is clear that the Eq. (11) modifies the results of Suzuki’s EOS (Eq. 5), for the compression behaviour of nanomaterials. The reason for this may be attributed to the mathematical consistency of the modified Suzuki EOS which was missing in the Suzuki EOS. Thus, it is convenient to use Eq. (11) i.e. modified Suzuki’s EOS to study the high pressure behaviour of nanomaterials. The theory may also be extended to study the pressure dependence of bulk modulus for these nanomaterials. The pressure dependence of bulk modulus can also be calculated from Eq. (9). It is pertinent to mention here that Kumar and Kumar\[17\] have also modified Shanker’s EOS on the empirical basis to study the compression behaviour of nanotubes (individual and bundles). Although, the results obtained by modified Shanker’s EOS were close in the range up to where

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Material</th>
<th>$B_0$ (GPa)</th>
<th>$B_0'$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zr0.1Ti0.9O2</td>
<td>213</td>
<td>17.9</td>
<td>[1]</td>
</tr>
<tr>
<td>2</td>
<td>3C-SiC</td>
<td>245</td>
<td>2.9</td>
<td>[2]</td>
</tr>
<tr>
<td>3</td>
<td>ε-Fe</td>
<td>179</td>
<td>3.6</td>
<td>[3]</td>
</tr>
<tr>
<td>4</td>
<td>CuO</td>
<td>81</td>
<td>4</td>
<td>[4]</td>
</tr>
</tbody>
</table>
Figure 1: Compression behavior of nano-Zr0.1Ti0.9O2

Figure 2: Compression behavior of nano-3C-SiC

Figure 3: Compression behavior of nano-5 Fe

the experimental data is available but Kholiya[18] have shown that their used EOS is thermodynamically and
mathematically inconsistent and hence may not be applicable for some other nanomaterials as well as for interpolation and extrapolation in to the regions in which the experimental data is not available.

From the overall discussion, it may be concluded that the present formulation follows the fundamental thermodynamic conditions and modifies the results of Suzuki’s EOS, which is mathematically and thermodynamically inconsistent also. Therefore, modified Suzuki’s EOS, should be favoured over mathematically and thermodynamically inconsistent Suzuki’s EOS.

REFERENCES

“Temperature dependence of Thermal expansivity and volume thermal expansion of Silver (Ag) and Gold (Au) nanometals”

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Abstract: There has been intense activity, both experimental and theoretical, in exploring fascinating thermo physical properties of noble metals like silver and gold. In the present study the authors have investigated the thermo-elastic properties such as volume thermal expansion and thermal expansivity of two nanometals using the equation of state based on thermodynamic variables as a function of temperature. A simple and straightforward method used for calculating the thermo-elastic properties of high temperature is based on the approximation that the temperature derivative of work done by thermal pressure approaches a constant value at high temperature. The results achieved in the present investigation are compared with the available experimental data. A good agreement is obtained.

Keywords: Equation of state, volume thermal expansion, thermal expansivity, nanometals.

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INTRODUCTION

The equation of state (EOS) plays a key role in analyzing the thermo physical properties of different class of solids. In general, the metals are characterized by the availability of large number of electrons, which can be easily removed from the parent atoms. The free electrons are mainly responsible for the high thermal and electrical conductivity since they absorb easily any energy from lattice vibration and thereby increase their energy and mobility. During past years, several experimental and phenomenological approaches have been proposed to analyze the various thermo dynamical properties of bulk metals under the effect of high temperature and high pressure. The knowledge of thermo-elastic properties of minerals at high temperature and pressure is required for the understanding of the earth’s deep interior. Considerable efforts have been made to predict the equation of state of minerals under varying conditions of pressure using diamond-anvil cells. However, fewer efforts are made under the effect of high temperature at zero pressure.

Several equations of state are available [1-5] for the study of temperature dependent properties of the different class of solids. Though the theoretical attempts based on interionic potentials [6-7] have been proposed earlier, however, there are some weaknesses in the theoretical models adopted by them. These models involve not only the various approximations but also the complex calculations. Among the number of isothermal and isobaric EOS described earlier we prefer the equation of state (EOS) due to Zheng-Hua Faug[8] because of its simple and straightforward application in high temperature physics. This model is however, applicable under the assumption that the Anderson parameter (δT) is a temperature independent parameter and remains constant even in high temperature range. It has been recently noted [8] that the results on the temperature dependent elastic moduli of bulk crystals improve if the product of thermal expansion coefficient and bulk modulus of material is assumed to be constant. In the present investigation we have employed the Zneng-Hua’s equation of state to calculate the thermoelastic properties of Ag and Au nanomaterials. The method of analysis is given in section 2 and the results are discussed in section 3.

METHOD OF ANALYSIS

Under the effect of temperature, the product of thermal expansion coefficient and bulk modulus remain constant [9], i.e.,

\[ \alpha_T B_T = \text{constant} \] (1)

where \( \alpha_T \) is thermal expansivity and \( B_T \) is bulk modulus.

On differentiating eq (1) with respect to T, at constant pressure, we get

\[ \alpha (dB_T/dT)_P + B_T (d \alpha/dT)_P = 0 \] (2)

or,

\[ (dB_T/dT)_P = - \frac{B_T (d \alpha/dT)_P}{\alpha} \] (3)
The isothermal Anderson-Gruneison parameter ($\delta_T$) is defined as:

$$
\delta_T = -B_T \frac{(dB_T/dT)_P}{\alpha} \tag{4}
$$

On substituting of $(dB_T/dT)_P$ from equation (3) in to equation (4), we get

$$
\delta_T = \frac{(d \alpha/dT)_P}{\alpha^2} \tag{5}
$$

Here $\alpha$ is defined as:

$$
\alpha = \frac{(dV/dT)_P}{V} \tag{6}
$$

In view of equation (5) and (6), $\delta_T$ can be defined as follows:

$$
\delta_T = \frac{V}{d \alpha/dV}_P / \alpha \tag{7}
$$

Following the work of Tallon [10], we may write the isothermal Anderson-Gruneison parameter in terms of volume expansion likewise.

$$
\delta_T = \delta_0 \frac{V}{V_0} \tag{8}
$$

where $\delta_0$ and $V_0$ are, respectively, the Anderson-Gruneison parameter $\delta_T$ and the volume $V$ both at zero pressure.

Now, integrating equation (4), over temperature at ambient pressure ($P=0$) and using equation (6), we get the following expression for the variation of isothermal bulk modulus $B_T$ with temperature $T$.

$$
B_T = B_0 \left[ 1 - \alpha_0 \delta_0 (T - T_0) \right] \tag{9}
$$

Substituting eq.(6) and (9) into equation (1), and integrating it over temperature at $P=0$, we get

$$
\frac{V}{V_0} = 1 - \frac{1}{\delta_0} \log \left[ 1 - \alpha_0 \delta_0 (T - T_0) \right] \tag{10}
$$

Thus the volume thermal expansion in nanomaterials at high temperature can be estimated from equation (10) provided the initial values of $\delta_0$ and $\alpha_0$ are known as ambient pressure. The expression for thermal expansivity is obtained from equation (9) and (1) as follows:

$$
\alpha_T / \alpha_0 = \left[ 1 - \alpha_0 \delta_0 (T - T_0) \right]^{-1} \tag{11}
$$

$$
\alpha_T = \alpha_0 \left[ 1 - \alpha_0 \delta_0 (T - T_0) \right]^{-1} \tag{12}
$$

In the present investigation we have thus employed equation (10) and (12) to determine the thermal expansion coefficient and thermal expansivity of Au and Ag nanomaterials at different temperatures.
RESULTS AND DISCUSSION

In present research work, we have analysed the thermo physical properties such as volume thermal expansivity ($\alpha$) and volume thermal expansion ($V/V_0$) under the effect of high temperature for Au and Ag nanomaterials. For this purpose we have used equation (10) and equation (12) which consists of only two input required parameters i.e., Anderson- Gruneison parameter ($\delta_0$) and volume thermal expansion coefficient ($\alpha_0$) at room temperature. The variation of volume thermal expansion and thermal expansivity with temperature are shown in figure 1-4 and compared with the available experimental data [15-17]. From figures 1-4, it is noted that like in bulk silver and gold metals, the volume thermal expansion also show the increasing trend with temperature. From overall discussion, it may thus be accomplished that present model theory merits the attention for the selection of the reference thermodynamic state required to generate the equation of state to explain the thermo-elastic properties of nanocrystals considered in the present study. Our methodology is useful especially for the solids which have the Debye temperature higher than the room temperature.
Figure 1: Temperature dependence of $\alpha_T \left(10^{-5}\right) K^{-1}$ in Silver metal (Ag)

Figure 2: Temperature dependence of $V/V_0$ in silver metal (Ag)

Figure 1 Temperature dependence of $\alpha_T \left(10^{-5}\right) K^{-1}$ in Silver metal (Ag)

Figure 2 Temperature dependence of $V/V_0$ in silver metal (Ag)
Figure 3 Temperature dependence of $V/V_0$ in Gold metal (Au)

Figure 4. Temperature dependence of $\alpha_T (10^{-5})$ K$^{-1}$ in Gold metal (Au)
REFERENCES

1) Friedli C. and Ashcroft N.W., phy. Rev. (1975), B12, p.5552
2) Ross M., Phys. Ru B (1980), B21, 3140
6) Born M. and Huang K. Dynamical theory of crystals, Oxford (1954), Oxford University
7) Bedi S S. Singh M and Singh J. solid state commun.(1994), 89, p.265
8) Zheng-Hua Faug, Solid state Sciences (2008), 10, p.950
Study of thermal expansion properties of 11% AlN/Al and 39% AlN/Al nanomaterials
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ABSTRACT: In the present study, a theoretical formulation is used to analyze the validity of temperature dependent equation of state in nanomaterials under the effect of high temperature. The authors have calculated the thermo-elastic properties such as the volume thermal expansion and thermal expansivity of two nanometals using the equation of state based on thermodynamic variables as a function of temperature. Two nanomaterials, viz. 11% AlN/Al and 39% AlN/Al are considered in the present study to test the validity and applicability of the equation of state. The results so obtained are compared with the available experimental data. A good agreement between the calculated values and experimental data is achieved.

Keywords: Equation of state, Volume thermal expansion, Thermal Expansivity, Nanomaterials

INTRODUCTION

Nanomaterials are expected to play an important and central role in all fields of science and technology. Therefore, the study of nanomaterials is of current interest in the field of nanoscience. During past years, several properties of nanomaterials have been studied including the mechanical, electrical, magnetic and optical. The knowledge of temperature dependent physical properties is important to understand the phase transition and structural behavior of nanomaterials. The thermal properties of nanomaterials have also attracted the attention of researchers because of their importance in nanoscience and technology [1-7]. Recently, Liu et al [8] have studied the thermal conductivity and the thermal expansion coefficient of Al composites at room and elevated temperature to explore the potential applications of nanocomposites for microelectronic engineering.

During past years some of the equations of state are used [9-13] to study of temperature dependent properties of the different class of nanomaterials, however, no satisfactory results have been achieved previously. It has been noted that the results on temperature dependent thermo physical properties of solids are calculated without considering the temperature dependence of Anderson-Gruneisen parameter (δν). So it is legitimate to present a theoretical approach in which the Anderson-Gruneisen parameter (δν) should also be the function of temperature. In the present study we have used the integral form of equation of state which does not include only the temperature dependence of Anderson-Gruneisen parameter 14 but also provide a simple and straightforward theoretical method to determine the temperature dependent properties of nanomaterials with more accuracy.

THEORETICAL FORMULATION:
Akaogi and Navrotsky [15] have made an attempt to estimate the volume of materials at an elevated temperature by incorporating the thermal effects. The materials generally expand on heating and their dimensions are usually linear related to the change in temperature. The variation of volume with temperature is written as;

\[
\frac{V}{V_0} = 1 + \alpha \delta_0 (T-T_0) + \alpha_1 \delta_0 (T-T_0)^2
\]

and \[\alpha = \left(\frac{V}{V_0}\right)^{-1} [\alpha_0 + 2\alpha_1 (T-T_0)] \]

Where \(\alpha_0\) is the thermal expansion coefficient, \(V_0\) is the initial volume and \(\alpha_1\) is the temperature derivative of \(\alpha\) at \(T=T_0\) and \(P=0\). It should be mentioned that equation (1) and (2) are consistent with each other, and based on the standard definition of \(\alpha\) given as;

\[
\alpha = \frac{1}{V^*} (dV/dT)_0
\]

Plymate and Stout [16] have presented in more detail the temperature dependence of \(\frac{V}{V_0}\) by taking into account the variation of isothermal bulk modulus (K) with the temperature and pressure. The expression obtained by Plymate and Stout is given as:
\[
\frac{V}{V_0} = [1 + (dK/dT)(T- T_0)]^{-\frac{1}{\alpha K_0}} \cdot \exp \left\{ \left[ \frac{\alpha_0}{K_0} + \frac{1}{K_0 K_0} (T- T_0)^2 \right] \right\}
\]

(4)

The expression of \( \alpha \) corresponding to Eq. (4) is obtained as follows:

\[
\alpha = \alpha_0 + \frac{1}{K_0 K_0} (dK/dT) - 1/ \left( \frac{K_0 + (dK/dT) (T- T_0)}{K_0 K_0} \right)^{1/2} + \frac{1}{K_0 K_0} (dK/dT)^2 (T- T_0).
\]

(5)

In deriving Eqs. (4) and (5), the bulk modulus (K) has been assumed to vary linearly with temperature. This implies that (dK/dT) is constant and its value is taken at room temperature. The expression for the temperature dependence of \( \alpha \) has also been obtained by Anderson et al. [17-18] which can be expressed as follows:

\[
\alpha = \alpha_0 [1 - \alpha_0 \delta_T (T-T_0)]^{1/2}
\]

(6)

Where \( \delta_T \) is the Anderson-Gruneisen parameter and is assumed to be a temperature independent parameter. It is defined as

\[
\delta_T = -1/ \alpha K_T (dK_T/dT)_p
\]

(7)

Eq. (6) has been derived by integrating the following relationship:

\[
1/ \alpha^2 (d\alpha/dT)_T = 1.
\]

(8)

In view of Eqs. (3) & (7), \( \delta_T \) can also be expressed as

\[
\delta_T = -V/K_T (dK_T/dV)_p
\]

(9)

Or

\[
dK_T/K_T = - \delta_T (dV/V)
\]

(10)

By integrating Eq. (10) at constant pressure and assuming \( \delta_T \) to be constant, we get

\[
K_T/K_T^0 = (V/V_0)^{-\delta_T}
\]

(11)

Or

\[
(K_T/K_T^0)^{-1/\delta_T} = (V/V_0)
\]

(12)

If the empirical temperature independent of \( \delta_T \) and the product of \( \alpha K_T \) [17] are assumed, then Eq. (7) can also be expressed as:

\[
dK_T/dT = - \alpha K_T \delta_T
\]

(13)

which gives on integration

\[
K_T = K_T^0 [1 - \delta_T \alpha_0 (T-T_0)]
\]

(14)

By substituting Eq. (14) in Eq. (12), we get the following expression for \( V/V_0 \)

\[
V/V_0 = [1 - \delta_T \alpha_0 (T-T_0)]^{-1/\delta_T}
\]

(15)

Anderson et al. [18] have pointed out that Eq. (6) is a high-temperature approximation. It only works above the Debye temperature \( \theta_D \). Moreover, the Eqs. (14) and (15) are derived assuming the fact that \( \delta_T \) and the product \( \alpha K_T \) to be the temperature independent and therefore the limitation of these expression are that these equations are applicable only at the temperature range higher than that of the Debye temperature. Motivated with this situation we have made an attempt to modify the expressions (Eqs. (6), (14) and (15)) assuming that \( \delta_T \).
is not the temperature independent parameter. It has been recently noted that the value of \( \delta_T \) changes with the temperature and hence cannot be considered to be temperature independent parameter. The empirical temperature dependence of \( \delta_T \) is considered in the present work as

\[
\delta_T = \delta_T^0(X)^k
\]  
(16)

Where \( \delta_T^0 \) is the value of Anderson-Gruneisen parameter at \( T = T_0 \), and \( X = T/T_0 \). \( T_0 \) is the reference temperature. \( k \) is the new dimensionless parameter which can be calculated from the slope of the graph plotted between \( \log \delta_T \) and \( \log(T/T_0) \). If we substitute the value of \( \delta_T \) from Eq. (16) in Eq. (8), we can obtain the modified expression for thermal expansion coefficient as follows:

\[
\delta_T^0(X)^k = 1/\alpha^2 \left( \frac{d\alpha_\delta}{dT}\right)_p
\]  
(17)

or

\[
\delta_T^0(T^{k}/T_0)^k = 1/\alpha^2 \left( \frac{d\alpha_\delta}{dT}\right)_p
\]  
(18)

By integrating Eq. (18)

\[
\frac{\delta_T^0}{T_0^k(k+1)} = -\frac{1}{\alpha_\delta} + C
\]  
(19)

Here C is an integration constant evaluated from initial conditions at \( T = T_0 \) and \( \alpha_\delta = \alpha_0 \).

\[
\frac{\delta_T^0}{T_0^k(k+1)} (T^{k+1} - T_0^{k+1}) = 1/\alpha_0 - 1/\alpha_\delta
\]  
(20)

The final expression for thermal expansivity is thus obtained as

\[
\alpha_\delta/\alpha_0 = \left[ 1 - \frac{\alpha_0 \delta_T^0}{T_0^k(k+1)} (T^{k+1} - T_0^{k+1}) \right]^{-1}
\]  
(21)

To obtain the expression for bulk modulus as a function of temperature, we consider the Eq. (7) assuming that the product \( \alpha K_T \) remains constant at \( P = 0 \) and \( \delta_T \) to be the temperature dependent as shown by Eq. (16). In view of the Eq. (16), the Eq. (7) can be written as follows:

\[
\delta_T^0 \frac{T^k}{T_0^k} = -1/\alpha_0 K_0 (dK_T/dT)_p
\]  
(22)

Integrating Eq. (22), i.e.,

\[
\int \frac{dK_T}{K_0} = -\alpha_0 \delta_T^0 \frac{K_0}{T_0^k(k+1)} \left( \frac{T}{T_0} \right)^k dT
\]  
(23)

\[
K_T = K_0 - \alpha_0 \delta_T^0 \frac{K_0}{T_0^k(k+1)} [T^{k+1} - T_0^{k+1}]
\]  
(24)

Or

\[
\frac{K_T}{K_0} = 1 - \alpha_0 \delta_T^0 \frac{K_0}{T_0^k(k+1)} [T^{k+1} - T_0^{k+1}]
\]  
(25)
The expression for thermal expansion \((V/V_0)\) can similarly be obtained by making use of Eq. (10) as follows:

\[
dK_1 = - K_1 \delta_T dV/V \tag{26a}
\]

Differentiating the Eq. (25) with respect to temperature, we get

\[
dK_1 = \frac{\alpha K_0 \delta_0}{T_0} T^k dT \tag{26b}
\]

Substituting Eq. (26b) into Eq. (26a), we get the following relation:

\[
dV = \frac{\alpha 0}{[1 - (\alpha 0 \delta T 0 / T 0k (k+1)) (T+k - T 0k+1)]} dT \tag{27}
\]

The integration of Eq. (27) gives us the final expression for \(V/V_0\) as follows:

\[
\frac{V}{V_0} = \frac{T}{T_0} \frac{\alpha 0}{[1 - A (T^k - T_0^k) / (k+1)]} dT \tag{28}
\]

Where \(A = \alpha 0 \delta T^0 / T_0^k (k+1)\).

**RESULT AND DISCUSSION:**

In present paper, we have reported the temperature dependence of volume thermal expansion and expansivity for different nanomaterials, viz. 11% AlN/Al and 39% AlN/Al and the compared results are shown in figures 1-4 respectively. Input data used in the present work are given in table 1 along with appropriate references. The results obtained for these nanomaterials have also seen compared with their available experimental values [8, 19]. There is a good agreement between theory and experiments for most of the nanomaterials considered in the present investigation. The values of thermal expansion coefficient \((\alpha_0/\alpha_0)\) and volume thermal expansion \((V/V_0)\) have been determined using equation (21) and equation (28) respectively. The value of dimensionless parameter \((k)\) appearing in equation (21, 28) is calculated from graph plotted between log \(\delta_T\) and log \(T/T_0\). On the basis of overall achievement in the present study, it may thus be emphasized that the our model theory is a simple and straightforward and can be applied to study the temperature dependent thermo physical properties of nanomaterials satisfactorily. The present study may be of the current interest to those researchers who are engaged in the field of nanoscience and nanotechnology.

**TABLE1. VALUES OF INPUT PARAMETER [1], [2], [3], [19]**

<table>
<thead>
<tr>
<th>Nanomaterials</th>
<th>(\delta_T^0)</th>
<th>(\alpha_0) (\times(10^5)) K(^{-1})</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11% AlN/Al</td>
<td>4</td>
<td>5.88</td>
<td>-0.67</td>
</tr>
<tr>
<td>39% AlN/Al</td>
<td>4</td>
<td>4.2</td>
<td>-0.85</td>
</tr>
</tbody>
</table>
Figure 1. Temperature dependence of $V/V_0$ in 11% AlN/Al

Figure 2. Temperature dependence of $\alpha_T (10^5) K^{-1}$ in 11% AlN/Al

Figure 3. Temperature dependence of $V/V_0$ in 39% AlN/Al

Figure 4. Temperature dependence of $\alpha_T (10^5) K^{-1}$ in 39% AlN/Al

REFERENCES:

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