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Bulk modulus of second-order pressure derivative for nanomaterials

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Abstract. The high-pressure compression behaviour of titanium dioxide (TiO_2) (Rutile phase), iron oxide (γ-Fe_2O_3), magnesium oxide (MgO) and copper oxide (CuO) nanomaterials are studied by several theoretical equation of state (EOS) model and compared with experimental results. In given theoretical EOS models, the pressure is considered as relative changes of volume and experimental data in terms of pressure. Moreover, the present EOS model specifies close conformity with the experimental data.

Keywords. Nanocrystalline materials; bulk modulus; high pressure; thermal analysis.

1. Introduction

In recent days, nanomaterials are gaining more attention due to its extraordinary properties like morphology, size, compressible properties, and their structural properties by changing the pressure, volume and temperature [1,2]. Among the nanomaterials, metal oxides play a vital role in optoelectronics and photocatalytic applications [3]. Recently Kholiya *et al* [4] studied large and high-pressure compression of magnesium oxide (MgO) using EOS. Olsen *et al* [5] reported macrocrystalline and nanocrystalline materials with synchrotron X-ray diffraction (XRD) of pressure-induced anatase TiO_2 (crystallite size 35 ± 5 nm) to 35 GPa. Similarly, Clark *et al* [6] reported XRD studies of baddeleyite structures under high-pressure (20–30 GPa) behaviours of nanocrystalline rutile TiO_2 at ambient temperature. Zhao *et al* [7] used analogously to study pressure-induced structural phase transition in nanocrystals and Kholiya and Chandra [8] studied high energy synchrotron radiation and Raman spectroscopy of copper oxide (CuO at 24 nm). Moreover, the structural transformation in cadmium selenide (CdSe) nanocrystals was studied by Tolbert and Alivisatos [9]. Zhou *et al* [10] and Tolbert and Alivisatos [9] reported the compression behaviour of Rb_3C_{60} [11]. Similar studies were studied in some other materials like nickel (Ni, 20 nm) and nanocrystalline 3C-SiC by Chen *et al* [12] and Liu *et al* [13]. As we know that the theoretical efforts are much useful for the understanding of nanomaterial behaviour under high pressure.

As a part of it, we studied a new theoretical approach for magnesium oxide (MgO), copper oxide (CuO), titanium dioxide (TiO_2) (Rutile phase) and γ-iron oxide (γ-Fe_2O_3) nanomaterials behaviour under high pressure.

2. Method of analysis

In this study, the equation of state (EOS) was used for determining the effect of pressure on nanomaterials, here P is a function of relative change in volume $\left(\frac{V}{V_0}\right)$ as follows:

$$P = a_0 + a_1\left(1 - \frac{V}{V_0}\right) + a_2\left(1 - \frac{V}{V_0}\right)^2 + a_3\left(1 - \frac{V}{V_0}\right)^3 \tag{1}$$

where a_0, a_1, a_2 and a_3 are the size-dependent parameters, which may be determined from bulk modulus and first/second-order pressure derivatives. In the above equation (1), there are no higher power terms since such terms will contain higher-order pressure derivatives of the bulk modulus. In the given study, the numerical results will be presented to reveal that equation (1) gives a satisfactory approximation. The bulk modulus, B, is given as

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T \tag{2}$$

According to the definition of bulk modulus, equation (2) is written as,

$$B = \frac{V}{V_0}\left[a_1 + 2a_2\left(1 - \frac{V}{V_0}\right) + 3a_3\left(-\frac{V}{V_0}\right)^2\right] \tag{3}$$

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Similarly, bulk modulus of the first-order pressure derivative is given as,

$$B' = \left(\frac{\partial B}{\partial P}\right)_T = \frac{-V}{B}\left(\frac{\partial B}{\partial V}\right)_T \tag{4}$$

Above equation (4) for first-order pressure derivative of bulk modulus can be written as,

$$B' = -\frac{1}{B}\left(\frac{V}{V_0}\right)\left[a_1 + 2a_2\left(1-\frac{V}{V_0}\right) + 3a_3\left(1-\frac{V}{V_0}\right)^2 - \left(\frac{V}{V_0}\right)\left\{2a_2 + 6a_3\left(1-\frac{V}{V_0}\right)\right\}\right] \tag{5}$$

The bulk modulus of second-order pressure derivative is defined as,

$$B'' = \left(\frac{\partial^2 B}{\partial P^2}\right)_T = \frac{V}{B^2}\left[\left(\frac{\partial B}{\partial V}\right) + V\left(\frac{\partial^2 B}{\partial V^2}\right)\right] \tag{6}$$

This gives the following relation:

$$B'' = \frac{V}{B^2}\left[\left(\frac{1}{V_0}\right)\left\{a_1 + 2a_2\left(1-\frac{V}{V_0}\right) + 3a_3\left(1-\frac{V}{V_0}\right)^2\right\} - \left(\frac{V}{V_0}\right)\left\{2a_2\left(\frac{1}{V_0}\right) + 6a_3\left(\frac{1}{V_0}\right)\left(1-\frac{V}{V_0}\right)\right\} - \frac{V}{V_0^2}\left\{4a_2 + 12a_3\left(1-\frac{V}{V_0}\right)\right\} + \frac{V}{V_0^3}(6a_3)\right] \tag{7}$$

Applying boundary conditions in equations (3), (5) and (7), i.e., $B = B_0$ at $V = V_0$, we get

$$a_0 = 0 \tag{8}$$

$$a_1 = B_0 \tag{9}$$

$$a_2 = B_0\left\{\frac{(B_0' + 1)}{2}\right\} \tag{10}$$

and

$$a_3 = B_0\left\{\frac{(B_0 B_0'' + 3B_0' + 2)}{6}\right\} \tag{11}$$

Thus, equation (1) takes the following form:

$$P = B_0\left(1-\frac{V}{V_0}\right) + B_0\left\{\frac{(B_0' + 1)}{2}\right\}\left(1-\frac{V}{V_0}\right)^2 + B_0\left\{\frac{(B_0 B_0'' + 3B_0' + 2)}{6}\right\}\left(1-\frac{V}{V_0}\right)^3 \tag{12}$$

Other EOS are studied for comparison purposes, the Mie–Gruneisen EOS, Tait EOS, Murnaghan EOS, Birch–Murnaghan EOS and Vinet EOS will be described as follows.

Mie–Gruneisen EOS reads as [14],

$$P = B_0\left(1-\frac{V}{V_0}\right) + \frac{B_0(B_0' + 1)}{2}\left(1-\frac{V}{V_0}\right)^2 \tag{13}$$

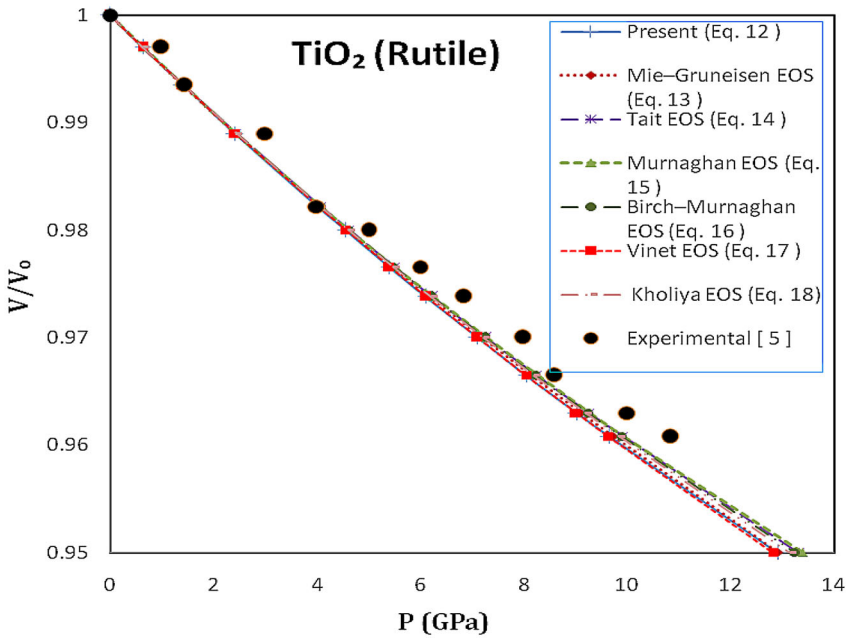

Figure 1. Several EOSs are used for calculating high-pressure behaviour $\frac{V}{V_0}$ for TiO_2 (Rutile phase).

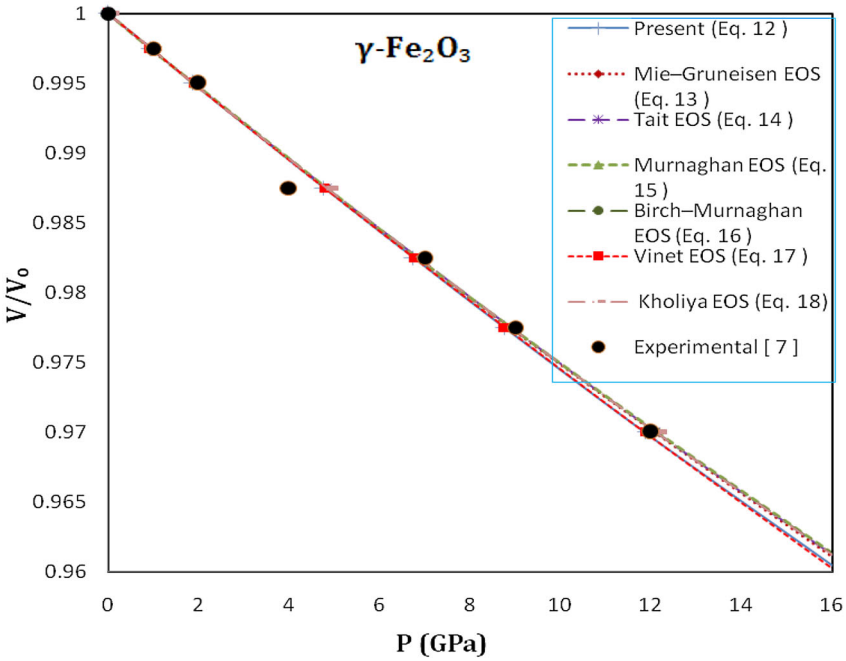

Figure 2. Several EOSs are used for calculating high-pressure behaviour $\frac{V}{V_0}$ for γ-Fe_2O_3.

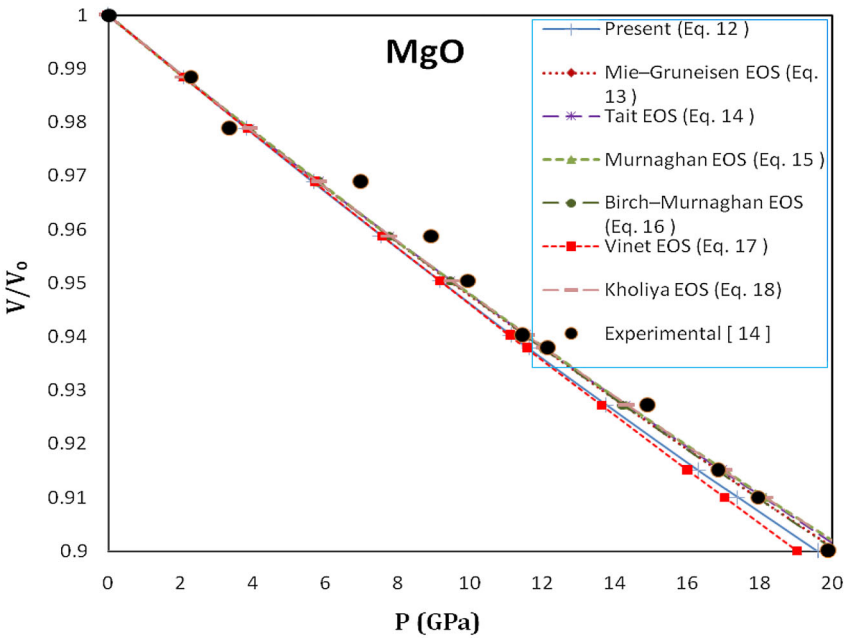

Figure 3. Several EOSs are used for calculating high-pressure behaviour $\frac{V}{V_0}$ for MgO.

Tait EOS reads as [15],

$$P = \frac{B_0}{(B_0' + 1)}\left[\exp\left\{(B_0' + 1)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right] \quad (14)$$

Murnaghan EOS reads as [16],

$$P = \frac{B_0}{B_0'}\left[\exp\left\{-B_0' \ln\frac{V}{V_0}\right\} - 1\right] \quad (15)$$

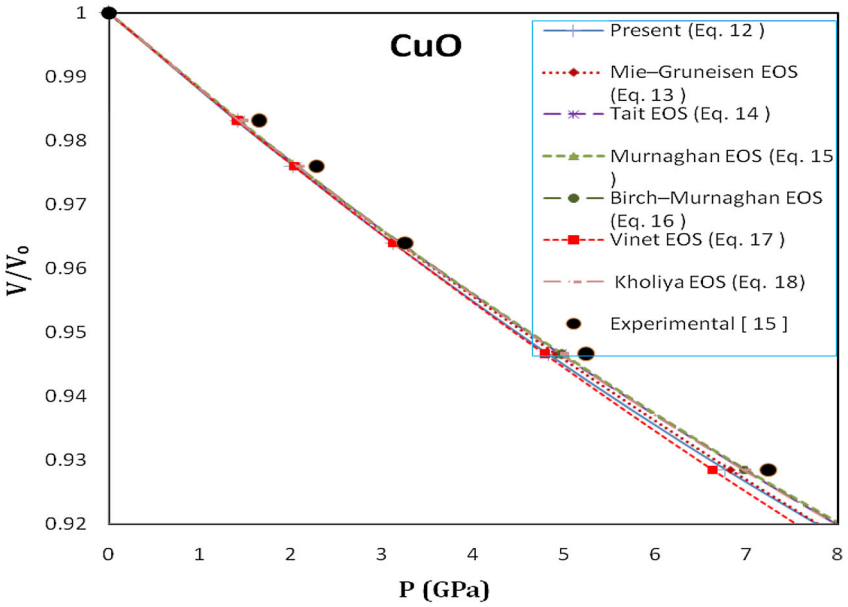

Figure 4. Several EOSs are used for calculating high-pressure behaviour $\frac{V}{V_0}$ for CuO.

Table 1. Values of B_0, B_0' and B_0'' and average percentage deviations using equation (12).

Nanomaterial	B_0 (GPa)	B_0'	B_0''	Max pressure (GPa)	Average % deviations (0 to max pressure)	References
TiO_2 (Rutile phase)	211.0	8.0	0.429	10.85	10.9519	[5]
γ-Fe_2O_3	374.0	4.0	0.191	12.00	0.0957	[7]
MgO	179.0	1.5	0.196	19.89	5.6567	[19]
CuO	81.00	4.0	0.708	7.25	8.4488	[20]

Birch–Murnaghan EOS reads as [17],

$$P = \frac{3}{2}B_0\left\{\left(\frac{V}{V_0}\right)^{7/3} - \left(\frac{V}{V_0}\right)^{5/3}\right\} \times \left[1 + \frac{3}{4}(B_0' - 4)\left\{\left(\frac{V}{V_0}\right)^{2/3} - 1\right\}\right] \quad (16)$$

Vinet EOS reads as [18],

$$P = 3B_0\left(\frac{V}{V_0}\right)^{-2/3}\left[1 - \left(\frac{V}{V_0}\right)^{1/3}\right] \times \exp\left[\frac{3(B_0' - 1)}{2}\left\{1 - \left(\frac{V}{V_0}\right)^{1/3}\right\}\right] \quad (17)$$

Kholiya and Chandra [8] EOS reads as,

$$p = \frac{B_0}{2}\left[(B_0' - 3) - 2(B_0' - 2)\left(\frac{V}{V_0}\right)^{-1} + (B_0' - 1)\left(\frac{V}{V_0}\right)^{-2}\right] \quad (18)$$

Sharma and Kumar group [2] studied experimental data for several nanomaterials and satisfactorily explains using equation (12), the high-pressure elastic behaviour of nanomaterials and gives results similar to those of the Mei–Gruneisen EOS, Tait EOS, Murnaghan EOS, Birch–Murnaghan EOS and Vinet EOS. Kholiya and Chandra [8] recently performed computational study on high-pressure compression behaviour of nanomaterials and provided great agreement with experimental data at high pressure. This is verified by average deviations.

3. Results and discussions

In this study, we suggested the effect of change by varying the pressure on several nanomaterials. From the equation (12), pressure have been calculated from the values of three input parameters such as B_0, B_0' and B_0'' are listed in table 1. Under different compressions of the nanomaterials (TiO_2 (Rutile phase), γ-Fe_2O_3, MgO and CuO), pressures and validity test were calculated using equation (12) and some other isothermal EOSs from equations (13–17). The results

calculated under these EOSs are presented in figure 1 for comparison between pressure and $\frac{V}{V_0}$. It is found that the experimental data [2] and equation (12) gives better agreement as compared with the other EOSs. The obtained results compared with experimental data are shown in figures 1–4, these values are calculated from equation (12) and closer to the experimental values for several nanomaterials studied. Sharma and Kumar [2] provide results within experimental uncertainty, as experimental measured P–V data is often pressuring calibration errors; therefore, in the present study, we considered these materials. Similarly, equation (12) is used to study the compression behaviour of TiO_2 (Rutile phase). The obtained results are reported in figure 1 along with the experimental data [5]. After observing satisfactory results, the authors extend a given application of the present approach to some other nanomaterials, such as TiO_2 (Rutile phase), γ-Fe_2O_3, MgO and CuO, corresponding results are presented in table 1. Furthermore, the obtained results are reported in figures 2–4 along with the experimental data. Noteworthy, the obtained results were a better agreement with the experimental data. Additionally, we have calculated the average percentage deviations corresponding to pressure results shown in table 1. The average deviation represents within the experimental results. This approach confirms the importance and validity of the application.

4. Conclusions

Here, we have suggested a second-order pressure derivative of bulk modulus EOS theory for isothermal compression of nanomaterials, which is useful for studying under high-pressure compression behaviour of solids and especially nanomaterials. The obtained results give good agreement compared with experimental data and other EOSs. The major advantage of this application is that the experimental data are not available, so an equation may be helpful under high-pressure compression behaviour of given nanomaterials. So, the present work is a simple and efficient method to study the effect of high-pressure compression on nanomaterials.

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