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Equation of State for the Compression of Nanocrystalline Anatase TiO_2

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ABSTRACT

The compression behavior of Nanocrystalline Anatase TiO_2 has been studied to test the validity of fundamental equation of state. To validate our results five fundamental equation of states (viz. Murnaghan EOS, Birch EOS, Usual-Tait EOS, Kholiya EOS and Vinet EOS) are used to compute the pressure upto the compression ratio of 0.9478. In the present work it is observed that the result obtained by using Murnaghan, Usual Tait and Vinet equation of state are consistently very close and in good agreement with the experimental results. The results obtained by using Murnaghan and Usual-Tait equation of sate are very close to the experimental values than Kholiya and Vinet equation of state while the Birch equation of state has no agreement with the compression behavior of Nanocrystalline Anatase TiO2. With the validity of Murnaghan and Usual-Tait equation of sate for TiO_2 the variation of isothermal bulk modulus of the sample has also studied and found its linear variation with pressure.

Keywords: Equation of state, nanocrytalline TiO_2, compression behavior of nanocrytalline Anatase TiO_2 and isothermal bulk modulus.
PACS: 64.30. +t; 62.10. +s; 62.25.+g

INTRODUCTION

Recently large number of nanocrystalline metals, semiconductors and ceramics has been studied theoretically and experimentally [1-2]. Physical properties of nanocrystalline Anatase TiO_2 has also been studied well using experimental techniques to reveal the information about local structure and interface of the material [3]. On the basis of their experimental findings many researchers have suggested that there is a significant effect of particle size on its physical properties such as melting point, hardness, stability compressibility and sintering ability etc [4-6]. During last two decades considerable experimental and theoretical investigations have been performed by different group of scientists [7-8] on the nanocrystalline metals. The compression behavior of nanocrystalline anatase TiO_2 has also been studied well using experimental techniques such as synchrotron X-ray diffraction study of pressure induced change in the selected sample able to reveal the information about local structure and interface of the material [3].

In the present work compression behavior of Nanocrystalline Anatase TiO_2 has been studied with the help of different equation of state. The obtained results suggest that Murnaghan and Usual- Tait equation of sate (UTE) is most suitable to predict the compression behavior of the sample. After getting the validity of Usual- Tait EOS, the variation of isothermal bulk modulus of nanocrystalline Nanocrystalline Anatase TiO2 has also been studied and found that it has linear variation with pressure

MATERIALS AND MEHTODS

METHODS OF ANALYSIS

To analyze the compression behavior of Nanocrystalline Anatase TiO_2 following five equation of states (EOS) are used. Most suitable EOS is used to study the variation of bulk modulus with pressure as in the case of carbon nanotubes and graphite [2].

1.1 Murnaghan Equation of State

Using the relation of bulk modulus with pressure Murnaghan derived an EOS [9-11] as follows

$$P = \frac{K}{K_0^{'}}\left[\left(\frac{V}{V_0}\right)^{-K_0^{'}} - 1\right] \quad (1)$$

1.2 Birch Equation of State

By expansion of free energy in terms of Eulerian strain based on finite strain theory, Birch derived an EOS [12-13] known as Birch EOS given as;

$$P = \frac{3K_0}{2}\left[\left(\frac{V}{V_0}\right)^{-\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{-\frac{5}{3}}\right]\left[1 - \frac{3(4-K_0^{'})}{4}\left\{\left(\frac{V}{V_0}\right)^{-\frac{2}{3}} - 1\right\}\right] \quad (2)$$

1.3 Usual-Tait Equation of State

A slight modification in Murnghan EOS performed by Usual-Tait yields a new EOS known as Usual-Tait EOS [10-11]

$$P = \frac{K_0}{(K_0^{'}+1)}\left[\exp\left\{(K_0^{'}+1)\left(1-\frac{V}{V_0}\right)\right\} - 1\right] \quad (3)$$

1.4 Kholiya Equation of State

To study the physical properties of nanocrystalline materials Kholiya suggest a EOS by expansion and approximation of UTE EOS [14]. The beauty of this equation is that it needs only one input parameter (K_0) to predict the compression behavior of nanocrystalline particles. This EOS is given as,

$$P = K_0\left[\left(1-\frac{V}{V_0}\right) + \frac{5}{2}\left(1-\frac{V}{V_0}\right)^2\right] \quad (4)$$

1.5 Vinet Equation of State

For a special interest of calculation of pressure at extreme compression ranges for solids Vinet proposed a new equation of state based on the relationship between binding energy and interatomic distances, known as Vinet EOS [15-17] given as

$$P = 3K_0 x^{-2}(1-x)\exp\{\eta(1-x)\} \quad (6)$$

where, $x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ and $\eta = \frac{3}{2}(K_0^{'} - 1)$

1.6 Isothermal bulk Modulus

The expression for the bulk modulus using Usual-Tait equation of state can be given as [2, 19]

$$\frac{K_T}{K_0} = \frac{V}{V_0}\left(1 + \frac{K_0'+1}{K_0}P\right) \quad (7)$$

RESULTS AND DISCUSSION

In case of some nanocrystalline materials it is observed that their high-pressure response is almost similar to the behavior of the bulk samples under compression, while in case of some other nanocrystalline materials it is quite different and displayed novel phase transitions. In the present work the pressure dependence of volume compression of nanocrystalline Anatase TiO_2 has been analyzed using five fundamental equations of states (viz. Murnaghan EOS, Birch EOS, Usual-Tait EOS, Kholiya EOS and Vinet EOS) upto the compression ratio of 0.9478. The bulk modulus for Anatase TiO_2 at zero pressure (K_0=243 GPa) and its derivative (K_0'= 4) has been taken from literature [3], which are used as input data required in the calculation. Computed results are tabulated in the table-1 and the variation of pressure with compression for this sample is depicted in figure-1. From the results it is obvious that the Murnaghan and Usual Tait equation of state are consistently very close and in good agreement with the experimental results than Vinet and Kholiya equation of state. The departure of the results obtained from Kholiya equation of state is only because of the approximation of higher terms in the expansion of Usual-Tait equation of state. Thus Kholiya EOS may be treated as the limiting case of Usual-Tait equation of state. Approximate validity of Vinet equation of state can be interpreted on the basis of the variation of lattice parameters at extreme conditions. Disagreement of Birch equation of state with the compression behavior of Nanocrystalline Anatase TiO_2 shows that the EOS derived on the basis of expansion of free energy in terms of Eulerian strain based on finite strain theory is not suitable for the prediction of compression behavior of Nanocrystalline materials. The validity of Murnaghan and Tait's formulation for Nanocrystalline Anatase TiO_2 can be justified on the basis of the fact that the product of bulk modulus and the coefficient of volume thermal expansion remain constant for the materials at nano as well as bulk level, similar explanation has also been suggested by Pandey et al [2] in case of carbon nanotubes. The agreement of fundamental EOS with the results obtained in case of nanocrystalline TiO_2 shows that there is no appreciable change in the compression ratio for bulk and nano $TiO_{2,}$ as it have been predicted in case of bulk modulus of bulk and anatase TiO_2 [18]. Thus it may be concluded that in the most of the cases of materials the widely used fundamental EOS are still most suitable and valid for the bulk as well as nanocrystalline materials to predict their compression with pressure.

Table-1: Variation of pressure with compression of Nanocrystalline Anatase TiO_2 using Murnaghan (P_m), Birch (P_B), Usual-Tait (P_{UT}), Kholiya(P_K) and Vinet(P_V)equation of states

V/V_0	P_{Exp} GPa	P_m Gpa	P_B Gpa	P_{UT} Gpa	P_K Gpa	P_V Gpa
0.9967	0.96	0.8086	1.2168	0.8086	0.8085	0.8086
0.9869	3.84	3.2903	5.0005	3.2899	3.2876	3.2898
0.9837	4.72	4.1277	6.2931	4.1268	4.1223	4.1267
0.9728	8.08	7.0847	10.919	7.0801	7.0591	7.0798
0.9662	9.68	8.9573	13.8957	8.9482	8.9074	8.9476
0.9597	11.84	10.8651	16.964	10.8493	10.7795	10.8483
0.9531	13.44	12.8694	20.2249	12.8438	12.733	12.8424
0.9478	16.96	14.53	22.9541	14.4939	14.3399	14.492

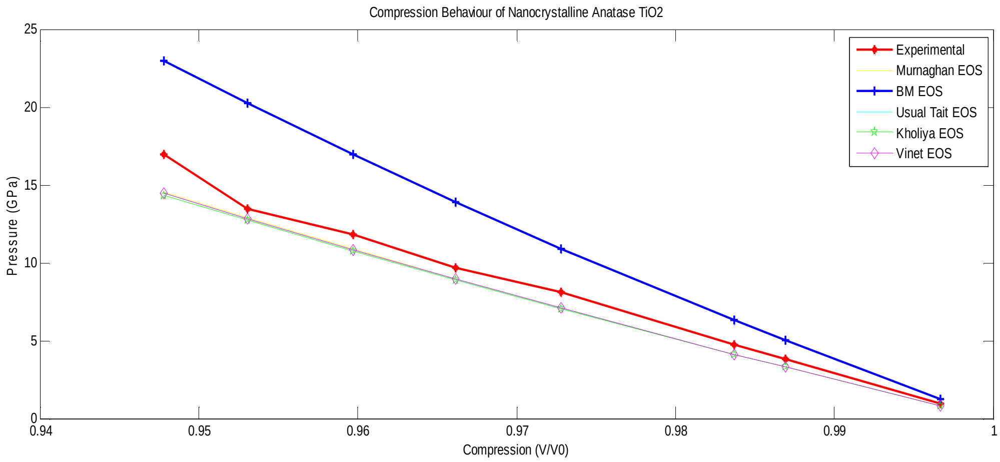

FIGURE 1. Compression Behaviour of Nanocrystalline Anatase TiO_2 using Murnaghan (P_m), Birch (P_B), Usual-Tait (P_{UT}), Kholiya(P_K) and Vinet(P_V)equation of states

With the validity of Murnaghan and its modified form of Usual- Tait equation of sate for nanocrystalline TiO_2 the variation of isothermal bulk modulus of the sample has also studied. For which the expression of isothermal bulk modulus has been derived within the frame work of UTE as mentioned in equation (7). Calculated values of isothermal bulk modulus at different pressure in given in table-1 and the graph plotted between pressure and bulk modulus is shown in figure-2. Obtained result shows the linear variation of K_T with pressure at a constant temperature. Same results are also predicted for carbon nanotubes by Chandra et al [19] and justified on the basis of the fact that isothermal bulk modulus K is linear function of pressure at any temperature for bulk as well as nanomaterials.

Table-2: Variation of isothermal bulk modulus with pressure in case of Nanocrystalline Anatase TiO_2

Compression V/V_0	P_{Exp} GPa	Isothermal Bulk Modulus(K_T) Gpa
0.9943	2.5	196.7720
0.9600	9	221.1840
0.9486	14	242.2724
0.9314	16.85	251.1520
0.8971	23.25	270.6102
0.8800	30	295.1520
0.8686	33	304.3574
0.8571	38	321.7553
0.8457	43	338.6183
0.8343	51	367.4257
0.8260	54	327.3444

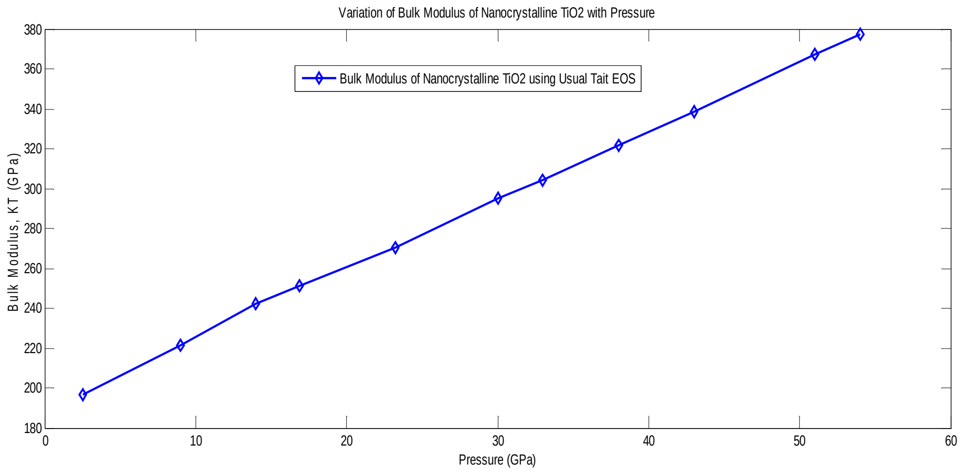

FIGURE 2. Variation of Bulk Modulus of Nanocrystalline Anatase TiO_2 with pressure

CONCLUSION

On the basis of our findings it may be concluded that in the most of the cases of materials the widely used fundamental EOS are still most suitable and valid for the bulk as well as nanocrystalline materials to predict their compression with pressure. In the present work it is found that the Murnaghan and Usual-Tait equation of state is most suitable and competent for this prediction of compression behavior of nanocrystalline TiO_2. The expression of isothermal bulk modulus has been derived within the frame work of UTE and the variation of isothermal bulk modulus of the sample has also studied, which shows the linear variation with pressure.

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