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Compression of nanomaterials under pressure

Jeewan Chandra [a,*], Kuldeep Kholiya [b]

[a] Department of Applied Sciences & Humanities, G. B. Pant Engineering College, Pauri Garhwal, Uttarakhand, India
[b] Department of Applied Science, B.T. Kumaon Institute of Technology Dwarahat, India

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Abstract

A simple equation of state (EOS) model is proposed to predict the high pressure compression behaviour of nanomaterials. The model is based on the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (B_T) (i.e., αB_T) remains constant under pressure. This model is used to study the compression behaviour of a number of nanomaterials, i.e., CuO, TiO_2 (anatase), α-Fe_2O_3, γ-Fe_2O_3, *n*-ZnO, *n*-CeO_2, *n*-PbS, carbon nanotube (individual), Ni-filled multi-wall carbon nanotube (MWCNT), Fe-filled MWCNT, AlN (hexagonal), γ-Al_2O_3 (67 nm), Ni (20 nm) and CdSe (rocksalt phase). The beauty of the model used in the present study is that it needs only one input parameter, the bulk modulus at zero pressure. The results obtained using the present formulation are in agreement with the existing experimental data. This shows the legitimacy of the present approach.

Keywords: Nanomaterial; Equation of state; Volume compression

1. Introduction

Studies of compressibility and pressure-induced phase transitions for nanocrystalline materials can improve our understanding of the stability of materials at the nanometre scale. Most of the high pressure research on nanocrystalline materials has been on semiconductors, although some work on insulators and metals has been reported recently. While applying high pressure on a nanomaterial, many effects may occur, such as the (i) transformation of the nano-constitutive elements, (ii) transformation of the interaction between nano-objects and (iii) modification of interactions between the nano-objects and the pressure transmitting medium. Due to such applications, the effects of pressure on nanomaterials have attracted the attention of researchers. The EOS of nanocrystalline CuO (24 nm) has been studied by Wang et al. [1] using high energy Synchrotron radiation and Raman spectroscopic techniques. Swamy et al. [2] presented a synchrotron XRD study of pressure-induced changes in nanocrystalline anatase TiO_2 (with a crystallite size of 30–40 nm) at 35 GPa and found that the bulk modulus value obtained for the nanocrystalline anatase is approximately 35% larger than that of the macrocrystalline counterpart. Olsen et al. [3] studied the high pressure behaviour of nanocrystalline rutile TiO_2 at ambient temperature by using X-ray diffraction and found it to be transforming to the monoclinic baddeleyite structure between 20 and 30 GPa. Clark et al. [4] observed a pressure-induced γ-Fe_2O_3 (maghemite) to α-Fe_2O_3 (hematite) structural phase transition in

* Corresponding author. Tel.: +91 9634183287.
E-mail address: j.jeewan@gmail.com (J. Chandra).
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nanocrystals, which was analogous to the findings of Zhao et al. [5]. Using energy dispersive synchrotron XRD produced wiggler radiation, Quadri et al. [6] investigated the effect of size on compressibility and phase transition in PbS nanocrystals.

The high pressure compression behaviour of carbon nanotubes was studied experimentally by Tang et al. [7]. With the help of synchrotron-based angle dispersive X-ray diffraction, the high pressure behaviour of Ni and Fe filled multiwalled carbon nanotubes was investigated by Poswal et al. [8] up to pressures of 27 and 19 GPa, respectively. These nanotubes do not show any structural transformation, even at the highest pressures studied.

The study of AlN nanocrystals under hydrostatic conditions was performed by Wang et al. [9] up to 36.9 GPa using an energy dispersive synchrotron-radiation technique in a diamond anvil cell (DAC). Shen et al. [10] have investigated the structural transition of AlN nanowires by in situ angle dispersive high-pressure X-ray diffraction using a synchrotron radiation source and found a pressure-induced wurtzite to rocksalt phase transition at 45.4 GPa.

At room temperature, Mao et al. [11] compressed nanocrystalline γ-Al_2O_3(67 nm) quasi-hydrostatically at pressures of up to 60 GPa in a Mao-Bell type DAC, and a X-ray diffraction study was carried out by Chen et al. [12]. The bulk modulus was found to be different during the two processes. To understand the size effect on the bulk modulus and to look for possible new high pressure phases, nanocrystalline Ni (20 nm) was studied under high pressure by Chen et al. [13]. The structural transformation in CdSe nanocrystals was studied [14] using high pressure X-ray diffraction and high pressure optical absorption at room temperature. The nanocrystal undergoes a wurtzite to rocksalt transition analogous to that observed in bulk CdSe. The nanocrystal phase transition pressures vary from 3.6 to 4.9 GPa for crystallite ranging from 21 to 10 Å in radius, respectively, in comparison to the value of 2 GPa for bulk CdSe.

In the present paper, we present a simple theoretical model to study the compression behaviour of nanosystems through several experimental studies to understand the high pressure behaviour of nanomaterials, but the theoretical efforts are deficient. In addition to the available models, the study of the high pressure compression behaviour requires two input parameters, the bulk modulus and the first order pressure derivative of the bulk modulus, and among these experimental values, the first order pressure derivative of the bulk modulus is not always available in the literature, especially for nanomaterials. Thus, it is justifiable and may be useful to present a simple theoretical method, which requires only a zero pressure value of the bulk modulus at zero pressure, to study the high pressure compression behaviour of nanomaterials. The method of analysis is given in Section 2. The results and discussion are given in Section 3 and the conclusion in Section 4.

2. Theory of analysis

Assuming the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (B_T) is constant under the effect of pressure [15], i.e.,

$$\alpha B_T = \text{constant}. \tag{1}$$

The differentiation of Eq. (1) with respect to the volume at a constant temperature gives

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

The Anderson–Grüneisen parameter is defined as

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

where δ_T is Anderson–Grüneisen parameter at constant temperature.

From Eqs. (2) and (3) we obtain

$$\delta_T = \frac{V}{\alpha}\left(\frac{d\alpha}{dV}\right)_T = -\frac{V}{B}\left(\frac{dB}{dV}\right)_T. \tag{4}$$

Assuming δ_T to be independent of V,

$$\delta_T = \left(\frac{dB}{dP}\right)_T = B_0' \tag{5}$$

and the Anderson–Grüneisen parameter δ_T and $\eta = V/V_0$ (where V_0 is the initial volume) are related by the following relation [16]

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

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

$$\frac{dB}{B} = \left[-\frac{A}{V_0} + \frac{1}{V}\right] dV. \tag{7}$$

Integrating the above equation, we obtain

$$\frac{B}{B_0} = \frac{V}{V_0}\exp A\left[1 - \frac{V}{V_0}\right], \tag{8}$$

where

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