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Short Communication

Pressure induced Phase Transition in Zinc sulfide (10 nm-ZnS) Nano-crystal

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Abstract

In the present paper, the authors have employed the usual Tait's equation of state to study the structural and electronic properties of ZnS-nanocrystal .The Tait's equation of state has been used to analyze the unit cell compression under high pressure. Phase transition of Wurtzite of 10 nm ZnS to rock salt occurs at 16.5 GPa, which is higher than that of corresponding bulk materials. Moreover, the resulting pressure is found higher than that of corresponding bulk material, which indicates that the ZnS nanomaterial has higher hardness than its bulk material. The phase transition pressure (16.5 GPa) obtained in the present study presents a better agreement with the experimental data as compared to the previous studies which show that the transition to rock salt phase occurs at 12.4 GPa [3].

Keywords: transition pressure, volume compression, Bulk modulus.

Introduction

The nanomaterials exhibit many promising characteristics on the aspects of mechanical and electronic properties as compared with conventional bulk materials[1,2]. The structural transition under pressure of nanomaterial has been of great interest and has been widely investigated in the high pressure research field. The II –VI semiconductor ZnS is an illuminant film component. The phase transition under high pressure of the bulk ZnS has been studied systematically in recent years[3, 4]. According to the corresponding results; ZnS possesses two structures of Wurtzite (W) and Zinc blende (Z) at ambient condition. They can undergo to rock salt (R) structure under high pressure and furthermore, into a distortion of rock salt structure. Till date a little research work on phase transition of nanocrystalline ZnS has been performed, especially under high pressure.

In recent years, the electronic structures of the zinc blende (W) compounds have been studied by only few research groups. Khenata et al[5] and Gangadharan et al[6] have calculated the electronic properties of ZnS by using the full potential linear augmented plane wave method plus local orbital method. Chen and Hu[7] calculated aggregate velocities of ZnS versus pressure for the zinc blende and wurtzite structures ZnS. Nazzal et al[8] calculated the energy volume curves of all the phases of ZnS using non linear exchange correlation core corrections (NLCC). The phase transition and the electronic structure of the zinc blende nanocrystal have thus attracted much interest during past years.

The aim of the present work is to give a complentary investigation on the phase transition properties and mechanical stability of nano-structured zinc blende crystal to fully understand the high pressure behavior of nano-particles and nanostructured crystals. In section II of the present paper, the theoretical formulation is presented. Section III contains the results and discussion on the applicability of the equation of state (EOS). Finally; the conclusions are summarized in section IV.

Method of Analysis

The usual Tait's equation of state has been found most useful nonlinear relation to explain the thermo-elastic properties of different class of solids and liquids[9]. This equation of state has been now applied to analyze the compression of unit cell volume and rigidity of ZnS nanomaterial under pressure in the present study. The usual Tait's equation of state is obtained by assuming the fact that the product of thermal expansion coefficient (α_T) and bulk modulus (B_T) is constant under the effect of pressure[10], i.e.

$$\alpha_T B_T = \text{constant} \quad (1)$$

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

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

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 T.
From equation (2) and (3), we get

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

Assuming δ_T to be independent of V,

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

Anderson-Gruneisen parameter δ_T and $\eta = V/V_o$ (where V_o is the initial volume) are related by the following relation [11],

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

Where A is a constant for a given nanomaterial. In view of equation (6), equation (4) can be written as

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

Integrating eq. (7), we get

$$\frac{B}{B_o} = \frac{V}{V_o} \exp A\left[1 - \frac{V}{V_o}\right] \quad (8)$$

Where B is equal to $B = -V\left(\frac{dP}{dV}\right)_T$ (9)

Using equation (8), equation (9) can be represented as

$$\frac{B}{B_o} \exp A\left[1 - \frac{V}{V_o}\right] dV = -dP \quad (10)$$

The integration of equation (10) gives

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

Here B_o is the bulk modulus at zero pressure and the constant A is determined from the initial conditions, i.e. at $V = V_o$,

$A = \delta_T^o + 1$

On substitution of constant A in equation (11) and taking natural log, we get the following final form of usual Tait's equation of state,

$$V(P,T_o)/V(o,T_o) = 1 - \frac{1}{B_o' + 1}\log\left[1 + \left\{\frac{B_o' + 1}{B_o}\right\}P\right] \quad (12)$$

Where $V(P, T_o)$ is the volume of the material at pressure required to compress it, keeping the temperature constant. V_o is the initial volume at room temperature T_o. B_o and B_o' are the isothermal bulk modulus and its first pressure derivative at $T = T_o$.

The above equation (12) provides a simple and straight forward approach to predict the relative compression in solids at high pressures. To test the validity of equation of state in nanomaterials, (as in bulk materials), we have therefore, employed Tait's equation of state also to determine the hardness (Bulk modulus) behavior of zinc- sulfide nanomaterial as an example. Within the framework of usual Tait's equation of state, the expression for the isothermal bulk modulus can be achieved as follows[11,12].

$$\frac{B_T}{B_o} = \frac{V}{V_o}\left[1 + \left\{\frac{B_o' + 1}{B_o}\right\}P\right] \quad (13)$$

The calculated values of isothermal bulk modulus (B_T) with different pressures are shown in figure 2.

Results and Discussion

It is evident from the figure 1 that the wurtzite structure of ZnS nanocrystal reduces to its rock salt structure at transition pressure (P_t) =16.5 GPa if the bulk modulus value K_o= 67.8 GPa is considered. The calculated value of transition pressure (P_t) is found very close to the available experimental data 16.2 GPa[13]. From figure 1 it may also be observed that there is a sharp reduction in volume at the transition pressure (P_t) during the transformation of zinc blende wurtzite structure to rock salt structure and the volumetric change of the wurtzite phase with pressure becomes discontinuous after the phase transition pressure. This is a typical first rule phase transition. It is pointed out that the compression is about 16.8% at 16.5 GPa for 10 nm ZnS nanocrystal. Nanomaterials have considerable surface atoms and thus store much higher surface energy than bulk materials. Thus, it is understandable that the ZnS nano-crystal need a high pressure than bulk ZnS to overcome the extra surface energy and further, the transition pressure may go up when the Nano- crystal size is reduced.

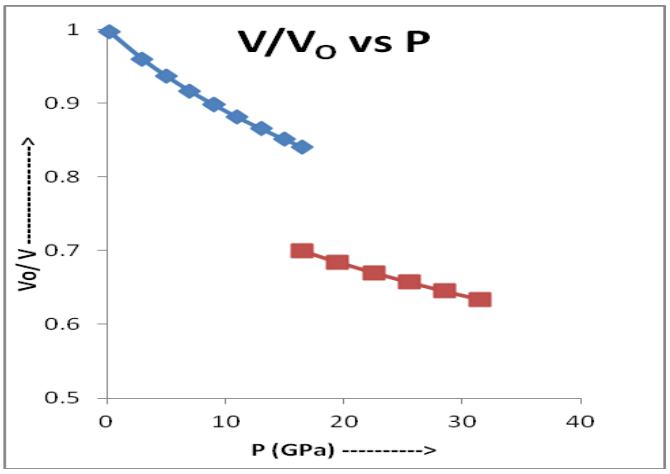

Figure-1
V/V_O versus Pressure P (GPa) for 10 nm ZnS nanocrystal

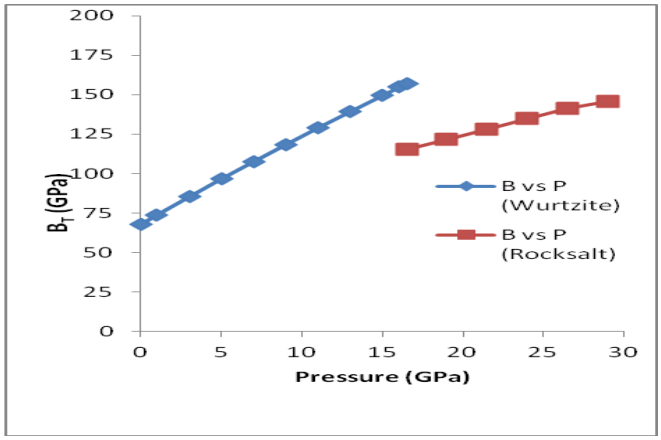

Figure-2
Isothermal Bulk modulus (B_T) as a function of pressure for 10 nm ZnS nanocrystal

From figure 2, it is clear that the bulk modulus of ZnS nanomaterial increases with pressure in both phases and shows a drastic change in unit cell volume at the transition pressure 16.5 GPa.

Conclusion

On the basis of the whole discussion, it may thus be concluded that the Tait's equation of state is capable of explaining the structural phase transition and structural stability of zinc blende structured nanocrystal under high pressure successfully. The present investigations on structural phase transition and elastic properties of nanomaterials, under high mechanical pressure will provide the significant uses of nanomaterials in various optical and electronic devices. The prediction of shear modulus and bulk modulus make the material usable in mechanical engineering to determine their tensile strength under high pressure. More-over, much of modern technology, such as the transistors, and integrated circuits, which are at the heart of modern computers and electronics, is the result of researches performed in the field of Nano-science and nanotechnology. Therefore, the study of electronic and thermophysical properties of nanostructured crystals may be very useful in all types of engineering which involve the application of physics in designing and fabricating the devices. The theoretical results reported in the present paper may also stimulate the further experimental investigations yet to be explored in future.

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