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THERMODYNAMIC PROPERTIES OF ZnO WITH IN MIE-GRÜNEISEN HYPOTHESIS

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Zinc oxide (mineral name: Zincite) is an attractive wide band gap semiconductor due to its large number of industrial applications such as in the production of solar cells, liquid-crystal displays, electrochromic devices, LED, as well as adhesive taps, automobile tires, ceramics, glass, varistors, etc. It is due to versatile nature of ZnO, in we have studied its thermal properties at high temperatures. Theoretically, complete ab initio investigations at elevated temperatures are restricted due largely to computational complexity of many-body nature. We have therefore used an consistent iterative scheme to include thermal effect by combining the universal equation of state (UEOS) to the Mie-Gruneisen hypothesis. It is demonstrated that from the knowledge of cohesive properties at ambient condition various thermodynamic properties can be predicted at finite temperatures and pressures. For example, presently calculated relative volume-thermal expansions, static EOS are in good accordance with experimental results.

Keywords: EOS, THERMAL EXPANSION, THERMAL PRESSURE, ZnO.

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1. INTRODUCTION

Zinc oxide (ZnO) has wurtzite phase at ambient condition. The ambient properties of such oxide is known experimentally and also through first principles calculation [1]. At elevated temperatures, characterization of materials pose difficulty at the complete *ab initio* level [2-4]. Theoretically situation becomes more complicated also due to the coexistence of partial covalent and metallic banding nature in these materials. It is due to this reason one may calculate various physical quantities at an extreme environment rather empirically. In this regard, we have combined universal equation of state (UEOS) formalism due to Vinet et al. [5] to Mie-Gruneisen hypothesis to include the temperature effect in a consistent manner [4, 6].

2. FORMULATION

Total pressure at temperature T is given by,

$$p(V, T) = p_0(x) + \left(\frac{\gamma_{th}(V)}{V} \right) 3k_B T, \quad (1)$$

where $p_0(x)$ is the cold pressure and is given by Vinet's UEOS scheme [5]. Thermal energy (E_{th}) corresponding to lattice vibrations is assumed to be linear in temperature and is taken as $-3 k_B T$. Thus, the second term in

Eq. (1) represents the thermal pressure in terms of thermodynamic Gruneisen parameter with,

$$\gamma_{th}(V) = \left[\gamma_0 + \frac{2}{3} \left(1 - \frac{V}{V_0} \right)^\delta \right], \tag{2}$$

where γ_0 is the Gruneisen parameter at ambient condition and is calculated from the Poisson ratio (σ) as suggested in Ref. [7], and $\delta = 2$ [4, 6].

To include thermal effect, we assume: (i) Pressure derivative of bulk modulus does not change with temperature and pressure and (ii) Temperature dependence of bulk modulus is controlled by the Gruneisen parameter.

$$B_T^{p=0} = B_0 + \left. \frac{\partial B}{\partial T} \right|_{p=0} T \quad \text{with} \quad \left. \frac{\partial B}{\partial T} \right|_{p=0} = \frac{-3 k_B \gamma_{th}(V) (\gamma_{th}(V) + 1)}{V} \tag{3}$$

3. RESULTS AND DISCUSSION

In the present calculation, experimental quantities as quoted in Ref. [1] are used to calculate the equations of state. At each temperature corresponding value of isothermal bulk modulus is evaluated using equation (3). And following zero-pressure condition, we obtained relative volume-thermal expansion. As shown in Fig. 1 intersection of $p - V$ curve on volume axis suggests volume-thermal expansion, and is the indication of proper treatment of anharmonic effect.

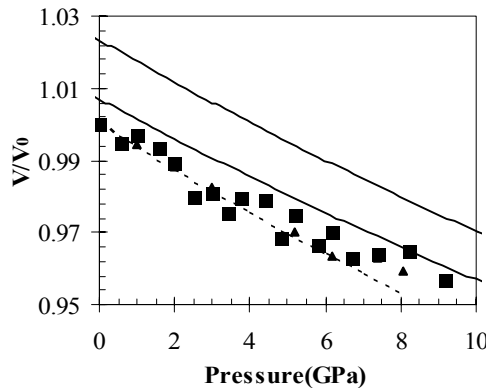


Fig. 1 – Isothermal EOS (solid line) at $T = 300, 1000 \text{ K}$ (from down to up) are compared with first principles (broken line) as well as experimental results (triangle and square) due to Decremps et al. [1] at 300 K

The thermal pressure as a function of temperature is shown in Fig. 2. Linearity confirms the assertion that the cold pressure governs the equations of state at finite temperatures and shift to the higher pressure side. The most stringent test of any high temperature methods is to account for thermal expansion. Relative volume (V/V_0) versus temperature is depicted in Fig. 3. At low temperatures discrepancy is observed, and is

typical of any finite temperature theories, where correlation effects are ignored. Nevertheless, above Debye temperature ($\theta_D = 399.5$ K) experimental trend, i.e., linear increase in V/V_0 is reproduced, which confirms the applicability of the present scheme.

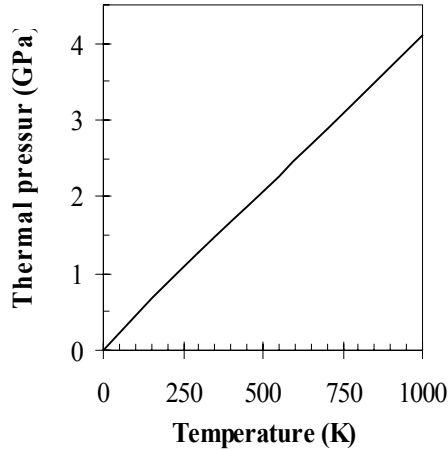


Fig. 2 – Thermal pressure as a function of temperature

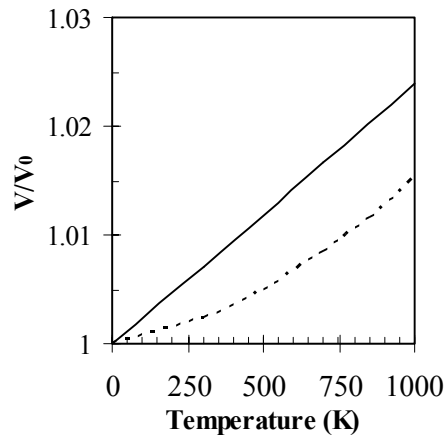


Fig. 3 – Results for relative volume-thermal expansion (solid line) is compared with experimental results (broken line) [8]

4. CONCLUSION

In summary, we have calculated isothermal equations of state, relative volume-thermal expansion and thermal pressure at high temperature. Good accordance with the available first principles and experimental data is therefore the justification of the present scheme. From the larger expansion ($\sim 15\%$ to 20%) even at $T = 1000$ K, we conclude that the ZnO is a soft

material. We also conclude that since the proposed scheme is unbiased to the bonding nature of a material, and it can be extended to verities of the substances.

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