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Analysis Of Thermophysical Properties And Melting Curves Of Rutile (Tio_2) At High Pressures

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Abstract : We have investigated pressure dependence of some thermophysical properties of TiO_2 (rutile) by using equations of state (EOS). We have used two different equations of state, viz. Birch-Murnaghan third order EOS and Vinet-Rydberg EOS. We have calculated pressure, bulk modulus and its pressure derivatives at different values of volume compression. These results have been used in the generalized free volume formula to determine Grüneisen parameter at different values of volume compression. We have used the model given by Burakovsky and Preston (B-P Model) to calculate volume dependence of the Grüneisen parameter. This model is based on the assumption that the Grüneisen parameter is an analytic function of $(V/V_0)^{1/3}$, and designed to accurately represent the theoretically determined low pressure behavior of Grüneisen parameter. Using the Burakovsky-Preston model in the Lindemann law we have calculated melting curves for rutile (TiO_2) at high pressure. The calculations have been performed by assuming that TiO_2 remains in the rutile structure for the entire range of volume compression.

Keywords : Bulk modulus, TiO_2 (rutile), Grüneisen parameter, melting temperature, equation of state.

1. Introduction

Rutile (TiO_2) is a material with many useful applications in various fields, including photovoltaic devices, integrated waveguides, humidity sensors, solar cells, catalysts and photocatalytic applications [1]. Under extreme compressions, TiO_2 exhibits unique behaviour and properties that make it suitable for specific applications. When TiO_2 is subjected to extreme compression, it undergoes structural changes, which affect its properties such as bulk modulus, first pressure derivative of bulk modulus, and volume dependence of Grüneisen parameter. These properties are crucial in understanding the thermophysical behaviour of TiO_2 under high pressure [2].

At high pressure, the phase diagrams of TiO_2 exhibits a series of structural phase transformations which are of particular interest in geophysics and geochemistry of the Earth mantle [3]. Understanding its properties and behaviour under high pressure can lead to the development of new materials with specific properties and applications [4-7]. Thermophysical properties such as melting temperature. Debye temperature, viscosity, thermal conductivity and diffusivity of rocks and minerals are important for strengthening our knowledge about the interior of the Earth. Temperature and pressure dependence of thermophysical properties of TiO_2 have been investigated by several researchers [8-13]. In some of the previous studies [9] the pressure dependences of the six elastic constants of single-crystalline rutile (TiO_2) have been measured using the ultrasonic techniques for a pressure range of 0-2 GPa. First-principle methods have been used to determine the pressure dependence of elastic and thermal properties of cubic TiO_2 [12].

The EOS have paramount important in geophysics and material science. There are two popular equations, the Birch-Murnaghan EOS [14] and the Vinet EOS [15], which are given below -

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

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

where K_0 and K_0' are the values of bulk modulus and its pressure derivative, respectively, both at zero pressure and $x = (V/V_0)^{1/3}$ and $\eta = 3(K_0' - 1)/2$. The Birch-Murnaghan EOS, Eq. (1), was derived using the Eulerian strain theory [14]; the Vinet EOS, Eq. (2), is based on the Rydberg interatomic potential function [16]. We have used Eqs. (1) and (2) to find the pressures at different compressions (V/V_0).

In the present study, we have considered TiO_2 for theoretical prediction of its thermophysical properties and melting curves. We have calculated bulk modulus and its pressure derivative by using the Birch-Murnaghan third order EOS and the Vinet-Rydberg EOS. The obtained results have been used in the generalized free volume formula to determine Grüneisen parameter at different values of compressions. We have used the model given by Burakovsky and Preston (B-P model) to calculate volume dependence of the Grüneisen parameter. This model has been used in the Lindemann law to calculate melting curves for rutile at high pressures.

2. Method of Analysis

According to the Birch-Murnaghan third order EOS, the bulk modulus K and its pressure derivative K' are given as follows [14]

$$K = \frac{1}{2}K_0\left(7x^{-7} - 5x^{-5}\right) + \frac{3}{8}K_0(K_0' - 4)\left(9x^{-9} - 14x^{-7} + 5x^{-5}\right) \quad (3)$$

$$K' = \frac{K_0}{8K}\left[(K_0' - 4)\left(81x^{-9} - 98x^{-7} + 25x^{-5}\right) + \frac{4}{3}\left(49x^{-7} - 25x^{-5}\right)\right] \quad (4)$$

and according to the Vinet-Rydberg the EOS, the bulk modulus K and its pressure derivative K' are given as follows [15]

$$K = K_0 x^{-2}\left[1 + \left\{\frac{3}{2}(K_0' - 1)x + 1\right\}(1 - x)\right]\exp\left[\frac{3}{2}(K_0' - 1)(1 - x)\right] \quad (5)$$

$$K' = \frac{1}{3}\left[\frac{x(1 - \eta) + 2\eta x^2}{1 + (\eta x + 1)(1 - x)} + \eta x + 2\right] \quad (6)$$

TABLE 1

Input Parameters for rutile (TiO_2) [17]

K_0 (GPa)	K'_0	γ_0	T_m (K)
213.5	6.3	1.62	2116

The Debye-Grüneisen definition of γ, can be written as follows [18]

$$\gamma = -\frac{d\ln\theta_D}{d\ln V} \quad (7)$$

The Lindemann melting criterion, which asserts that the root-mean square atomic displacement of atoms from their equilibrium positions in a solid is a fixed fraction of the interatomic distance at the melting point, can be rewritten in the form of Gilvarry law, which relates the melting temperature T_m, to the Grüneisen parameter [19]

$$\frac{d\ln T_m}{d\ln V} = -2\left[\gamma - \frac{1}{3}\right] \quad (8)$$

There have been various attempts to develop a model for γ [20-23]. They are summarised by the single generalized formula [16,19]

$$\gamma = \frac{\left(\frac{K'}{2}\right) - \left(\frac{1}{6}\right) - \left(\frac{t}{3}\right)\left(1 - \frac{P}{3K}\right)}{1 - 2t\left(\frac{P}{3K}\right)} \quad (9)$$

Now, at P = 0 (i.e. atmospheric pressure) $\gamma = \gamma_0$, $K = K_0$ and $K' = K_0'$ then

$$\gamma_0 = \frac{K'_0}{2} - \frac{1}{6} - \frac{t}{3}. \tag{10}$$

We have calculated t = 4.09 for TiO_2 at zero pressure, taking $K'_0 = 6.3$ and $\gamma_0 = 1.62$.

An analytic model for the volume dependence of Grüneisen parameter γ has been developed by Burakovsky and Preston [24] which is written as follows

$$\gamma = \gamma_\infty + a_1\left(\frac{V}{V_0}\right)^{1/3} + a_2\left(\frac{V}{V_0}\right)^n \tag{11}$$

where

a_1, a_2 and n are constant for a given material. Burakovsky and Preston have taken $\gamma_\infty = 1/2$ in the limit of extreme condition (V→0). This value of γ_∞ has been supported by previous workers [25, 26]. Eq. (11) can then be written as follows

$$\gamma = \frac{1}{2} + a_1\left(\frac{V}{V_0}\right)^{1/3} + a_2\left(\frac{V}{V_0}\right)^n \tag{12}$$

Now, at $V = V_0$, P = 0, and $\gamma = \gamma_0$

We get

$$a_1 + a_2 = \gamma_0 - \frac{1}{2} \tag{13}$$

Assuming that $a_1 = a_2 = a$ [27-29] Eq. (13) gives

$$a = \frac{1}{2}\left(\gamma_0 - \frac{1}{2}\right) \tag{14}$$

by using Eq. (14), Eq. (12) can be written as follows

$$\gamma = \frac{1}{2} + \frac{1}{2}\left(\gamma_0 - \frac{1}{2}\right)\left(\frac{V}{V_0}\right)^{1/3} + \frac{1}{2}\left(\gamma_0 - \frac{1}{2}\right)\left(\frac{V}{V_0}\right)^n \tag{15}$$

Using Eq. (15), in the Lindemann law, Eq. (8) can be integrated to yield the melting temperatures

$$T_m = T_{m0}\left(\frac{V}{V_0}\right)^{-1/3} \exp\left[6a\left\{1 - \left(\frac{V}{V_0}\right)^{1/3}\right\} + \frac{2a}{m}\left\{1 - \left(\frac{V}{V_0}\right)^n\right\}\right] \tag{16}$$

3. Results and Discussion

We have used Eqs. (1) and (2) to find out the pressure (P) at different compressions (V/V_0) for TiO_2 using the input given in Table 1. Figure 1 represents the plots between pressure (P) and V/V_0 based on the Birch-Murnaghan EOS and the Vinet-Rydberg EOS down to a compression of 0.60. We have used Eqs. (3) and (5) to find values of bulk modulus (K) at high pressure (P). Figure 2 represents the plot between K and P. The bulk modulus is increases very rapidly with the increase in pressure for both the EOSs. We have used Eqs. (4) and (6) to calculate pressure derivative of bulk modulus (K') with the increasing pressure. The results are plotted in figure 3. Values of P, K and K' determine from both the EOSs are comparable with each other.

The volume dependence of Grüneisen parameter γ has been computed using the generalized free volume formula Eq. (9), the results based on the two EOSs. We have fitted the B-P Model with the results determined from the generalized free volume formula. It is found that the results based on the Birch-Murnaghan EOS give n = 1, and those based on the Vinet-Rydberg EOS fit Eq. (15) with n = 3.2 (Figure 4).

Values of melting temperatures for TiO_2 as function of V/V_0 are computed from Eq. (16). The results for T_m are then transformed as function of pressure with the help of EOSs. The melting curves given in figure 5 reveal that T_m increases with the increase in pressure in a nonlinear manner such that the melting slope decreases with the increasing pressure [30].

$$\left(\frac{dT_m}{dP}\right)_\infty = 0 \tag{17}$$

Equation (17) reveals that melting slope becomes zero in the limit of infinite pressure.

It should be mentioned that at the maximum value of melting slope is found at zero pressure. We can write [30]

$$\left(\frac{dT_m}{dP}\right)_0 = \frac{2T_{m0}\left(\gamma_0 - \frac{1}{3}\right)}{K_0} \tag{18}$$

where T_{m0}, γ_0 and K_0 are the zero pressure value. Value of the melting slope at zero pressure for rutile determined from Eq. (18) turns out to be 25.6 K $(GPa)^{-1}$. In the limit of infinite pressure, $T_{m\infty}$ varies as $(V/V_0)^{1/3}$ as is evident from Eq. (16) in the limit of extreme compression V→ 0. This would imply

$$\left(\frac{d\ln T_m}{d\ln V}\right)_\infty = \left(-\frac{1}{3}\right) \tag{19}$$

Eq. (8) at infinite pressure can be written as follows

$$\left(\frac{d\ln T_m}{d\ln V}\right)_\infty = -2\left[\gamma_\infty - \frac{1}{3}\right] \tag{20}$$

On comparing Eq. (19) and Eq. (20), we get $\gamma_\infty = \frac{1}{2}$. This result supports the B-P model for volume dependence of the Grüneisen parameter

4. Conclusion

Values of the Grüneisen parameter γ computed from the generalized from formula using the results based on the Birch-Murnaghan EOS and the Vinet-Rydberg EOS are found to be consistent with the Burakovsky Preston model for the volume dependence of Grüneisen parameter for the entire range of compressions. The Burakovsky and Preston model has been used in the Lindemann law to determine melting curves for rutile up to very high pressures corresponding to a volume compression V/V_0 = 0.60. It has been found that T_m increases with increasing pressure in a nonlinear manner such that the melting slope decreases with increase in pressure.

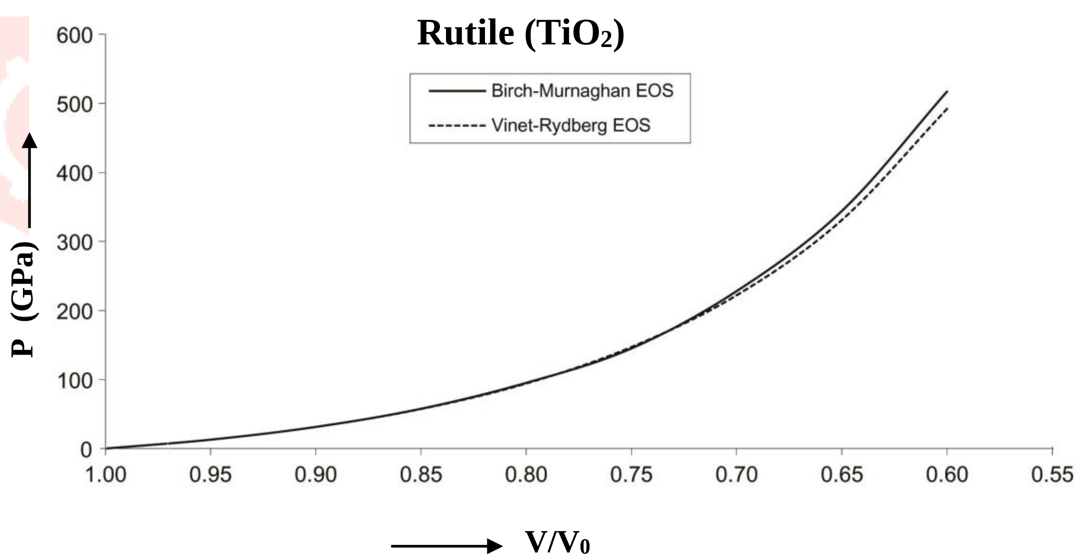

Figure 1 : Plots of pressure (P) versus volume compression (V/V_0) for Rutile (TiO_2)

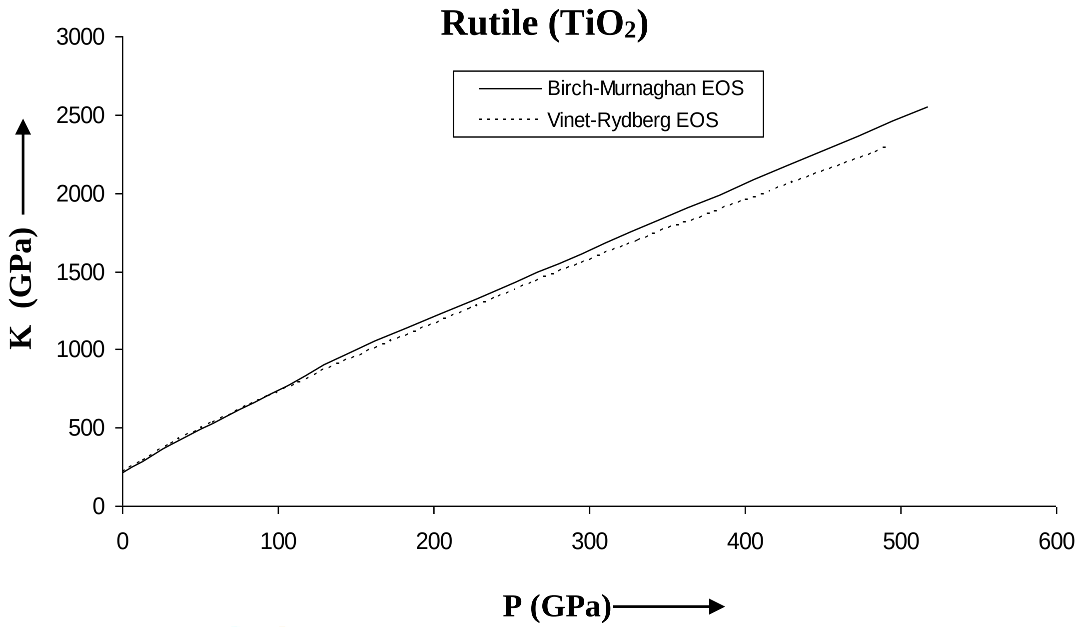

Figure 2 : Plots of bulk modulus (K) versus pressure (P) for Rutile (TiO_2)

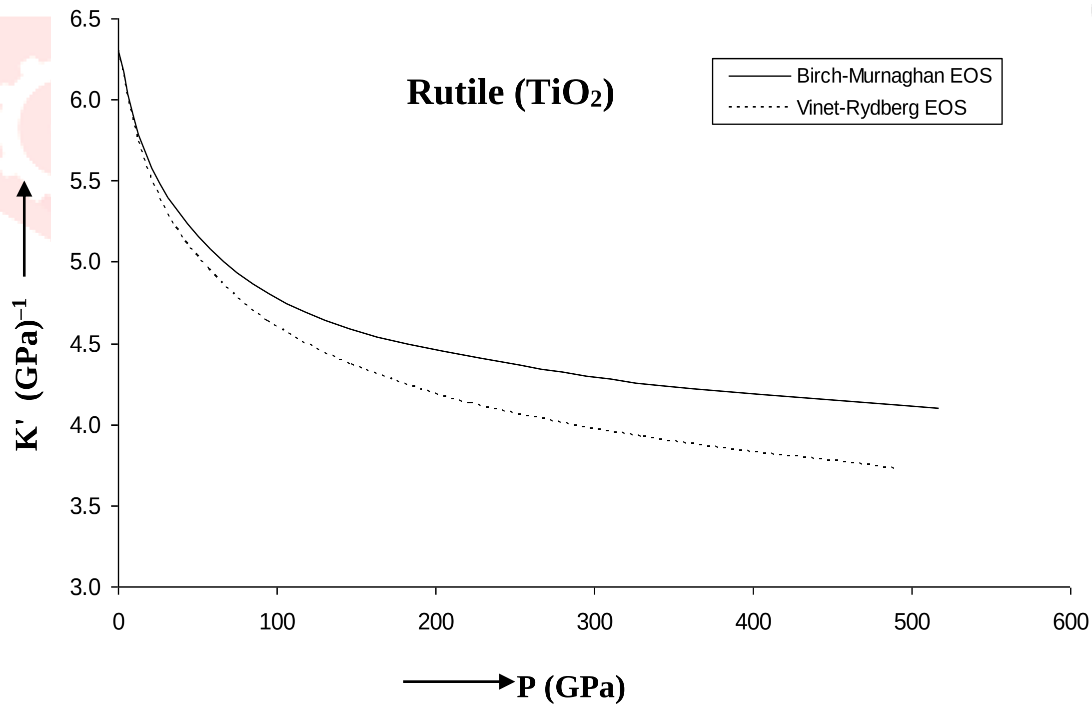

Figure 3 : Plots of pressure derivative of bulk modulus (K') versus pressure (P) for Rutile (TiO_2)

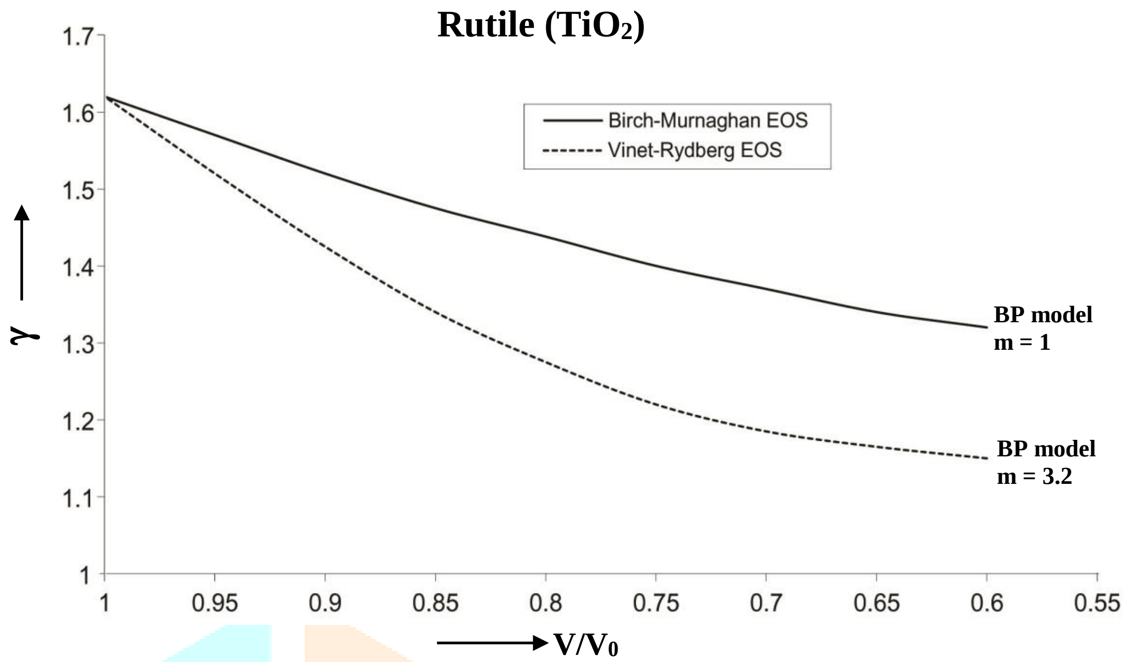

Figure 4 : Plots of γ versus volume compression (V/V_0) for Rutile (TiO_2) obtained by fitting the B-P model with the results based on generalized free volume formula.

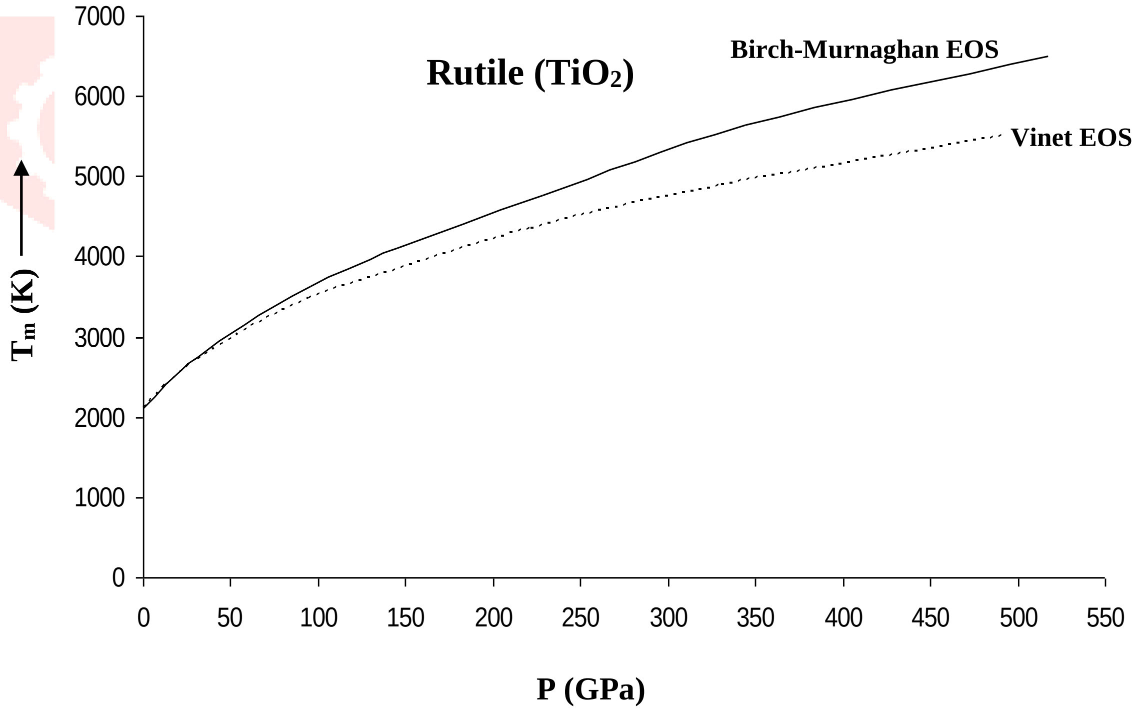

Figure 5 : Plots of melting curves (T_m Versus P) for Rutile (TiO_2) using the B-P model in the Lindemann law of melting Eq. (16)

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