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Thermal and physical properties of titanium oxide at high pressure

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ABSTRACT

We have investigated the pressure dependence of the thermal and physical properties of titanium oxide (rutile) by utilizing the semi-empirical relation developed following the Lindemann's melting law. Grüneisen parameter and the bulk modulus are the basic inputs of the empirical relation. The formalism has been applied to estimate the pressure dependence of melting temperature, Debye temperature, viscosity, conductivity and diffusivity of rutile. The pressure range used in the present study is 0–20 GPa. The results show that the properties of TiO_2 as a function of pressure are close to linear at low pressures ($P \leq 6.0$GPa) but starts deviating from being linear for ($P > 6.0$GPa). Similar trends are also exhibited for viscosity, thermal conductivity, and diffusivity.

1. Introduction

There are several naturally occurring (rutile, anatase and brookite) and, synthesized polymorphs (columbite, baddeleyite, cotunnite and fluorite) of titanium oxide (TiO_2). Rutile is the most common naturally occurring and most stable polymorph of TiO_2 with a tetragonal symmetry. It is a common accessory mineral in metamorphic rock and also found in igneous rocks, mantle xenoliths, lunar rocks and meteorites. Out of the total mass of the Earth's crust, amount of rutile found in nature ranges from 0.5% at the upper crust to 0.8% at the bottom crust [1].

Titanium dioxide has two interesting properties. When water comes in contact with TiO_2 under the influence of light irradiation, it forms an extremely small contact angle ($\approx 0^\circ$) with water. Materials having this property of superhydrophilicity can defog glass, and it can also enable oil spots to be wiped away easily with water. Such materials are used as door mirrors for cars, coatings for buildings, self-cleaning glass, etc. Another property of TiO_2 is called photocatalysis, which is the acceleration of a photoreaction in the presence of a catalyst. The practical application of this feature was made possible by water electrolysis using titanium dioxide. These two properties have made TiO_2 an interesting problem [2] of research in material science and engineering besides its industrial uses in photovoltaic devices, integrated waveguides, gas and humidity sensors, and solar cells. It is of special importance because more than twenty compounds share the same structure, allowing for detailed comparison of different properties [3]. It has the largest refractive index (2.903) of all known minerals and exhibits high dispersion [4,5].

At high pressures, the phase diagrams of TiO_2 exhibits a series of structural phase transformations, which are of particular interest in geophysics and geochemistry because these phases serve as accessible analog of minerals in the Earth's mantle [6]. A complete understanding of the composition and thermal state of the Earth's interior depends on information about the thermal properties of the mineral at high pressure and temperature [7]. Both the naturally grown anatase and rutile transform to meta stable columbite structure at high pressure. The pressure at which this transformation occurs ranges between 4 and 8 GPa in case of anatase and 10 GPa for rutile. In case of rutile, the transformation to columbite structure is very slow. The columbite structured TiO_2 transforms to a baddeleyite structured phase at pressure between 12 and 20 GPa [8–13]. Elastic and thermal properties of rutile and anatase have been studied [14] using first-principles calculations based on density functional theory (DFT).

Earlier work on TiO_2 reported [15–17] measurement of heat capacities of rutile and anatase at low temperatures (0–300 K).The major research works [18,19] on lattice dynamics of rutile phase were aimed at determining the dielectric properties and phonon frequencies at the gamma point of the rutile structure using variational density functional perturbation theory (DFPT). The phonon band structure and density of states have also been reported using the local density approximation (LDA) and generalized gradient approximation (GGA) [20] and the straight super cell method [21]. The state of the art DFT calculations have been used to show the existence of two soft phonon modes in rutile and anatase which are absent in high pressure Raman spectrum [22].

More recently TiO_2 has been studied under compression, both for bulk materials and nanoparticles [23–25]. Outcomes of these studies are interesting. A strong dependence of bulk modulus of

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nanocrystalline TiO_2 anatase on its grain size between 20 and 40 nm has been reported in [23]. It was suggested [24] that, in case of nanocrystalline TiO_2 anatase, the effect of pressure on atomic positions, bond distances, and bond angles increases the distortion in the TiO_6 octahedra making anatase phase unstable and triggering the observed transition to baddeleyite. First principles study [25] predicted a novel ten-fold coordinated TiO_2 polymorph with CaC_2-type symmetry which is thermodynamically stable at pressures greater than 690 GPa.

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 [7,26–31]. In some of the previous studies [26] 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-principles method has been used [29] to determine the pressure dependence of elastic and thermal properties of cubic TiO_2. Information on the pressure dependence of the melting temperature and the Debye temperature of rutile is scanty and the present study is intended to abridge the gap.

We present here a semi-empirical approach based on Lindemann law to determine the pressure dependence of these properties which can be extrapolated to very high pressures relevant to the interior of the terrestrial and other planets.In our formalism we have used second degree polynomial equations for Grüneisen parameter, ξ and bulk modulus B as a function of pressure, P. These equations have been used in Debye and Lindemann's formalisms to derive expressions for Debye temperature, Θ_D and melting temperature, T_m as a function of pressure. The values of Θ_D(P) and T_m(P) are then utilized to estimate viscosity, thermal conductivity and diffusivity of rutile. We have used the seismic velocity data [31] and the density data [6] of rutile in the original form of Lindemann's equation. to determine Θ_D as a function of pressure. The latter is one of the important characteristics of substance, which reflects its structure stability, the strength of bonds between its separate elements, structure defects availability (dislocations in crystalline structure of mineral grains, pores, micro cracks) and its density. Actually, any alteration of the external conditions of rock formation and transformation can cause a change in the Debye characteristic temperature [32]. The formalism has further been extended to investigate the pressure dependence of the melting temperature, Debye temperature, thermal conductivity and diffusivity of rutile using the semi-empirical relations for a pressure range of 0–20 GPa.

The layout of the paper is as follows: theoretical formalism is presented in Section 2, results and discussions of pressure dependence of the melting temperature, Debye temperature, thermal conductivity and diffusivity of rutile in the pressure range of 0–20 GPa are given in Section 3, which is followed by conclusions in Section 4.

2. Theoretical formalism

We present here briefly the mathematical formalism leading to semi empirical relation to determine the pressure dependence of melting temperature and the Debye temperature.

2.1. Melting temperature

A detailed formalism to derive the relation of melting temperature as a function of pressure can be found in our earlier works [33–36]. The Debye model of solids was incorporated into it to obtain a relation for the variation of the melting temperature, T_m with pressure, P in terms of bulk modulus, $B(P)$ $\left[=1/\Omega\left(\frac{\partial\Omega}{\partial P}\right)_T\right.$, Ω is the molar volume$\left.\right]$ and the Grüneisen parameter, $\xi(P)\left[=-(\Omega/\Theta_D)(\partial\Theta_D/\partial\Omega)\right.$, Θ_D is the Debye temperature for solids$\left.\right]$,

$$\frac{d(lnT_m)}{dP}=\frac{2}{B}\left(\xi-\frac{1}{3}\right) \tag{1}$$

Grüneisen parameter, ξ is a measure of the anharmonicity of thermal vibrations in solids. In order to get better information, B and ξ are further expanded in terms of P as

$$B(P)=B_0+b_1P+b_2P^2+\ldots \tag{2}$$

$$\xi(P)=\xi_0+a_1P+a_2P^2+\ldots \tag{3}$$

ξ_0 and B_0 are values at ambient conditions which have been extensively measured for various materials. In absence of such data, one can determine them from the thermoelastic relations,

$$B_0=\frac{(1+\sigma)\varrho v_P^2}{3(1-\sigma)};\ \xi_0=\frac{\beta}{\varrho c_P\kappa_S};\ \kappa_S=\frac{1}{\rho\left(v_p^2-\frac{4}{3}v_s^2\right)} \tag{4}$$

where σ is the Poisson ratio, β is the coefficient of thermal expansion, c_P is the specific heat at constant pressure, κ_S is the isentropic compressibility and ρ stands for density.

If we retain the terms of Eqs. (2) and (3) up to 2nd order and substitute those in Eq. (1), we obtained [34] the equation for $T_m(P)$ for two conditions:

Solution for Condition I: If $b_1^2<4B_0b_2$

$$T_m(P)=T_{m0}\left[\left(1+\frac{b_1}{B_0}P+\frac{b_2}{B_0}P^2\right)^{n'}exp\left\{\frac{2a_2}{b_2}P\right\}\right]exp\left\{\frac{2C}{A}arctan\left(\frac{AP}{2B_0+b_1P}\right)\right\} \tag{5}$$

$$with\quad A=\sqrt{4B_0b_2-b_1^2} \tag{6}$$

$$n'=\frac{a_1}{b_2}-\frac{a_2b_1}{b_2^2} \tag{7}$$

and

$$C=\left\{2\xi_0-\frac{2}{3}-\frac{a_1b_1}{b_2}+\frac{a_2\left(b_1^2-2B_0b_2\right)}{b_2^2}\right\} \tag{8}$$

Here $T_{m0}=T_m(0)$ is the melting temperature at ambient pressure (atmospheric pressure $\approx$0). It is determined from Eq. (25).

Solution for Condition II: If $b_1^2>4B_0b_2$

$$T_m(P)=T_{m0}\left[\left(1+\frac{b_1}{B_0}P+\frac{b_2}{B_0}P^2\right)^{n'}exp\left\{\frac{2a_2}{b_2}P\right\}\right]\left\{\frac{(b_1+A')P+2B_0}{(b_1-A')P+2B_0}\right\}^{C/A'} \tag{9}$$

$$with\ A'=\sqrt{b_1^2-4B_0b_2} \tag{10}$$

2.2. Pressure dependence of Debye temperature, Θ_D

The evaluation of the Debye temperature for minerals and rocks is very important to investigate the structural stability and defects. The difference between Θ_D of the separated facies of the metamorphic rocks is maximum in case of regional metamorphism. It is lower at intermediate level of metamorphism and is minimum in case of extremely altered rocks.

The Debye model is intrinsically harmonic in the sense that the dependence of potential energy on displacement of the atoms shows quadratic behavior. The anharmonic effects such as