Melting behaviour of the candidate minerals for planetary models

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Abstract. The discovery of super-Earths and extra solar giant planets has made high pressure physics relevant for determining the formation and composition of these planets. We have developed a model to determine the pressure dependence of melting temperature, $T_m$ and the Debye temperature, $\Theta_D$ of materials utilizing Grüneisen parameter, $\xi$ and the bulk modulus, $B$ as the basic ingredients. The formalism has been applied to estimate the pressure dependence of melting temperature and Debye temperature of one of the candidate minerals such as quartz (stishovite, $SiO_2$). The pressure range used in the present study is 0-6000GPa commensurate with the interior pressures of giant exoplanets. The results show an excellent agreement with the available experimental and other theoretical results.

1. Introduction
For developing realistic planetary models, knowledge of the melting behavior of the candidate minerals like quartz (stishovite, $SiO_2$) and MgO at high temperature and pressure is essential. Melting is the most important thermodynamic process that determines the physical and chemical evolution of the interiors of the planets of all sizes. Chemical differentiation and gravitational separation of liquid phase are responsible for the evolution of a terrestrial planet\cite{1}. The melting temperatures, at very high pressures, of the end-members of chemical differentiation such as silicates, iron, iron alloys, and $H_2O$ play an important role with regard to better constraining the internal structure and the physical properties of super-Earths\cite{2}. Silica is not only the most abundant oxide component of the mantles of the terrestrial planets, but also important as a model system to study polymorphic phase changes and interatomic potentials\cite{2,3}. Although free silica may exist locally along the subducted oceanic crust, it may form the bulk composition of super-Earths whose extremely high pressure and temperature conditions allow for greater presence of silica\cite{4-7}. Under these conditions silica and stishovite can have very different properties\cite{8}. The phase diagram of silica becomes, therefore, fundamental to the understanding of the interior of the planets in question.

The pressure variation of melting temperature of silica, at present, is known only up to 500GPa\cite{1} experimentally. Simulations results have reported the melting curve up to 200GPa\cite{9}, and recently up to 3400GPa\cite{10}. Since the multimegabar regime corresponds to the conditions found in the core of giant planets and super-Earths\cite{11}, it is desirable to explore it for even higher pressures, and from different approaches.

In the present work, we have used a semi-empirical formalism to deal with phase transitions at extremely high pressure and temperature conditions that may exist in the cores of extrasolar
planets. Our formalism involves $\xi$ and $B$ and their pressure dependence. Experimentally available values of $\xi_0$ and $B_0$ at ambient conditions are the principal ingredients of the present formalism. At higher pressure, we found that the pressure dependence of $B$ and $\xi$ are very sensitive and, change substantially around the structural transformation. We have also incorporated Debye temperature $\Theta_D$ in our analysis because of its importance in characterization of rocks and minerals[12]. Any change in the external condition of rocks and other materials formation and transformation can lead to a change in $\Theta_D$.

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 of silica in the pressure range of 0-6000GPa 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. A detailed formalism to derive the relation of melting temperature as a function of pressure can be found in our earlier works[13-15].

2.1. Melting temperature
The Debye model of solids was incorporated into the present formalism to obtain a relation for the variation of the melting temperature, $T_m$ with pressure, $P$ in terms of bulk modulus $B(P)$, and the Grüneisen parameter $\xi(P)$,

$$(\ln T_m)' = (2/B)(\xi - 1/3),$$

where prime denotes differentiation w.r. to $P$. $\xi$ is a measure of the anharmonicity of thermal vibrations in solids. In order to get better information, $B$ and $\xi$ are further expanded in terms of $P$ as

$$B(P) = B_0 + b_1 P + b_2 P^2 + \ldots,$$

$$\xi(P) = \xi_0 + a_1 P + a_2 P^2 + a_3 P^3 + \ldots.$$  

We have expanded $\xi$ up to third order to account for its sensitivity on melting at higher pressures where contributions from second order phase transformations may be important. Further expansion of $B$ has been avoided because of complexity in deriving an analytical solution. $\xi_0$ and $B_0$ are values at ambient conditions which have been extensively measured for various materials. The coefficients $a_n$ and $b_n$ are the pressure derivatives of $\xi$ and $B$. Inserting Eqs.(2)-(3) in Eq.(1) and, integrating from pressure 0 to $P$ one can get two solutions for two conditions[13,14].

**Solution for condition I:** For $b_1^2 < 4B_0b_2$

$$T_m(P) = T_0 \left[ \left( 1 + \frac{b_1}{b_0} P + \frac{b_2}{B_0} P^2 \right)^n \exp \left( 2DP + \frac{a_3}{b_2} P^2 \right) \exp \left( \frac{2C}{A} \tan^{-1} \frac{AP}{2B_0 + b_1 P} \right) \right],$$

$$A = \sqrt{4B_0b_2 - b_1^2},$$

$$C = \left[ 2\xi_0 - 2/3 - a_1b_1/b_2 + ((b_1^2 - 2B_0b_2)/b_2^2) \left( a_2 - a_3b_1/b_2^2 \right) + a_3B_0b_1/b_2^2 \right],$$

$$D = a_2/b_2 - a_3b_1/b_2^2,$$

$$n = a_1/b_2 - a_2b_1/b_2^2 - a_3B_0/b_2^2 + a_3b_1^2/b_2^2.$$  

References:
[12] [Insert reference here]
[13] [Insert reference here]
[14] [Insert reference here]
[15] [Insert reference here]
Solution for condition II: For $b_1^2 > 4B_0b_2$

$$T_m(P) = T_0 \left[ \left( 1 + \frac{b_1}{b_0}P + \frac{b_2}{B_0}P^2 \right)^n \exp \left( 2DP + \frac{a_3}{b_2}P^2 \right) \right] \left\{ \frac{(b_1 + A')P + 2B_0}{(b_1 - A')P + 2B_0} \right\}^{C/A'},$$

where $A' = \sqrt{b_1^2 - 4B_0b_2}$; $T_0$ is the melting temperature at atmospheric pressure. \( \tag{9} \)

### 2.2. Pressure dependence of Debye temperature, $\Theta_D$

It has been shown\[15\] earlier that within the Debye-Grüneisen Model the relationship among $\xi$, $B$ and $\Theta_D$ as a function of pressure, $P$ may be written in the form:

$$\frac{1}{\Theta_D(P)} \frac{d\Theta_D(P)}{dP} = \frac{\xi(P)dP}{B_T(P)} \tag{11}$$

Inserting Eqs.(2)-(3) in Eq.(11) and integrating from pressure 0 to $P$, we get two solutions in terms of Debye temperature $\Theta_{D0}$ at ambient condition.

**Solution for condition I:** For $b_1^2 < 4B_0b_2$

$$\Theta_D(P) = \Theta_{D0} \left[ \left( 1 + \frac{b_1}{b_0}P + \frac{b_2}{B_0}P^2 \right)^{n/2} \exp \left( DP + \frac{a_3}{2b_2}P^2 \right) \right] \exp \left( \frac{2C'}{A}\tan^{-1} \frac{AP}{2B_0 + b_1P} \right). \tag{12}$$

**Solution for condition II:** For $b_1^2 > 4B_0b_2$

$$\Theta_D(P) = \Theta_{D0} \left[ \left( 1 + \frac{b_1}{b_0}P + \frac{b_2}{B_0}P^2 \right)^{n/2} \exp \left( DP + \frac{a_3}{2b_2}P^2 \right) \right] \left\{ \frac{(b_1 + A')P + 2B_0}{(b_1 - A')P + 2B_0} \right\}^{C'/A'} \tag{13}$$

$$C' = \left[ \xi_0 - a_1b_1/2b_2 + ((b_1^2 - 2B_0b_2)/2b_2^2) \left( a_2 - a_3b_1/b_2^2 \right) + a_3B_0b_1/2b_2^2 \right] \tag{14}$$

The constants $A$, $D$, $n$ and $A'$ are defined earlier in Eqs.(5), (7), (8) and (10) respectively.

### 3. Results and discussions

The results of our study are presented in Fig.1(A-C). Figure 1A is a plot of low and high pressure melting curves together. It shows an excellent fit of our melting curve (thick solid line) with that of\[2\] obtained from first principles molecular dynamics simulations for pyrite, cotunnite and Fe2P phases of silica. Since it is difficult to show discontinuity in the melting curve from theoretical formulations, we have determined the melting curves for the low pressure (0-500GPa) and high pressure (300-6000GPa) regions separately for two sets of parameters (Table 1) to account for the reported phase transition of silica melting curve at about 300GPa. The melting curve obtained from the present formalism shows a minimum slope of 1.34K-GPa$^{-1}$ at 3400GPa.

Characteristic points of a melting curve such as maximum and inflexion point are often interpreted to be associated with phase transition. The low pressure region of the present melting curve plotted separately in figure 1B has an excellent fit with that of the experimental curve \[1\]. Our melting curve shows a minimum slope of 8.09K-GPa$^{-1}$ at 350GPa. This value is comparable with the phase transition value of 330GPa found in molecular dynamic simulations studies \[2\]. Figure 1C which is a plot of $\Theta_D$ against pressure, shows a minimum slope of 0.215K-GPa$^{-1}$ at 3800GPa. This value of pressure is close to the value, 3400GPa obtained in the case of the melting curve. It can be noticed that the shape of the $T_m$-$P$ curve is very similar to that of $\Theta_D$-$P$ curve indicating an intimate relationship between the two.
Table 1. Grüneisen parameter, $\xi_0$ and bulk modulus, $B_0$(GPa) at ambient conditions. $a_n$(GPa$^{-n}$) and $b_n$(GPa$^{-n+1}$) are the derivatives of $\xi$ and B.

| Minerals   | $\xi_0$ | $a_1$     | $a_2$          | $a_3$ | $B_0$ | $b_1$ | $b_2$ |
|------------|---------|-----------|----------------|-------|-------|-------|-------|
| $\alpha$-quartz | 1.35    | -0.0001035 | 1.2022x10$^{-5}$ | -     | 37$^{[8]}$ | 6.0$^{[8]}$ | 0.1539 |
| stishovite | 1.28    | -0.00022  | 5.1044x10$^{-10}$ | 2.1969x10$^{-11}$ | 295$^{[8]}$ | 1.3$^{[8]}$ | 0.001882 |

Figure 1. (A) Comparison of the melting curve determined in this study (thick solid line) with those of$^{[1,2,9]}$. (B) $T_m$-$P$ curve for low pressure region (0-500GPa). (C) $\Theta_D$ -$P$ curve is computed from Eq.(13) using the parameters for high pressure only.

4. Conclusions

An empirical relation to compute $T_m$-$P$ variation at high pressures is formalised in terms of bulk modulus($B$) and Grüneisen parameter($\xi$). This is applied to compute the melting temperature of quartz(stishovite, SiO$_2$) as a function of pressure in the range 0 - 6000GPa. Such a pressure is commensurate to the interior pressure of giant planets. Our computed results are in excellent agreement with available experimental results in the low pressure region. Results exhibit a discontinuity in slope around 350GPa which is comparable with the phase transition value of 330GPa found from molecular dynamic simulation. It has been observed that the value of $B$ and $\xi$ of stishovite at high pressures are quite different from those of $\alpha$-quartz in the low pressure region.

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