Thermodynamic Properties of $CaSiO_3$ Perovskite at High Pressure and High Temperature

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The thermodynamic properties of tetragonal $CaSiO_3$ perovskite are predicted at high pressures and temperatures using the Debye model for the first time. This model combines the ab initio calculations within local density approximation using pseudopotentials and a plane wave basis in the framework of density functional theory, and it takes into account the phononic effects within the quasi-harmonic approximation. It is found that the calculated equation of state is in excellent agreement with the observed values at ambient condition. Based on the first-principles study and the Debye model, the thermal properties including the Debye temperature, the heat capacity, the thermal expansion and the entropy are obtained in the whole pressure range from 0 to 150 GPa and temperature range from 0 to 2000 K.

Key words: Thermodynamic Property; High Pressure; First Principles.
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1. Introduction

$CaSiO_3$ perovskite is believed to be an important phase in the Earth's transition zone and lower mantle [1 – 3]. Experimental studies have shown that $CaSiO_3$ perovskite forms in mantle-relevant compositions under deep Earth conditions [4, 5], and its physical properties are important to understand the transition zone seismic structure [6]. It is, however, very difficult to perform detailed structural studies at lower-mantle pressures in the laboratory. The stability and equation of state of $CaSiO_3$ perovskite were investigated to core-mantle boundary conditions [7, 8] by energy-dispersive synchrotron X-ray diffraction in the laser-heated diamond anvil cell. Within the resolution of these studies, $CaSiO_3$ has a cubic perovskite structure. Theoretical studies based on ionic models [9, 10], periodic Hartree-Fock [11], pseudopotential density functional theory calculations [12, 13] have supported this observation. However, other theoretical calculations have proposed a orthorhombic structure [14, 15]. Recent progresses in both the theoretical and experimental studies of $CaSiO_3$ perovskite are due to the improvements in the methods used. High-resolution synchrotron X-ray diffraction measurements were performed at 20 – 46 GPa on $CaSiO_3$ perovskite synthesized in a laser heated diamond cell, it was found that $CaSiO_3$ perovskite favored a tetragonal structure [16]. Li et al. [17] reported the dynamics of the structure of $CaSiO_3$ perovskite from ab initio molecular dynamics calculations at high pressure and high temperature. His calculations indicate the tetragonal phase dominating the pressure and temperature region between room temperature and 4000 K. Using density functional simulations, within the generalized gradient approximation and projector augmented wave method, Jung and Oganov [18] studied structures and energetics of $CaSiO_3$ perovskite in the pressure range of the Earth's lower mantle. At zero Kelvin temperature the cubic structure is unstable in the whole pressure range, at 14.2 GPa there is a phase transition to the tetragonal phase. In addition, a early theoretical study [19] also proposed that the tetragonal phase of $CaSiO_3$ perovskite is more stable at all pressures at 0 K. Therefore, the physical properties of tetragonal $CaSiO_3$ perovskite may well be of geophysical importance. However, theoretical and experimental studies have placed constraints on structure, equation of state and elastic properties of the perovskite phase [16, 17, 19 – 21]. As yet, there has been no experimental study that di-

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rectly compares the thermodynamic properties of the perovskite phases over a broad range of pressure conditions for a mantle-relevant chemical composition. In order to better understand the relative importance of the perovskite phase we need to know its thermodynamic properties at relevant pressures and temperatures.

This work is devoted to the investigation of the thermal properties of CaSiO$_3$ perovskite phases. For the sake of this, the Debye model, which combines the ab initio calculations and takes into account the phononic effects within the quasi-harmonic approximation, is adopted. The equilibrium structure of CaSiO$_3$ perovskite phase is also investigated via the minimization of the total energy within local density approximation using pseudopotentials and a plane wave basis. Based on the first principles study and the Debye model, the thermal properties including the Debye temperature, the heat capacity and the thermal expansion and the entropy are obtained in detail.

2. Method

Computations employ the density functional theory plane-wave pseudopotential method [22, 23]. The exchange-correlation functional theory is adopted in the local density approximation [24]. The pseudopotentials for Ca and Si are norm-conserving [25], while an ultrasoft pseudopotential [26] is used for O. All the pseudopotentials are non-local. The use of an ultrasoft pseudopotential for oxygen allows us to use a relatively small basis set with plane wave cut-off energy of 550 eV without any loss of accuracy and with excellent convergence of all properties with respect to the basis set (the maximum stress is only 0.02 GPa). The Brillouin zone is sampled on an 8 × 8 × 8 Monkhorst-Pack k-point mesh [27], which provides convergence of the total energy to a value within $5.0 \cdot 10^{-6}$ eV/atom. The Kohn-Sham equations are solved iteratively to self-consistency within $5.0 \cdot 10^{-7}$ eV/atom.

To investigate the thermodynamic properties of CaSiO$_3$ perovskite, we here apply the quasi-harmonic Debye model [28], in which the non-equilibrium Gibbs function $G^*(V;P,T)$ takes the following form:

$$G^*(V;P,T) = E(V) + PV + A_{\mathrm{vib}}(\Theta(V);T), \quad (1)$$

where $E(V)$ is the total energy per unit cell for CaSiO$_3$ perovskite, PV denotes the constant hydrostatic pressure condition, A_{vib} is the vibrational Helmholtz free energy, and $\Theta(V)$ denotes the Debye temperature. Using the Debye model of phonon density of states and allowing for the quasi-harmonic approximation, the vibrational term A_{vib} can be written as [29, 30]

$$A_{\mathrm{vib}}(\Theta;T) = nkT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-\mathrm{e}^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right)\right], \quad (2)$$

where $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. Θ is expressed as [29]

$$\Theta = \frac{\hbar}{k}[6\pi^2 V^{1/2} n]^{1/3} f(\sigma)\sqrt{\frac{K_{\mathrm{S}}}{M}}, \quad (3)$$

where M is the molecular mass per formula unit and K_{S} the adiabatic bulk modulus, which can be approximated by the static compressibility [28]

$$K_{\mathrm{S}} \approx K(V) = V\left(\frac{\mathrm{d}^2E(V)}{\mathrm{d}V^2}\right). \quad (4)$$

Here the Poisson ratio σ is taken as 0.25 [31], $f(\sigma)$ is given in [32, 33]. Therefore, the non-equilibrium Gibbs function $G^*(V;P,T)$ as a function of $(V;P,T)$ can be minimized with respect to volume V as follows:

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \quad (5)$$

By solving (5) we obtain the thermal equation of state. The volume heat capacity C_{V}, the entropy S and the thermal expansion coefficient α are given respectively by [33]

$$C_{\mathrm{V}} = 3nk\left[4D\left(\frac{\Theta}{T}\right) - \frac{3\Theta/T}{\mathrm{e}^{\Theta/T}-1}\right], \quad (6)$$

$$S = nk\left[4D\left(\frac{\Theta}{T}\right) - 3\ln(1-\mathrm{e}^{-\Theta/T})\right], \quad (7)$$

$$\alpha = \frac{\gamma C_{\mathrm{V}}}{K_T V}, \quad (8)$$

where γ is the Grüneisen parameter and it is expressed as $\gamma = -\mathrm{d}\ln\Theta(V)/\mathrm{d}\ln V$.

3. Results and Discussion

Self-consistent total energies are calculated for different volumes, with isotropic volume changes. A series of different values of lattice constants are set to

Table 1. Unit cell volume, bulk modulus and pressure derivatives of CaSiO^3 perovskite from the calculations and measurements.

EOS third order BM	V_0 [Å^3]	K_0 [GPa]	K'_0
This work	45.46	238	4.4
Li et al. (2006) [20]	45.56	237	3.99
Jung and Oganov (2005) [18]	46.90	219	4.08
Akber-Knutson et al. (2002) [14]	45.90 ± 0.02	228 ± 2	4.3 ± 0.1
Magyari-Köpe et al. (2002) [15]	45.69	216	4.82
Karki and Crain (1998) [37]	45.35	241	4.14
Chizmeshya et al. (1996) [38]	45.62	227	4.29
Wentzcovitch et al. (1995) [12]	46.15	254	4.4
Wolf and Bukowinski (1987) [10]	55.74	263	4.13
Wolf and Jeanloz (1985) [9]	56.13	270	3.86
Experiment			
Ono et al. (2005) [21]	45.38	248 ± 8	4
Shim et al. (2002) [16]	45.58	255 ± 5	4
Wang et al. (1996) [35]	45.58 ± 0.04	232 ± 8	4.8 ± 0.3
Mao et al. (1989) [7]	45.37 ± 0.08	281 ± 4	4
Tamai and Yagi (1989) [36]	45.58 ± 0.07	352 ± 10	4

calculate the total energy E and the corresponding unit cell volume V. Based on the computed $E-V$ relations, we fit $E-V$ data points to the third-order Birch-Murnagham equations of state [34]. The calculated equilibrium volume, bulk modulus, and their pressure derivatives are given in Table 1. We find that the calculated equilibrium volume is in good agreement with the experimental [7, 16, 21, 35, 36] and theoretical [12, 14, 15, 18, 20, 37, 38] ones. The results concerning the V_0 of Wolf and Jeanloz [9] and Wolf and Bukowinski [10] are higher than the rest. This can be explained by the fact that they did not use ab initio methods fully and had to use models which introduced a certain amount of ambiguity. Our predicted equilibrium volume and bulk modulus agree well with the latest theoretical result [20]. The pressure dependence of the volume for CaSiO$_3$ perovskite calculated with CA-PZ [25, 39] is shown in Figure 1. It is found that the calculated equation of state of CaSiO$_3$ perovskite is in excellent agreement with the available experimental [7, 35, 40] and theoretical data [37]. However, Jung and Oganov [18] overestimate the equation of state over a wide pressure range.

From Fig. 2, we can see that at low pressure, the Debye temperature Θ decreases significantly when the temperature changes from 0 to 2000 K, it can be noted that Θ decreases by 7.57, 2.28, and 0.36% at the pressures of 0, 60, 100 GPa when the used temperature is from 0 to 2000 K, respectively. And when the used pressure is from 0 to 100 GPa, Θ increases by 54.15, 57.48, 63,91% at the temperatures of 300, 1000, and 2000 K, respectively. As the pressure goes higher, the decreased magnitude of Θ becomes small. When the pressure approaches to 100 GPa, the variation of Θ is very small in the whole changed temperature range from 0 to 2000 K. Therefore, it can be concluded that the effect of the temperature on the Debye temperature Θ is not as important as that of the pressure on Θ. And the higher the pressure, the smaller the effect of the pressure on the Debye temperature Θ.

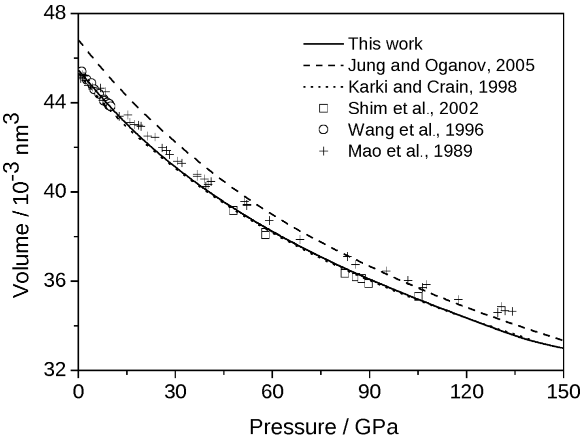

Fig. 1. Static equation of state of CaSiO$_3$ perovskite.

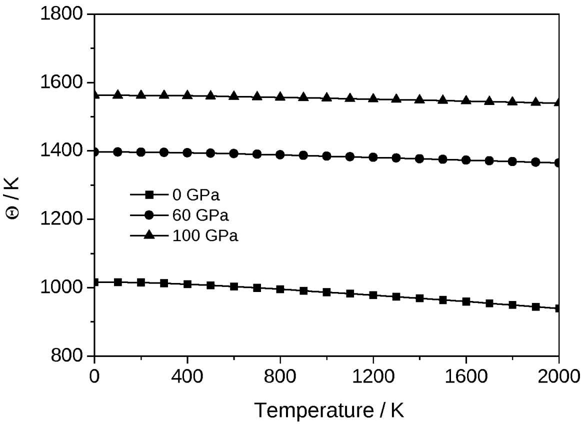

Fig. 2. Variation of the Debye temperature Θ with the temperature at different pressures of $P = 0$, 60, and 100 GPa.

The relations between the constant volume heat capacity C_V and the ratio of T/Θ are shown in Figure 3. It can be seen that the trend of variation of the constant volume heat capacity C_V with the ratio of T/Θ is similar at different pressures of $P = 0$, 60, and 150 GPa when $T/\Theta > 0.15$, respectively. At fixed T/Θ, the value of C_V is the same. While there exists a subtle discrepancy of the variation of C_V at different pressures of $P = 0$, 60, and 150 GPa when $T/\Theta < 0.15$,

	T [K]	P [GPa]					
		0	10	30	60	100	150
C_V [J/mol K]	300	74.8972	69.3350	60.6436	51.3727	43.0094	36.1005
C_V [J/mol K]	600	108.8835	106.3744	102.0363	96.6864	90.9900	85.4210
C_V [J/mol K]	1000	118.8492	117.7930	115.9253	113.5340	110.8635	108.1123
C_V [J/mol K]	1500	122.1791	121.6716	120.7811	119.6307	118.3275	116.8676
C_V [J/mol K]	2000	123.3532	123.0558	122.5343	121.8624	121.0993	120.2445

Table 2. The values of the constant volume heat capacity C_V at different temperatures and different pressures.

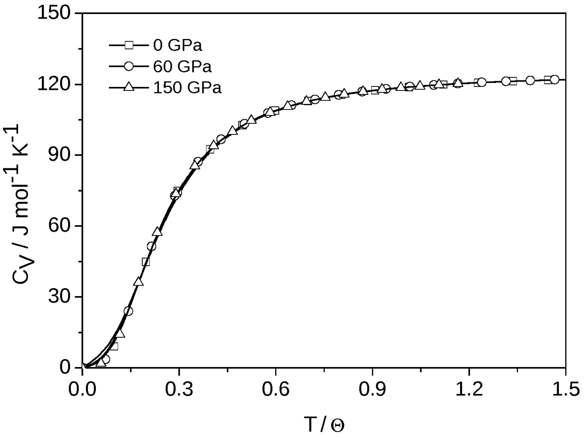

Fig. 3. Variation of the constant volume heat capacity C_V with the ratio of T/Θ at different pressures of $P = 0$, 50, and 150 GPa, respectively.

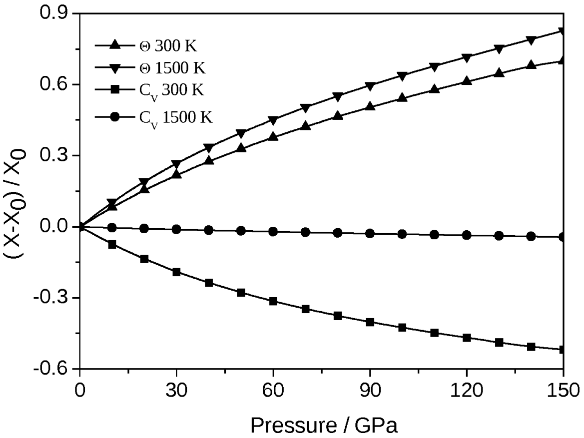

Fig. 4. Variation of the thermal parameters X (Debye temperature Θ or constant volume heat capacity C_V) with pressure P. They are generalized by $(X-X_0)/X_0$, where X and X_0 are the Debye temperature Θ or constant volume heat capacity C_V at any pressure P and zero pressure at the temperatures of 300 and 1500 K.

respectively. The higher the ratio of T/Θ, the larger is the constant volume heat capacity C_V. And this is due to the limitation of the Debye model at low temperatures and owing to different Debye temperature Θ at different temperatures as shown in Figure 2. However, according to the trend of the variation of the $C_V(T/\Theta)$, one can confirm the experimental data of the constant volume heat capacity C_V. This is an important case in the future experimental work.

The variation of the Debye temperature Θ and the constant volume heat capacity C_V with pressure P are shown in Figure 4. They are generalized by $(X - X_0)/X_0$, where X and X_0 denote the Debye temperature Θ or the constant volume heat capacity C_V at any pressure P and zero pressure. We find that at a given temperature, the Debye temperature Θ increases almost linearly with pressures. As the pressure goes higher, the discrepancy between Θ at fixed pressures increases gradually at different temperatures of $T = 300$ K and $T = 1500$ K, respectively. By contraries, the constant volume heat capacity C_V decreases with pressures at different temperatures. It can be seen that at $T = 1500$ K, almost keeps constant in the whole pressure range from 0 to 150 GPa. While at $T = 300$ K, there is a dramatic decrease in C_V with pressures from 0 to 150 GPa. This is due to the fact that the effect of increasing pressure on the constant volume heat capacity C_V of $CaSiO_3$ perovskite is the same as decreasing temperature on that of $CaSiO_3$ perovskite. In Table 2, we also list the constant volume heat capacity C_V at different pressures and different temperatures. It can be seen that when the used pressure ranges from 0 to 150 GPa, C_V decreases by 51.80, 21.55, 9.03, 4.35, and 2.52% at the temperatures of 300, 600, 1000, 1500, and 2000 K, respectively. It means that the higher the temperature, the smaller is the decreased magnitude of the constant volume heat capacity C_V. On the other hand, comparing C_V at the different temperatures of $T = 300$ K and $T = 1500$ K, we find that C_V at $T = 1500$ K is almost 0.63, 0.75, 0.99, 1.33, 1.75, and 2.24 times larger than those at $T = 300$ K at different pressures of 0, 10, 30, 60, 100, and 150 GPa, respectively.

The volume thermal expansion coefficient α can be directly obtained from (8). Figure 5 shows the variation of the volume thermal expansion coefficient α with the pressures and temperatures. From Fig. 5a we can see that the volume thermal expansion coefficient α

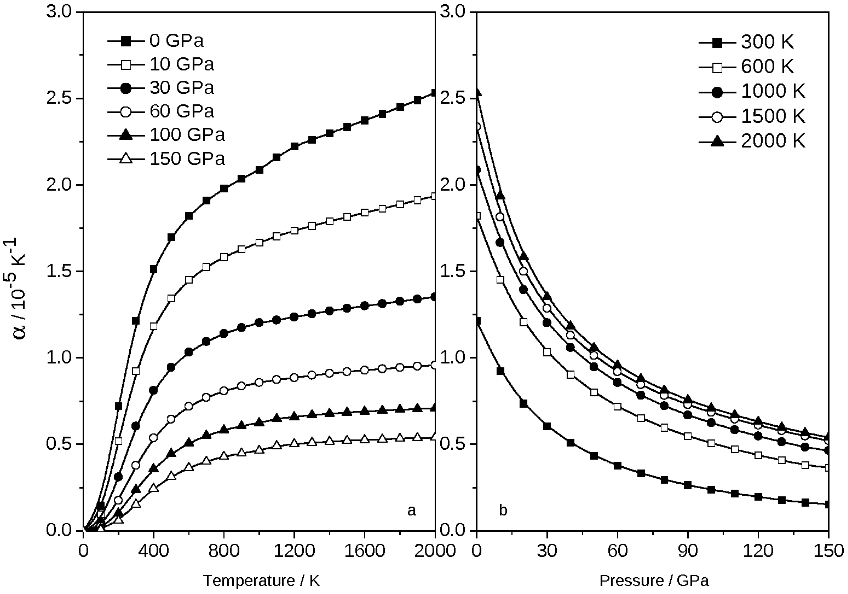

Fig. 5. Variation of the volume thermal expansion coefficient α with (a) the temperature and (b) the pressure.

increases with T^3 at low temperature T and gradually increases linearly with the increment of the temperatures, and then the increasing trend becomes gentler. The effects of the pressure on the volume thermal expansion coefficient α are very small at low temperatures; the effects are increasingly obvious as the temperature increases. As pressure increases, the volume thermal expansion coefficient α decreases rapidly and the effects of temperature become less and less pronounced, resulting in linear high temperature behaviour. It is noted that the high temperature dependence of the volume thermal expansion coefficient α is not linearly at low pressure, this is an indication of the inadequacy of the quasi-harmonic approximation at high temperatures and low pressures. It can be seen that at a given temperature, α decreases drastically with the increment of the pressures as shown in Figure 5b. When $P = 0$ GPa, the volume thermal expansion coefficient α of $T = 2000$ K is much larger than that of $T = 300$ K. As the pressure goes higher, the volume thermal expansion coefficient α gradually decreases, and the higher the temperature is, the faster the volume thermal expansion coefficient α decreases, which means that the effect of the temperature on the volume thermal expansion coefficient α plays a prominent role at low pressures, while the effect of the temperature on α decreases at high pressures. These results are in accordance with the results of the Debye theory which applies to many kinds of material. Comparing Figs. 5a and b, we conclude that the increasing temperature dependence of thermal expansion coefficient α is as important as the decreasing pressure dependence of the volume thermal expansion coefficient α, the volume thermal expansion coefficient α converge to a constant value at high temperatures and pressures. As shown in Fig. 6, unlike the volume thermal expansion coefficient α and the volume heat capacity C_V, the high temperature dependence of the entropy is nearly insensitive to pressure.

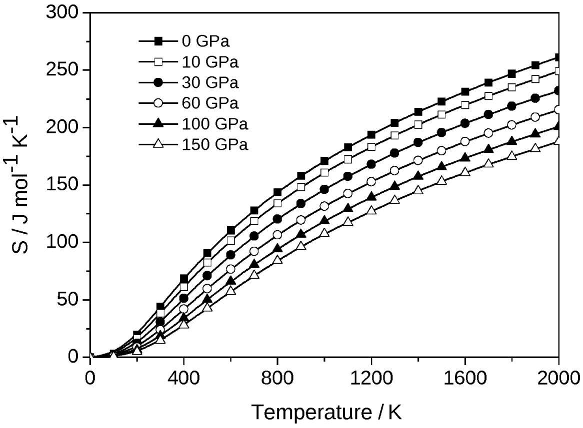

Fig. 6. Variation of the entropy S with the temperature.

4. Conclusions

In summary, the thermodynamic properties of $CaSiO_3$ perovskite are predicted using the quasi-harmonic Debye model in this work. It is found that the calculated equation of state is in excellent agreement with the experimental value. The thermal properties including the Debye temperature, the heat capacity, the thermal expansion and the entropy are obtained. We see that the high temperature leads to a smaller Debye temperature Θ, a larger heat capacity, and a bigger thermal expansion coefficient α. But the high pressure gives birth to a larger Debye temperature Θ, a smaller heat capacity, and a smaller thermal expansion coefficient α in the wide range of pressures and temperatures. It is also shown that the thermal expansion coefficient α and heat capacity are shown to converge to a nearly constant value at high pressures and temperatures. And the data concerning the thermal properties of $CaSiO_3$ perovsite will be useful in the studies of deep planetary interiors.

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