First-principles study of the elastic and thermodynamic properties of CaSiO$_3$ perovskite

First-principles study of the elastic and thermodynamic properties of CaSiO₃ perovskite

Z J Liu[1,2,3], X W Sun[4], Q F Chen[2,5], L C Cai[2], H Y Wu[3] and S H Ge[3]

[1] Department of Physics, Lanzhou City University, Lanzhou 730070, People's Republic of China
[2] Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics,
Academy of Engineering Physics, PO Box 919-102, Mianyang 621900,
People's Republic of China
[3] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065,
People's Republic of China
[4] School of Mathematics and Physics, Lanzhou Jiaotong University, Lanzhou 730070,
People's Republic of China

E-mail: lzjcaep@126.com

Abstract

The thermodynamic and elastic properties of CaSiO₃ perovskite are investigated at high pressures and temperatures using the plane wave pseudopotential method within the local density approximation. The athermal elastic moduli of CaSiO₃ perovskite are calculated as a function of pressure up to 200 GPa. The calculated results are in excellent agreement with available experimental data at high pressure, and compare favourably with other pseudopotential predictions over the pressure regime studied. It is also found that the elastic anisotropy drops rapidly with the increase of pressure initially, and then decreases more slowly at higher pressures. The thermodynamic properties of CaSiO₃ perovskite are predicted using the quasi-harmonic Debye model for the first time; the heat capacity and the thermal expansion coefficient agree with the observed values at ambient conditions and the other calculations at high pressures and temperatures.

1. Introduction

CaSiO₃ perovskite is thought to constitute between 6 and 12 wt% of the lower half of the Earth's transition zone and lower mantle [1–3] and is the third most abundant phase after (Mg, Fe)SiO₃ perovskite and magnesiowüstite (Mg, Fe)O, under the assumption that the lower mantle is pyrolytic. The single-crystal elastic properties of CaSiO₃ perovskite are important for our understanding of processes including brittle failure, flexure, and the propagation of

---

[5] Author to whom any correspondence should be addressed.

elastic waves. However, many of its physical properties are still relatively poorly understood because it is non-quenchable at ambient conditions. Available results on the elastic properties are restricted to analogue [4] and theoretical studies [5]. Recently, Shieh *et al* reported an *in situ* strength and elasticity of CaSiO$_3$ perovskite using energy dispersive radial x-ray diffraction together with lattice strain theory in the pressure range 19–61 GPa [6]. Up to now, there have not been any measurements reported of the thermodynamic properties of CaSiO$_3$ perovskite at high pressures and temperatures. Moreover, the crystal structure of CaSiO$_3$ perovskite in the mantle is still controversial. Most experimental studies have reported that CaSiO$_3$ perovskite crystallizes in the cubic structure [7, 8], and first-principles calculations also supported this observation [9–13]. However, other theoretical calculations favoured a tetragonal structure [14–17] or even lower symmetry [18–20]. Calculated energy differences between the proposed phases are sufficiently small that the crystal structure under mantle conditions is uncertain and may be cubic even if a lower symmetry phase is favoured at 0 K [5]. Therefore, the physical properties of cubic CaSiO$_3$ perovskite may well still be of geophysical importance.

In this paper, we present first-principles predictions of the elastic properties of cubic CaSiO$_3$ perovskite at lower mantle pressures using the plane-wave pseudopotential within the local density approximation. The predicted elastic constants are used to study the elastic modulus, elastic anisotropy and Cauchy violation. To further investigate this mineral, the quasi-harmonic Debye model, which takes into account the thermal effects, is adopted to research the thermal properties of CaSiO$_3$ perovskite, such as the bulk modulus, the heat capacity, the thermal expansion and the entropy on a first-principles basis. Our results demonstrate that this method can provide amply reliable predictions for the temperature and pressure dependence of these quantities.

2. Method

Our computations employ the density functional theory [21, 22] plane-wave pseudopotential method. The exchange–correlation functional theory is adopted in the local density approximation [23]. The pseudopotentials for Ca and Si are norm-conserving [24], while an ultrasoft pseudopotential [25] is used for O. All the pseudopotentials are non-local. The core radii are 1.06 Å for Ca, 0.95 Å for Si and 0.69 Å for O. 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 $8 \times 8 \times 8$ Monkhorst–Pack k-point mesh [26], which provides convergence of the total energy to a value within 5.0×10^{-6} eV/atom. The Kohn–Sham equations are solved iteratively to self-consistency within 5.0×10^{-7} eV/atom.

The determination of the elastic constants requires the knowledge of the equilibrium structure at a given pressure. We first fully optimize a single primitive cell of CaSiO$_3$ perovskite at several pressures. The structural optimization technique uses the Broydon–Fletcher–Goldfarb–Shanno (BFGS) [27] method with variable cell shape [28]. The elastic constants are then determined from direct computation of the stresses generated by small deformations of the equilibrium unit cell. Strains of different amplitudes (-0.003 to 0.003) are used and the elastic constants are derived from the resulting nonlinear stress–strain relation [29]. The details of the computational method have been given elsewhere [30].

To investigate the thermodynamic properties of CaSiO$_3$ perovskite, we here apply the quasi-harmonic Debye model [31], in which the non-equilibrium Gibbs function $G^*(V; P, T)$ takes the following form [31]:

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

where $\Theta(V)$ is the Debye temperature, and the vibrational term A_{vib} can be written as [32, 33]

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

where $D(\Theta/T)$ represents the Debye integral, and n is the number of atoms per formula unit. For an isotropic solid, Θ is expressed as [32]

$$\Theta = \frac{\hbar}{k} \left[6\pi^2 V^{1/2} n \right]^{1/3} f(\sigma) \sqrt{\frac{K_S}{M}}, \tag{3}$$

where M is the molecular mass per formula unit, and K_S the adiabatic bulk modulus, which can be approximated by the static compressibility [31]

$$K_S \simeq K(V) = V \left(\frac{\mathrm{d}^2 E(V)}{\mathrm{d}V^2} \right). \tag{4}$$

Here the Poisson ratio σ is taken as 0.25 [34]; $f(\sigma)$ is given in [35, 36]. 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:

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

By solving equation (5) we obtain the thermal equation of state (EOS). The isothermal bulk modulus K_T, the heat capacity C_V, the entropy S and the thermal expansion coefficient α are given respectively by [36]

$$K_T(P, T) = V \left(\frac{\partial^2 G^*(V; P, T)}{\partial V^2} \right)_{P,T}, \tag{6}$$

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

$$S = nk \left[4D \left(\frac{\Theta}{T} \right) - 3 \ln \left(1 - e^{-\Theta/T} \right) \right], \tag{8}$$

$$\alpha = \frac{\gamma C_V}{K_T V}, \tag{9}$$

where γ is the Grüneisen parameter [31].

3. Results and discussion

3.1. Static equation of state

The equilibrium volume, bulk modulus, and its pressure derivative are obtained by calculating the total energy and pressure for different values of the unit cell volume and by fitting the calculated data to the third-order Birch–Murnaghan (BM) equation of state [37]. The calculated equilibrium volume (V_0), bulk modulus (K_0), and their pressure derivatives (K_0') are given in table 1. We find that the calculated equilibrium volume is in good agreement with the experimental [7, 8, 38–40] and theoretical [5, 11, 14, 16–19] ones. The results concerning the V_0 of Wolf and Jeanloz [41] and Wolf and Bukowinski [42] 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
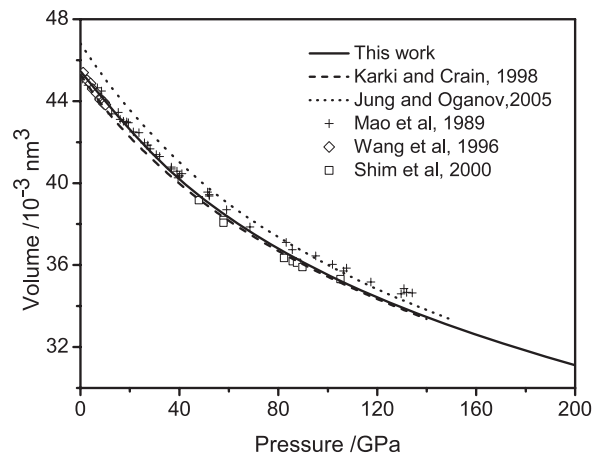
Figure 1. Static equation of state of CaSiO$_3$ perovskite. The present calculated equation of state is indicated by the solid line, and the experimental data of Mao *et al* [7], Wang *et al* [8] and Shim *et al* [44] are shown by the cross, open diamond and open square, respectively. The dashed line and dotted line represent the theoretical values of Karki *et al* [5] and Jung *et al* [16], respectively.

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	240	4.15
Li *et al* (2006) [17]	45.56	237	3.99
Jung and Oganov (2005) [16]	46.90	219	4.08
Akber-Knutson *et al* (2002) [18]	45.90 ± 0.02	228 ± 2	4.3 ± 0.1
Magyari-Köpe *et al* (2002) [19]	45.69	216	4.82
Karki and Crain (1998) [5]	45.35	241	4.14
Chizmeshya *et al* (1996) [14]	45.62	227	4.29
Wentzcovitch *et al* (1995) [11]	46.15	254	4.4
Wolf and Bukowinski (1987) [42]	55.74	263	4.13
Wolf and Jeanloz (1985) [41]	56.13	270	3.86
Experiment			
Ono *et al* (2005) [38]	45.38	248 ± 8	4
Shim *et al* (2002) [39]	45.58	255 ± 5	4
Wang *et al* (1996) [8]	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) [40]	45.58 ± 0.07	352 ± 10	4

agree well with the latest theoretical result [17]. The pressure dependence of the volume for CaSiO$_3$ perovskite calculated with CA-PZ (Ceperley–Alder-Perdew–Zunger) [23, 43] 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, 8, 44] and theoretical data [5]. However, Jung and Oganov [16] overestimate the equation of state over a wide pressure range.

3.2. Elastic moduli

The single-crystal elastic properties of mantle minerals are essential for interpreting seismic wave velocities and their lateral variations. However, the single-crystal elastic constants of
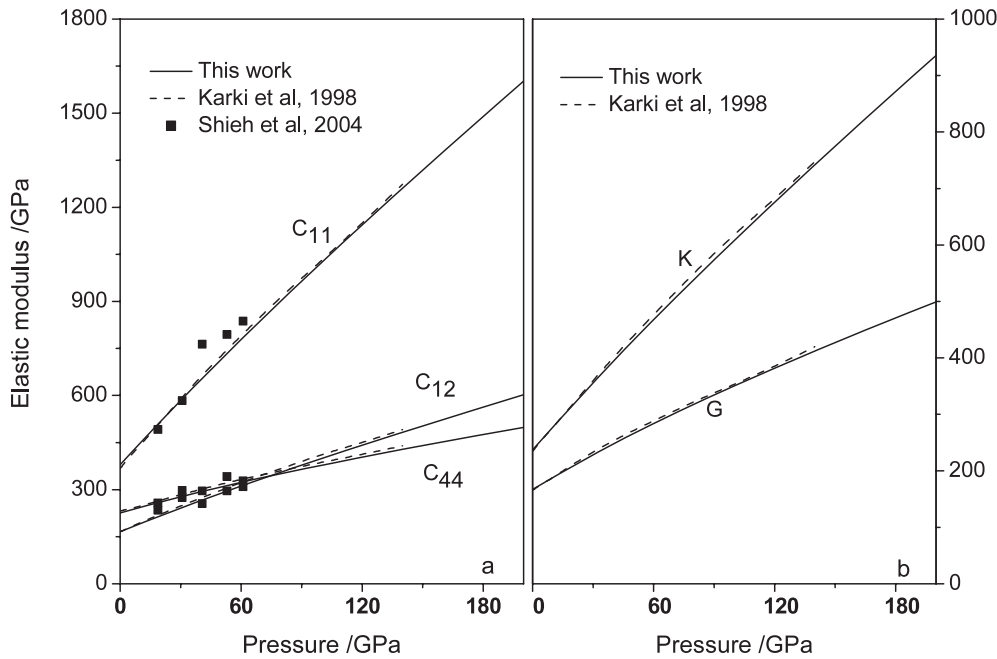
Figure 2. Pressure dependence of elastic modulus of $CaSiO_3$ perovskite. The solid lines represent the present results. The calculated values of Karki *et al* [5] are denoted by the dashed line. The experimental data are shown by the solid squares [6].

Table 2. Three elastic constants (c_{ij}), and bulk (K) and shear (G) moduli in GPa of $CaSiO_3$ perovskite compared with previous results at zero pressure.

Source	c_{11}	c_{12}	c_{44}	K	G
This work	380	166	225	237	167
Karki and Crain (1998) [5]	367	168	229	234	164
Sherman (1993) [45]	367	222	290	290	208

$CaSiO_3$ perovskite have not yet been measured in experiments at zero pressure. The calculated athermal elastic constants at zero pressure are shown in table 2 along with the previous calculations [5, 45]. It is seen that the calculated isotropic bulk modulus is consistent with the experimental value of 232 GPa [8]. There are not yet experimental data for the elastic constants and hence for the shear modulus. The periodic Hartree–Fock calculations [45] gave much higher bulk modulus and hence must have overestimated the shear modulus by several per cent. However, the calculated isotropic shear modulus is in excellent agreement with the previous one [5].

The effect of pressure on the elastic constants of $CaSiO_3$ perovskite is large, so theoretical results at ambient pressure cannot be used to reliably estimate the elasticity at mantle pressures. Therefore, we predict the high-pressure elastic constants of $CaSiO_3$ perovskite. The bulk modulus of an isotropic aggregate of cubic crystals is related to the elastic constant $K = (c_{11}+2c_{12})/3$. The pressure dependence of the isotropic aggregate shear modulus G of $CaSiO_3$ perovskite is obtained using the Voigt–Ruses–Hill [46] averaging scheme. In figure 2, the elastic constants of $CaSiO_3$ perovskite are shown as a function of pressure and compared with the experimental data [6]. The calculated values of local elastic constants of $CaSiO_3$ perovskite
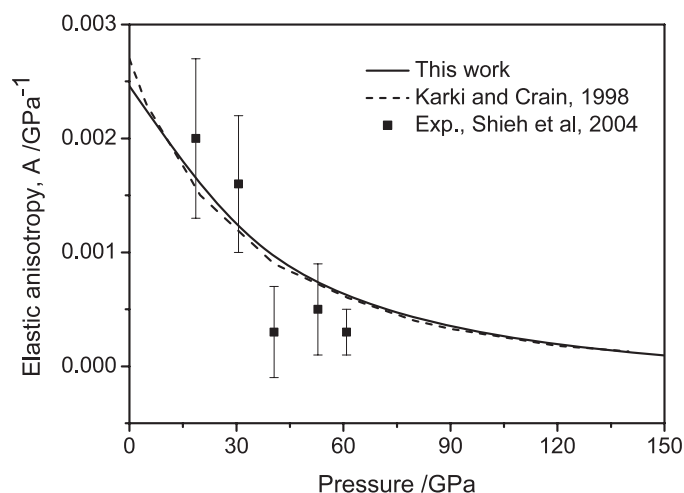
Figure 3. Pressure dependence of elastic anisotropy A of $CaSiO_3$ perovskite. The present elastic anisotropy is indicated by the solid line; the dashed line is the calculated values of Karki *et al* [5]. The solid squares are the experimental data of Shieh *et al* [6].

are slightly underestimated in comparison with the experimental values [6], which, however, are in good agreement with the recently theoretical data [5] over a wide pressure range.

The evolution of elastic anisotropy of the Earth's deep minerals with increasing pressure and temperature is of fundamental importance for the understanding of the seismic anisotropy of the Earth's interior. The elastic anisotropy of a cubic crystal can be described using $A = S_{11} - S_{12} - S_{44}/2$ [6]. The pressure dependence of the elastic anisotropy A of $CaSiO_3$ perovskite is shown in figure 3. The elastic anisotropy A drops rapidly with the increase of pressure initially, and then decreases more slowly at higher pressures. The theoretically predicted behaviour of $CaSiO_3$ perovskite is consistent with the experimental observations [6] and the previous calculations [5].

The Cauchy relation $c_{12} - c_{44} = 2P$ is valid only when all interatomic forces are central under static lattice conditions. At zero pressure, $c_{12} - c_{44}$ is equal to -59.6 GPa. As shown in figure 4, the value of Cauchy violation $c_{12} - c_{44} - 2P$ for $CaSiO_3$ perovskite is found to be large and negative and to increase in magnitude with increasing pressure (greater Cauchy violation). Our results are in good agreement with other ones [5]. The large violations of the Cauchy relation in $CaSiO_3$ perovskite require an important contribution from noncentral (many-body) forces. $CaSiO_3$ perovskite cannot be thought of as a material composed of rigid ions. Band-structure calculations indicate that $CaSiO_3$ remains a wide-gap insulator to pressures well beyond those in the mantle, and that covalent bonding is not important, so metallic binding or covalent forces cannot explain the Cauchy violations. The potential-induced breathing model appears to capture the essential physics, as this simplified model correctly predicts the Cauchy violation in the alkaline earth oxides [47, 48]. The relevant many-body force arises from a spherically symmetric breathing of the oxygen ion in response to strain-induced variations in the Madelung potential at the oxygen site.

3.3. Thermodynamic properties

In figure 5, we have displayed the relations of the bulk modulus of $CaSiO_3$ perovskite as a function of pressure up to 150 GPa at temperatures $T = 300$ K, 600 K, 1000 K, 1500 K, and
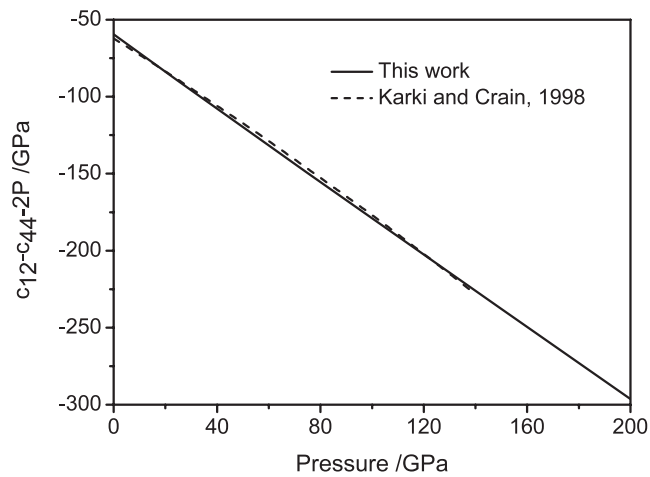
Figure 4. Pressure dependence of Cauchy violation of CaSiO$_3$ perovskite. The solid line is the present work; the dashed line represents the calculated values of Karki *et al* [5].
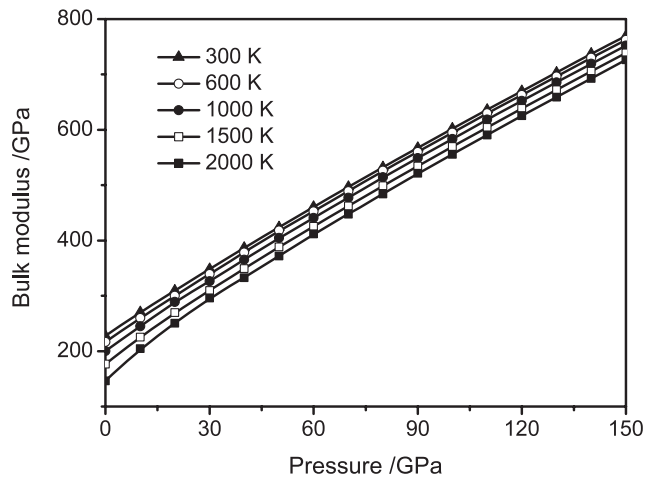

Figure 5. Pressure dependence of bulk modulus of CaSiO$_3$ perovskite. The isotherms at 300, 600, 1000, 1500, and 2000 K are represented by the solid lines from top to bottom.

2000 K, respectively. It is found that the relationships between bulk modulus and pressure are nearly linear at various temperatures of $T = 300$ K, 600 K, 1000 K, 1500 K, and 2000 K, respectively. The bulk modulus decreases with increasing temperature at a given pressure and increases with increasing pressure at a given temperature. These results are due to the fact that the effect of increasing pressure on the material is the same as that of decreasing temperature on the material.

The temperature and pressure dependences of the thermal expansion coefficient α of CaSiO$_3$ perovskite are shown in figure 6. It can be seen from figure 6(a) that the calculated thermal expansion coefficient α is in accord with the recently measured value [39] at ambient conditions and the latest calculations [17] at high pressures and temperatures are quite different from the experimental value [8] at zero pressure and 300 K. The thermal expansion coefficient α increases with T^3 at low temperatures and gradually approaches a linear increase at high
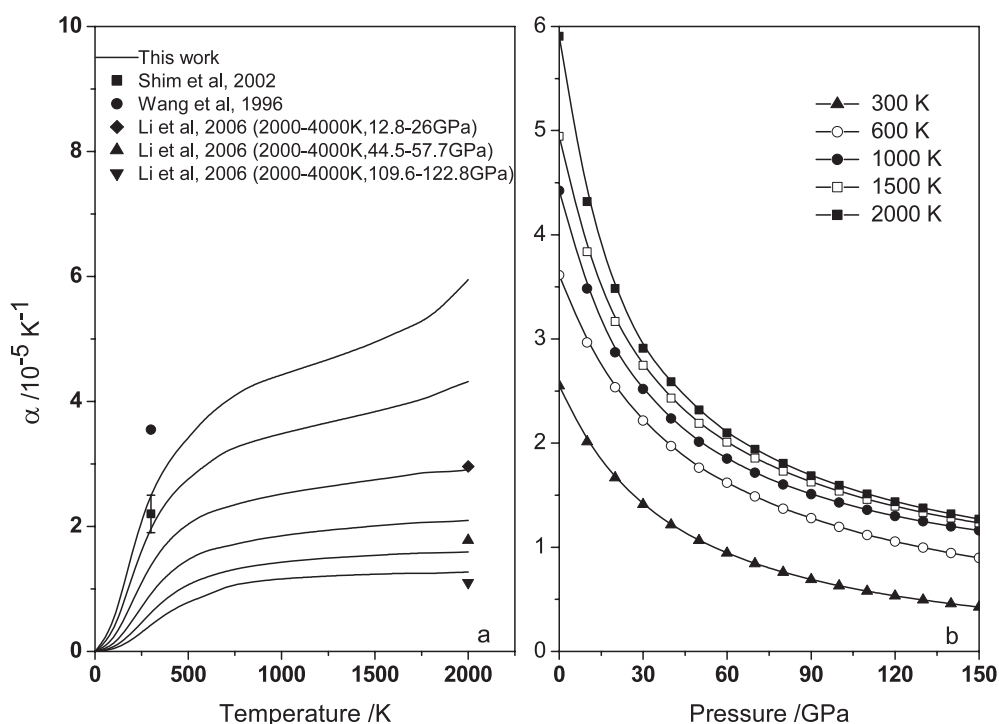
Figure 6. Temperature (a) and pressure (b) dependence of the thermal expansion coefficient α of CaSiO$_3$ perovskite. The isobars at 0, 10, 30, 60, 100, and 150 GPa are represented by the solid lines from top to bottom. The experimental values at ambient conditions of Shim *et al* [39] and Wang *et al* [8] are denoted by the solid squares and solid circle, respectively. The solid diamond, solid upper triangle and solid lower triangle are for the calculated data of Li *et al* [17] at high pressures and temperatures, respectively.

temperatures, and then the increasing trend becomes gentler. The effects of pressure on the thermal expansion coefficient α are very small at low temperatures; the effects are increasingly obvious as the temperature increases. As pressure increases, the thermal expansion coefficient α decreases rapidly and the effects of temperature become less and less pronounced, resulting in linear high-temperature behaviour. It is noteworthy that the high-temperature dependence of the thermal expansion coefficient α is not linear at low pressure (0 and 10 GPa); this is an indication of the inadequacy of the quasi-harmonic approximation at high temperatures and low pressures. It is shown that the thermal expansion coefficient α converges to a constant value at high temperatures and pressures. However, it is noted from figure 6(b) that, as the pressure increases, the thermal expansion coefficient α decreases almost exponentially, and the higher the temperature is, the faster the thermal expansion coefficient α decreases. This shows that the impact of temperature is much greater than the impact of pressure on the thermal expansion coefficient α of this material. These results are in accordance with the results of the Debye theory, which applies to many kinds of material.

The heat capacity at a constant pressure C_P of CaSiO$_3$ perovskite vary with temperature T and pressure P as displayed in figure 7. The calculated value of C_P at ambient conditions is 84.29 J mol^{-1} K^{-1}, compared to the experimental value of $C_P = 85.3$ J mol^{-1} K^{-1} [49]. Figure 7 illustrates that the anharmonic effects are suppressed at high pressures and C_P is very close to a constant value at high pressures and temperatures.
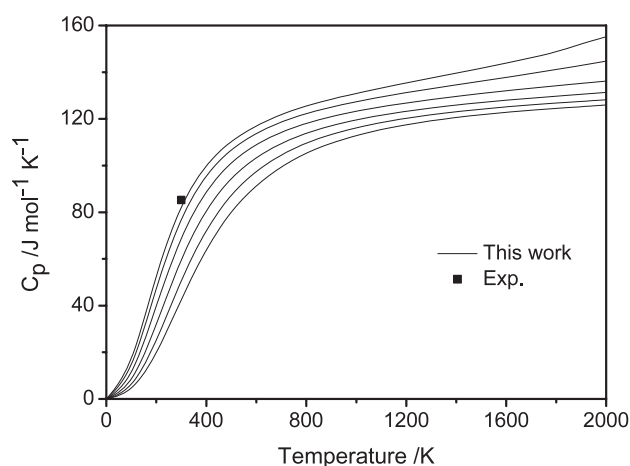
Figure 7. Temperature dependence of the heat capacity C_P of CaSiO$_3$ perovskite. The isobars at 0, 10, 30, 60, 100, and 150 GPa are represented by the solid lines from top to bottom. The experimental value at zero pressure and 300 K is denoted by a solid square [49].

4. Conclusions

First-principles plane wave pseudopotential calculations are performed for the analysis of the structural properties of CaSiO$_3$ perovskite under high-pressure conditions. Our calculated elastic moduli at pressures up to 200 GPa are in good agreement with the available experimental data and the previous calculations at high pressures. The calculated elastic anisotropy is consistent with the experimental observations and the previous calculations. Furthermore, the value of Cauchy violation is found to be large and negative and to increase in magnitude with increasing pressure. The thermodynamic properties of CaSiO$_3$ perovskite are predicted using the quasi-harmonic Debye model. We see that the predicted heat capacity and thermal expansion coefficient α are in accordance with the observed values at ambient conditions and the other calculations at high pressures and temperatures. The thermal expansion coefficient α and heat capacity are shown to converge to a nearly constant value at high pressures and temperatures.

Acknowledgments

References

[1] Fiquet G 2001 *Z. Kristallogr.* **216** 248
[2] Irifune T 1994 *Nature* **370** 131
[3] Ita J J and Stixrude L 1992 *J. Geophys. Res.* **97** 6849

[4]   Kung J, Angel R J and Ross N L 2001 *Phys. Chem. Miner.* **28** 35
[5]   Karki B B and Crain J 1998 *Geophys. Res. Lett.* **25** 2741
[6]   Shieh S R, Duffy T S and Shen G Y 2004 *Phys. Earth Planet. Inter.* **143** 93
[7]   Mao H K, Chen L C, Hemley R J, Jephcoat A P, Wu Y and Bassett W A 1989 *J. Geophys. Res.* **94** 17889
[8]   Wang Y, Weidner D J and Guyot F 1996 *J. Geophys. Res.* **101** 661
[9]   Hemley R J, Jackson M D and Gordon R G 1987 *Phys. Chem. Minerals* **14** 2
[10] Sherman D M 1993 *J. Geophys. Res.* **98** 19795
[11] Wentzcovitch R, Ross N L and Price G D 1995 *Phys. Earth Planet. Inter.* **90** 101
[12] Warren M C, Ackland G J, Karki B B and Clark S J 1998 *Mineral. Mag.* **62** 585
[13] Kurashina T, Hirose K, Ono S, Sata N and Ohishi Y 2004 *Phys. Earth Planet. Inter.* **145** 67
[14] Chizmeshya A V G, Wolf G H and McMillan P F 1996 *Geophys. Res. Lett.* **23** 2725
[15] Stixrude L, Cohen R E, Yu R and Krakauer H 1996 *Am. Mineral.* **81** 1293
[16] Jung D Y and Oganov A R 2005 *Phys. Chem. Minerals* **32** 146
[17] Li L, Weidner D J, Brodholt J, Alfè D, Price G D, Caracas R and Wentzcovitch R 2006 *Phys. Earth Planet. Inter.*
       155 249
[18] Akber-Knutson S, Bukowinski M S T and Matas J 2002 *Geophys. Res. Lett.* **29** 4
[19] Magyari-Köpe B, Vitos L, Grimvall G, Jonasson B and Kollar J 2002 *Phys. Rev.* B **65** 193107
[20] Magyari-Köpe B, Vitos L, Johansson B and Kollar J 2002 *Comput. Mater. Sci.* **25** 615
[21] Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864
[22] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133
[23] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[24] Hamann D R, Schluter M and Chiang C 1979 *Phys. Rev. Lett.* **43** 1494
[25] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[26] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[27] Fischer T H and Almlof J 1992 *J. Phys. Chem.* **96** 9768
[28] Wentzcovitch R M, Martins J L and Price G D 1993 *Phys. Rev. Lett.* **70** 3947
[29] Karki B B, Stixrude L, Clark S J, Warren M C, Ackland G J and Crain J 1997 *Am. Mineral.* **82** 52
[30] Payne M C, Teter M P, Allan D C, Arias T A and Joannopolous J D 1992 *Rev. Mod. Phys.* **64** 1045
[31] Blanco M A, Francisco E and Luaña V 2004 *Comput. Phys. Commun.* **158** 57
[32] Blanco M A, Martín Pendás A, Francisco E, Recio J M and Franco R 1996 *J. Mol. Struct. Theochem.* **368** 245
[33] Flórez M, Recio J M, Francisco E, Blanco M A and Martín Pendás A 2002 *Phys. Rev.* B **66** 144112
[34] Poirier J P 2000 *Introduction to the Physics of the Earth's Interior* (Cambridge: Cambridge University Press)
[35] Francisco E, Recio J M, Blanco M A and Martín Pendás A 1998 *J. Phys. Chem.* **102** 1595
[36] Francisco E, Sanjurjo G and Blanco M A 2001 *Phys. Rev.* B **63** 094107
[37] Birch F 1978 *J. Geophys. Res.* **83** 1257
[38] Ono S, Ohishi Y and Mibe K 2005 *Am. Mineral.* **89** 1480
[39] Shim S H, Jeanloz R and Duffy T S 2002 *Geophys. Res. Lett.* **29** 242166
[40] Tamai H and Yagi T 1989 *Phys. Earth Planet. Inter.* **54** 370
[41] Wolf G H and Jeanloz R 1985 *Geophys. Res. Lett.* **12** 413
[42] Wolf G H and Bukowinski M S T 1987 *High-Pressure Research in Mineral Physics* (Tokyo: Terra Scientific)
[43] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
[44] Shim S H, Duffy S and Shen G 2000 *Phys. Earth Planet. Inter.* **120** 327
[45] Sherman D M 1993 *J. Geophys. Res.* **98** 19795
[46] Hill R 1952 *Proc. Phys. Soc.* A **65** 349
[47] Isaak D G, Cohen R E and Mehl M E 1990 *J. Geophys. Res.* **95** 7055
[48] Mehl M J, Hemley R J and Boyer L L 1986 *Phys. Rev.* B **33** 8685
[49] Ahrens T J 1995 *Mineral Physics and Crystallography: a Handbook of Physical Constants* (Washington:
       American Geophysical Union)