

HEAT CAPACITY OF MgSiO_3 PEROVSKITE

Masaki Akaogi

Department of Chemistry, Gakushuin University, Tokyo, Japan

Eiji Ito

Institute for Study of the Earth's Interior, Okayama University, Misasa, Japan

Abstract. Heat capacity of MgSiO_3 perovskite has been measured in the temperature range 140-295 K by differential scanning calorimetry. The Kieffer model approach has been used to calculate the heat capacity beyond the measured temperature range. The estimated entropy of MgSiO_3 perovskite is 57.2 ± 1.0 J/mol.K at 298 K which is higher than that of ilmenite, in accord with the negative pressure-temperature slope for the ilmenite-perovskite transition. From the heat capacity thermodynamic Debye temperature of MgSiO_3 perovskite is evaluated to be 980 ± 15 K at 298 K and 1030 ± 20 K at temperatures above about 700 K. Thermodynamic Gruneisen parameter of MgSiO_3 perovskite at 30 GPa and above 1000 K is also estimated as 1.45 ± 0.15 . An adiabatic temperature profile in the pyrolitic lower mantle is calculated with the average gradient of 0.32 ± 0.04 K/km. The temperature at the top of the D" layer is estimated to be 2500 ± 100 K.

Introduction

Magnesium-rich (Mg, Fe) SiO_3 perovskite is accepted to be the most abundant constituent mineral in the lower mantle [e.g. Ito and Takahashi, 1989]. Thermophysical and thermochemical properties of the silicate perovskite are of essential importance to calculate the phase relations and to estimate the thermal state in the lower mantle. Although heat capacity is a fundamental thermodynamic quantity which allows us to calculate entropy, Debye temperature, Gruneisen parameter etc., no experimental measurement has been made on the silicate perovskite. In this study we have measured directly the isobaric heat capacity (C_p) of MgSiO_3 perovskite in the temperature range of 140-295 K at 1 bar. The heat capacity of MgSiO_3 perovskite at 0-1000 K is also calculated by the Kieffer's lattice vibrational model. The entropy and thermodynamic Debye temperature of perovskite are calculated directly from the heat capacity. Thermodynamic Gruneisen parameter of perovskite at high pressure is also estimated using the heat capacity, and is used to calculate an adiabatic geotherm in the lower mantle.

Experimental Method

MgSiO_3 orthorhombic perovskite of about 12 mg was synthesized at 25 GPa and 1950 K using a uniaxial split-sphere apparatus [Ito and Yamada, 1982] from a starting material of synthetic MgSiO_3 orthopyroxene provided by Dr. M. Ozima. The starting material was put into a tubular rhenium furnace. Microfocused x-ray diffraction analysis

showed that the high-temperature central part of the run products was perovskite, while the low-temperature margins consisted of the low-pressure phases. The margins of the products were removed completely. The powder x-ray diffraction of the pulverized perovskite part showed the single phase perovskite. Microscopic observation, however, indicated perovskite plus very small amount (<1%) of impurities (ilmenite and rhenium). A differential scanning calorimeter [Akaogi et al., 1990] was used for the heat capacity measurements of MgSiO_3 perovskite and orthopyroxene in the temperature range of 140-295 K. The sample temperature was measured by a chromel-alumel thermocouple in the calorimeter with the accuracy of ± 1 K. The maximum temperature of 295 K in the present measurements was selected to avoid retrograde phase change of perovskite which was observed at temperatures above about 400 K [Parise et al., 1990; Ito and Akaogi, unpublished data, 1988]. The powdered sample (11.48 mg for perovskite and 14.20 mg for orthopyroxene) was packed in a tightly crimped aluminum pan. Pure $\alpha\text{-Al}_2\text{O}_3$ powder was used as the heat capacity standard. The sample in the differential scanning calorimeter was first cooled by liquid nitrogen, and then the heat capacity was measured at constant heating rate of 5 or 10 K/min in argon gas flow with the sensitivity of 20 mJ/s. The heat capacity data were collected at the interval of 5 K. The sample and standard $\alpha\text{-Al}_2\text{O}_3$ were measured alternately. Nine and seven measurements for perovskite and orthopyroxene, respectively, were repeated and averaged, with the average reproducibility of ± 1.0 % for perovskite and ± 0.9 % for orthopyroxene. No correction to the heat capacity was made for presence of the very small amount of impurities. Powder x-ray diffraction and microscopic observation showed no change in the perovskite sample after the heat capacity measurements in the present temperature range.

Measured and Calculated Heat Capacities

Figure 1 illustrates the measured heat capacities of MgSiO_3 perovskite and orthopyroxene. The present data of orthopyroxene are in excellent agreement with those measured by adiabatic calorimetry [Krupka et al., 1985], confirming accuracy of the measurements in this study. The heat capacity of MgSiO_3 perovskite is smaller than that of orthopyroxene in the measured temperature range. The difference between the two phases decreases with increasing temperature, suggesting a possible cross-over at a temperature around 400 K. The heat capacity of perovskite is very close to that of ilmenite [Ashida et al., 1988] at about 170-200 K, above which it exceeds ilmenite.

Since the heat capacity of MgSiO_3 perovskite was measured only at temperatures 140-295 K, C_p was estimated beyond the measured temperature range using the Kieffer's

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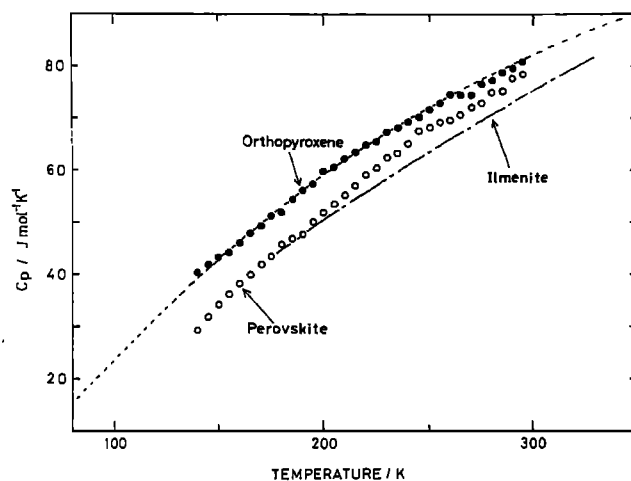


Fig. 1. Heat capacities of MgSiO₃ perovskite and orthopyroxene. Open and closed symbols represent measured heat capacities of perovskite and orthopyroxene, respectively. A dashed curve and dash-dot line show the data of orthopyroxene by Krupka et al. (1985) and ilmenite by Ashida et al. (1988), respectively.

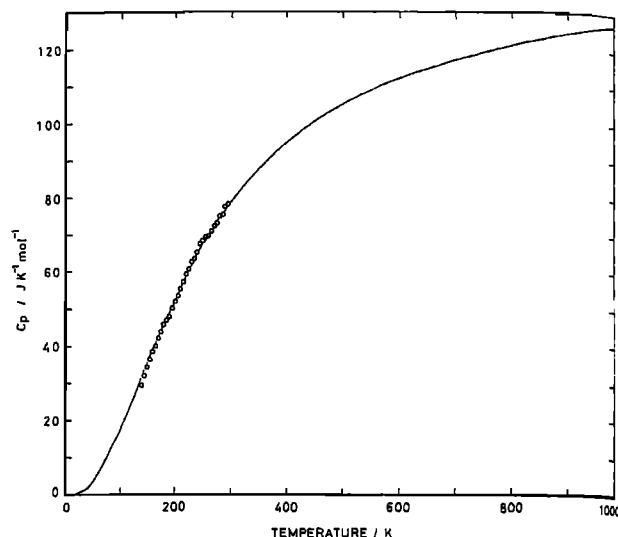


Fig. 2. Measured and calculated heat capacities of MgSiO₃ perovskite. Open symbols represent the measured heat capacities. A solid curve shows the calculated heat capacity by the Kieffer model.

model approach [Kieffer, 1979a,b,c, 1980]. In the Kieffer model isochoric heat capacity (C_V) is calculated using the vibrational model which consists of three acoustic modes and several optic continua. The calculated C_V is converted to C_P by the relation $C_P = C_V + \alpha^2 K_T V T$, where α and K_T are volume thermal expansivity and isothermal bulk modulus, respectively, and V is volume. The parameters used in the Kieffer model calculation are listed in Table 1. A single optic continuum was adopted in the present vibrational model with the upper- and lower-cutoff frequencies, ω_u and ω_l , respectively. The ω_u was determined to be 900 cm⁻¹ from the zero-pressure infrared and Raman spectra [Williams et al., 1989; Hemley et al., 1989; Madon and Price, 1989]. The calculated C_P was fitted to the measured C_P by varying the ω_l , because the ω_l could not be estimated accurately from the measured vibrational spectra. The determined ω_l was 210 cm⁻¹. Fractions of the optic mode and acoustic modes were 0.95 and 0.05, respectively, for the orthorhombic perovskite [Navrotsky, 1989]. Figure 2 shows that the calculated C_P is in good agreement with the measured C_P within $\pm 2\%$ except for the data point at 140 K. It should be noted that the calculated C_P below 300 K is not affected by the adopted values of α and K_T , because the $\alpha^2 K_T V T$ term is negligible in this temperature range.

Discussion

The entropy of MgSiO₃ perovskite is calculated to be 57.2 ± 1.0 and 188.5 ± 2.5 J/mol·K at 298 and 1000 K, respectively, by the equation $\int_0^T C_P/T dT$ using the heat capacity calculated above. The entropy of MgSiO₃ ilmenite was also calculated by the Kieffer model: 54.1 ± 0.5 and 182.4 ± 1.8 J/mol·K at 298 and 1000 K, respectively [Hofmeister and Ito, 1992]. These calculations show positive entropy changes of about 3–6 J/mol·K for the ilmenite-perovskite transition at the two temperatures. The positive entropy change of about 9 ± 3 J/mol·K at 1000 K is also calculated for the dissociation of Mg₂SiO₄ spinel to MgSiO₃ perovskite plus MgO, using the present entropy of perovskite and the previous data for spinel and MgO [Robie et al., 1978; Akaogi et al., 1989]. The positive entropy changes for both of the transitions are generally consistent with the negative P-T slopes for the ilmenite-perovskite transition and the spinel dissociation reaction determined experimentally by Ito and Takahashi [1989].

Thermodynamic Debye temperature (θ_D) of MgSiO₃ perovskite is calculated by applying the Debye model to the heat capacity (C_V) calculated above. Figure 3 shows the θ_D vs. temperature. The θ_D is 980 ± 15 K at 298 K and 1030 ± 20 K at temperatures above about 700 K. The thermodynamic

Table 1. Physical properties used for the Kieffer model calculation of heat capacity of MgSiO₃ perovskite.

V_{298}	24.44 cm ³ /mol	[1]	$\alpha = a_0 + a_1 T + a_2 T^{-2}$, K ⁻¹	
K_T	246 GPa	[2]	$a_0 = 3.01 \times 10^{-5}$	[3]
dK_T/dP	4	[3]	$a_1 = 1.50 \times 10^{-8}$	[3]
dK_T/dT	-6.3×10^{-2} GPa/K	[3]	$a_2 = -1.14$	[3]
v_1	6.550 km/s	[4]	ω_u 900 cm ⁻¹	[5]
v_2	6.842 km/s	[4]	ω_l 210 cm ⁻¹	[5]
v_3	10.940 km/s	[4]		

1: Ito and Yamada [1982]; 2: Yeganeh-Haeri et al. [1989]; 3: Mao et al. [1991];
4: directionally averaged velocities by the method of Kieffer [1979a] using the elastic data by Yeganeh-Haeri et al. [1989]; 5: see text.

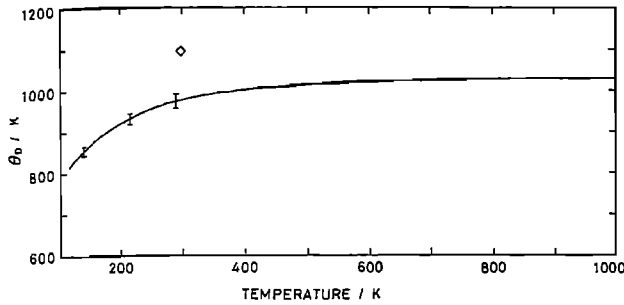


Fig. 3. Debye temperature of MgSiO₃ perovskite. A solid curve shows thermodynamic Debye temperature vs. temperature. Error bars with the solid curve represent uncertainties in the thermodynamic Debye temperature due to $\pm 2\%$ change in the heat capacity. A diamond shows the elastic Debye temperature at 298 K, estimated from the elastic constants [Yeganeh-Haeri et al., 1989].

Debye temperature estimated previously by the various methods spans a range from 525 to 1340 K [Knittle et al., 1986; Williams et al., 1989; Hemley et al., 1989]. The present θ_D is much more tightly constrained, based on the direct measurement of the heat capacity. At 298 K this thermodynamic θ_D is about 115 K smaller than the elastic Debye temperature (1094 K) from the elastic properties of MgSiO₃ perovskite [Yeganeh-Haeri et al., 1989].

Using the present heat capacities, thermodynamic Grüneisen parameter (γ_{th}) can be estimated by the equation

$$\gamma_{th} = \alpha V K_S / C_p = \alpha V K_T / C_v,$$

where K_S is adiabatic bulk modulus. Since thermal expansion of MgSiO₃ perovskite at 1 bar and high temperature is in controversy [Knittle et al., 1986; Wang et al., 1991], we use thermal expansivity at high pressure and high temperature, recently measured by Mao et al. [1991]: the thermal expansivity is approximated as $\alpha = 1.56 \times 10^{-5} + 7.8 \times 10^{-9} T$ at 30 GPa and temperatures above 1000 K with the estimated uncertainty of $\pm 10\%$. Since effect of compression on C_v is negligible near and above θ_D , C_v at 1 bar is used for the γ_{th} calculation. The bulk modulus and its pressure and temperature dependences in Table 1 are also used. The calculated γ_{th} is 1.45 ± 0.15 at 30 GPa and temperatures above 1000 K, which is smaller than the previous values at 1 bar, 1.7–2.2, estimated from thermal expansion measurements [Knittle et al., 1986] and spectroscopic studies [Williams et al., 1989; Hemley et al., 1989].

It is generally accepted that temperature distribution in the convecting mantle is close to adiabatic [e.g. Jeanloz and Morris, 1986]. The adiabatic temperature gradient is given by the equation $(dT/dP)_S = \gamma_{th} / K_S$. We assume the lower mantle with pyrolite composition to be approximated as a mixture of 1 part (Mg,Fe)SiO₃ orthorhombic perovskite and 1/2 part (Mg,Fe)O in molar ratio. It is also assumed that structural phase transitions of the orthorhombic perovskite do not occur in the lower mantle and that γ_{th} and K_S of perovskite and magnesiowüstite do not change significantly with small degree of Mg-Fe substitution. Since γ_{th} is generally insensitive to temperature above θ_D , volume dependence of γ_{th} is only considered in the calculation: $\gamma_{th}/\gamma_{th,r} = (V/V_r)^4$, where $\gamma_{th,r}$ and V_r are Grüneisen parameter and volume, respectively, at reference condition. As the reference Grüneisen parameter at 30 GPa above 1000 K, we adopt 1.45 ± 0.15 for perovskite estimated in this study and

1.25 ± 0.03 for MgO [Anderson et al., 1992]. The bulk modulus and the pressure and temperature dependences of perovskite are from Table 1 with conversion of K_T to K_S , and those of magnesiowüstite are from Anderson et al. [1992]. The q parameter is assumed to be unity. Effects of pressure and temperature on volume are calculated by the same method as that in Akaogi et al. [1989]. The temperature of 1873 K at 655 km depth in the mantle [Ito and Katsura, 1989] is adopted to anchor the adiabatic temperature profile. A temperature change associated with the spinel dissociation reaction ($\Delta T \sim 65$ deg) is estimated by the previous method [Navrotsky and Akaogi, 1984] and included in the calculation of the temperature profile. Figure 4 shows the adiabatic temperature profile for the pyrolitic upper and lower mantle. The average gradient in the lower mantle is 0.32 ± 0.04 K/km. We emphasize that this temperature distribution is based on the measured thermodynamic properties of the major constituent minerals of the lower mantle, without theoretical estimation from the seismic velocities. This gradient is a little higher than 0.27 K/km estimated by Brown and Shankland [1981] from the seismic velocity model. The temperature at depth of the top of the D'' layer is estimated as 2500 ± 100 K in this study.

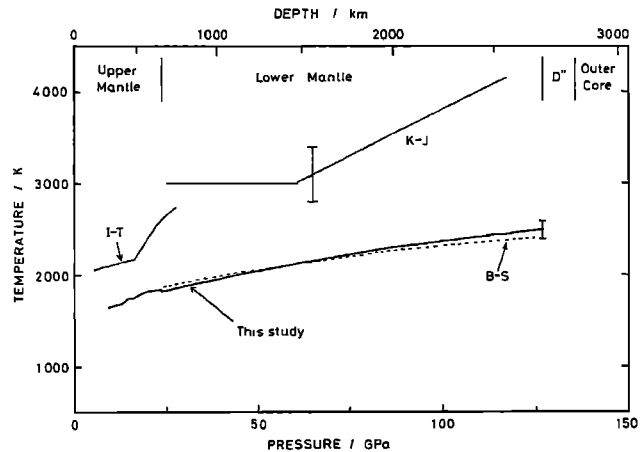


Fig. 4. The adiabatic temperature profile in the pyrolitic mantle. The profile in the lower mantle is calculated in this study, while that in the upper mantle by the previous studies [Akaogi et al., 1989; Ito and Katsura, 1989]. B-S shows the adiabatic geotherm by Brown and Shankland [1981]. I-T and K-J show, respectively, solidus of dry peridotite [Ito and Takahashi, 1987] and melting curve of (Mg_{0.9}Fe_{0.1})SiO₃ perovskite with the uncertainty [Knittle and Jeanloz, 1989].

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M. Akaogi, Department of Chemistry, Gakushuin University, Toshima-ku, Tokyo, 171 Japan.

E. Ito, Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken, 682-02 Japan.

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