LETTER

Thermal expansion of brucite, Mg(OH)$_2$

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Abstract

The lattice parameters of brucite, Mg(OH)$_2$, have been measured between 20 and 310 °C at atmospheric pressure. The thermal expansion is strongly anisotropic with a high coefficient of linear expansion (α_3) parallel to the **z** axis. This leads to an overall volume coefficient of expansion (average of 10.9×10^{-5}/K) that is several times greater than estimates based on amphiboles and other hydrous minerals. Our results for the individual expansion coefficients are $\alpha_1 = \alpha_2 = 1.73 \times 10^{-5} - 0.13 \times 10^{-7}T \pm 0.17 \times 10^{-5}$, $\alpha_3 = 3.23 \times 10^{-5} + 2.65 \times 10^{-7}T \pm 0.32 \times 10^{-5}$, and $\alpha_{vol} = 6.70 \times 10^{-5} + 2.37 \times 10^{-7}T \pm 0.67 \times 10^{-5}$, where T is the temperature between 20 and 310 °C.

Introduction

The stabilities of hydrous phases at high pressure and temperature control the compositions and behavior of many of the fluids that attend geologic processes. Interest in the role of H$_2$O in mantle processes has been stimulated recently by suggestions that its concentration in the Earth is much higher than previously believed (Liu, 1987; Ahrens, 1989), as well as by observations that nominally anhydrous mantle phases may contain appreciable H$_2$O (Aines and Rossman, 1984; Smyth, 1987). In addition, dense high-pressure hydrated silicates (Ringwood and Major, 1967) and brucite, Mg(OH)$_2$, may store H$_2$O in the deepest parts of the mantle, particularly in the *P-T* regimes present in subduction zones. Our work was stimulated by recent shock wave measurements (Duffy et al., 1991) and calculations (Sherman, 1991) of the equation of state of brucite. Both studies suggested that brucite is extremely compressible ($K_s = 51$ GPa), which implies that the brucite hydration reaction should have a positive dP/dT to very high pressures. Apart from the (recently ignored) pioneering work of Megaw (1933), no study has been made of the temperature dependence of the thermal expansion of brucite, and hence there is no unequivocal way of using the shock wave data, which depend on assumptions about the Gruneisen relation. We therefore set out to determine the thermal expansion of brucite as a function of temperature at 1 atm.

The most recent refinement of the crystal structure of brucite was carried out by Zigan and Rothbauer (1967). It has a layer structure and comprises sheets of hexagonally close-packed OH ions with Mg bonded (principally ionically) to six OH. The sheets are parallel to (0001) in the $P\bar{3}m1$ structure. These Mg(OH)$_2$ sheets are bonded to one another by weak OH-OH dipole forces.

In this study, the high-temperature lattice parameters of brucite are presented in the temperature range 20–310 °C at atmospheric pressure, conditions below the dehydration reaction. The temperature-dependent thermal expansion is calculated in the same temperature range, and the results discussed in the light of related work.

Experimental details and results

Brucite was synthesized by hydrothermal recrystallization of reagent grade MgO. This material was ground by hand in an agate mortar and sealed in air at atmospheric pressure in a glass capillary of 0.7-mm diameter. The capillary was placed at the oscillation center of a Huber 620 heating Guinier camera, surrounded by a U-form horseshoe heater. High-resolution powder X-ray diffraction patterns were collected isothermally at nine temperatures between room temperature and 310 °C; 20 °C above that highest temperature the capillary seal failed, and the brucite began to dehydrate to periclase.

Powder diffraction maxima were measured to a precision of 0.005° 2θ and an accuracy of ±0.01° 2θ using a video traveling microscope system. Lattice parameters were refined by standard least-squares methods with a typical error of one part in 1000.

Temperature measurement was carried out using a Pt-Rh thermocouple placed in contact with the top of the glass capillary. The heating apparatus and sample were enclosed in Kapton shielding, and temperature stability was maintained to within ±2 °C of the set temperature using a linearized temperature controller. The tempera-

TABLE 1. Unit-cell parameters of brucite as a function of temperature

T (°C)	a (Å)	c (Å)	Volume (Å³)
20	3.149	4.749	40.77
56	3.150	4.757	40.88
93	3.152	4.769	41.04
129	3.154	4.776	41.15
165	3.156	4.789	41.30
202	3.157	4.806	41.48
238	3.159	4.818	41.65
274	3.161	4.833	41.83
310	3.162	4.858	42.06

ture calibration of the furnace was determined by the measurement of critical temperatures of phase transitions in standards (benzoic acid and sodium nitrate) through the temperature region of interest.

The refined unit-cell parameters of brucite as a function of temperature are given in Table 1 and presented graphically in Figure 1. These data have been fitted by linear least-squares analysis to a second-order polynomial to obtain

$$a = 3.1473 + 5.431 \times 10^{-5}T$$
$$- 2.049 \times 10^{-8}T^2 \pm 0.003 \text{ Å} \quad (1)$$

$$c = 4.7468 + 1.510 \times 10^{-4}T$$
$$+ 6.494 \times 10^{-7}T^2 \pm 0.015 \text{ Å} \quad (2)$$

$$V = 40.720 + 2.701 \times 10^{-3}T$$
$$+ 5.130 \times 10^{-6}T^2 \pm 0.12 \text{ Å}^3 \quad (3)$$

where T is the temperature over the range 20–310 °C.

The increase in cell volume between room temperature and 310 °C is 3.2%. This is related to the linear thermal expansions of the a and c cell edges, which are described by the principal coefficients of the thermal expansion representation quadric. The anisotropy of the thermal expansion is evident, and the c/a ratio is not constant but varies with temperature between 1.508 and 1.537 at the lower and upper temperature ranges of the experiments, respectively (Fig. 2), and fits a second-order polynomial of the form $c/a = 1.508 + 2.18 \times 10^{-5}T + 2.16 \times 10^{-7}T^2$. The instantaneous isobaric thermal expansion is related to the unit-cell parameter, x, and may be approximated as $\alpha_x = (1/x_0)(\partial x/\partial T)_P$ where x_0 is a reference lattice constant at T_0 °C. This may be obtained directly from the expression for the temperature dependence of the unit-cell parameters and unit-cell volume by taking the first derivative of those expressions to give

$$\alpha_1 = \alpha_2 = 1.73 \times 10^{-5} - 0.13 \times 10^{-7}T$$
$$\pm 0.17 \times 10^{-5} \quad (4)$$

$$\alpha_3 = 3.23 \times 10^{-5} + 2.65 \times 10^{-7}T$$
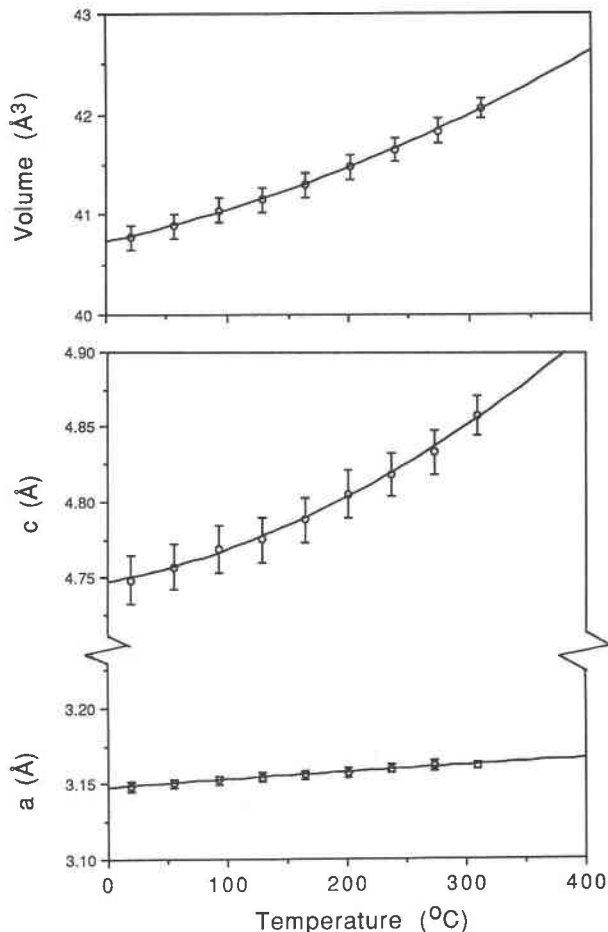$$\pm 0.32 \times 10^{-5} \quad (5)$$

Fig. 1. The lattice parameters of brucite as a function of temperature. Error bars represent $\pm 2\sigma$.

$$\alpha_{vol} = 6.70 \times 10^{-5} + 2.37 \times 10^{-7}T$$
$$\pm 0.67 \times 10^{-5} \quad (6)$$

where T is the temperature between 20 and 310 °C. If one takes into account the accuracy of the temperature control and measurement, the thermal expansion coefficients of the unit-cell edges and unit-cell volume are accurate to within approximately 10%. The thermal expansion (both linear expansion parallel and perpendicular to the z axis as well as the volume expansion) is itself strongly dependent upon temperature (Fig. 3). These measurements compare favorably with the average thermal expansion (between room temperature and 100 °C) determined by Megaw (1933) for a natural sample (her values: $\alpha_1 = 1.10 \pm 0.15 \times 10^{-5}$, $\alpha_3 = 4.47 \pm 0.20 \times 10^{-5}$). It is interesting to note that the measured thermal expansion is far greater in brucite than in either periclase or hornblende (data that were used to model the behavior of brucite by Duffy et al., 1991) and is approximately 1 order of magnitude greater than that estimated for brucite by Saxena (1989) on the basis of C_P and phase equilibrium data.
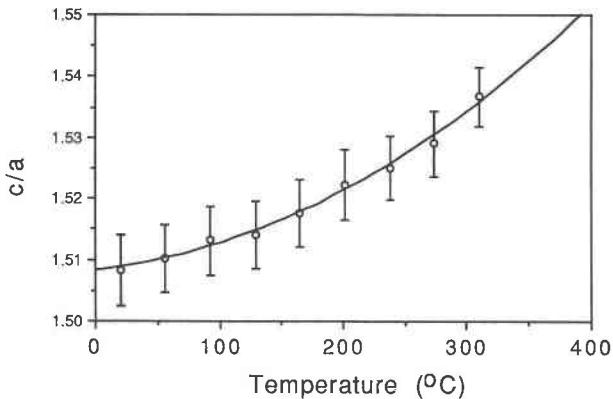
Fig. 2. The variation with temperature of the axial ratio (c/a) of the unit cell of brucite.

Fig. 3. The temperature dependence of the linear (α_1 and α_3, shown dashed) and volume (α, solid line) isobaric thermal expansion coefficients of brucite. The marked anisotropy in thermal expansion is evident.

Thermal expansion in minerals has been very often described in terms of a mean value, averaged over a wide range of temperature (usually the range of temperature of the particular study; see for example Cameron et al., 1973). Such an average thermal expansion may be defined as $\bar{\alpha}_x = \Delta x/(x_0/\Delta T)$ and is often given the abbreviation MTEC (mean thermal expansion coefficient). MTEC values for brucite over the temperature range of this study are

$$\bar{\alpha}_1 = \bar{\alpha}_2 = 1.45 \times 10^{-5}/\text{K} \qquad (7)$$

$$\bar{\alpha}_3 = 7.96 \times 10^{-5}/\text{K} \qquad (8)$$

$$\bar{\alpha}_{\text{vol}} = 10.9 \times 10^{-5}/\text{K} \qquad (9)$$

which conform to the general criterion that $\bar{\alpha}_{\text{vol}} = \bar{\alpha}_1 + \bar{\alpha}_2 + \bar{\alpha}_3$. The considerable temperature variation of the instantaneous isobaric thermal expansion (Eqs. 4, 5, 6) indicates the caution with which such mean values must be applied.

DISCUSSION

The results show that the thermal expansion of brucite is considerably higher than previous estimates. The value for the average volume coefficient of expansion is, for example, several times greater than the estimates of Duffy et al. (1991), Berman (1988), and Holland and Powell (1990). In addition, the thermal expansion is seen to be strongly anisotropic. This may be understood in terms of the weak dipole-dipole interaction between the $Mg(OH)_2$ layers of the brucite structure, which is susceptible to enhanced anharmonic extension with increasing temperature, and hence explains the high coefficient of linear expansion (α_3) parallel to the z axis. In contrast the relatively strongly polarizing character of the Mg^{2+} cation ensures ionic Mg-OH bonding within the layers and smaller linear thermal expansion parallel to the layers (α_2 and α_3). The high volume expansion is principally the result of the increased layer separation within the brucite structure with increasing temperature, which itself becomes more pronounced as the brucite-periclase reaction temperature is approached from below. An increase in lattice defects
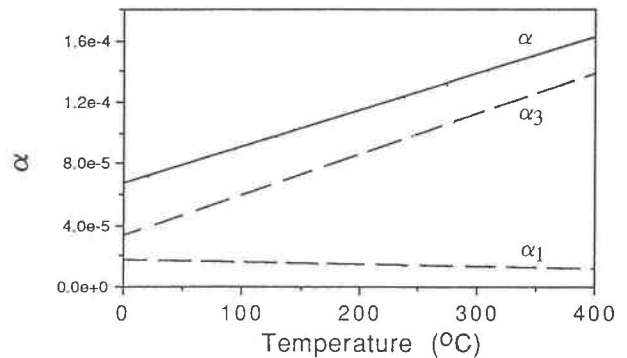
as a precursor stage to the dehydration reaction might account for some of the increased thermal expansion at the upper temperature range of this study, since incremental changes in entropy can be related directly to α.

Duffy et al. (1991) reported a Gruneisen parameter γ_0 of 0.43 ± 0.40 for brucite and observed that the third-order Birch-Murnaghan equation of state and the shock-wave equation of state cannot be equivalent descriptions of this phase. Their calculation was, however, based on an assumed value of α of $2.5 \times 10^{-5}/\text{K}$ and our value of $6.75 \times 10^{-5}/\text{K}$ at room temperature would yield γ_0 of 1.16 and much closer agreement between the two equations of state. Recent measurements of brucite breakdown to periclase and H_2O indicate that it is stable to about 1200 °C at 10 GPa (Johnson et al., 1991) and that the dehydration reaction does not have a strong negative slope at higher pressures. Johnson and Walker (in preparation) show a slightly positive slope for this reaction to 15 GPa. Combination of these results and our thermal expansion data on brucite should provide a good measure of the P-V-T properties of H_2O at pressures above 10 GPa. Experimental data on H_2O at <1 GPa have been extrapolated using a variety of empirical and semiempirical equations of state. Particularly promising, however, are equations of state based on simulations that begin with realistic two-body potentials. Brodholt and Wood (1992) have, for example, used such a potential to simulate H_2O at pressures above 10 GPa. With the properties of H_2O they have determined, the measured stability field of brucite requires an anomalously large thermal expansion coefficient of about $7 \times 10^{-5}/\text{K}$. This agrees with our results and confirms the utility of simulations.

ACKNOWLEDGMENTS

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