An *in situ* high-pressure X-ray diffraction experiment on hydroxyapophyllite*

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The compression behavior of a natural hydroxyapophyllite is investigated up to about 10.01 GPa at 300 K using *in situ* angle-dispersive X-ray diffraction and a diamond anvil cell at the High Pressure Experiment Station, Beijing Synchrotron Radiation Facility (BSRF). Over this pressure range, no phase change or disproportionation is observed. The isothermal equation of state is determined for the first time. The values of zero-pressure volume V_0, isothermal bulk modulus K_0, and K_0' refined with a third-order Birch–Murnaghan equation of state are $V_0 = 1276.3 \pm 0.9$ Å^3, $K_0 = 71 \pm 3$ GPa, and $K_0' = 8 \pm 1$. Furthermore, we confirm that the values of linear compressibility β along the a and c directions of hydroxyapophyllite are elastically anisotropic.

Keywords: hydroxyapophyllite, X-ray diffraction, equation of state, high pressure

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1. Introduction

Apophyllite is a specific group of phyllosilicate minerals with the chemical formula (K, Na)$Ca_4Si_8O_{20}$(F, OH)·$8H_2O$.[1] The apophyllite is tetragonal with space group *P*4/*mnc*.[1] Originally, the group name was referred to a specific mineral, but was redefined in 1978 to represent a class of minerals of similar chemical makeup that comprise a solid solution series and include fluorapophyllite (KF), hydroxyapophyllite (KOH), and natroapophyllite (NaF).[2,3] The apophyllite group is layered with alternating silicate sheets and potassium, sodium, calcium, fluorine, and water layers.[3,4] However, unlike other phyllosilicates, the apophyllite group silicate sheets are composed of inter-connected four and eight member rings.[1,4] This is why these minerals have typical tetragonal or pseudo-tetragonal symmetries. Only apophyllite group members have this unique inter-connected four and eight member ring structure. These minerals are typically found as secondary minerals in holes in basalt or other igneous rocks.[5]

Apophyllite is often thought of as a zeolite group mineral, but its members have different structures. Zeolites are network silicates belonging to the tectosilicate subclass, whereas apophyllite is a layered phyllosilicate.[1,6] However, apophyllite and zeolites are associated with each other in low temperature and low pressure metamorphic environments.[5] Another typically associated mineral is the prehnite that forms a rolling carpet, on the top of which is pseudo-cubic apophyllite crystals.[7]

To date, the elastic properties of zeolites have been studied extensively.[6,8–11] In addition, Detrie *et al*.[12] investigated the equations of state and the high-pressure behaviors of a natural sample of prehnite by single crystal X-ray diffraction at pressures up to 9.75 GPa. Using a second-order Birch–Murnaghan equation of state, they determined the bulk modulus of prehnite at 109.29 GPa. However, there is no report on the physical properties including the equation of state (EOS) and the elasticity of apophyllite at high pressure. High pressure X-ray diffraction experiments not only provide us with information about phase transitions, but also give us access to basic properties of elasticity,[13–15] e.g., the bulk modulus.[16] For a further understanding of the elastic property of apophyllite, it is useful to investigate the high pressure EOS of this mineral. Therefore, we study the EOS of apophyllite under high pressure conditions for the first time, and the isothermal bulk modulus is derived based on our observed pressure–volume (*P*–*V*) data.

2. Experiment

A natural apophyllite of an unknown source was carefully crushed and thoroughly ground under acetone in an agate mortar to an average grain size of 5 μm before drying. The chemical composition of the apophyllite was determined by an electron probe, and the chemical formula of the crystal was calculated to be $(K_{0.95}Na_{0.05})Ca_{3.97}Si_8O_{20}(OH_{0.94}F_{0.06})\cdot 8H_2O$, so it was a hydroxyapophyllite.

The high pressure experiment was performed using a modified Merill–Bassett type diamond anvil cell (DAC),[17] equipped with two diamond anvils (culet face diameter: 500 μm) and tungsten–carbide supports. By using the anvils,

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a T301 stainless steel gasket of 200 μm in thickness was pre-indented to a thickness of about 70 μm, and a 200 μm diameter hole was drilled in the center of the pre-indentation to be used as a sample chamber. The sample powder was loaded with the inner pressure standard Pt powder in the sample chamber. The cell pressure was determined by fitting the *P*–*V* data of Pt using the equation of state given by Holmes *et al*.[18] The pressure transmitting medium was a 16:3:1 mixture of methanol–ethanol–water.[19] The *P*–*V* experiments were conducted at the High Pressure Experiment Station, Beijing Synchrotron Radiation Facility (BSRF). The incident X-ray beam was monochromatized to a wavelength of 0.6199 Å. The doubly focused X-ray beam size was 12 μm×27 μm. The angle-dispersive X-ray diffraction patterns were obtained on an imaging plate X-ray data collection system. The typical exposure time for collecting diffraction patterns of the sample and the pressure marker was 600 s and it was then integrated as a function of 2θ using the Fit2D code software package[20] to obtain conventional, one-dimensional diffraction profiles. The cell parameters were calculated using the UnitCell process.[21] For all patterns, sample diffraction lines (103), (200), (211), (212), (220), (105), (301), (311), (312), (224), (322), (411), (330), (420), and (422) were used to refine the parameters.

3. Result and discussion

Typical X-ray diffraction spectra at selected pressures are shown in Fig. 1. The diffraction patterns in this study are similar to each other up to 10.01 GPa, the Bragg peaks shift toward higher 2θ and the diffraction lines broaden and weaken slightly as the pressure increases. Thus we find no evidence for any phase transition to another crystalline phase of hydroxyapophyllite, or an amorphous structure.

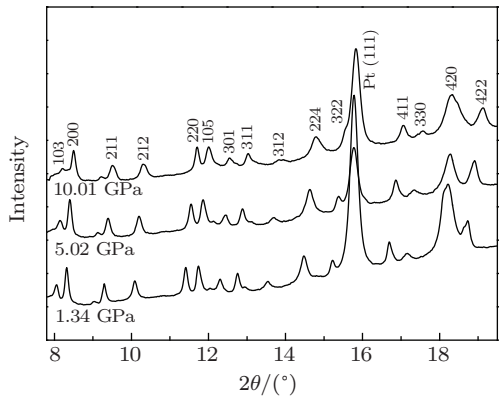


Fig. 1. Typical X-ray diffraction patterns of hydroxyapophyllite.

The effects of pressure on the unit-cell parameter and volume of hydroxyapophyllite are shown in Table 1. The pressure–volume data are fitted to the third-order Birch–Murnaghan equation of state[22] to determine the elastic parameter

$$P = (3/2)K_0[(V_0/V)^{7/3} - (V_0/V)^{5/3}] \times \{1 + (3/4)(K_0' - 4)[(V_0/V)^{2/3} - 1]\}, \quad (1)$$

where V_0, V, K_0, and K_0' are the zero-pressure volume, and high-pressure volume, isothermal bulk modulus and its pressure derivative, respectively. The results from a least-square fitting using the EOSFIT program[23] are $V_0 = 1276.3 \pm 0.9$ Å^3, $K_0 = 71 \pm 3$ GPa, and $K_0' = 8 \pm 1$. When K_0' is set to be 4, the isothermal bulk modulus is determined to be 86(3) GPa. The unit-cell volume data as a function of pressure and the curve of compression versus pressure calculated from these fitted parameters are plotted in Fig. 2.

Table 1. Cell parameters at different pressures for hydroxyapophyllite. Estimated standard deviations are given in parentheses.

P/GPa	*a*/Å	*c*/Å	*V*/Å^3
0.0001	8.9345(6)	15.9831(7)	1275.9(9)
1.34	8.8788(4)	15.9175(5)	1254.0(5)
2.77	8.8211(3)	15.8504(4)	1234.6(7)
3.39	8.7964(5)	15.8250(8)	1225.9(8)
5.02	8.7458(4)	15.7592(4)	1205.4(6)
7.27	8.6832(7)	15.6773(7)	1182.0(5)
10.01	8.6272(8)	15.5954(3)	1160.7(7)

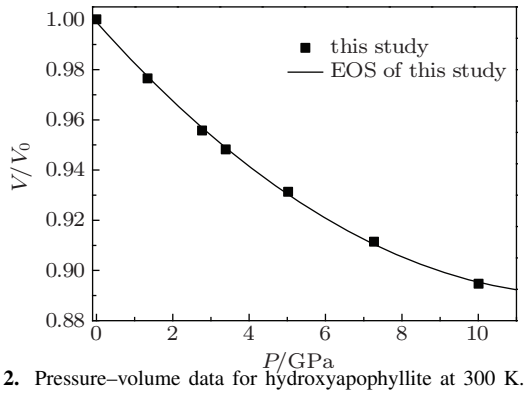


Fig. 2. Pressure–volume data for hydroxyapophyllite at 300 K. The solid curve is the Birch–Murnaghan equation fitting with K_0 and K_0' being 71 GPa and 8, respectively.

We infer that there are two possible reasons for the differences in the elastic behavior among apophyllite, zeolite, and prehnite. Firstly, the differences can be attributed to their different compositions and structures, since the prehnite has an orthorhombic structure belonging to the *Pncm* space group, the zeolite, according to the different components, possesses an orthorhombic, monoclinic, trigonal, or hexagonal structure, and in contrast, the apophyllite has a tetragonal structure with space group *P*4/*mnc*.[7] Second, the water content of the samples are different. From Table 2, we can find that the water content of zeolites are the highest, but their bulk moduli are the smallest. The water content of prehnite is the smallest, but its bulk modulus is the largest. According to the investigation of Smyth *et al*.,[24] the addition of 1 wt.% H_2O reduces the bulk modulus of olivine by about 6% (from 130 GPa to 120 GPa). They also believed that the reduced bulk modulus is a common feature of water-bearing minerals. So, we infer that the difference in water content among the samples is a possible reason for this.

Table 2. Bulk moduli of apophyllite, zeolite, and prehnite. Estimated standard deviations are given in parentheses.

Pressure range/GPa	Sample	Formula	K_0/GPa	K_0'	Reference
0–5	heulandite	$Na_{1.7}Ca_{2.7}Al_{9.3}Si_{26.7}O_{72}\cdot 27H_2O$	27.5(2)	4(fixed)	[8]
0–5	heulandite	$Na_{1.7}Ca_{2.7}Al_{9.3}Si_{26.7}O_{72}\cdot 27H_2O$	26.4(1.0)	4.9(8)	[8]
0–5	scolecite	$Ca_{7.9}(Al_{15.7}Si_{24.3}O_{80})\cdot 24H_2O$	54.6(7)	4(fixed)	[9]
0–6.9	zeolite Na-A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$	22.3(3)	4(fixed)	[6]
0–6.9	zeolite Na-A	$Na_{12}Al_{12}Si_{12}O_{48}\cdot 27H_2O$	19.6(6)	5.1(3)	[6]
0–5	zeolite levyne	$(Ca_{0.5},Na,K)_6(Al_6Si_{12}O_{36})\cdot 18H_2O$	48(1)	4(fixed)	[11]
0–9.75	prehnite	$Ca_{2.07}(Al_{0.98})(AlSi_{3.09}O_{10})(OH)_2$	109.3(2)	4(fixed)	[12]
0–10.01	apophyllite	$K_{0.95}Ca_{3.97}Si_8O_{20}OH_{0.94}\cdot 8H_2O$	71(3)	8(1)	this work

To assess the quality of the Birch–Murnaghan equation of state fitting obtained from the plot of unit cell volume against pressure, the relationship between the Eulerian strain ($f_E = 0.5[(V_0/V)^{2/3} - 1]$) and the normalized pressure ($F_E = P/[3f_E(2f_E+1)^{5/2}]$) is plotted[23] and shown in Fig. 3. The F_E–f_E plot provides a visual indication of which higher order terms, such as K_0' and K_0'', are significant in the EOS. The hydroxyapophyllite data show a relatively large positive slope (Fig. 3). This indicates that the pressure derivative of the bulk modulus (K_0') is larger than 4. Therefore, the value, estimated to be 8(1), is consistent with the F_E–f_E plot analysis.

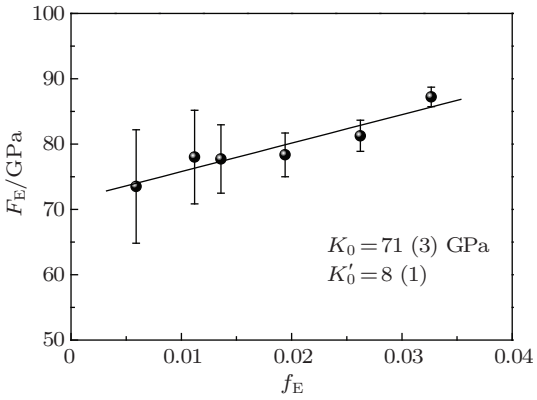


Fig. 3. Eulerian strain–normalized pressure (F_E–f_E) plot of the data based on the Birch–Murnaghan equation of state. The solid line represents the linear fitting.

The linear compressibility $\beta_l = -(\partial l/\partial P)_{P=0}/l_0$, where l_0 is the length of a unit-cell axis at 1 bar, is estimated by fitting the axial compression data of hydroxyapophyllite to a linearized Birch–Murnaghan equation of state.[23] Zero-pressure compressibilities from the hydroxyapophyllite P–V experimental data are found to be 4.6×10^{-3} GPa^{-1} and 2.8×10^{-3} GPa^{-1} for the a-axis and c-axis, respectively, with K_{l0}' fixed at 4.0 for both axes. The evolutions of unit-cell parameters a/a_0 and c/c_0 with pressure are plotted in Fig. 4, which indicate that the hydroxyapophyllite is elastically anisotropic.

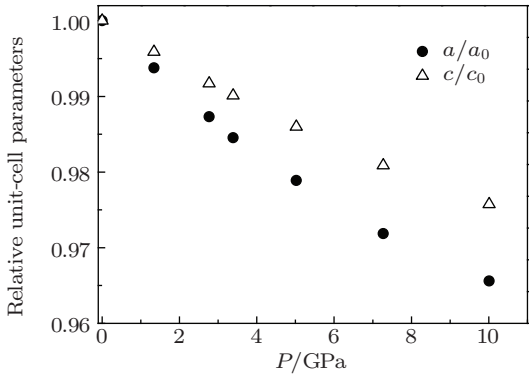


Fig. 4. Relative compression of hydroxyapophyllite, showing the variation of relative axial ratio with pressure. The data points marked by error bars are smaller than the size of the symbols.

4. Conclusion

The P–V measurements on hydroxyapophyllite at pressures up to 10.01 GPa are carried out using the angle-dispersive X-ray diffraction technique. The experimental data demonstrate that the hydroxyapophyllite does not undergo any phase transition at pressures up to 10.01 GPa. The P–V EOS for the hydroxyapophyllite, fitted using the third-order Birch–Murnaghan EOS, gives $V_0 = 1276.3 \pm 0.9$ Å^3, $K_0 = 71 \pm 3$ GPa, and $K_0' = 8 \pm 1$. Furthermore, we confirm that the values of linear compressibility β along the a and c directions of hydroxyapophyllite are elastically anisotropic ($\beta_a = 4.6 \times 10^{-3}$ GPa^{-1} and $\beta_c = 2.8 \times 10^{-3}$ GPa^{-1}), with the compressibility along the a-axis being almost twice that along the c-axis.

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