Synchrotron X-ray diffraction study of phenacite at high pressure*

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Abstract: We report the results of a natural phenacite from 0 to 30.9 GPa using in situ angle-dispersive X-ray diffraction and a diamond anvil cell at the National Synchrotron Light Source, Brookhaven National Laboratory. Over this pressure range, no phase change or disproportionation has been observed. The isothermal equation of state was determined. The values of V_0, K_0, and K_0' refined with a third-order Birch-Murnaghan equation of state are V_0=1116.1±1.2 Å^3, K_0=223±9 GPa, and K_0'=5.5±0.8. Furthermore, we confirm that the linear compressibilities (β) along a and c directions of phenacite are elastically isotropic (β_a=1.50×10^{-3} and β_c=1.34×10^{-3} GPa^{-1}). Consequently, it can be concluded that the compressibility of phenacite under high pressures has been accurately constrained.

Key words: X-ray diffraction, high pressure, equation of state, phenacite

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1 Introduction

Phenacite (Be_2SiO_4), which contains one silicon atom, two inequivalent beryllium atoms, and four inequivalent oxygen atoms, is a fairly rare nesosilicate mineral consisting of beryllium orthosilicate. It is a beryllium silicate with a hardness of 7.5 to 8. Its crystal system is hexagonal (trigonal) and it often crystallizes in short prisms. The structure of phenacite consists of an ordered three-dimensional framework formed by tetrahedra of different types (SiO_4 and BeO_4) with approximately equal geometrical parameters [1]. These tetrahedra are joined together into chains oriented parallel to the threefold crystallographic axis and form cavities in the form of wide hexagonal channels.

The crystal structure of phenacite was first solved by Zachariasen [2]. Later, several studies have been devoted to the crystal chemistry/physics of phenacite [3–6]. Zachariasen [2] and Downs [3] reported that phenacite has anisotropic temperature parameters, Hazen and Au [4] considered that phenacite has an isotropic compressibility. Hazen and Finger [6] reported the thermal expansion and high temperature structures of phenacite. The pressure and elastic behaviour of natural phenacite were investigated by Hazen and Au [4] by means of X-ray methods, and Yeganeh-Haeri and Weidner [5] by Brillouin spectroscopy. The high pressure lattice parameters have been measured up to about 4.9 GPa by Hazen and Au [4]. The bulk modulus has been calculated on the basis of the volume data collected up to 4.9 GPa with

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a third-order Birch-Murnaghan equation of state. However, it is necessary to obtain accurate lattice parameters at P >6.8 GPa for determining the K_0' of the hard mineral (the hardness of phenacite is 7.5 to 8) [7]. Moreover, the K_0' values (2±4 and −1.70±1.82) have been obtained by Hazen and Au [4] and Yeganeh-Haeri and Weidner [5], respectively. But the error for the K_0' value of Hazen and Au [4] and the negative value for the K_0' value of Yeganeh-Haeri and Weidner [5] were unreasonable. In addition, Hazen and Au [4] obtained the results of phenacite from single-crystal diffraction, but not with appropriate techniques in modern high pressure crystallography (e.g. synchrotron X-ray diffraction). So it would have been worth measuring the compressibility of phenacite within the scope of this study. Therefore, the aim of this study is to investigate the high pressure elastic behavior of a natural phenacite by means of in situ synchrotron X-ray diffraction up to pressures in excess of 20 GPa, which will allow a full description of the elastic parameters (i.e. K_0, K_0', axial bulk moduli and elastic anisotropy).

2 Experiment

The sample used in this study is colorless, inclusion free, a perfect crystal with a hexagonal system, collected from pegmatite in the Yunnan Province, China. The chemical composition of phenacite was determined by electron probe, and the chemical formula of the crystal was calculated to be Be_2SiO_4. The sample was ground under acetone in an agate mortar to an average grain size of 5 μm before further drying.

A T301 steel plate with an initial thickness of 200 μm was used as a gasket. The powdered sample, loaded in the stainless steel gasket, was pressurized using a diamond anvil cell. The diamonds had 400 μm flat culet faces. The central area of the plate was pre-indented to a thickness of about 50 μm, and then drilled to give a 100 μm hole. The sample powder and a few grains of ruby were loaded with the pressure medium (a 16:3:1 methanol-ethanol-water mixture) into the hole of the gasket. The sample pressure was determined by the ruby technique [8].

The in situ high-pressure X-ray angle dispersive diffraction experiments on phenacite were carried out with a diamond anvil cell (DAC) at the Beamline X17C, National Synchrotron Light Source, Brookhaven National Laboratory. The incident synchrotron radiation beam was monochromatized to a wavelength of 0.4066 Å, and the beam size was collimated to ∼26.6 μm×24 μm. Two-dimensional images were recorded by using an online CCD detector. CeO_2 was used to calibrate the sample-detector distance. The typical exposure time for collecting diffraction patterns of the sample was 900–1500 s, and later integrated as a function of 2θ using the Fit2D code software package [9] to obtain conventional, one-dimensional diffraction profiles. The diffraction peak positions were determined using a peak fitting program. The cell parameters of phenacite were calculated and refined by using the UnitCell process [10] (Table 1) with all of the diffraction lines (012), (211), (300), (220), (21-2), (31-1), (11-3), (140), (303), (330), (104).

3 Results and discussion

The typical X-ray diffraction spectrums at selected pressures are shown in Fig. 1. The diffraction patterns at each pressure of the study are similar to one another up to 30.9 GPa, with the Bragg peaks shifted to higher 2θ and the diffraction lines broaden and weaken slightly as the pressure increases. Thus we found no evidence for any phase transformations to another crystalline phase of phenacite, or an amorphous structure. The pressure dependency of the d-spacings is shown in Fig. 2, which shows a continuous decrease with the increase in pressure, also indicates that the sample is stable up to 30.9 GPa. The d-spacings of (012), (220), (11-3), (140), (303) diffraction reflections that were prominent, non-overlapping, and observable until the end of the experiment are shown.

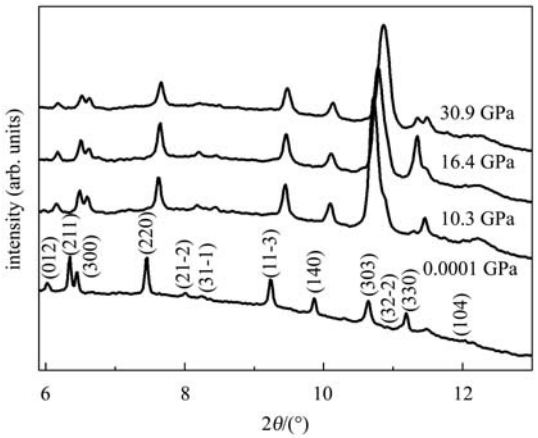

Fig. 1. Representative X-ray diffraction patterns of phenacite in this study.

The unit-cell parameters of phenacite at various pressures are given in Table 1. The pressure-volume data were fitted using a third order Birch-Murnaghan

Table 1. Cell parameters versus pressure for phenacite.

P/GPa	a/Å	c/Å	V/Å^3	P/GPa	a/Å	c/Å	V/Å^3
0.0001	12.481(5)	8.261(5)	1116.2(4)	12.9	12.281(8)	8.149(8)	1064.4(7)
1.1	12.467(8)	8.256(8)	1111.2(6)	14.4	12.266(3)	8.118(4)	1057.8(7)
3.6	12.425(5)	8.221(5)	1099.1(8)	16.4	12.239(3)	8.106(4)	1051.6(6)
4.2	12.410(5)	8.220(5)	1096.4(9)	18.1	12.210(3)	8.085(4)	1043.8(6)
5.1	12.394(5)	8.206(5)	1091.6(8)	20.0	12.178(4)	8.078(6)	1037.5(8)
6.0	12.375(5)	8.200(7)	1087.5(7)	22.7	12.151(2)	8.046(2)	1028.8(3)
7.2	12.360(4)	8.189(5)	1083.4(8)	25.5	12.125(6)	8.024(8)	1021.6(3)
8.0	12.342(3)	8.173(4)	1078.1(7)	28.1	12.089(8)	8.006(8)	1013.3(7)
9.3	12.323(3)	8.153(5)	1072.1(7)	29.9	12.073(5)	7.986(7)	1008.1(4)
10.3	12.303(2)	8.155(3)	1068.9(5)	30.9	12.056(5)	7.976(9)	1003.9(4)

Numbers in brackets are 1s error in last digits.

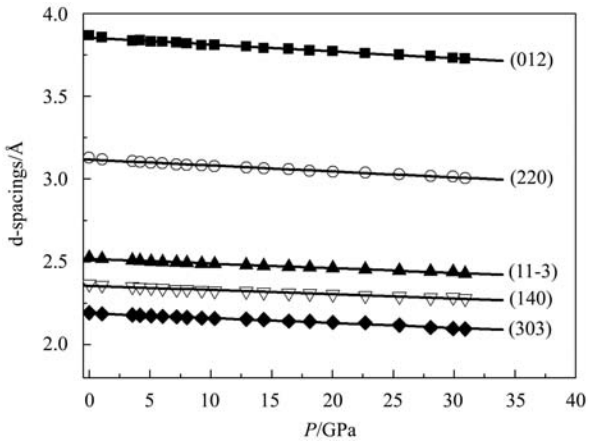

Fig. 2. The pressure dependence of d-spacings of phenacite. The solid lines are guides.

equation of state:

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

where V_0, K_0 and K_0' are the zero-pressure volume, isothermal bulk modulus and its pressure derivative, respectively. The results from a least-squares fitting using the EoSFit program [11] are V_0=1116.1(1.2) Å^3, K_0=223(9) GPa, and K_0'=5.5(8), respectively. The unit-cell volume data as a function of pressure and the compression curve calculated from these fitted parameters are plotted in Fig. 3.

To assess the quality of the Birch-Murnaghan equation of state fit 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 ($F_E = P/[3f_E(2f_E+1)^{5/2}]$) was plotted, and it is shown in Fig. 4(a). 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 equation of state. The phenacite data show a relatively large positive slope (Fig. 4(a)). This indicates that the pressure derivative of the bulk modulus (K_0') is higher than 4. Therefore, the value, estimated to be 5.5(8), is consistent with the F_E-f_E plot analysis.

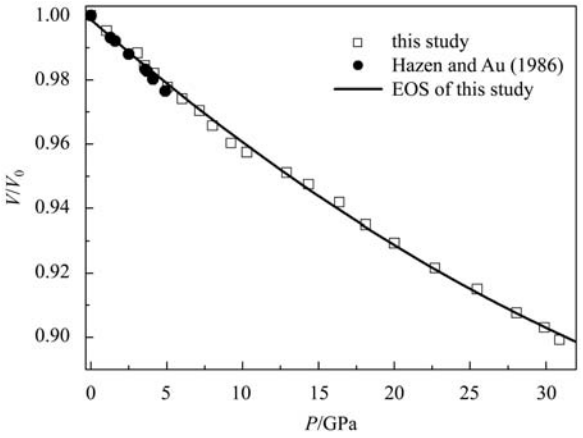

Fig. 3. The pressure-volume data for phenacite at 300 K. The solid curve: Birch-Murnaghan equation fit with K_0 and K_0' is 223 GPa and 5.5, respectively. The size of the symbols exceeds the uncertainties.

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] was estimated by fitting the axial compression data of phenacite to a linearized third-order Birch-Murnaghan equation of state [11], yielding: a_0=12.485(9) Å, K_{a0}=222(11) GPa, K_{a0}'=6.1(9) for the a axis; c_0=8.265(5) Å, K_{c0}=249(15) GPa, K_{c0}'=3.6(7) for the c axis. Then, the zero-pressure compressibilities from the phenacite P-V experimental data were found to be 1.50×10^{-3} GPa^{-1}, 1.34×10^{-3} GPa^{-1}, for the a-, and c-axis, respectively. The slopes fairly positive and negative obtained from the linear fits of the F_E-f_E plots for the a and c unit-cell parameters, respectively, are in good agreement with the K_0' values larger and smaller than 4 given by the III-BM-EoS fits (Fig. 4(b) and (c)). And the

evolution of unit-cell parameters a/a_0 and c/c_0 with pressure is plotted in Fig. 5. The unit-cell parameters of the phenacite show a non-linear dependence on pressure over the pressure range. The $(c/c_0)/(a/a_0)$ ratio of the phenacite ranges from 0.9992 to 1.0020, essentially constant at 1, in the present pressure range, which indicates that the phenacite is elastically isotropic (see Fig. 5).

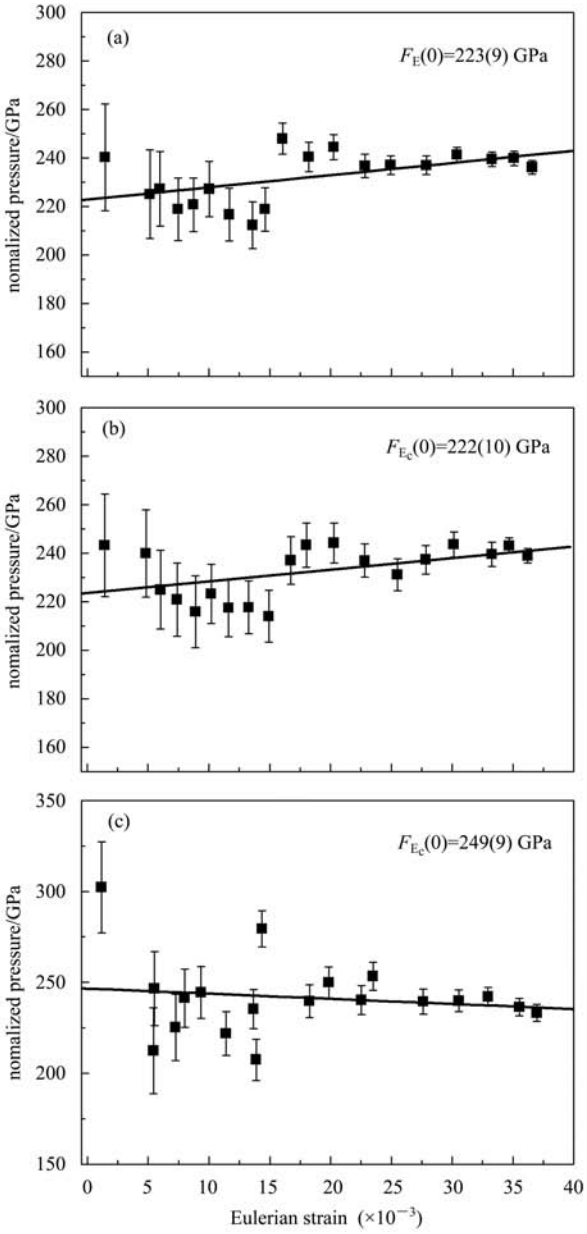

Fig. 4. Eulerian strain-normalized pressure (F_E-f_E) plot of the data based on the Birch-Murnaghan equation of state. The solid line represents the linear fit. (a) volume; (b) a-axis; (c) c-axis.

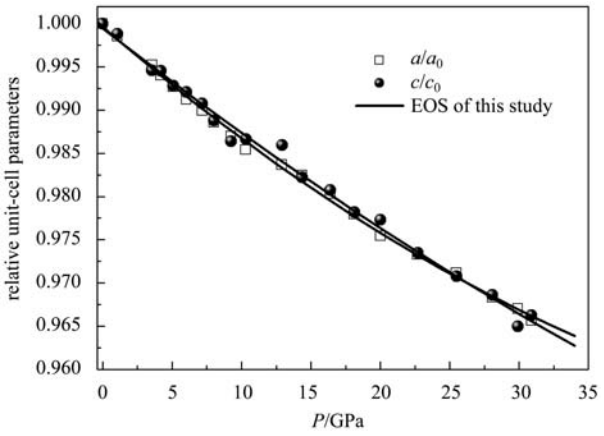

Fig. 5. Relative compression of phenacite, showing the variation of relative axial ratios as a function of pressure. The size of the symbols exceeds the uncertainties.

The precise determination of the unit-cell volume allowed us to refine both the bulk modulus and its pressure derivative. The isotropic behavior of phenacite obtained in this study (β_a:β_c=1.15:1.00) is in general agreement with the results reported by Hazen and Au [4], which provided the axial compressibility coefficient up to 4.9 GPa on the basis of a linear regression through the data point (β_a:β_c=1.10:1.00). However, the bulk modulus value obtained in this study is slightly higher than the K_0 value obtained by Hazen and Au [4], and by Yeganeh-Haeri and Weidner [5] (Table 2). The difference between the K_0 of this study and those of Hazen and Au [4] and Yeganeh-Haeri and Weidner [5] may be due to the different K_0' used, since Hazen and Au [4] and Yeganeh-Haeri and Weidner [5] implied a K_0' value of less than 2 whereas from our data K_0' is 5.5. However, Hofmeister [12] shows that the values of K_0' outside the range of 3.8–8.0 lead to physically unrealistic potentials and hence are not appropriate for the Birch-Murnaghan's equations of state. Therefore, we consider that K_0'=5.5 for phenacite in this study is better.

Table 2. Bulk moduli and its first pressure derivative of phenacite.

reference	this study			Hazen and Au (1986) [4]	Yeganeh-Haeri and Weidner (1989) [5]
methods	synchrotron radiation X-ray diffraction			X-ray diffraction	Brillouin spectroscopy
	a	c	V	V	V
K_0/GPa	222(11)	249(15)	223(9)	201(8)	212(3)
K_0'	6.1(9)	3.6(7)	5.5(8)	2(4)	−1.70(1.82)

Numbers in brackets are 1s error in last digits.

4 Conclusion

The P-V measurements on phenacite at pressures of up to 30.9 GPa were carried out using an angle-dispersive X-ray diffraction technique. The experimental data demonstrate that phenacite does not undergo any phase transition up to 30.9 GPa. The P-V equation of state for the phenacite, fitted using the third-order Birch-Murnaghan equation of state, gives V_0=1116.1(1.2) Å^3, K_0=223(9) GPa, and K_0'=5.5(8). The mean axial compressibilities of phenacite are determined to be 1.50×10^{-3} GPa^{-1}, 1.34×10^{-3} GPa^{-1} for the a-, and c-axis, respectively, and the axial ratio of the phenacite ranges from 0.9992 to 1.0020, respectively, essentially constant at 1, implying an elastically isotropic behavior of phenacite.

References

1 Bragg L, Claringbull G F. Crystal Structure of Minerals. Bell, London, 1965
2 Zachariasen W H. Soviet Physics Crystallography, 1972, **16**: 1021
3 Downs J W. PhD Thesis. Virginia Polytechnic Institutc and State University, Blacksburg, Virginia, 1983
4 Hazen R M, Au A Y. Physics and Chemistry of Minerals, 1986, **13**: 69
5 Yeganeh-Haeri A, Weidner D J. Physics and Chemistry of Minerals, 1989, **16**: 360
6 Hazen R M, Finger L W. Physics and Chemistry of Minerals, 1987, **14**: 426
7 Gatta G D, Nestola F, Ballaran T B. Physics and Chemistry of Minerals, 2006, **33**: 235
8 MAO H K, XU J, Bell P M. Journal of Geophysical Research, 1986, **91**: 4673
9 Hammersley J. Fit2d User Manual. ESRF, Grenoble, France, 1996
10 Holland T J, Tedfern S A. Mineralogical Magazine, 1997, **61**: 65
11 Angel R J. Reviews in Mineralogy and Geochemistry, 2001, **41**: 35
12 Hofmeister A M. Geophysical Research Letters, 1993, **20**: 635