Zeitschrift für Kristallographie 173, 305–312 (1985)

The effect of pressure on helvite $Mn_8S_2[Be_6Si_6O_{24}]$

Yasuhiro Kudoh and Yoshio Takéuchi

Mineralogical Institute, Faculty of Science, University of Tokyo,
Hongo, Tokyo 113, Japan

Received: October 21, 1985

Helvite / Phase transition / High pressure

Abstract. The effect of pressure on the helvite structure has been studied up to 45 kbar, using the single-crystal diffraction technique. The result has shown that an abrupt shrinkage of the BeO_4 tetrahedra takes place at around 30 kbar, thus showing that the compression of the helvite framework is not a simple function of the rotation of the tetrahedra. At around that pressure, the BeO_4 tetrahedra contracted by about 3.2%, while SiO_4 seems to show a slight expansion by about 1.4%

Introduction

The crystal structure of helvite $Mn_8S_2[Be_6Si_6O_{24}]$, which is isotypic with sodalite $Na_8Cl_2[Al_6Si_6O_{24}]$ (Pauling, 1930), has been refined by Holloway et al. (1972). The framework is characterized by four-membered rings consisting of two BeO_4 and two SiO_4 tetrahedra that occur on each face of the cubic cell. They are linked together to form six-membered rings around the cube corners.

The framework of this type in general may expand or shrink by rotation of tetrahedra about the axes parallel to the cube edges, provided that the tetrahedra are kept rigid. The relationship between the angle of rotation, Φ, of the tetrahedron from its position of fully-expanded structure, the cell parameters and the length of the tetrahedron edge has been provided by Taylor (1972).

When pressure is applied, the compression of the framework may be effected by an increase of Φ. This situation, however, implies a decrease of the $T-O-T$ angle. In addition, the framework is firmly held with the links of bonds between the framework oxygen atoms and cations located in the large cage. It is then conceivable that the compression of the framework, now considered, would not necessarily be a simple function of Φ particularly if the angle becomes large. The present study was undertaken to elucidate the effect of pressure on the helvite framework. The helvite structure is, in particular, suited for the purpose because its T—O—T angle at ordinary condition is as small as 128.2° (Holloway et al., 1972) and it contains BeO_4 tetrahedra having a relatively small bulk modulus.

Experimental

The crystals used for the present study came from Schwarzenberg, Saxony. Electron microprobe analyses revealed the existence of cations such as Fe and Zn that substitute Mn with the Mn:Fe:Zn ratio of 1:0.12:0.06.

A small piece of crystal with the dimensions as listed in Table 1 was mounted in a pressure cell of the Merrill-Bassett type (Merrill and Bassett, 1974) together with a piece of NaCl crystal as pressure indicator. A 1:1 mixture of pentane-isopentane was used as fluid pressure medium. An Inconel 750X plate, 0.250 mm thick, was used for the gasket material; the radius of a hole opened in the gasket was 0.15 mm.

The unit-cell dimensions were obtained with a least-squares procedure applied to $\sin 2\theta$ values of $11 \sim 15$ reflections measured on a Syntex $P2_1$ four-circle single-crystal diffractometer, using graphite monochromated Mo$K\alpha$ radiation [in the particular case of 14 kbar, Ag$K\alpha$ was used]. They are listed in Table 1. The unit cell contains $(Mn, Fe, Zn)_8S_2[Be_6Si_6O_{24}]$. No variation of space group symmetry $P\bar{4}3n$ was observed in the pressure range covered.

The fixed-φ scan technique (Finger and King, 1978) was used to collect diffraction intensities with the four-circle diffractometer, using Mo$K\alpha$ radiation (Ag$K\alpha$ at 14 kbar). Reflections with intensities greater than two times the estimated error were regarded as measured. Among each set of intensities of symmetrically equivalent reflections, the one having the least estimated error was selected. The number of independent reflections thus obtained at each pressure is listed in Table 1. The reflections were then subjected to a check for overlapping with those of the diamonds and with powder lines from the Be disks, using the procedure provided by Denner et al. (1978). After correcting for Lorentz and polarization factors, the intensities were corrected for absorption. The final number of reflections used for structure refinement at each pressure is given in Table 1. The pressures were calibrated based on the cell dimension of a NaCl crystal, using Decker's equation of state (Decker, 1971).

The atomic parameters reported by Holloway et al. (1972) at 1 atm served as initial set of atomic coordinates for the refinement with LINUS (Coppens and Hamilton, 1970). A weighting scheme was used of the form $1/\sigma^2 \, |F_o|$. Throughout calculations, the neutral atomic form factors were used given in *International Tables for X-ray Crystallography* (1962). The final values of R are listed in Table 1.

Table 1. Cell dimension and intensity-study data. Those at 1 atm are from Holloway et al. (1972)

Pressure	1 atm	14 kbar	27 kbar	36 kbar	40 kbar	45 kbar
Crystal size (μm)	260[a]	88 × 88 × 38	150 × 150 × 50	150 × 100 × 50	150 × 100 × 50	88 × 100 × 30
Cell dimension (Å)	8.294(7)	8.261(1)	8.223(1)	8.214(1)	8.203(1)	8.190(1)
Number of reflexions						
measured		90	120	123	129	111
observed		63	90	114	111	100
used	116	54	77	102	100	78
R (%)	4.0	7.9	4.9	5.6	6.3	5.9
R_w (%)		3.3	2.5	3.7	4.0	3.4

[a] The edge length of a tetrahedral crystal

Table 2. Positional atomic parameters and isotropic temperature factors. Those at 1 atm are from Holloway et al. (1972)

Pressure		1 atm	14 kbar	27 kbar	36 kbar	40 kbar	45 kbar
Mn	*x*	0.1693(1)	0.1680(3)	0.1703(2)	0.1702(2)	0.1708(2)	0.1700(2)
	y	0.1693	0.1680	0.1703	0.1702	0.1708	0.1700
	z	0.1693	0.1680	0.1703	0.1702	0.1708	0.1700
	$B(\text{Å}^2)$	1.04(3)	0.03(7)	0.66(3)	0.82(5)	0.87(5)	0.77(4)
Si	*x*	0	0	0	0	0	0
	y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	$B(\text{Å}^2)$	0.60(10)	0.04(23)	0.48(10)	0.32(12)	0.61(13)	0.47(14)
Be	*x*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	y	0	0	0	0	0	0
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	$B(\text{Å}^2)$	0.60(41)	9.6(29)	7.7(16)	3.0(9)	5.8(14)	4.0(11)
O	*x*	0.1418(3)	0.1414(12)	0.1399(6)	0.1399(8)	0.1382(10)	0.1387(8)
	y	0.1404(3)	0.1400(12)	0.1405(6)	0.1422(8)	0.1400(10)	0.1402(8)
	z	0.4171(4)	0.4151(9)	0.4134(5)	0.4156(7)	0.4147(7)	0.4137(7)
	$B(\text{Å}^2)$	0.68(11)	0.38(25)	0.68(11)	0.38(11)	0.58(12)	0.71(12)
S	*x*	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	y	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	z	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
	$B(\text{Å})$	1.24(6)	7.25(83)	2.0(2)	2.5(3)	3.1(3)	3.1(3)

Results and discussion

The final sets of atomic parameters are listed in Table 2. The mode of variation of relative cell volume versus pressure shows a gap at around 30 kbar (Fig. 1), suggesting the existence of a phase transition at around that pressure. Although the gap is not conspicuous by itself, the mode of variations in structural data, which will be given below, shows that the existence of the phase transition is conclusive. This transition has been found to be reversible.

In Table 3 we give some important bond lengths and angles at the pressures covered. The variations of the T–O bond lengths according to pressure are shown in Fig. 1. In this diagram, we observe a significant contraction of the Be–O bonds taken place at around 30 kbar, which corresponds to the above-mentioned pressure for the gap in change of relative cell volume. Thus the high-pressure transition in helvite is basically characterized by an abrupt shrinkage of the BeO_4 tetrahedra that takes place at around 30 kbar.

We next consider the mode of variation in the angle, Φ, for the rotation of tetrahedra. In Fig. 2 (*top*), which shows the variation in the value of $\cos\Phi$ versus pressure, we observe gaps at around 30 kbar. Up to around this

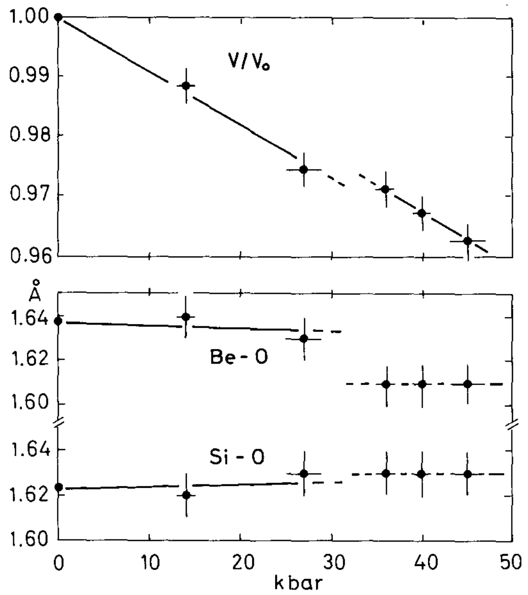

Fig. 1. Variation of relative cell volume (*top*) and tetrahedral bond lengths (*bottom*) versus pressure

pressure, the values show a gradual decrease, showing that the shrinkage of the framework is effected by an increase of the Φ angle. At 36 kbar in the diagram, however, the values change nearly back to those at 1 atm and then decrease again with further increase of pressure. In conformity with such a change in Φ, the Be – O – Si angle varies with pressure as shown in Fig. 2 (*bottom*).

The above observations may now be summarized to show the mechanism of compression of the helvite framework. When pressure is applied, the framework starts contracting by rotations of tetrahedra. When the cell volume is reduced by about 3% at around 30 kbar, an abrupt shrinkage of the BeO_4 tetrahedra takes place. This situation would presumably be rationalized in the following way. Since the helvite framework is firmly held by the links of MnO_3S tetrahedra located in the large cage, the BeO_4 and SiO_4 tetrahedra have less freedom of rotation. It then follows that the two kinds of tetrahedra themselves would be considerably subjected to compression with an increase of pressure. The energy of compression would thus be released by the contraction of BeO_4 which has a small bulk modulus relatively to SiO_4.

In general a shrinkage of tetrahedra of the helvite framework gives an effect on the cell dimension in a way which is similar to an increase of the Φ angle. Specifically, the edge length *a* of the cubic unit cell is related in

Table 3. Bond lengths (Å) and bond angles (°). Those at 1 atm are from Holloway et al. (1972)

Pressure		1 atm	14 kbar	27 kbar	36 kbar	40 kbar	45 kbar
SiO_4 tetrahedron							
Si – O	[×4]	1.623(3)	1.62(1)	1.63(1)	1.63(1)	1.63(1)	1.63(1)
O – O	[×4]	2.622(4)	2.62(2)	2.64(1)	2.64(2)	2.64(2)	2.64(1)
	[×2]	2.704(6)	2.71(2)	2.72(1)	2.72(1)	2.69(2)	2.70(1)
O – Si – O angle	[×4]	107.8(1)	107.8(3)	107.9(1)	107.9(2)	108.5(2)	108.3(2)
	[×2]	112.9(2)	112.9(3)	112.6(1)	112.6(2)	111.4(2)	111.9(2)
Volume ($Å^3$)		2.19(2)	2.19(4)	2.22(2)	2.22(2)	2.21(4)	2.21(2)
BeO_4 tetrahedron							
Be – O	[×4]	1.638(3)	1.64(1)	1.63(1)	1.61(1)	1.61(1)	1.61(1)
O – O	[×4]	2.649(4)	2.65(2)	2.62(1)	2.60(1)	2.61(2)	2.61(1)
	[×2]	2.725(6)	2.73(2)	2.71(1)	2.68(1)	2.66(2)	2.68(1)
O – Be – O angle	[×4]	107.9(1)	107.9(3)	107.9(1)	107.7(2)	108.4(2)	108.1(2)
Volume ($Å^3$)	[×2]	112.6(2)	112.6(3)	112.7(1)	113.1(2)	111.7(2)	112.2(2)
		2.25(2)	2.25(4)	2.20(2)	2.13(2)	2.14(4)	2.15(2)
Si – O – Be angle		128.2(2)	127.2(3)	126.4(2)	127.4(3)	127.3(3)	126.7(3)
MnO_3S tetrahedron							
Mn – S		2.432(2)	2.404(2)	2.426(1)	2.421(1)	2.427(1)	2.412(1)
Mn – O	[×3]	2.082(4)	2.066(8)	2.029(4)	2.045(5)	2.034(5)	2.027(5)
S – O	[×3]	3.835(5)	3.80(2)	3.77(1)	3.79(1)	3.77(1)	3.75(1)
O – O	[×3]	3.238(7)	3.21(2)	3.18(1)	3.19(1)	3.20(2)	3.18(1)
S – Mn – O angle	[×3]	116.1(1)	116.4(3)	115.3(1)	115.7(1)	114.8(2)	115.2(1)
O – Mn – O	[×3]	102.1(1)	101.8(3)	103.1(2)	102.6(2)	103.6(2)	103.2(2)
Volume ($Å^3$)		5.07(4)	4.93(3)	4.80(5)	4.86(5)	4.84(1)	4.77(5)

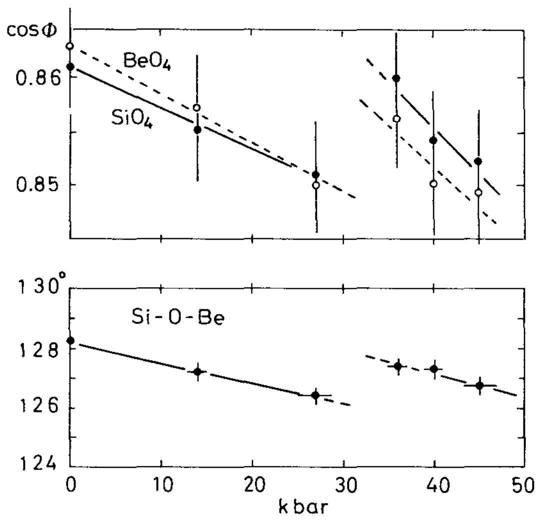

Fig. 2. Variation of cos Φ (*top*) and the Si—O—Be angle (*bottom*) versus pressure

the following way to the length l of the edges of the BeO_4 tetrahedron parallel to the cube face and the width w of SiO_4 along the cube axis:

$$a = 2\,l \cos \Phi + 2\,w\,.$$

Since the geometrical change in SiO_4 is small compared to that of BeO_4, w is assumed to be constant. Then, the reduction of the cell dimension, Δa, due to a small change Δl may be given by

$$\Delta a = 2\,\Delta l \cos \Phi$$

for a fixed value of Φ. As a rough measure, the mean O—O distance may be used instead of l.

The mean O—O distance of the BeO_4 tetrahedra at 1 atm, 2.674 Å, after the transition changes to 2.63 Å, giving a difference of 0.044 Å (Table 3). Using the above relation, we find that this amount of reduction in the O—O distance reduces the cell dimension by 0.076 Å for a fixed value of $\Phi = 30°$. This value is nearly the same with the difference 0.074 Å, between the cell dimension 8.294 Å at 1 atm and the estimated cell dimension 8.22 Å at around the transition (Table 1). This situation well explains the mode of variation of the Φ angle at the transition pressure [Fig. 2 (*top*)].

The computation was carried out on HITAC M-200H at the Computer Center of the University of Tokyo.

References

Coppens, P., Hamilton, W. C.: Anisotropic extinction corrections in the Zachariasen approximation. Acta Crystallogr. **A26**, 71–83 (1970)

Decker, D. L.: High-pressure equation of state for NaCl, KCl, and CsCl. J. Appl. Phys. **42**, 3239–3244 (1971)

Denner, W., D'Amour, H., Schulz, H., Stoeger, W.: A new measuring procedure for data collection with a high-pressure cell on an X-ray four-circle diffractometer. J. Appl. Crystallogr. **11**, 260–264 (1978)

Finger, L. W., King, H.: A revised method of operation of the single-crystal diamond cell and refinement of the structure of NaCl at 32 kbar. Am. Mineral. **63**, 334–342 (1978)

Holloway, W. M. Jr., Giordano, T. J., Peacor, D. R.: Refinement of the structure of helvite, $Mn_4(BeSiO_4)_3S$. Acta Crystallogr. **B28**, 114–117 (1972)

International Tables for X-ray Crystallography. Vol. 3, Kynoch Press, Birmingham (1962)

Merrill, L., Bassett, A.: Miniature diamond anvil pressure cell for single crystal X-ray diffraction studies. Rev. Sci. Instrum. **45**, 290–294 (1974)

Pauling, L.: The structure of sodalite and helvite. Z. Kristallogr. **74**, 213–225 (1930)

Piermarini, G. J., Block, S., Barnett, J. D.: Hydrostatic limits in liquids and solids to 100 kbar. J. Appl. Phys. **44**, 5377–5382 (1973)

Taylor, D.: The thermal expansion behaviour of the framework silicates. Mineral. Mag. **38**, 593–604 (1972)