Crystal structure of humite, $Mg_7Si_3O_{12}(OH, F)_2$ at 2.7 GPa

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Introduction

Humite, $Mg_7Si_3O_{12}(OH, F)_2$, belongs to humite minerals described as $nMg_2SiO_4{\cdot}Mg(OH, F)_2$ (n=1, 2, 3 and 4). Humite minerals such as chondrodite (n=2) and clinohumite (n=4) were stable under high pressure and high temperature conditions about -10 GPa, -1000ºC [1-2]. It is therefore considered that humite minerals would play an important role for the transportation and as a reservoir of water in the subduction zone. However the behaviors of humite structure under high pressure and temperature condition is little known. In this study, we report the cell parameters and the crystal structure of humite at 2.7 GPa to understand the effects of pressure on the structures of humite minerals.

Experimental Procedure

The sample used for this study is from Tilley Foster Mine, Brewster New York, U.S.A.. A single crystal of humite (50×40×30 mm in size) was mounted in a modified diamond anvil cell [3] with a small piece of ruby, which used for pressure marker. The 4:1 fluid mixture of methanol and ethanol was used for pressure medium and SUS301 plate was used for gasket. Pressure was determined by ruby fluorescence method [4]. The wavelength of synchrotron radiation (λ=0.6958 Å) is calibrated by the unit cell constants of a ruby standard crystal at ambient condition. The X-ray diffraction data were measured with an automated four-circle diffractometer at the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization. The unit cell parameters were determined from 25 centered reflections in the 2θ range between 15.6º and 30.2º. Lattice constants of humite displayed as orthorhombic symmetry within the limit of standard deviation. The X-ray reflection intensity data of humite at 2.7 GPa were collected up to $\sin\theta/\lambda<0.79$ Å^{-1} (maximum 2θ is 66.7º). The 3/8 of a reciprocal sphere was measured and a total of 2467 reflections were obtained. After background and Lorentz corrections, the symmetrically equivalent reflections were averaged by the Laue symmetry of mmm. 343 reflections ($Io > 2.0\sigma(Io)$) were used for the structure refinement of data set at 2.7 GPa. The model (space group Pbnm (No.62)) by Ribbe and Gibbs (1971) was used for the initial parameters of humite structure. Final agreements factors were R=9.4 and Rw=7.6%, applying the $1/\sigma^2(Fo)$ weight for all reflections. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation (1992).

Results

The unit cell parameter of humite at 2.7 GPa is a=4.715(4) Å, b=10.165(7) Å, c=20.714(4) Å and V=992.8(10) Å^3. The a/a_0, b/b_0, c/c_0 and V/V_0 ratios are 0.995, 0.991, 0.993 and 0.979. The stacking direction [100] is most stiff and the [010] direction is most compressible. This trend is the same as the other humite minerals (*ex*. the linear compressibility of each direction of chondrodite is β_a=1.88(3), β_b=2.80(3), β_c=2.79(3) ($\times10^{-3}$/GPa), respectively (data from [5]). The predicted isothermal bulk modulus of humite is calculated as K_{0T}=117 GPa using the Birch-Murnaghan equation of state with assuming a pressure derivative K′=4. This value is consistent to the trend in humite minerals. The final atomic coordinates are given in Table 1. The mean distances of both tetrahedra (1.62(2) Å for Si1 and 1.64(2) Å for Si2) at 2.7 GPa are almost unchanged. In contrast, the mean distance of each octahedron is 2.09(3) Å for M1, 2.14(4) Å for M2, 2.08(3) Å for M3 and 2.09(3) Å for M4, respectively. Although M1-O, M2-O and M4-O mean distances are almost unchanged under this pressure, M3-O is significantly shortened.

References

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Table 1. Final atomic coordinates of humite at 2.7 GPa

Site	x	y	z	Biso
M1	0.0000(23)	0.3778(13)	0.1766(4)	0.3(2)
M2	0.5143(33)	0.1521(19)	0.25	0.4(3)
M3	0.0108(20)	0.0964(12)	0.1108(4)	1.1(2)
M4	0.4930(22)	0.8644(14)	0.0278(4)	1.1(2)
Si1	0.0706(24)	0.9718(19)	0.25	0.9(3)
Si2	0.5732(14)	0.2835(12)	0.1049(4)	0.8(2)
O11	0.7356(52)	0.9580(42)	0.0366(12)	1.9(8)
O12	0.2855(72)	0.3139(60)	0.25	1.4(10)
O13	0.2192(49)	0.0281(46)	0.1873(11)	1.0(8)
O21	0.2310(41)	0.2713(45)	0.1048(13)	1.4(7)
O22	0.7794(30)	0.9259(28)	0.1081(9)	0.7(4)
O23	0.7321(35)	0.2064(50)	0.1698(10)	1.7(5)
O24	0.7250(35)	0.2069(33)	0.0470(9)	0.8(4)
OH	0.2698(43)	0.0289(42)	0.0366(12)	0.6(5)

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