



Evolution of the brewsterite structure at high pressure: A single-crystal X-ray diffraction study

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ABSTRACT

The structural evolution of natural brewsterite $\text{Sr}_{1.30}\text{Ba}_{0.66}(\text{H}_2\text{O})_{10}[\text{Al}_{4.00}\text{Si}_{12.00}\text{O}_{32}]$, compressed in penetrating (water:ethanol 1:4 mixture) and non-penetrating (paraffin) media up to 3.5 GPa, was studied using single-crystal X-ray diffraction data from a diamond-anvil cell. The results clearly demonstrate the absence of pressure-induced hydration in the brewsterite structure. In both media, the behaviour of brewsterite under compression is similar. A nearly isotropic compression of brewsterite up to 2 GPa proceeds through a slight decrease of the framework T–O–T angles. At $P > 2$ GPa a phase transition occurs, which is evinced by an abrupt volume reduction by about 1%. The structure contracts mainly along the *a* axis and exhibits almost regular changes along the two other axes. The high-pressure phase is characterized by a doubled *c* parameter of the unit cell; the space group remains the same as for the initial phase.

1. Introduction

The microporous compounds, including zeolites, are characterized by a developed system of channels and cavities, whose dimensions allow the diffusion of molecules and cations during the interaction with external medium. This provides an easy exchange of the extraframework cations [1], as well as (for a number of zeolites) variations of the H_2O content in the structure cavities, depending on the external conditions. For example, the H_2O content in large-pore zeolites of heulandite-clinoptilolite group can increase by one third depending on the air humidity change [2]. Upon the increase of the partial H_2O pressure up to ~ 29 mbar, lomontite undergoes a structural transformation with an abrupt increase of the H_2O content [3]. No less important is the possibility of the interaction of microporous compound with compressing medium under pressure. In this sense the pressure-transmitting media can be divided onto “penetrating” (whose molecules can diffuse into the channels due to steric reasons) and “non-penetrating”. The atomic gaseous compounds of the environment (e.g. He, N, Ne, Ar, Xe) and small molecules (H_2O , CO_2) are potentially penetrating. On the contrary, the compounds with larger molecules such as alcohols, glycerol, silicon oils, paraffin and others are used as non-penetrating media.

The compression in non-penetrating medium usually proceeds through the deformation of tetrahedral framework [4], which

sometimes leads to the phase transitions involving the rearrangement of extraframework subsystem. The compression in water-containing (penetrating) medium results, as a rule, in a pressure-induced hydration (PIH) [5]; this, in its turn, can be accompanied by various structural transformations including the changes in the configuration of the extraframework water-cation subsystem.

Brewsterite $[(\text{Sr},\text{Ba},\text{Ca})_2(\text{H}_2\text{O})_{10}][\text{Al}_4\text{Si}_{12}\text{O}_{32}]$, space group $P2_1/m$, is a rare zeolite of heulandite group. The structure of brewsterite was determined by Perrotta and Smith [6] and refined by Schlenker et al. [7] using X-ray diffraction method. Multiple hydrogen positions were located by neutron diffraction [8]. This zeolite has been described only in five localities [9], which apparently explains a relatively small number of publications devoted to its study. For example, the structure evolution of brewsterite during thermal dehydration was studied, involving single-crystal method [10,11]. No drastic changes in the brewsterite structure were found, but only the migration of cations in new positions in the framework cavities was observed during the water loss. As concerns the high-pressure behaviour of brewsterite, it was not studied.

The aim of the present contribution is to compare the structural evolution of brewsterite under the compression in water-containing and anhydrous fluids.

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Table 1
Lattice parameters and volumes of brewsterite at high pressure.

P, GPa	a, Å	b, Å	c Å	β , °	V, Å ³
0.0001	6.7808(2)	17.4973(5)	7.7334(2)	94.049(3)	915.25(5)
Compression in ethanol:water 4:1					
0.17	6.77179(13)	17.4597(17)	7.72677(14)	94.0573(15)	911.27(9)
0.66	6.75257(10)	17.3763(12)	7.68848(12)	94.2871(13)	899.60(7)
1.32	6.72837(11)	17.2591(12)	7.63848(12)	94.5531(13)	884.22(6)
1.96	6.70028(12)	17.1584(13)	7.59089(13)	94.7238(14)	869.73(7)
2.52	6.62237(11)	17.0947(10)	15.1501(2)	93.5420(13)	1711.83(11)
2.99	6.59951(10)	16.9895(10)	15.0853(2)	93.6484(12)	1687.97(11)
3.69	6.58219(11)	16.8821(12)	15.0409(2)	93.6684(13)	1667.94(12)
Compression in paraffin					
0.40	6.76412(11)	17.4374(13)	7.71447(17)	94.1379(16)	907.54(7)
1.19	6.73390(14)	17.2833(14)	7.64946(15)	94.5060(17)	887.52(8)
2.08	6.70260(13)	17.1635(13)	7.59656(17)	94.6331(17)	871.05(7)
2.33	6.6996(3)	17.111(4)	7.5889(5)	94.741(4)	867.0(2)
2.50	6.6886(8)	17.060(8)	7.5790(11)	94.702(11)	861.9(4)
2.50	6.6456(16)	17.018(5)	15.129(3)	93.92(2)	1707.0(7)
3.28	6.61004(9)	16.9117(11)	15.0803(3)	93.9904(13)	1681.69(12)
In air, after decompression					
0.0001	6.7808(3)	17.4989(6)	7.7378(3)	94.019(3)	915.89(6)

2. Experimental

The sample of brewsterite (Strontian, Argyllshire, Scotland) was provided by Igor A. Belitsky. The chemical composition was determined using wavelength-dispersive spectroscopy on Cameca Camebax Micro electron microprobe at 20 nA and 20 kV with a defocused beam of 20 μm and counting time of 20 s. The water content was measured by thermogravimetric analysis using Mettler TA3000 equipment (temperature range 20–750 °C, heating rate 10 °C/min). The resulting composition is $\text{Sr}_{1.30}\text{Ba}_{0.66}\text{Na}_{0.06}\text{K}_{0.02}(\text{H}_2\text{O})_{10.1}[\text{Al}_{4.00}\text{Si}_{12.00}\text{O}_{32}]$.

Several fragments of a large crystal were first inspected using a polarizing microscope to exclude twinned crystals, and a

0.19 \times 0.14 \times 0.04 mm prismatic crystal was selected for the X-ray diffraction study. Diffraction data were first collected at room conditions (crystal in air) on an Oxford Diffraction Xcalibur Gemini diffractometer (MoK α radiation, 0.5 mm collimator, graphite monochromator, ω scan with step of 1°, 30 s per frame). Data reduction, including the background correction and Lorentz and polarization corrections, was performed with the *CrysAlis Pro* 171.37.35 program package. A semi-empirical absorption correction was applied using the multi-scan technique. The structure was solved and refined with SHELX-97 program package [12]. The Si/(Al + Si) ratio for each tetrahedral site was estimated using the method described in Ref. [13]. The occupancy of mixed (Sr,Ba) position was refined assuming its full population. All four Ow positions in the brewsterite structure were found to be fully occupied, and their occupancies were constrained to 1.0 in the final cycles of structure refinement. All atoms were refined with anisotropic displacement parameters.

The same crystal was used for the high-pressure measurements in a Boehler–Almax diamond–anvil cell (DAC) [14] (0.200 mm stainless steel gasket pre-indented to 0.107 mm, hole diameter 0.3 mm). In all experiments, the pressure was estimated from the shift of the ruby R1 band (\pm 0.05 GPa) [15]. An ethanol–water (4:1) mixture was used as a pressure-transmitting fluid in the first series of high-pressure experiment. Single-crystal X-ray diffraction experiments were carried out at 7 pressure points in the pressure range from 0.17 to 3.69 GPa (Table 1). Data were collected using ω scan technique, with scan step of 0.5° and a time of 30 s per frame with the strategy of *CrysAlis Pro* for high-pressure experiments in DAC.

After the first series of high-pressure experiment, DAC was decompressed to ambient pressure, and the DAC was opened and dried to remove ethanol–water mixture from the sample chamber. Then the sample chamber was filled with paraffin as a non-penetrating medium. The second series (6 pressure points) was carried out using the same crystal and the same experimental parameters as in the first series.

Table 2
Parameters of data collection and structure refinement for brewsterite compressed in penetrating medium.

Pressure (GPa)	0.0001	0.17	0.66	1.32	1.96	2.52	2.99	3.69	0.0001 ^a
a (Å)	6.7808(2)	6.77179(13)	6.75257(10)	6.72837(11)	6.70028(12)	6.62237(11)	6.59951(10)	6.58219(11)	6.7808(3)
b (Å)	17.4973(5)	17.4597(17)	17.3763(12)	17.2591(12)	17.1584(13)	17.0947(10)	16.9895(10)	16.8821(12)	17.4989(6)
c (Å)	7.7334(2)	7.72677(14)	7.68848(12)	7.63848(12)	7.59089(13)	15.1501(2)	15.0853(2)	15.0409(2)	7.7378(3)
β (°)	94.049(3)	94.0573(15)	94.2871(13)	94.5531(13)	94.7238(14)	93.5420(13)	93.6484(12)	93.6684(13)	94.019(3)
V (Å ³)	915.25(5)	911.27(9)	899.60(7)	884.22(6)	869.73(7)	1711.83(11)	1687.97(11)	1667.94(12)	915.89(6)
Space group	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> 2 ₁ / <i>m</i>
d (g/cm ³)	2.438	2.449	2.481	2.524	2.566	2.607	2.644	2.676	2.436
μ (MoK α) (mm ⁻¹)	3.231	3.245	3.287	3.344	3.400	3.455	3.504	3.546	3.229
Scan width (°/frame)	1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1
Exposure (s/frame)	30	30	30	30	30	30	30	30	30
2 θ range (°)	5.28–63.66	5.28–62.30	5.32–62.72	5.36–62.16	5.38–62.42	5.38–62.18	5.42–62.40	9.48–52.30	2.58–63.66
Number of I_{hkl} measured	18258	9013	8904	8721	8513	16890	16516	9949	17965
Number of unique F_{hkl}^2	3132	951	940	904	866	1766	1731	1242	3098
R _{int}	0.0665	0.0766	0.0777	0.0766	0.0755	0.0926	0.1031	0.0912	0.0715
Reflections with $I > 2\sigma(I)$	2749	817	821	788	757	1428	1337	1010	2642
Number of variables	146	126	121	126	126	243	262	267	146
R1, wR2 for observed reflections [$I > 2\sigma(I)$]	0.0451, 0.0962	0.0470, 0.1008	0.0467, 0.1006	0.0425, 0.0947	0.0391, 0.0915	0.0504, 0.1033	0.0513, 0.1079	0.0422, 0.0858	0.0453, 0.0959
R1, wR2 for all data	0.0538, 0.0999	0.0586, 0.1053	0.0566, 0.1041	0.0523, 0.0983	0.0481, 0.0952	0.0702, 0.1119	0.0773, 0.1171	0.0594, 0.0927	0.0566, 0.1012
Goof	1.186	1.173	1.144	1.214	1.186	1.058	1.194	1.097	1.147
Residual electron density (e/Å ³)	0.888, -0.603	0.472, -0.336	0.445, -0.340	0.538, -0.356	0.405, -0.330	0.669, -0.585	1.000, -0.733	0.428, -0.456	1.330, -0.641

^a After decompression, in air.

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