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

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ABSTRACT

The structural evolution of natural bikitaite $Li_2(H_2O)_2[Al_2Si_4O_{12}]$, compressed in penetrating (water-containing) medium up to 4 GPa, was studied using single-crystal X-ray diffraction data from a diamond-anvil cell. A nearly isotropic compression of bikitaite up to 1.2 GPa proceeds through a slight decrease of the framework T—O—T angles. Further pressurizing leads to anisotropic compression: the compressibility of *b*-axis is half as smaller compared to *c*-axis, and the *a*-axis is the least compressible. The structure can be described as hexagonal sheets of six-membered rings parallel to (001), connected by pyroxene-like chains. Upon the compression, the hexagonal sheets approach each other, leading to the shortening of the *c*-parameter. The deformation of hexagonal sheets, reinforced by O—Li bonds, is defined by the corrugation of 6-membered rings. The deformation of more flexible pyroxene chains, responding to the deformation of hexagonal sheets, consists of axial rotation of tetrahedra with only minor change in T—O—T angles. The arrangement of extraframework species changed slightly. The system of H-bonds between water molecules remains intact upon pressurizing. At the same time, the formation of new H-bonds with framework O-atoms becomes possible above 2 GPa due to the shortening of the distances between O_W positions and framework O-atoms. All pressure-induced structural changes are completely reversible and the recovered crystal structure returns to its ambient structure.

The results clearly demonstrate the absence of pressure-induced hydration in the bikitaite structure. The pressure-induced changes in the unit cell metrics are similar for bikitaite compressed in water-containing medium, silicon oil, and glycerol.

1. Introduction

The high-pressure behavior of zeolites significantly depends on the composition of pressure-transmitting medium [1,2]. Zeolites are characterized by open structures with wide channels and cavities, where additional H_2O molecules can intercalate under pressurizing in water-containing ("penetrating") medium. The latter phenomenon (so-called "pressure-induced hydration" – PIH [3]) can cause either volume increase (abrupt as in Refs. [2–6] or gradual as in Ref. [7]), or just decrease in compressibility compared with that in non-penetrating medium, due to the site occupancy increase of the already existing water sites [8,9]. The absence of the PIH effect, however, is also possible [10]. The high-pressure behavior of zeolite structure depends both on the framework topology and Si,Al-ordering, as well as on the type, quantity, and configuration of the extraframework species. The water content in pressure-transmitting medium can also be essential (see for example Refs. [5,11]).

Zeolite bikitaite $Li_2[Al_2Si_4O_{12}]\cdot 2H_2O$ is one of the most dense species among natural zeolites [12], whose crystal structure is characterized by narrow channels where H_2O molecules are arranged in linear chains. The extraframework Li^+ cations located in trigonal 6-fold rings, coordinate the H_2O molecules. The high pressure behavior of bikitaite in non-penetrating media was studied by both powder [13] and single-crystal [14] X-ray diffraction. The single-crystal experiments demonstrated that bikitaite compressibility significantly differs depending on glycerol or

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silicon oil was used as a pressure-transmitting medium [14]. Such a result implies that penetrating (water-containing) medium could also have a pronounced effect on the compressibility of bikitaite, which is the subject of the present study.

2. Experimental

The sample of bikitaite (King's Mountain, North Carolina, USA) was provided by Igor A. Belitsky. The chemical composition excluding Li content 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 Li^+ content was constrained from charge balance. 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 close to ideal formula $Li_{2.00}(H_2O)_{2.1}[Al_{2.00}Si_{4.00}O_{12}]$.

Several fragments of a large crystal were first inspected using a polarizing microscope to exclude twinned crystals, and a 0.24 × 0.12 × 0.06 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 (MoKα radiation, 0.5 mm collimator, graphite monochromator, ω scan with step of 1°, 15.9 s per frame). Data reduction, including a 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 [15]. All non-H atoms were refined with anisotropic displacement parameters.

The same crystal was used for high-pressure measurements in a Boehler–Almax diamond-anvil cell (DAC) [16] (0.200 mm stainless steel gasket pre-indented to 0.120 mm, hole diameter 0.3 mm). In all experiments, the pressure was estimated from the shift of the ruby R1 band (±0.05 GPa) [17]. An ethanol–water (1:1) mixture was used as a pressure-transmitting fluid. Single-crystal X-ray diffraction experiments were carried out at 6 pressure points in the pressure range from 0.16 to 4.13 GPa (Table 1). The data were collected using ω scan technique, with the scan step of 0.5° and a time of 30 s per frame.

Starting from 2.15 GPa, the reflections of ice have been observed in diffraction frames. Above that pressure, the data are collected under quasi-hydrostatic conditions, and, hence, the results should be considered questionable. At the same time, the quality of the diffraction data and structure refinement parameters at 2.15 and 3.47 GPa are comparable with those at lower pressure (see Table 1). The maximum pressure achieved was limited by the quality of the diffraction data, which decreased with pressure.

The recovered crystal was broken into three fragments; one of them (0.13 × 0.11 × 0.06 mm) was used to estimate the reversibility of pressure-induced changes in bikitaite structure.

The high-pressure diffraction data were reduced using *CrysAlis Pro* software. The data were reduced as from a single-crystal sample, without taking the diamond reflections into account. Under compression in water-containing medium, the reflections of ice appeared above 2 GPa. The overlapping of the sample and diamond or ice reflections was checked manually afterwards and the reflections with the contribution of more than one phase were excluded. The absorption by diamonds, the gasket and the crystal was corrected numerically using Absorb6.1 software [18]. The structures were refined with SHELX-97 program package; the structural parameters found at the previous pressure point were applied as the starting model. The H atoms were refined as described above. If the refinement of proton positions led to non-realistic results, the corresponding positions were removed from the refinement and were not considered later on. The full experimental details of the data collection and structure determination are given in Table 1. The atomic coordinates, occupancies, and displacement parameters are given in Tables 2 and 3; the interatomic distances and angles are presented in Tables 4–6.

3. Results and discussion

The crystal structure of bikitaite at ambient conditions is shown in Fig. 1a. Bikitaite is pseudomonoclinic, its triclinic symmetry is related to ordered Si,Al distribution in the framework [14,19]. The Si- and Al-tetrahedra alternate to form sublayers of six-membered

Table 1
Parameters of data collection and structure refinement for bikitaite compressed in penetrating medium.

Pressure (GPa)	0.0001	0.16	1.22	2.15	3.47	4.13	0.0001[a]
a (Å)	8.6191(5)	8.6022(8)	8.5592(8)	8.5450(8)	8.515(2)	8.507(4)	8.6075(4)
b (Å)	4.9608(3)	4.94857(14)	4.91368(14)	4.88293(14)	4.8304(3)	4.8065(7)	4.9530(2)
c (Å)	7.6070(4)	7.5965(8)	7.5540(8)	7.4654(9)	7.303(2)	7.241(5)	7.6001(5)
α (°)	90.123(5)	90.128(4)	90.198(5)	90.307(5)	90.534(11)	90.62(3)	90.101(4)
β (°)	114.411(5)	114.453(10)	114.655(10)	114.823(10)	114.45(3)	114.09(6)	114.449(5)
γ (°)	90.028(5)	90.016(4)	89.944(4)	89.725(4)	89.469(9)	89.36(2)	90.043(4)
V ($Å^3$)	296.18(3)	294.37(4)	288.74(4)	282.71(4)	273.42(10)	270.3(2)	294.96(3)
Space group	*P*1	*P*1	*P*1	*P*1	*P*1	*P*1	*P*1
d (g/cm^3)	2.289	2.303	2.348	2.398	2.479	2.508	2.298
μ (MoKα) (mm^{-1})	0.729	0.734	0.748	0.764	0.790	0.799	0.732
Scan width (°/frame)	1.0	0.5	0.5	0.5	0.5	0.5	1.0
Exposure (s/frame)	15	30	60	30	30	30	25
2θ range (°)	8.22–68.28	8.24–62.54	8.30–63.06	8.34–63.50	8.44–63.94	8.48–62.56	8.22–68.56
Number of I_{hkl} measured	6995	1967	1902	1907	1775	1659	7382
Number of unique F^2_{hkl}	4527	928	903	907	869	839	4637
R_{int}	0.0262	0.0405	0.0414	0.0423	0.0572	0.0978	0.0249
Reflections with $I > 2\sigma(I)$	4341	878	886	882	822	727	4440
Number of variables	215	135	159	178	177	162	217
$R1$, $wR2$ for observed reflections [$I > 2\sigma(I)$]	0.0300, 0.0706	0.0352, 0.0939	0.0331, 0.0861	0.0309, 0.0777	0.0381, 0.0921	0.0654, 0.1588	0.0312, 0.0873
$R1$, $wR2$ for all data	0.0321, 0.0706	0.0362, 0.0953	0.0326, 0.0966	0.0320, 0.0792	0.0407, 0.0957	0.0766, 0.1734	0.0336, 0.0901
Flack *x* parameter	0.07(8)	−0.1(2)	−0.07(17)	−0.09(18)	−0.1(2)	−0.4(5)	0.07(9)
GooF	1.060	1.208	1.182	1.056	1.073	1.150	1.078
Residual electron density ($e/Å^3$)	0.547, −0.358	0.218, −0.205	0.209, −0.202	0.183, −0.179	0.302, −0.235	0.702, −0.480	0.469, −0.363

[a] Data collected in air after decompression.