Single-crystal Diffraction Studies of Pressure-induced Phase Transitions in H_2O Ice and $BaCuSi_2O_6$

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Introduction

Diffraction experiments with single-crystal samples (surface x-ray diffraction or SXD) are unique and important sources of information about the structure of crystalline solids. In every scientific discipline where the objects of investigation are solids, these experiments have the ability to provide ultimate answers to the questions about microscopic mechanisms of the observed phenomena. The need for SXD experiments is especially pronounced in research involving experiments at extreme conditions of pressure and temperature. At sufficiently high pressures (usually above 15 GPa), all known substances, including ambient-pressure gases and liquids, become solids, often crystalline. The crystalline solids can undergo extremely dramatic changes when pressure is further increased or temperature is changed. In the quest to improve the quality of the diffraction data from a single crystal squeezed at high pressure, especially in the case of weakly scattering samples, much can be gained by using synchrotron facilities.

Synchrotron experiments provide the ability to change the wavelength of the incident beam. This ability provides an immediate advantage, by allowing an increase in the portion of reciprocal space accessible in a diamond-anvil cell (DAC) experiment. (With short λ, the reflections appear at lower Bragg angles, and absorption by sample and cell components is minimized.) In March 2001, our group performed the first of a series of pilot experiments at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) at APS. The main purposes were to develop a successful experimental and computational methodology for *in situ* high-pressure single-crystal experiments with charge-coupled device (CCD) detection and to study the compression behavior of H_2O ice as well as cyclosilicate $CuBaSi_2O_6$.

Methods and Materials

H_2O is one of the most abundant molecules on the earth. Despite the simplicity of the molecule, it has one of the richest and most complex phase diagrams amongst all the substances. So far, 14 different phases of H_2O have been identified (e.g., Ref. 1), with varying pressure and temperature regions of stability. Understanding the phase diagram of H_2O is crucial for several different disciplines of science. From a physical point of interest, clear understanding of H_2O phase equilibria is important in revealing the nature of the "anomalous" properties of water. From a chemical viewpoint, water is the most common solvent. For biologists, it is a molecule essential for all living organisms. Geologists' interests in different phases of ice as substantial components of the earth's lithosphere cannot be understated. Ice VI is the central phase in the H_2O phase diagram (Fig. 1). It has a phase boundary with the liquid phase as well as with solid phases V, VI', VII, VIII, and IX. Thus, detailed knowledge of the structure and properties of ice VI is crucial for understanding the phase behavior and mechanisms of phase transformation. Unfortunately, the structure of phase VI is not simple, and the H_2O molecules are disordered among several different orientations.

Silicates with isolated $SinO_{3n}$ rings display properties typical of both ionic and molecular crystals. In this regard, the cyclosilicate $BaCuSi_2O_6$ is of special interest because of its relatively simple structure that incorporates Si_4O_{12} rings as well as the presence of Cu in square-planar coordination (Fig. 2). When synthesized in 1988, deep magenta crystals of this phase were observed to crystallize in the acentric space group I4m2. Our reexamination of the crystals in 2000 revealed a distinctive color change to purple. The space group of the crystals has increased in symmetry to I4/mmm. We anticipated that the purple phase, with its greater unit-cell volume and undistorted silicate ring, would be subject

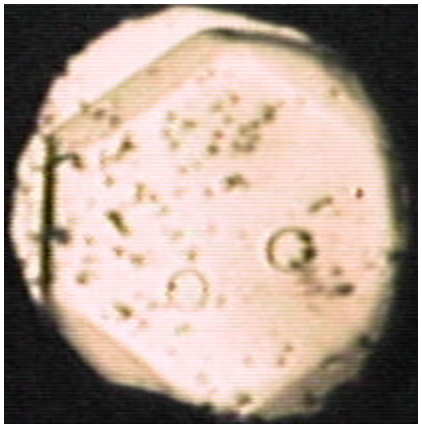

FIG. 1. Single crystal of ice VI was obtained at about 1.2 GPa by pressure cycling and freezing (no heating was involved).

to reversible high-pressure transitions. Such behavior has been documented previously (e.g., in gillespite BaFeSi4O10, which also features a silicate ring of four tetrahedra).

Results

Our experiment with BaCuSi2O6 was fully successful and revealed a phase transition occurring in the vicinity of 2 GPa (see Fig. 3). The use of synchrotron radiation and the CCD detector turned out to greatly improve the quality of obtained intensity data. A comparison of some of the parameters describing both in-house and synchrotron experiments with a 25-μm^3 sample crystal of $BaCuSi_2O_6$ in DAC at 4.5 GPa is presented in Table 1. The 13-BM beamline at the APS is equipped with a CCD detection system very similar to the one in our laboratory and uses the same software package. Therefore, we were able to easily use all the specialized high-pressure software written in our lab for CCD data processing. The high-pressure phase of $BaCuSi_2O_6$ has a monoclinic symmetry, with a C2 space group. In this structure, the silicate ring is distorted to 2 point-group symmetry. Preliminary results of this *in situ* structure determination were presented at the AIRAPT Conference in Beijing, China [2].

The experiment with H_2O ice VI was less successful because of the loss of quality of the single-crystal specimen in the high-pressure cell after irradiation with the very intense synchrotron beam. In a standard high-pressure experiment with a sample that is a solid at ambient conditions, a smear of Vaseline™ is used to fix the sample to the surface of diamond anvil. For the purpose of our ice VI experiment, the crystal was grown *in situ*, and partial melting caused by the beam caused its instability during data collection. Nevertheless, the diffraction data for ice VI collected at our lab, although inferior to the expected quality of synchrotron SXD data, are good enough to discuss details of the compression mechanism related to the proton disorder. The oxygen framework structure of ice VI has been known since 1965 [3], although not much information on the hydrogen atom properties was found in this study. The most recent structural study for ice VI [4] applied neutron diffraction with a powder sample. Although the symmetry and the unit cell were determined with satisfactory confidence, because of experimental difficulties, the poor quality of the data prevented these studies from performing full structure refinement and from drawing definite conclusions. The existing results reveal some information about the nature of the proton disorder. However, the lack of precise structural data has made it impossible to propose an ultimate structural interpretation of observed phenomena. From our laboratory data, collected at pressures from 1.2 to 2.4 GPa, it was possible to determine positions of H atoms from the difference Fourier map and to refine occupancy of sites between which these atoms are disordered. A detailed analysis of pressure effects on hydrogen bonding and proton disorder is underway. Preliminary results were presented during the IUCr workshop in Paris, France [5].

Table 1. Comparison of the quality of SXD data obtained from in-house and synchrotron experiments with a 25-mm^3 sample of $BaCuSi_2O_6$ in DAC at 4.5 GPa.

Parameter	In-house experiment	Synchrotron experiment
Best resolution (Å)	0.92	0.6
% of reflections with intensity of <2 σ to 1 Å	60.7	14.0
No. of symmetry-independent reflections collected	263	561
R_{merge} to 1 Å (%)	16.7	4.2
e.s.d of unit cell volume ($Å^3$)	1.24	0.46

Discussion

Our general conclusion from the experiments performed at the APS during the spring of 2000 is that SXD experiments can be successfully performed at the GSECARS microdiffraction station, and that the quality of diffraction data, especially from very small samples, is significantly superior to laboratory data. The new high-pressure structure of $BaCuSi_2O_6$ that we determined by using data collected at the GSECARS sheds some new light on the crystal chemistry of ring silicates and their behavior at high pressure.

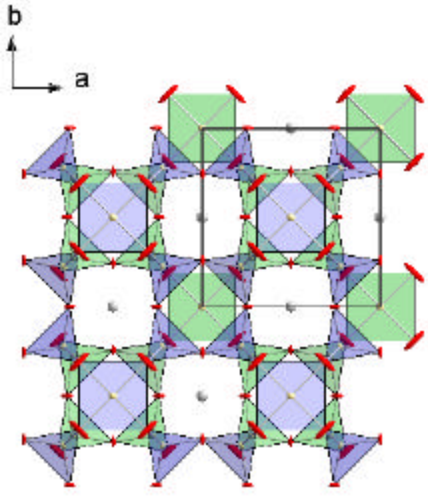

FIG. 2. The structure of $BaCuSi_2O_6$ in (001) projection.

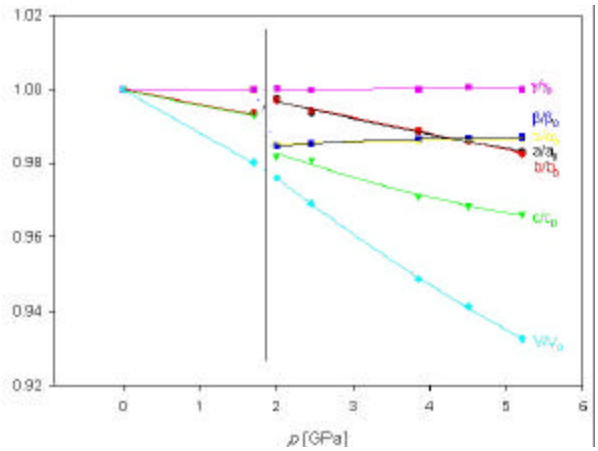

FIG. 3. Pressure dependence of unit cell parameters of $BaCuSi_2O_6$ showing phase transition in the vicinity of 2 GPa.

Acknowledgments

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