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High-pressure synchrotron x-ray diffraction and infrared microspectroscopy: applications to dense hydrous phases

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Abstract
Synchrotron x-ray diffraction (XRD) and infrared (IR) absorption spectra of
hydrous and 'anhydrous' forms of phase X were measured to 30 GPa at room
temperature. Three OH stretching modes were found in the hydrous phase, and
surprisingly one sharp OH mode was observed in the previously characterized
anhydrous phase. All OH stretching modes soften and broaden with increasing
pressure and become very weak above $\sim$20 GPa. XRD indicates that the crys-
tal structure remains stable up to 30 GPa. Combining IR absorption and XRD
results, the behaviour is attributed to pressure-induced distortion of the Si_2O_7
groups and disorder of the hydrogen atoms. The bulk moduli of the hydrous
and 'anhydrous' phases are in the region of 74 GPa.

1. Introduction

Infrared microspectroscopy at high pressure has greatly benefited from the development of
synchrotron radiation sources. It is often essential to study the same sample at the same
pressure and temperature with a broad range of techniques, including spectroscopy and x-ray
diffraction (XRD). However, synchrotron infrared (IR) and XRD techniques have not been
widely used together.

Recently, we have constructed a new beamline, U2A [1] (upgraded from our earlier
U2B beamline [1, 2]), on the VUV ring of the National Synchrotron Light Source (NSLS),
Brookhaven National Laboratory (BNL). Combining this with another x-ray beamline, X17C,
at the NSLS, both synchrotron IR and x-ray experiments can be performed routinely on
these two fully operational facilities using the same sample at the same pressure. This
provides improved capabilities for new classes of experiments in high-pressure condensed-
matter physics, geoscience, and materials science. As examples, we have applied synchrotron
IR microspectroscopy as well as XRD techniques in studying hydrous phase minerals, because

the information on the crystal structures and lattice vibrations is of great importance in understanding the mineralogy of the Earth's interior.

Extensive laboratory studies and theoretical modelling over the past two decades have indicated that the upper mantle is dominated by ultramafic minerals, principally olivine, pyroxene, and garnet phases, but substantial amounts of plagioclase feldspar, kaersutitic amphibole, phlogopite mica, and many other accessory minerals may be found [3–7]. Recent studies reveal that K-rich amphibole breaks down to produce a hydrous K-rich silicate [8, 9], named phase X, $K_{1.54}Mg_{1.93}Si_{1.89}O_7H_{1.04}$. This phase is found to be stable to 20 GPa and 1700 °C, which makes phase X a potential host for sodium, potassium, and water in metasomatized upper mantle and transition zone settings as well as a suitable host for trace elements with large ionic radii such as Rb, Cs, and Ba.

In this paper, we report combined synchrotron IR and XRD studies of hydrous and nominally anhydrous phase-X crystals under pressure up to 30 GPa. The purpose of this work is to study the effect of high pressure on phase stability and speciation of hydrogen for phase X.

2. Experimental details

Two different samples of phase X, namely a hydrous form (JKW56, $K_{1.54}Mg_{1.93}Si_{1.89}O_7H_{1.04}$) and a previously characterized anhydrous form (JKW62, $K_{1.85}Mg_{2.06}Si_{2.01}O_7$) [10], were studied in these experiments. Symmetrical diamond anvil cells [11] with type-II diamonds were used for both high-pressure XRD and IR absorption measurements. To eliminate orientational effects, single crystals of phase X were crushed into fine powder first and then loaded into the pressure chamber with ruby (as pressure gauge) and argon (as pressure transmitting medium as well as pressure gauge) for XRD and IR absorption studies.

Synchrotron IR experiments are performed at the U2A IR beamline. The beam is extracted through a wedged diamond window, then collimated and delivered through a vacuum pipe system before entering a Fourier transform infrared (FTIR) spectrometer. The U2 port provides approximately 80 mrad horizontal and 40 mrad vertical aperture, which particularly improves brightness at long wavelength. Figure 1 shows schematically an optical path of the set-up. The core equipment consists of a Bruker IFS 66s/V FTIR spectrometer equipped with three microscope systems. *Microscope 1* is a commercial, high-magnification infrared microscope for diffraction-limited micro-infrared measurements of samples at 1 bar as well as high pressures. *Microscope 2* is a custom designed, long-working-distance microscope system for high-pressure (and variable-temperature) applications. Laser and grating spectrometer systems also permit a variety of complementary optical experiments (e.g., Raman and luminescence) to be performed concurrently on the same samples. *Microscope 3* is custom designed for far-IR high-pressure measurements. In order to eliminate vapour absorption, *Microscope 1* and *Microscope 3* can be purged and/or evacuated. The spectra were collected from 650 to 8000 cm^{-1} with a nitrogen-cooled MCT detector and a resolution of 4 cm^{-1} and 1024 scans were used for all spectra collections.

The XRD experiments were performed at the wiggler beamline X17C of the NSLS, using the energy dispersive x-ray diffraction (EDXD) technique with white radiation and the intrinsic Ge solid-state detector. The size of incident x-ray beam was set to 50 μm × 50 μm using pairs of slits. The diamond cell was mounted on the rotating axis of a goniometer stage with a motorized X, Y, Z stage [12].
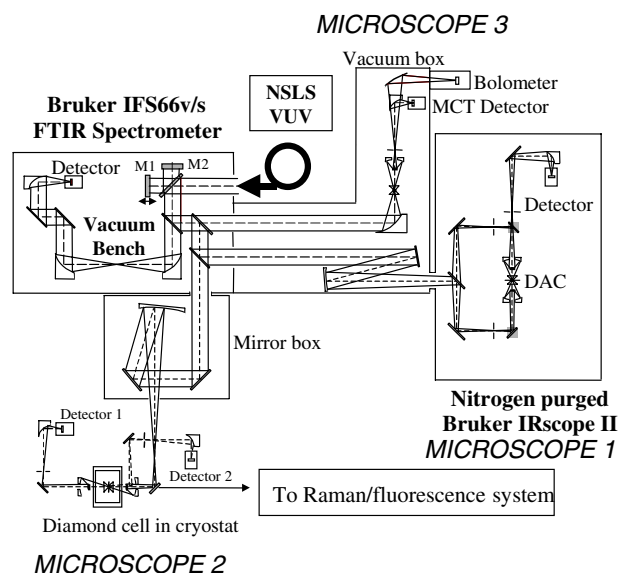
Figure 1. A schematic diagram of the optical facility at the U2A beamline.

3. Results and discussion

Figure 2(a) shows representative IR absorption spectra of the JKW56 sample measured at room temperature for different pressures. At low pressures, the IR absorption spectra in the OH stretching region are dominated by three peaks labelled as ν_1, ν_2, and ν_3. All peaks soften and broaden with increasing pressure and merge into a broad-band background above 18 GPa. As shown below, pressure-induced broadening and disappearance of the OH stretching vibrations will be discussed on the basis of both IR absorption and XRD results.

Powder EDXD patterns in the range of 1.7–2.8 Å for the same JKW56 sample at different pressures are shown in figure 2(b). At pressure above 2 GPa, diffraction peaks from solid argon start to appear and are labelled as Ar. The difference between the relative intensities at ambient and high pressures is probably due to the difference between the crystal orientation preferences before and after argon loading. As shown in figure 2(b), the diffraction peaks shift with pressure and have slight broadening up to 20 GPa. If the argon diffraction peaks are subtracted from the diffraction patterns, the main features of the patterns are similar for all pressures studied, indicating that the crystal structure remains stable above 20 GPa. For comparison, both IR absorption spectra and EDXD patterns of the JKW62 sample at room temperature for different pressures are shown in figure 3. Unlike the case for hydrous phase X, only one sharp peak at 3597 cm^{-1} is observed. This peak softens and broadens with increasing pressure and finally merges into the broad band as well. However, the peak is detectable until 30 GPa. On the other hand, the XRD pattern of JKW62 at high pressure is quite comparable to that of JKW56. The crystal structure of JKW62 appears not to change up to 30 GPa. At pressures above 20 GPa, however, the widths of the diffraction peaks broaden significantly with increasing pressure. For example, the width of the 104 diffraction peak increases from 0.0282 Å at room pressure to 0.0741 Å at 30 GPa. This is probably due to inhomogeneous lattice distortion, perhaps as a result of nonhydrostaticity.

Single x-ray diffraction studies indicate that both JKW56 and JKW62 samples have the same hexagonal symmetry and are characterized by MgO$_6$ octahedral layers that are stacked
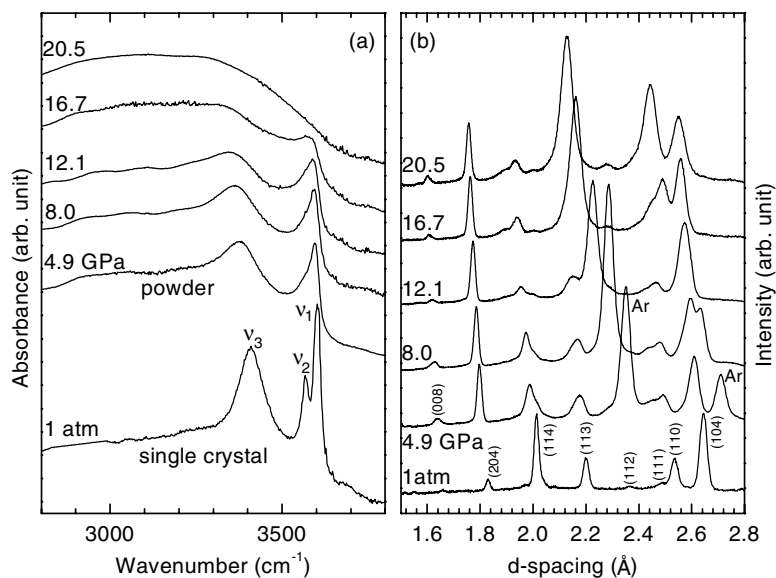
Figure 2. IR absorption spectra (a) and XRD patterns (b) of the JKW56 sample at room temperature for selected pressures.
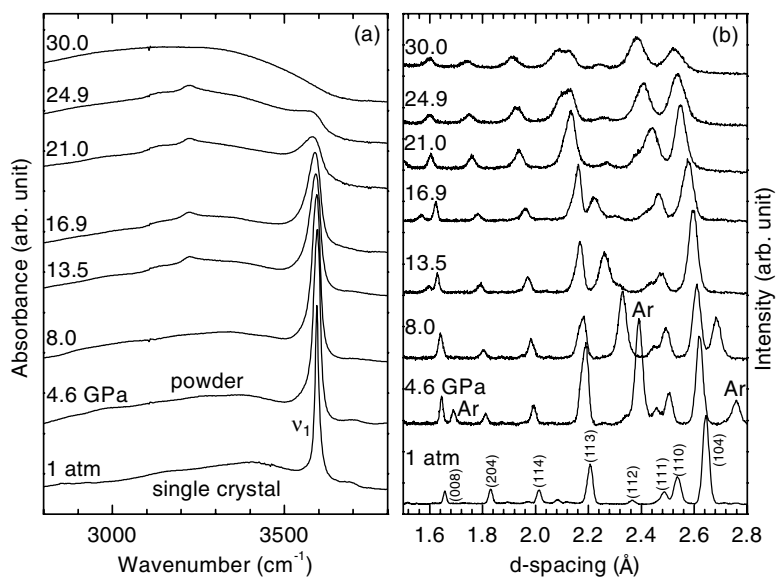

Figure 3. (a) IR absorption spectra and (b) XRD patterns of sample JKW62 at room temperature for selected pressures.

along the c-axis and inter-linked by Si_2O_7 tetrahedral dimers and K cations [10]. There are three symmetrically nonequivalent oxygen atoms in the phase X structure, and they are directly bonded to Si to form Si_2O_7 dimers. Among them, O1 is the bridging atom connecting Si1 and Si2 atoms, and O2 and O3 are nonbridging atoms. Since three OH stretching modes are observed in hydrous phase X, we assume that the all three oxygen atoms are available for
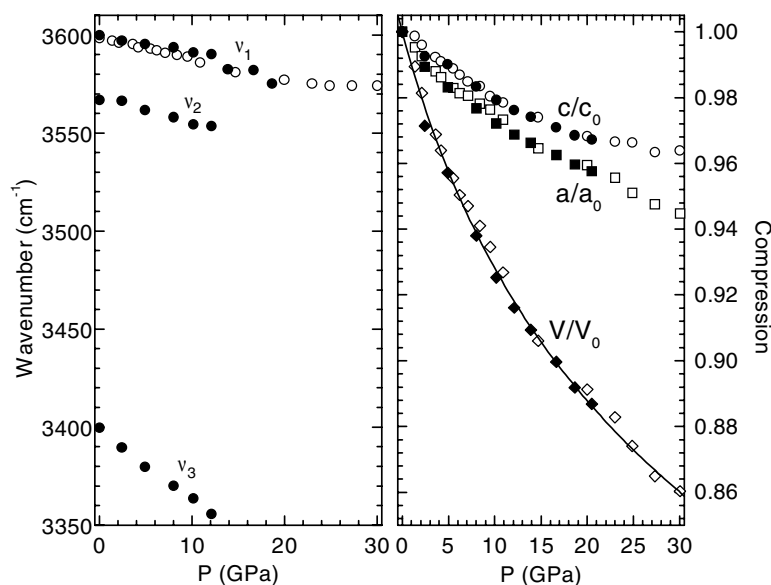
Figure 4. Pressure dependences of the OH stretching frequencies (left) and compression of the lattice parameters (right) for samples JKW56 and JKW62. Solid circles, JKW56; open circles, JKW62.

H bonding. In contrast to the case for hydrous phase X, only one peak is found in the OH stretching region for nominally anhydrous phase X. This presents an interesting question as to whether this material has been correctly characterized previously. The results indicate much less H bonding (no sharp lower-frequency OH mode and no splitting). Here, IR spectroscopy shows the great advantage of detecting OH stretching vibration in crystals with lower water concentration.

In figure 4, we summarize the pressure dependences of the OH stretching frequencies, volume, and lattice parameters. To allow comparison, solid and open symbols are used to represent the results for JKW56 and JKW62 samples, respectively. It can be seen that the frequencies of all OH stretching modes decrease with increasing pressure, but ν_3 has a large negative slope (-3.55 cm^{-1} GPa^{-1}) compared to that for ν_1 and ν_2 (-1.22 cm^{-1} GPa^{-1}). Above 20 GPa, ν_1 shows almost no shift for JKW62. The c-axis is less compressible than the a-axis; the difference between a/a_0 and c/c_0 increases with increasing pressure. This is consistent with the crystal structure model obtained from the single-crystal x-ray diffraction in which low compressibility of the lattice along the c-axis is expected due to the existence of Si_2O_7 tetrahedral dimers in the structure. The equation of state is also shown in the right-hand panel. The solid line represents a least-squares fit of the Birch equation to the experimental data. The bulk modulus is $B_0 = 74 \pm 38$ GPa and $B' = 16 \pm 9$ for both JKW56 and JKW62 samples. The broadening and disappearing of the OH stretching modes with increasing pressure may be related to the disorder and/or delocalization of hydrogen atoms at higher pressure.

4. Conclusions

The combination of the synchrotron IR microspectroscopy and x-ray diffraction techniques is a powerful tool for studying properties of OH stretching vibrations and crystal structures for hydrous minerals at high pressure. X-ray diffraction studies indicate that the crystal structure

of phase X is stable up to 30 GPa on room temperature compression. OH stretching modes broaden and greatly weaken with increasing pressure, which is attributed to pressure-induced distortion of Si_2O_7 dimers and disorder and/or delocalization of hydrogen atoms.

Acknowledgments

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