Re-examination of the hydrogarnet structure at high pressure using neutron powder diffraction and infrared spectroscopy

GEORGE A. LAGER,1,* WILLIAM G. MARSHALL,2 ZHENXIAN LIU,3 AND ROBERT T. DOWNS4

1Department of Geography and Geosciences, University of Louisville, Louisville, Kentucky 40292, U.S.A.
2ISIS Facility, CLRC Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, U.K.
3Geophysical Laboratory, Carnegie Institute of Washington, Washington, D.C. 20015, U.S.A.
4Department of Geosciences, University of Arizona, Tucson, Arizona 95721, U.S.A.

ABSTRACT

Time-of-flight neutron powder data and synchrotron infrared absorption spectra were collected for katoite hydrogarnet \([\text{Ca}_3\text{Al}_2(\text{O}_4\text{D}_4)\text{H}_4]\) at pressures to 9.4 and 9.8 GPa, respectively. The phase transition from space group \(\text{Ia}3d\) to \(\text{A}3d\) was observed in the neutron spectrum at \(\sim 7.5\) GPa, as indicated by the presence of two weak reflections (730 and 530) that violate the \(hkl\) conditions \((h\neq 0, h \neq 2n)\) imposed by the \(a\)-glide operation. However, attempts to refine the high-pressure structure in space group \(\text{A}3d\) did not significantly improve the fit and produced a chemically unreasonable O-D bond length at the second D position. Structure refinements in \(\text{Ia}3d\) indicate that (1) the O-D bond length, corrected for the effects of thermal motion, remains essentially constant \((\sim 0.95\ \text{Å})\) with increasing pressure; (2) hydrogen bond lengths shorten with increasing pressure; however, the variation in O-D–O angles indicates a preferential strengthening of H bonds; and (3) the compression mechanism is characterized by bond shortening rather than bond bending. The new results are in excellent agreement with both high-pressure X-ray diffraction experiments and ab initio calculations, and illustrate the need to eliminate peak broadening in high-pressure neutron powder experiments. IR spectra collected for the same sample showed discontinuities in both O-H and O-D vibrational frequencies at \(\sim 5\) GPa, suggesting that deuteration does not significantly affect the pressure of the transition. The higher pressure observed for the transition in the neutron data is probably due to lower signal-to-noise levels, which mask the weaker, symmetry-forbidden reflections at lower pressure.

INTRODUCTION

Katoite hydrogarnet \([\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)]\) is a model for the incorporation of OH in garnets and other silicate minerals that occur in the mantle, e.g., coesite (Koch-Muller et al. 2003). In natural systems, Ca-silicate garnets may be important water-bearing phases in eclogitic regions of the upper mantle (O’Neill et al. 1993). Recent deformation experiments carried out at 3 GPa suggest that very small amounts of fluids released by garnets and pyroxenes in eclogites can migrate to grain boundaries where they induce melting and cause brittle failure (Zhang et al. 2002). For these reasons, there has been continued interest in the high-pressure crystal chemistry of katoite.

The first high-pressure structural study of katoite was carried out using neutron powder diffraction methods (Lager and Von Dreele 1996). In their experiment, the sample was mixed with both fluorinert (pressure-transmitting medium) and NaCl (pressure calibrant) and pre-pressed into a sphere, which was then inserted between the WC anvils in a Paris-Edinburgh cell. Significant peak broadening was observed in the spectra above 2–3 GPa due to non-hydrostatic conditions within the cell. The results of that neutron powder study have been shown to be inconsistent with both theoretical and experimental studies (Knittle et al. 1992; Nobes et al. 2000a, 2000b), suggesting that peak broadening plus overlap between garnet and NaCl peaks may have introduced systematic errors in the data above \(\sim 3\) GPa. In the present study, the powder data were recollected from a fully deuterated katoite using a fluid pressure medium (deuterated ethanol:methanol). As the equation of state is well-determined (Lager et al. 2002), the sample was loaded without an internal pressure calibrant. In addition, the same sample was studied with high-pressure synchrotron IR spectroscopy to determine the effect of deuteration on the pressure of the phase transition.

EXPERIMENTAL METHODS

The polycrystalline samples of deuterated katoite (\(\sim 1\) g) were synthesized from tricalcium aluminate \((\text{Ca}_3\text{Al}_2\text{O}_6)\) at 473 K in a Parr vessel (45 mL) filled to approximately 70% capacity with D\(_2\)O (99.9 at% D, Aldrich 15,188-2). The tricalcium aluminate was synthesized following the procedure described by Lager et al. (1987).

About 170 mg of powdered sample were loaded into a type V4b Paris-Edinburgh high-pressure cell (Besson et al. 1992) equipped with standard profile WC Ni-binder anvils. The sample was confined between the anvils with a soft-metal-encapsulated (SME), single-torsoid gasket machined from null-scattering Ti/Zr alloy (Marshall and Francis 2002). A standard 4:1 by volume mixture of deuterated methanol and ethanol was used as the pressure-transmitting medium. Oil pressure in the in situ ram was raised using a hand-operated hydraulic pump. Time-of-flight (TOF) neutron powder diffraction data were collected at 0.08, 0.80, 1.72, 2.98, 4.05, 5.40, 6.65, 7.55, 8.56, and 9.42 GPa with the PEARL/HiPr diffractometer at the U.K. pulsed spallation source, ISIS. Integrated ISIS currents ranged from 560 \(\mu\text{A}\) h (\(-3\) h at 0.08 GPa) to 1883 \(\mu\text{A}\) h (\(-11\) h at 9.42 GPa). The equation of state determined by Lager et al. (2002) from single-crystal X-ray diffraction measurements was used to calculate the pressure (\(\pm 0.1\) GPa).

The overall \(d\)-spacing focused time-of-flight powder diffraction pattern obtained using the PEARL/HiPr 90° detector bank was corrected for neutron attenua-