High-pressure single-crystal X-ray diffraction study of katoite hydrogarnet: Evidence for a phase transition from \( Ia3d \rightarrow I\bar{4}3d \) symmetry at 5 GPa

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ABSTRACT

The crystal structure of katoite hydrogarnet has been refined at 0.0001, 2.15, 4.21, 5.09, 6.00, 7.09, and 7.78 GPa from single-crystal X-ray diffraction data using a 4:1 methanol:ethanol mixture as pressure medium in a Merrill-Bassett X-ray diamond-anvil cell. Below \(~5\) GPa, the katoite structure has \( Ia3d \) symmetry and compresses by bond shortening rather than bond bending, in agreement with recent neutron and theoretical results (Lager and Von Dreele 1996) below 4 GPa but differs in sign and magnitude from neutron data at higher pressures. If fluorinert is used as the pressure-transmitting medium, the katoite structure has \( Ia3d \) symmetry at 5 GPa determined from least-squares refinement of 25 reflections (8°< θ < 50°). In the \( I\bar{4}3d \) structure, there are two non-equivalent \((O_4H_4)\) groups. Both the Ca and Al atoms are displaced along \( a \) relative to their positions in \( Ia3d \). It is proposed that compression of the short H-H distance between \((O_4H_4)\) groups destabilizes the structure and may initiate the observed phase transition. Corroboration of this model will require accurate information on the hydrogen atom positions at pressures above 5 GPa.

INTRODUCTION

Katoite garnet [Ca₃Al₂(O₄H₄)₃], the Si-free end-member of the hydrogrossular solid-solution series, has received considerable attention in the literature because it is a model for the incorporation of OH in silicate garnets that occur in the Earth’s crust and mantle (Lager et al. 1987). The structure and bulk modulus of this garnet (\( Ia3d \) symmetry) has recently been determined to 70 GPa using ab initio quantum mechanical calculations (Nobes et al. 2000a, 2000b). It was proposed that bond shortening, as opposed to bond bending, was the primary mechanism of compression. This conclusion was based, in part, on the relative change in the tetrahedral-octahedral rotation angle, which shows only a small variation with pressure. The calculated trend is in agreement with neutron powder diffraction results (Lager and Von Dreele 1996) below 4 GPa but differs in both sign and magnitude from neutron data at higher pressures. If fluorinert is used as the pressure-transmitting medium, it is well known that deviatoric stress in the neutron diffraction experiment can cause significant strain broadening of Bragg reflections and loss of resolution above \(~2–3\) GPa. In this study, single-crystal X-ray diffraction data were collected to 7.78 GPa to re-examine the compression mechanism based on the neutron data and evaluate the discrepancy between the neutron and theoretical results.

EXPERIMENTAL METHODS

The katoite single crystals were synthesized in a Teflon-lined Parr vessel (~80% filled with \( H_2O \)) using a stoichiometric mixture of Al foil (in the form of strips) (Aldrich 35,685-0, 0.05 mm thick, 99.8%) and reagent-grade lime (CaO). After seven days at 423 K, this method produced relatively large single crystals (up to 800 \( \mu \)m) in a matrix of fine-grained material (<10 \( \mu \)m).

A crystal fragment with dimensions 120 × 100 × 50 \( \mu \)m was first examined in air outside the diamond-anvil cell on a Picker automated four-circle diffractometer (45 kV; 40 mA; unfiltered, non-monochromatic MoKα radiation). Reflection profiles (ω scans) were sharp (FWHM = 0.08°) with no indication of twinning. A small subset of reflections, e.g., (400), showed significant thermal diffuse scattering. Intensity data were collected in air assuming space group symmetry \( Ia3d \) and the structure was refined using RFINE4 (Finger and Prince 1975). The unit-cell parameter and atomic coordinates were consistent with the single-crystal X-ray results of Lager et al. (1987) and are not reported in this study.

High-pressure experiments were carried out using a 4-pin Merrill-Bassett diamond-anvil cell with 600 \( \mu \)m culets. The crystal was mounted in a 350 \( \mu \)m diameter sample hole drilled into an Inconel steel gasket (250 \( \mu \)m thickness; preindented to 100 \( \mu \)) with an electrostatic discharge machine. A 4:1 methanol:ethanol mixture was used as pressure-transmitting medium. The pressure was determined from the shift in the fluorescence lines of a small ruby chip mounted in the sample hole. The \( R_1 \) and \( R_2 \) peaks at each pressure were fit with Lorentzian functions; pressure was calculated using the relationship given by Mao et al. (1978). Errors in the pressure are estimated to be ±0.05 GPa.

Unit-cell parameters at ten pressures up to 7.78 GPa were determined from least-squares refinement of 25 reflections (8°< θ < 10°). The crystal structure of katoite hydrogarnet has been refined at 0.0001, 2.15, 4.21, 5.09, 6.00, 7.09, and 7.78 GPa from single-crystal X-ray diffraction data using a 4:1 methanol:ethanol mixture as pressure medium in a Merrill-Bassett diamond-anvil cell. Below ~5 GPa, the katoite structure has \( Ia3d \) symmetry and compresses by bond shortening rather than bond bending, in agreement with recent neutron and theoretical results (Lager and Von Dreele 1996) below 4 GPa but differs in sign and magnitude from neutron data at higher pressures. If fluorinert is used as the pressure-transmitting medium, the katoite structure has \( Ia3d \) symmetry at 5 GPa determined from least-squares refinement of 25 reflections (8°< θ < 50°). In the \( I\bar{4}3d \) structure, there are two non-equivalent \((O_4H_4)\) groups. Both the Ca and Al atoms are displaced along \( a \) relative to their positions in \( Ia3d \). It is proposed that compression of the short H-H distance between \((O_4H_4)\) groups destabilizes the structure and may initiate the observed phase transition. Corroboration of this model will require accurate information on the hydrogen atom positions at pressures above 5 GPa.