Crystal structure of a new high-pressure polymorph of topaz-OH

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ABSTRACT

A new high-pressure form of topaz-OH (denoted here topaz-OH II) was obtained at 14 GPa and 1400 °C. The X-ray diffraction pattern of this phase can be indexed by an orthorhombic cell with \( a = 4.72318(5) \), \( b = 8.91480(9) \), and \( c = 2.77276(3) \) Å. The lengths of \( a \) and \( b \) are similar, but \( c \) is approximately a third of that for a previously reported topaz-OH (denoted topaz-OH I). The structural formula of topaz-OH II can be written as \( (Al_{0.66}Si_{2.3})(OH_{0.66}Si_{2.3}) \), suggesting significant cation disorder in the structure. The crystal structure of topaz-OH II is solved using powder synchrotron X-ray diffraction data, and refined with constraints provided by a separate multi-nuclear NMR study. The structure has similarities with topaz-OH I and diaspore \((\alpha-AlOOH)\) structures, having partially occupied double edge-shared octahedral chains, and 2 \( \times \) 1 tunnels with partially occupied tetrahedral and octahedral sites.

Keywords: Crystal structure, high-pressure studies, phase transition, order-disorder

INTRODUCTION

Topaz-OH \([Al_2SiO_5(OH)_2]\), the OH end-member of the topaz solid-solution series, was discovered at pressures 5.5–10 GPa and 700–1000 °C (Wunder et al. 1993). Subsequent phase equilibrium studies revealed that topaz-OH is stable to 13 GPa and temperatures up to 1500 °C, beyond which topaz-OH breaks down to kyanite \((Al_2SiO_4)\) plus fluid at higher temperature, and to phase Egg \((Al_2SiO_5OH)\)-containing assemblages at higher pressure (Schmidt et al. 1998; Ono 1999).

The crystal structure of topaz-OH has been refined in space group \( Pbnm \) from single-crystal X-ray diffraction (XRD) obtained at 10 GPa and 1000 °C by Wunder et al. (1993). Northrup et al. (1994) also conducted single-crystal XRD of topaz-OH synthesized at the same \( P-T \) conditions, and revealed that the proton is located in two non-equivalent, half-occupied sites. Later, Chen et al. (2005) studied a topaz-OD sample synthesized at 1023 K and 7.5 GPa by neutron powder diffraction, and confirmed the conclusions of the previous studies. The latter two studies suggested the possibility of lower symmetry \((Pbn2)\) by long-range order of the proton positions, although it was not confirmed. The possibility of \( Pbn2 \), at room temperature was supported by ab-initio calculations and infrared spectroscopic study (Churakov and Wunder 2004; Watenphul and Wunder 2010). In all these structural studies, the samples were synthesized at pressures below 10 GPa and temperatures below 1000 °C, and the cation distributions except the proton were shown to be fully ordered. This established phase is referred as “topaz-OH I” in this paper.

Recently, we have applied multi-nuclear (\( ^1H, ^29Si, ^27Al \)) nuclear magnetic resonance (NMR) and Raman spectroscopy to phase Egg \((Al_2SiO_5OH)\) and other phases in the system \( Al_2O_3-SiO_2-H_2O \) (Xue et al. 2006). In the course of this study, we discovered the existence of a new high-pressure polymorph of topaz-OH (Kanzaki et al. 2006). The stability of the phase has been studied using in situ high-pressure X-ray diffraction (Kanzaki unpublished) and found to be stable at 13–14 GPa and 1300–1500 °C, located at the high-pressure and high-temperature corner of the topaz-OH stability field estimated (Schmidt et al. 1998; Ono 1999). Here we report the crystal structure of this phase (topaz-OH II hereafter) solved using powder synchrotron X-ray diffraction data. A combined multi-nuclear NMR and Raman study of both phase I and II is reported in a separate paper (Xue et al. 2010).

EXPERIMENTAL METHODS

Sample synthesis

The topaz-OH II sample used for the present study was synthesized using a Kawai-type double stage multi-anvil system with a DIA-type guide block driven by a 1500 ton press (SPEED1500) installed at the beamline BL04B1 of SPring-8 (Utsumi et al. 1998). The starting material was a mixture of dried reagent-grade \( SiO_2, Al_2O_3, \) and \( Al(OH)_3 \), with a nominal \( Al_2SiO_5(OH)_2 \) composition, and was put into a \( Pd_{25}Ag_{25} \) capsule (1.40/1.25 mm in o.d./i.d.). A 14 mm edge-length Cr-doped MgO octahedral cell assembly with a tube heater (made of hBN plus TiB_2) was employed. A thermocouple \((W_3Re_7-W_3Re)\) was broken during compression, and thus temperature was estimated from applied electric power (with an uncertainty of ±50 °C). The pressure cell is identical to that used for in situ high-pressure and high-temperature X-ray diffraction study of topaz-OH phase, in which gold powder was used as a pressure standard (Kanzaki unpublished). However, the present synthesis experiment was conducted without in situ X-ray diffraction. Therefore, to estimate the pressure, a pressure calibration curve against press load was constructed based on 10 in situ X-ray runs. The pressure reported here is based on that curve, and the estimation error is <1 GPa.

The sample was kept at 14 GPa and 1400 °C for an hour, and then quenched by cutting off the heating power. The recovered sample (K071126) was checked in situ X-ray runs. The pressure reported here is based on that curve, and the estimation error is <1 GPa.

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