Unique crystal chemistry of two polymorphs of topaz-OH: A multi-nuclear NMR and Raman study

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ABSTRACT

A new polymorph of topaz-OH (denoted as topaz-OH II) was recently discovered at higher P-T conditions than has been known thus far (denoted as topaz-OH I). High-resolution 1H, 29Si, and 27Al nuclear magnetic resonance (NMR) and micro-Raman spectroscopy are applied to shed light on the crystal chemistry of both polymorphs. Topaz-OH I, synthesized at 7 GPa and 640 °C, is stoichiometric (Si/Al = 0.5) with a largely ordered local structure. Higher P-T topaz-OH I synthesized at conditions close to the polymorphic phase transition boundary, on the other hand, shows lower Si/Al ratios (0.44–0.45) and greater local structural disorder [including a small fraction (~3%) of octahedral Si with a unique 29Si chemical shift near –133 ppm]. The latter may be accounted for by the development of defects (Si/Al in normally vacant octahedral sites and vacancies in the tetrahedral sites) at higher P-T conditions. Topaz-OH II synthesized at 13.5–14 GPa and 1300–1400 °C similarly exhibits low Si/Al ratios (0.41–0.46). The NMR and Raman spectra for these topaz-OH II are, in general, broader and revealed a substantial fraction (33–37%) of octahedral Si with a range of 29Si chemical shifts (–130 to –190 ppm), a small fraction (2–3%) of tetrahedral Al, and a range of (and overall shorter) hydrogen-bonding distances than topaz-OH I. Therefore, the phase transition from topaz-OH I to II is characterized by both a significant increase in the occupied octahedral/tetrahedral site ratio as well as disordering of cation distribution, which is unique from the viewpoint of crystal chemistry.

Keywords: NMR spectroscopy, Raman spectroscopy, high pressure, crystal structure, phase transition, vacancy, vacant site, Al-Si disorder, hydrogen bonding

INTRODUCTION

Naturally occurring topaz [Al8Si4O16(F,OH)2] are generally limited to F-rich compositions. Topaz-OH [Al8Si4O16(OH)2], the OH end-member of the F-OH solid-solution series of topaz, was first synthesized at 5.5–10 GPa and 700–1000 °C (Wunder et al. 1993). Subsequent studies in the Al8Si4O16·H2O system reported that topaz-OH can occur at pressures up to ca. 13 GPa and temperatures up to ca. 1500 °C, and breaks down to phase egg (AlSiO4OH)-bearing assemblages at higher pressures and to kyanite (Al2SiO5) + fluid at higher temperatures (Ono 1999; Schmidt et al. 1998).

Despite the reported high-temperature stability (up to ca. 1500 °C at 13 GPa) (Ono 1999), only topaz-OH samples synthesized at relatively low P-T (up to 10 GPa and 1000 °C) have been well characterized. Wunder et al. (1993) first refined the crystal structure of topaz-OH synthesized at 10 GPa and 1000 °C (space group Pbnm) from single-crystal X-ray diffraction (XRD). Subsequent studies of topaz-OH synthesized at 10 GPa and 1000 °C by single-crystal XRD (Northrup et al. 1994) and topaz-OD synthesized at 7.5 GPa and 750 °C by powder neutron diffraction (Chen et al. 2005) located the H (D) positions, and reported that the single H position found in F-rich topaz is split into two nonequivalent, half-occupied H (D) positions in topaz-OH (OD). The reported infrared and Raman spectra for topaz-OH synthesized at 9–10 GPa and 800–1000 °C both contain two O-H stretching bands near 3600 and 3520 cm⁻¹ with a low-frequency shoulder (Komatsu et al. 2005; Wunder et al. 1993). These bands have been attributed to O-H stretching of different OH groups from ab-initio calculations (Churakov and Wunder 2004).

We have applied a combined nuclear magnetic resonance (NMR) and micro-Raman spectroscopic study on hydrous phases (topaz-OH, phase egg, and δ-AlOOH) in the Al8Si4O16·H2O system synthesized under a range of P-T conditions to place additional constraints on their structures and potential roles as water reservoirs in the Earth’s mantle (Kanzaki et al. 2006; Xue et al. 2006). During this study, we discovered a new polymorph of topaz-OH (denoted here as topaz-OH II) (Kanzaki et al. 2006). In-situ XRD measurements over a wide range of P-T using synchrotron radiation at SPring-8, Japan, revealed that topaz-OH II occurs at the highest P-T corner of the previously reported stability field for topaz-OH, and the phase transition between topaz-OH II and the polymorph known thus far (denoted as topaz-OH I) is reversible (Kanzaki, unpublished results). The crystal structure of topaz-OH II has recently been refined in space group Pbnm using powder XRD data obtained with synchrotron radiation at SPring-8, and was found to bear some resemblance to that of topaz-OH I, but with a disordered cation distribution.