

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