

X-ray single-crystal structure refinement of an OH-rich topaz from Sulu UHP terrane (Eastern China) – Structural foundation of the correlation between cell parameters and fluorine content

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Abstract: An OH-rich topaz, $\text{Al}_2\text{SiO}_4\text{F}_{1.4}\text{OH}_{0.6}$, occurring in a kyanite quartzite of the Sulu UHP terrane (eastern China) has been optically and chemically (electron microprobe) characterised and its crystal structure refined by single-crystal X-ray diffraction data. Anisotropic refinement converged to $R = 0.024$ in the $Pbnm$ space group with cell parameters $a = 4.6696(8)$ Å, $b = 8.8486(17)$ Å, $c = 8.3915(22)$ Å. The position of the hydrogen atom has been detected; because the OH \rightarrow F substitution is less than 50 %, the disorder of H does not lower the overall symmetry. The influence of the OH \rightarrow F substitution on the lattice parameters is discussed in terms of crystal structure and shown to affect primarily the a and b cell edges; instead c is almost constant. A critical revision of earlier linear correlations of the F content (w_F) vs the lattice parameters and the availability of new data recently published, allowed to obtain improved regression lines for w_F vs a ($r^2 = 0.982$) and b ($r^2 = 0.968$) cell edges.

Key-words: OH \rightarrow F substitution, OH-rich topaz, crystal structure, cell dimensions vs structure, prediction of fluorine content.

Introduction

Topaz is one of the principal fluorine-bearing silicates that occurs as accessory mineral in fluorine-rich granitic rocks and associated hydrothermally altered rocks. The composition of topaz usually ranges from a nearly OH-free end-member, $\text{Al}_2\text{SiO}_4\text{F}_2$, in acid igneous rocks, to $\text{Al}_2\text{SiO}_4\text{F}_{1.4}(\text{OH})_{0.6}$, with $X_{\text{OH}} = \text{OH}/(\text{OH}+\text{F}) = 0.30$, in hydrothermal deposits (Barton *et al.*, 1982). Higher OH contents have been reported (Zhang & Liou, 1999; Zhang *et al.*, 2002) for topazes found in UHP units at Hushan ($X_{\text{OH}} \sim 0.35$), Hanshan and Wanshan ($X_{\text{OH}} = 0.40\text{--}0.55$) from the Sulu terrane, eastern China. Furthermore, a series of OH-rich topazes, from $X_{\text{OH}} = 0.22$ up to the pure end-member $\text{Al}_2\text{SiO}_4(\text{OH})_2$, has been synthesised by Wunder *et al.* (1993 and 1999) in high-pressure experiments (up to 100 kbar). The OH-rich topaz studied in this paper occurs within a kyanite quartzite (sample RPC547) collected at the mentioned Hushan locality. The quartzite contains also white mica and accessory barite, rutile, pyrite, zircon and apatite, and retrograde diaspore (Ferrando *et al.*, 2002).

The topaz structure usually shows orthorhombic $Pbnm$ space group, with F and OH statistically distributed on the same crystallographic site. By a single-crystal structure refinement, based on neutron-diffraction data collected from an OH-rich topaz ($X_{\text{OH}} = 0.28$), Zemmann *et al.* (1979) established that the hydrogen atom of the OH group substituting

F [hereafter indicated as F(O)] points towards the atoms O2 and F(O) belonging to adjacent octahedra (Fig. 1). The relevant distances and angles are: F(O)-H = 0.98 Å, H...F(O) = 2.38 Å, H...O2 = 2.22 Å, F(O)...O(2) = 3.02 Å, F(O)...F(O) = 3.20 Å, F(O)-H...O(2) = 138°, F(O)-H...F(O) = 140°. Consequently, taking into account that the observed O-H...F hydrogen bonds have maximum lengths around 3 Å (Chiari & Ferraris, 1982), we conclude that a very weak bifurcated hydrogen bond reasonably occurs between F(O), as donor, and the pair O2 plus an equivalent F(O) as acceptors. A triclinic $P1$ structure, with possible ordered F/OH arrangement, has been reported by Akizuki *et al.* (1979) and confirmed by a neutron diffraction refinement (Parise *et al.*, 1980). After heating at 950°C for 4 hours, the triclinic topaz inverts to orthorhombic with consequent F/OH disordering (Akizuki *et al.*, 1979). Parise *et al.* (1980) suggested that the proton-proton avoidance, related to two hydroxyls on adjacent sites, would imply the non existence of a fully hydrated topaz and concluded that the maximum OH \rightarrow F substitution should be 50 %. Nonetheless, the OH-pure end-member, $\text{Al}_2\text{SiO}_4(\text{OH})_2$, has been synthesised at high pressures (55–100 kbar) (Wunder *et al.*, 1993). An X-ray single-crystal structure determination on this end-member showed that H is distributed on two non-equivalent half-occupied sites, thus allowing full OH \rightarrow F substitution (Northrup *et al.*, 1994). The structure is still orthorhombic but the (001) mirror plane is lost and the sym-