

Crystal chemistry and thermal behavior of Fe-carpholite from the Pollino Massif, southern Italy

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ABSTRACT

The crystal chemistry and thermal behavior of Fe-carpholite from the Pollino Massif have been investigated by a multi-method approach. A combination of optical microscopy, scanning electron microscopy, μ Raman spectroscopy, thermal analysis, room-temperature single-crystal X-ray diffraction, and high-temperature X-ray powder diffraction was employed.

Field and micromorphological observations showed that the studied carpholite occurs in veins embedded in fine-grained matapelites and coexist with quartz, calcite, chlorite, and phengite. In particular, the tiny carpholite crystals are closely associated with quartz, suggesting simultaneous formation.

Structure refinements from single-crystal X-ray diffraction confirm that carpholite crystallizes in the *Ccce* space group. Anisotropic refinements converged at $2.3 \leq R$ (%) ≤ 2.6 and yielded unit-cell parameters $a \sim 13.77$ Å, $b \sim 20.16$ Å, $c \sim 5.11$ Å, and $V \sim 1419$ Å³. An X_{Fe} [i.e., the molar fraction $\text{Fe}^{2+}/(\text{Mg}+\text{Fe}^{2+}+\text{Mn})$] of ~ 0.6 was derived from the refined occupancy at the *M1* site and is correlated to structural expansion mainly along the *b* and *a* axes and to geometrical distortions of the *M1*, *M2*, and *M3* octahedra. μ Raman spectrum of unoriented Fe-carpholite crystals exhibits several bands in the 200–1200 cm^{-1} region, a strong peak at 3630 cm^{-1} and a weak peak at 3593 cm^{-1} , the latter two of which account for the presence of two independent OH groups, as also revealed by the X-ray structure refinement.

The TG curve indicates a total mass loss of 15.6% in the temperature range 30–1000 °C, and the DTA curve shows a broad endothermic band at ~ 400 °C, extending up to ~ 650 °C, and weak exothermic peaks at ~ 700 and 750 °C. The latter may be ascribed to the breakdown of the Fe-carpholite structure and crystallization of new phases. The in situ high-temperature X-ray powder diffraction from 30 to 1105 °C revealed no significant changes in XRD patterns from 30 to 355 °C but reflection splittings from 380 °C due to a Fe-oxidation/deprotonation process. The carpholite and deprotonated carpholite phases coexist in the temperature range 380–580 °C, whereas only the deprotonated phase is observed up to 630 °C. Above this temperature, the carpholite structure collapses and the characteristic peaks of spinel and quartz phases are observed. At 1105 °C, spinel, mullite, garnet, cristobalite, and tridymite can be clearly identified. Our results provide insight into the thermal stability of Fe-carpholites and may help understand the thermal evolution of HP/LT metasediments.

Keywords: Fe-carpholite, crystal chemistry, thermal evolution, SEM, single-crystal XRD, high-temperature powder XRD, thermal analysis, μ Raman spectroscopy