

Thermal behavior of a Ti-rich phlogopite from Mt. Vulture (Potenza, Italy): An in situ X-ray single-crystal diffraction study

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ABSTRACT

The structural evolution of a trioctahedral mica from Cava St. Antonio, Mt. Vulture, Potenza, Italy, has been studied in the temperature range 100–1023 K using in situ single-crystal X-ray diffraction techniques. The sample used shows a Ti-rich composition close to the phlogopite-annite join with the following crystal-chemical formula: $(K_{0.85}Na_{0.11}Ba_{0.03})(Al_{0.17}Mg_{1.98}Mn_{0.01}Fe_{0.29}^{2+}Fe_{0.37}^{3+}Ti_{0.18})(Si_{2.75}Al_{1.25})O_{10.66}(F_{0.13}OH_{1.20}Cl_{0.01})$. In the present study, the chemical and structural changes and the deprotonation process involved during heating have been characterized. Analysis of the data showed that *a*, *b*, and *c* cell parameters expand almost linearly up to 823 K, while the β angle remains constant. A sharp decrease in the unit-cell dimensions was observed at 873 and 1023 K. Linear trends obtained during reversal experiments from 1023 K to room temperature demonstrated the irreversibility of these events.

Structure refinements of single-crystal XRD data collected at 100, 200, 298, 473, 673, 873, and 1023 K converged to $2.14 \leq R$ (%) ≤ 8.47 , $2.47 \leq R_w$ (%) ≤ 10.83 . In the temperature range 100–673 K, the thermal expansion along the *c* direction is mainly due to interlayer thickness dilation. The tetrahedral ring approaches the ideal hexagonal shape with increasing temperature to match the expanding octahedral sheet. In the range 873–1023 K, a strong shrinking of the interlayer is associated with the shortening of the M1-O4 and M2-O4 distances and to the consequent reduction of octahedral thickness. Such structural features indicate the occurrence of Fe oxidation process, involving loss of structural H, which is responsible for a phase transition. Mössbauer spectroscopy supported this hypothesis.

Keywords: Trioctahedral mica, single-crystal X-ray diffraction, deprotonation, thermal expansion