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

Gennaro Venturti,1 Michele Zema,2,3 Fernando Scordari,1,* and Giuseppe Pedrazzi4

1Dipartimento Geomineralogico, Università degli Studi di Bari, Via E. Orabona 4, I-70125 Bari, Italy
2Dipartimento di Scienze della Terra, Università degli Studi di Pavia, via Ferrata 1, I-27100 Pavia, Italy
3CNR-IGG, Sezione di Pavia, via Ferrata 1, I-27100 Pavia, Italy
4Dipartimento di Sanità Pubblica, Sezione di Fisica, Plesso Biotecnologico Integrato, via Volturino 39, I-43100 Parma, Italy

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: (K0.85Na0.11Ba0.03)(Al0.17Mg1.98Mn0.01Fe2+0.29Fe30.37Ti0.18)(Si2.75Al1.25)O10.66(F0.13OH1.20Cl0.01). 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 % ≤ R (%) ≤ 8.47, 2.47 % ≤ Rw (%) ≤ 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

INTRODUCTION

Micas are very common minerals occurring in a wide variety of geological environments. They are important because they control the introduction of H2O into the mantle. This strongly influences melting conditions and other properties of the subcrustal material. High-temperature studies are mostly devoted to (1) understanding the mechanisms of storage and release of H2O in micas under extreme conditions, through thermal activation, and (2) investigating the effects of the oxygen fugacity upon phase relation diagrams. Understanding the thermal behavior of this mineral family is crucial to provide a reliable basis for further interpretation and prediction of phase equilibria, phase transformations, and most reactions occurring in a variety of rocks, and the development of geothermometers as well.

Several spectroscopic and structural studies have been performed on trioctahedral micas at high temperature, most of them on powdered samples. As concerns Fe-bearing phlogopites, complications arise from the multiple oxidation states of iron and the ability of the Fe-rich structure to compensate for oxidation or reduction. In this case, the modification of Fe-oxidation is shown by a marked change in slope of the lattice parameters and hence of the cell volume upon increasing T. However, the temperature range can be variable, depending on the rate of the change in T and the possible non-equilibrium conditions of the sample, and the particular environmental conditions of the process.

Takeda and Morosin (1975) first pioneered a high-temperature structural study of a synthetic fluorophlogopite single crystal. In their study the authors successfully related a geometrical model to deduce structural changes of the micas from the observed lattice expansion. They also observed a kink in the lattice parameter expansivities at 400 °C and a change in the expansion mode of Mg-octahedra. Takeda and Ross (1975) examined two polytypes (1M, 2M1) of Fe-rich phlogopites hydrogenated by a flow of hydrogen gas at 700 °C, while Ohta et al. (1982) used hot argon gas to produce a hydrogen-depleted and oxidized (oxy-mica) counterpart of each polytype for comparison. These studies clearly showed that interlayer separation is significantly affected by H content due to electrostatic repulsions between the interlayer cation and the H, in addition to cell parameter change caused by the reduction/oxidation process effects on the iron cation.

Rancourt et al. (2001) performed a detailed study, by means of a combination of several techniques, of the transformations annite → oxyannite, through the reaction Fe2+ + OH− → Fe3+ +