3T-phlogopite from Kasenyi kamafugite (SW Uganda): EPMA, XPS, FTIR, and SCXRD study

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ABSTRACT

A 3T mica polytype from Kasenyi (southwest Uganda), kamafugite, was studied by electron probe microanalysis (EPMA), single-crystal X-ray diffraction (SCXRD), micro-Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) to characterize its crystal chemistry and the relationships with phlogopites from the same rock but showing different stacking sequence and to get insights into factors affecting polytypism in Ugandan phlogopites. EPMA data gave: SiO$_2$ = 38.7(2), Al$_2$O$_3$ = 13.08(9), MgO = 20.4(2), TiO$_2$ = 4.8(1), MnO = 0.03(3), FeO$_{tot}$ = 5.51(9), Cr$_2$O$_3$ = 0.90(7), NiO = 0.11(5), SrO = 0.03(3), ZnO = 0.04(3), ZrO$_2$ = 0.01(2), K$_2$O = 9.64(5), Na$_2$O = 0.29(1), BaO = 0.15(5), F = 0.13(5), and Cl = 0.01(1) wt%.

X-ray photoelectron spectroscopy provided Fe$^3+$/Fe$^2+$ and O$^2-/OH$ equal to ~0.75 and 7.14, respectively, which are in agreement with the results of previous Mössbauer investigation on the BU1 phlogopites from the same rock and with the structural formula of the studied crystal. Infrared spectra showed a shoulder at ~3660 cm$^{-1}$ in the OH$^-$ stretching region (~3740–3600 cm$^{-1}$), which is assigned to MgMgFe$^{3+}$-OH$^-$< K-O$^2-$ local configurations. No evidences of vacancy configurations were observed.

Structure refinement based on single-crystal X-ray diffraction data was performed in space group $P3_112$ using anisotropic displacement parameters and converged to $R_I$ = 4.34 and $wR_2 = 3.33\%$. Unit-cell parameters are: $a=b=5.3235(3)$ Å and $c=30.1882(2)$ Å. Geometrical and chemical considerations point to a disordered cation distribution over T1 and T2 tetrahedral sites, whereas partial cation ordering characterizes the octahedral sites with high-charge cations preferentially located as expected on M2 and M3. Tetrahedral bond length distortion and angular variance parameters describe more distorted polyhedra in 3T polytype than those found in coexisting 1M and 2M polytypes.

Finally, the overall crystal-chemical features indicate the occurrence of the following substitution mechanisms in the studied sample: Ti-oxo ($^{\text{VI}}$M$^{2+}$+2(OH)) ↔ $^{\text{IV}}$Ti$^{4+}$+2(OH$^-$)+H$_2$O and Al, Fe$^{3+}$, Cr-oxo ($^{\text{VI}}$M$^{2+}$+(OH)) ↔ $^{\text{IV}}$M$^{3+}$+O$^2-$+½(H$_2$O)); Al, Fe$^{2+}$-Tschermak ($^{\text{VI}}$M$^{2+}$+Si$^{4+}$ ↔ $^{\text{IV}}$(Al$^{3+}$, Fe$^{2+}$)+$^{\text{IV}}$Al$^{3+}$); $^{\text{VI}}$K$^{+}$-$^{\text{IV}}$Al$^{3+}$ ↔ $^{\text{IV}}$Si$^{4+}$+$^{\text{IV}}$[O]; tetraferriphlogopite ($^{\text{VI}}$Fe$^{3+}$↔$^{\text{IV}}$Al$^{3+}$).

Keywords: 3T-phlogopite, SCXRD, EPMA, FTIR, XPS, crystal chemistry, cation partitioning

INTRODUCTION

1M, 2M, and 3T are the most common MDO mica polytypes classified as “Subfamily A polytypes” on the basis of successive layer rotation of 2$n\times60^\circ$ [with $n = 0$ for 1M, $n = 1$ and 2 for 2M, and $n = 1$ or 2 for 3T; Nespolo (1999); Ferraris and Ivaldi (2002)]. Among these, the 1M and 2M are the most abundant polytypes in trioctahedral and dioctahedral micas, respectively, whereas the 3T polytype is very frequently occurring in dioctahedral micas (see Sassi et al. 2010 and references therein). The total number of layers polytypes, derived by Ross et al. (1966) is six, out of which only two belong to the subfamily A. They are indicated as 3T[222] and 3Tc[022] in RTW notation (Ross et al. 1966) and can be distinguished by their symmetry where 3T has space group $P3_112$ and 3Tc has space group $CT$ (Takeda and Ross 1995). The characterization of mica polytypes is complicated by the fact that it may not be easy to distinguish between true polytypes and twinning that simulates a polytype with longer period, an issue known as “apparent polytypism” (Nespolo 1999 and references therein). Two cases of apparent 3T polytypes (really due to 1M polytypes twinned by pseudo-merohedry, each twin being composed of three individual components rotated by ±120° around e*) have been recently reported by Nespolo and Kuwahara (2001) and Scordari et al. (2013). However, although very rare, trioctahedral 3T polytype really occurs. The first structure model of a 3T-phlogopite dates back to Hendricks and Jefferson (1939). Sadanaga and Takeuchi (1961) identified a 3T trioctahedral mica by the analysis of diffraction intensities. Since then, most of the single crystals of 3T trioctahedral micas found in nature resulted to be Li-rich, mostly belonging to the muscovite-polythionite-annite system. X-ray diffraction studies were carried out on these mica samples to describe their structure and define their cation partitioning (Brown 1978; Pavlishin et al. 1981; Weiss et al. 1993; Brigatti et al. 2003). Based on average octahedral distances and refined scattering powers, it was argued that in most cases cation distribution with M1 = M3 >