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

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ABSTRACT

A 3*T* 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_2O_3 = 13.08(9), MgO = 20.4(2), TiO_2 = 4.8(1), MnO = 0.03(3), FeO_{tot} = 5.51(9), Cr_2O_3 = 0.90(7), NiO = 0.11(5), SrO = 0.03(3), ZnO = 0.04(3), ZrO_2 = 0.01(2), K_2O = 9.64(5), Na_2O = 0.29(1), BaO = 0.15(5), F = 0.13(5), and Cl = 0.01(1) wt%. The analyzed sample may be classified as a Ti-rich phlogopite.

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 substitutions 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_1 = 4.34 and wR_2 = 3.33%. Unit-cell parameters are: $a = b = 5.3235(3)$ and $c = 30.188(2)$ 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 3*T* polytype than those found in coexisting 1*M* and 2*M*₁ polytypes.

Finally, the overall crystal-chemical features indicate the occurrence of the following substitution mechanisms in the studied sample: Ti-oxy [$^{VI}M^{2+}+2(OH)^- \leftrightarrow {}^{VI}Ti^{4+}+2(O^{2-})+H_2\uparrow$] and Al, Fe^{3+}, Cr-oxy [$^{VI}M^{2+}+(OH)^- \leftrightarrow {}^{VI}M^{3+}+O^{2-}+\frac{1}{2}(H_2)\uparrow$]; Al, Fe^{3+}-Tschermak [$^{VI}M^{2+}+{}^{IV}Si^{4+} \leftrightarrow {}^{VI}(Al^{3+}, Fe^{3+})+{}^{IV}Al^{3+}$]; $^{XII}K^++{}^{IV}Al^{3+} \leftrightarrow {}^{IV}Si^{4+}+{}^{XII}\square$; tetraferriphlogopite [$^{IV}Fe^{3+} \leftrightarrow {}^{IV}Al$].

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