Crystal chemistry and surface configurations of two polylithionite-1*M* crystals

CHIARA ELMI[1], MARIA FRANCA BRIGATTI[1], STEPHEN GUGGENHEIM[2,*], LUCA PASQUALI[3,4], MONICA MONTECCHI[3,4] AND STEFANO NANNARONE[3,4]

[1]Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, 41121 Modena, Italy
[2]Department of Earth and Environmental Sciences, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607-7059, U.S.A.
[3]Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy
[4]IOM INFM-CNR Area Science Park, Building MM, S.S. 14, Km 163.5, 34012, Basovizza (TS), Italy

ABSTRACT

This paper explores the crystal chemical features of the bulk and the outermost (001) surface layers of two trioctahedral Li-rich mica-1*M* (space group *C*2) polytypes, i.e., a polylithionite (MLG-114) from Li-mica granitic pegmatite at St. Austell (SW England) and a Fe^{2+}-rich polylithionite (Ch-140) from a rhyolite at Profitis Ilias, Chios Island, Greece. Structural formulas are $^{[xii]}(K_{0.952}Na_{0.019}Rb_{0.019})$ $^{[vi]}(Al_{1.034}Li_{1.459}Fe^{2+}_{0.389}Fe^{3+}_{0.046}Mn_{0.038}Mg_{0.002}Zn_{0.002}Ti_{0.001})$ $^{[iv]}(Al^{3+}_{0.477}Si_{3.523})O_{10.081}(F_{1.735}OH_{0.184})$ and $^{[xii]}(K_{0.992}Na_{0.014})$ $^{[vi]}(Al^{3+}_{0.980}Li_{1.028}Fe^{2+}_{0.787}Fe^{3+}_{0.022}Mn_{0.059}Mg_{0.052}Zn_{0.010}Ti_{0.024})$ $^{[iv]}(Al^{3+}_{0.857}Si_{3.143})O_{10.095}(F_{1.617}OH_{0.288})$ for MLG-114 and Ch-140, respectively. Each mineral is characterized by a high F content in the anion site and has tetrahedral and octahedral compositions related to the exchange vector $^{[vi]}Li_{-1}^{[iv]}Si_{-1}^{[vi]}Fe^{2+[iv]}Al$. Unit-cell dimensions are *a* = 5.251(1), *b* = 9.066(2), *c* = 10.087(2) Å; β = 100.694(5)° for polylithionite MLG-114 and *a* = 5.282(1), *b* = 9.121(3), *c* = 10.080(3) Å; β = 100.764(5)° for Ch-140. Crystal structure refinements (agreement factors are *R* = 3.58% and 3.75% for MLG-114 and Ch-140, respectively) demonstrate that the $^{[vi]}Li_{-1}^{[vi]}Fe^{2+[iv]}Si_{-1}^{[iv]}Al$ exchange vector produces a decrease in the lateral dimensions of the tetrahedral and octahedral sheets. The decrease in basal oxygen distances results from the effect of the strain caused by the orientation of opposing tetrahedral sheets within a 2:1 layer. The decrease reduces the strain so that the basal oxygen plane can remain nearly planar. Changes in these dimensions via distortions of the tetrahedral basal-oxygen ring (α = 3.3° and 4.1° for MLG-114 and Ch-140, respectively) are limited. Octahedral M1 and M3 sites are similar in size and much larger than M2 and the mean electron count is M3 < M1 < M2 in MLG-114 and M1 ≈ M2 < M3 in Ch-140. Al preferentially occupies the M2 site, whereas Fe and Li are nearly disordered between M1 and M3 sites with a slight preference of Fe for the M1 site in MLG-114 and for M3 site in Ch-140.

Element concentrations on the (001) surface, obtained through X-ray photoelectron spectroscopy (XPS) high-resolution spectra for Si_{2p}, Al_{2p}, Fe_{2p}, K_{2p}, Li_{1s}, and F_{1s} core levels, indicate that a greater amount of lithium and a smaller amount of potassium characterize the surface with respect to the bulk. The decrease in K content, commonly observed in micas, is related to its location on the cleavage surface, because the cation must be distributed equally between the two (001) surfaces generated upon cleavage. The increase in Li content on or near the (001) cleavage surface suggests a preference for cleavage near lithium-enriched regions. The surface structure of the polylithionite crystals suggests that Al, Li, and Fe cations maintain coordination features at the surface similar to the bulk. Silicon, however, which is generally in fourfold coordination, shows also a small number of [1]-fold coordinated components at a binding energy of 99.85 eV.

Keywords: Polylithionite, crystal chemistry, crystal structure, surface features