A STRUCTURAL STUDY OF NATURAL OLIVINE-TYPE PHOSPHATES

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Minerals of the triphylite-lithiophilite series, $Li(Fe^{2+},Mn^{2+})PO_4$-$Li(Mn^{2+},Fe^{2+})PO_4$, are primary phosphates which occur in the geological context of rare-element granitic pegmatites. The oxidation processes, affecting the pegmatites during their evolution, provoke a progressive oxidation of triphylite in ferrisicklerite [$Li_{1-x}(Fe^{3+},Mn^{2+})PO_4$] and in heterosite [$(Fe^{3+},Mn^{3+})PO_4$], and of lithiophilite in sicklerite [$Li_{1-x}(Mn^{2+},Fe^{3+})PO_4$] and in purpurite [$(Mn^{3+},Fe^{3+})PO_4$] (1,2). These phosphates exhibit the olivine structure, but the detailed structural modifications induced by these oxidation processes were not previously investigated. It is noteworthy that these olivine-type phosphates are good candidates for the development of new cathode materials for Li-ion batteries.

In this study, we investigated a natural sample from the Altai Mountains, China, in which a progressive transition from lithiophilite to sicklerite is observed. Under the polarizing microscope, lithiophilite is colorless, whereas sicklerite shows a deep orange color. Several grains show intermediate colors, suggesting a progressive transition from lithiophilite to sicklerite. This progressive transition if confirmed by SIMS (Secondary Ion Mass Spectrometry) analyses, which indicate Li values from 0.96 to 0.69 Li atoms per formula unit (*p.f.u.*).

Five single-crystals, corresponding to zones with different colors, were extracted from this sample and investigated by single-crystal X-ray diffraction techniques (Oxford Diffraction Gemini PX Ultra 4-circle diffractometer, 50 kV, 40 mA, MoK_α). The samples are orthorhombic, space group *Pbnm*, with unit-cell parameters ranging from a = 4.736(1), b = 10.432(2), c = 6.088(1) Å (lithiophilite) to a = 4.765(1), b = 10.338(2), c = 6.060(1) Å (sicklerite). The structures were refined to R_1 values ranging from 2.19 to 2.94 %, and show a topology identical to that of olivine-type phosphates reported in the literature (3). Li occurs on the M(1) site, and shows occupancy factors from 0.99 Li *p.f.u.* (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS.

Two triphylite samples from a pegmatite near Brandberg, Namibia, and from Hagendorf-süd, Germany, were also investigated, and show the unit-cell parameters a = 4.711(1), b = 10.369(1), c = 6.038(1) Å and a = 4.704(1), b = 10.365(1), c = 6.025(1) Å, respectively. Their crystal structures were refined to R_1 values between 3.56 and 3.93 %. Correlations were established between the unit-cell parameters of olivine-type phosphates from this study and from the literature, and the mean ionic radius of the cations occurring on the M(2) site.

References

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