

Iron-Manganese Phosphates with the Olivine- and Alluaudite-Type Structures: Crystal Chemistry and Applications

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Iron-manganese phosphates play an essential geochemical role in the evolution processes affecting rare-element granitic pegmatites. Among these minerals, primary olivine-type phosphates of the triphylite-lithiophilite series $[\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4\text{-Li}(\text{Mn}^{2+}, \text{Fe}^{2+})\text{PO}_4]$ are affected by oxidation processes which induce a progressive transformation from triphylite to ferrisicklerite $[\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})\text{PO}_4]$ and to heterosite $[(\text{Fe}^{3+}, \text{Mn}^{3+})\text{PO}_4]$, and from lithiophilite to sicklerite $[\text{Li}_{1-x}(\text{Mn}^{2+}, \text{Fe}^{3+})\text{PO}_4]$ and to purpurite $[(\text{Mn}^{3+}, \text{Fe}^{3+})\text{PO}_4]$ [1,2]. The genetic evolution affecting these phosphates is also characterized by Na-metasomatic processes, leading to the formation of secondary phosphates of the alluaudite group. These minerals exhibit chemical compositions ranging from $\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$ to $\text{NaMnFe}^{3+}_2(\text{PO}_4)_3$, with Mn^{2+} or some Ca^{2+} replacing Na^+ , Fe^{2+} replacing Mn^{2+} , and some Mg^{2+} or Mn^{2+} replacing iron.

Minerals of the triphylite-lithiophilite series, as well as their oxidation products, exhibit the olivine structure, but the detailed structural modifications induced by these oxidation processes were not previously investigated. In this study, we performed single-crystal X-ray diffraction measurements (Oxford Diffraction Gemini PX Ultra 4-circle diffractometer, 50 kV, 40 mA, $\text{MoK}\alpha$) on a natural sample from the Altai Mountains, China, in which a progressive transition from lithiophilite to sicklerite is observed. Five single-crystals, corresponding to zones with different colors, were extracted from the sample and 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 $M(2)$ site, and shows occupancy factors from 0.99 Li atoms per formula unit (*p.f.u.*) (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS (Secondary Ion Mass Spectrometry), which indicate Li values from 0.96 to 0.69 Li *p.f.u.*

A good knowledge of the crystal chemistry of these phosphates is absolutely necessary, since Padhi *et al.* [4] demonstrated their efficiency as cathode material for Li-ion batteries. Such LiFePO_4 -based batteries are actually produced industrially, and are used as power sources for electric cars, laptops, or mobile phones. As a consequence, the number of scientific publications related to these phosphates increased linearly, from a few papers in 1997, to more than 250 publications in 2009.

The alluaudite structure was described by Moore [5] on a natural sample from the Buranga pegmatite, Rwanda. The mineral is monoclinic, space group $C2/c$, and the structural formula corresponds to $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$, with four formula units per unit cell. The structure consists of kinked chains of edge-sharing octahedra stacked parallel to $\{101\}$. These chains are formed by a succession of $M(2)$ octahedral pairs linked by highly distorted $M(1)$ octahedra. Equivalent chains are connected in the b direction by the $P(1)$ and $P(2)$ phosphate tetrahedra to form sheets oriented perpendicular to $[010]$. These interconnected sheets produce channels parallel to the c axis, channels which contain the X sites.

Over the past twenty years a variety of synthetic alluaudite-like compounds have been reported; see Hatert [6] for a brief summary of this work. The study of these new alluaudite-like structures reveals more structural complexity than that reported by Moore [5], a