

Oral Contributions

[MS18-02] Structural Variations of Olivine-type Phosphates: a good Example of how Minerals can inspire the Development of new Materials. Frédéric Hatert, Fabrice Dal Bo, Maxime Bajjot.

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Phosphates of the triphylite-lithiophilite series [$\text{LiFe}^{2+}\text{PO}_4$ - LiMnPO_4] occur in the geological context of granitic pegmatites, where they form masses that can reach several meters in diameter. During the oxidation processes affecting the pegmatites, these olivine-type phosphates progressively transform to ferrisicklerite-sicklerite [$\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})(\text{PO}_4)$ - $\text{Li}_{1-x}(\text{Mn}^{2+}, \text{Fe}^{3+})(\text{PO}_4)$] and to heterosite-purpurite [$(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{PO}_4)$ - $(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{PO}_4)$], according to the substitution mechanism $\text{Li}^+ + \text{Fe}^{2+} \rightarrow \square + \text{Fe}^{3+}$. This oxidation mechanism was described by mineralogists in the 1940's, based on petrographic observations of phosphates under the polarizing microscope and on chemical data [1,2]. In 1997, Padhi *et al.* [3] demonstrated the efficiency of triphylite-type phosphates 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. The crystal structure of minerals of the triphylite-lithiophilite series (triphylite: $a = 4.690$, $b = 10.286$, $c = 5.987$ Å, *Pbnm*) is characterized by two types of octahedral sites: the *M*(1) octahedra occupied by Li, and the *M*(2) sites occupied by Fe and Mn. A natural sample from the Altai Mountains, China, was recently investigated by Hatert *et al.* [4], in order to understand the structural variations occurring during the oxidation of lithiophilite into sicklerite. Five single-crystals, corresponding to intermediate members of the lithiophilite-sicklerite series, were extracted from a thin section 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 show a topology identical to that of olivine-type phosphates, with Li occurring on the *M*(2) site and showing occupancy factors from 0.99 Li atoms per formula unit (*p.f.u.*) (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). Natrophilite, NaMnPO_4 , is another pegmatite phosphate with the olivine structure, in which the *M*(1) site is occupied by Na while the *M*(2) site contains the smaller divalent cations. Recently, the Fe-analogue of natrophilite was found at the Malpensata granitic pegmatite, Colico commune, Lecco province, north Italy [5]. This phosphate, $\text{Na}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$, is orthorhombic, space group *Pbnm*, $a = 4.882(1)$ Å, $b = 10.387(2)$ Å, $c = 6.091(1)$ Å, $V = 308.9(1)$ Å³, and $Z = 4$. The mineral shows the olivine structure, with *M*(1) occupied by Na and *M*(2) occupied by Fe and Mn. In order to elucidate the phase relations among lithium-iron phosphates, we decided to investigate the $\text{Li-Fe}^{2+}\text{-Fe}^{3+}$ (+ PO_4) system hydrothermally between 400 and 700°C, at 1 kbar pressure. These experiments first allowed to determine the stability fields of several phosphate assemblages. A black crystal of partially oxidized triphylite has been synthesized during these experiments, and its crystal structure has been solved in the *Pnma* space group ($a = 10.306(4)$, $b = 6.004(2)$, $c = 4.69(1)$ Å, $R1 = 0.041$). The structural data, electron-microprobe analysis, as well as the colour of this phosphate, indicate that this triphylite-type compound contains both Fe^{2+} and Fe^{3+} ; the insertion of Fe^{3+} in the structure is achieved through the substitution mechanism $3\text{Fe}^{2+} = 2\text{Fe}^{3+} + \square$ [6].

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