

***In-situ* XRD and PDF investigation of battery fluoride materials $\text{MF}_3 \cdot 3\text{H}_2\text{O}$ (M = Fe, Cr) in controlled atmosphere: accessing new phases with controlled chemistry**

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Iron fluoride ($\text{FeF}_3 \cdot n\text{H}_2\text{O}$) shows high capacity as cathode material for lithium-ion batteries combined to low toxicity and low cost. The water content of iron fluoride has been shown to be of prime importance in the performances of the cathode. So far, the various synthesis route doesn't allow for a precise water content control, especially on the low amount regime which is the most interesting range of composition [1]. In addition, CrF_3 has been shown to significantly increase the conductivity of LiF film [2]. Consequently, it is of interest to look for the *in-situ* formation of the various $\text{MF}_{3-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ phases (M = Cr, Fe).

In this contribution, we report on the *in-situ* formation of $\text{MF}_{3-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ (M = Fe, Cr) phases using self-generated atmosphere. Traditionally, the heating $\text{MF}_3 \cdot 3\text{H}_2\text{O}$ in open air results in the full oxidation and decomposition of the fluorides giving rise to nano based oxides. Here, we make use of self-generated atmosphere to control the precise crystal chemistry of those phases upon heating preventing full oxidation at mild temperatures while stabilizing new phases relevant for battery applications.

Some of the results are presented in Figure 1 about the $\text{FeF}_{3-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ phases. Precise controlled of the water content of the $\text{FeF}_{3-x}(\text{OH})_x \cdot n\text{H}_2\text{O}$ series could be reached with n ranging from 1/3 to 0 with about 10 new pure phases. We demonstrate experimentally the initial assumption on the role played by the water in the stabilisation of the $\text{FeF}_3 \cdot 1/3\text{H}_2\text{O}$ phase, phase which is relevant for battery application [1]. In addition, the controlled *in-situ* decomposition of $\text{CrF}_3 \cdot 3\text{H}_2\text{O}$ led to the formation of a new $\text{CrF}_{3-x}(\text{OH})_x$ pyrochlore which was characterized structurally and magnetically. This work demonstrates the added value of *in-situ* experiment using self-generated atmosphere for synthesising new phases.

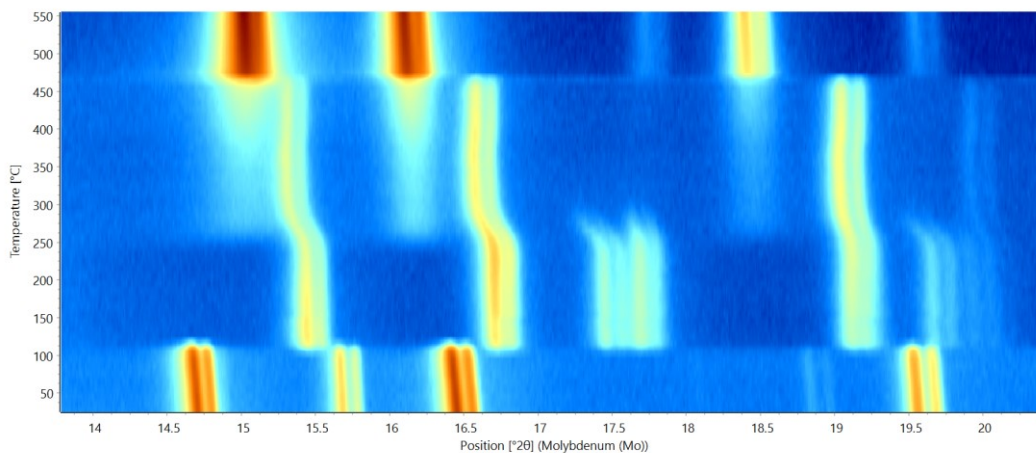


Figure 1. Isoline plot of the *in-situ* diffraction upon heating of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ illustrating the various stable phases obtained using self-generated atmosphere.

[1] Kim *et al.*, (2010) *Adv. Mater.* **22**, 5260; Ma *et al.* (2012), *Energy Environ. Sci.* **5**, 8538.

[2] Tetsu O. (1984), *Materials Research Bulletin* **19**, 451.

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