A simple Capillary Reactor to Study Solid/Solid and Solid/Gas Reactions in the Lab by *in situ* XRD with Coupled Mass Spectrometry (XRD-MS)

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The rational planning of solid-state synthesis experiments is almost always hindered by the fact that in general little is known on reaction mechanisms. Additionally, such experiments often involve extreme conditions (high temperatures, high pressures, gas flow, corrosive reactants…) and time scales in the wide range of µs to weeks. These issues are especially relevant when dealing with metastable compounds, which are at local minima in the thermodynamic energy landscape. Solid state synthesis therefore almost always consists of the well-known trial-and-error cycle, which either ends with satisfactory results or even more often with the neglection of the initial idea. *In situ* studies are an efficient way to target these problems as they enable the study of formation as well as decomposition reactions and may help in screening the multi-parameter space.[1]

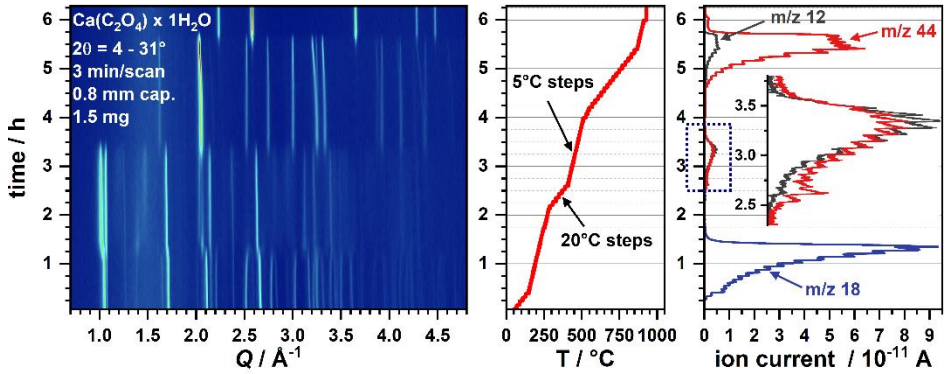


Figure 1. *Contour level plot of the XRD patterns obtained for the thermal decomposition of $Ca(C_2O_4)$ x 1 H_2O. The MS data in form of ion current for selected m/z ratios is additionally displayed.*

A currently studied class of metastable materials are oxyfluorides of the Ruddlesden-Popper structure type. Selected representatives are $La_2NiO_{2.5}F_3$ which is obtained from the reaction of La_2NiO_4 with polyvinylidene fluoride (PVDF) at 350 °C, and $La_2CoO_3F_3$ which plays an important role in solid state fluoride ion battery research. For the fluorination of La_2NiO_4 detailed *in situ* XRD and NPD investigations previously revealed a complex reaction mechanism consisting of several partially fluorinated reaction intermediates. [2,3]
In order to further study the reaction mechanism of such fluorination reactions we constructed a capillary reactor which is coupled to a mass spectrometer enabling *in situ* XRD-MS investigations of solid/solid and solid/gas reactions on a laboratory powder diffractometer. In our contribution we report first results that are obtained from this setup. These investigations include the thermal decomposition of $Ca(C_2O_4)$ x 1 H_2O which is used as benchmark experiment, the topochemical fluorination of La_2CoO_4 with AgF [4], and the thermal defluorination of $La_4Ni_3O_{8.4}F_{3.5}$ [5]. We hereby obtained insight in the type, and amount of the gaseous reaction products as well as the dependence of their appearance on the crystalline phases that are observed.

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