$M(C_2O_4)\cdot 2H_2O$ (M = Mg, Fe, Co) – Chained to Stacking Faults

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Metal oxalates are of multiple interest as they appear as minerals, in biological processes as well as in synthetic chemistry.[1-3] For various functional materials, e.g. battery materials or catalysts, they are used as precursors to prepare the corresponding oxides by thermal treatment. Given that the compounds $M(C_2O_4)\cdot 2H_2O$ with M = Mg, Mn, Fe, Co, Ni are structurally similar and easy to prepare by precipitation they are an appealing starting point for mixed metallic compounds.[3,4] The challenge starts with the interpretation of the powder diffraction patterns. The primary building unit of the compounds are chains that are packed into layers. The stacking of these – directed by hydrogen bonds – gives rise to various polytypes. It is long known that the compounds are prone to stacking faults[5], the degree of which is depending on the synthesis conditions. We use these materials as precursors for preparing catalysts and the aim of the work presented here is to guide the analysis of the often puzzling results from powder diffraction by methods beyond the state of the literature, e.g. the use of average crystal structures.[6]

In this work the various mono- and bimetallic samples with M = Mg, Fe & Co are analysed using XRPD, PDF and complementary chemical analytics. To outline in Fig. 1 calculated XRPD data for the two known polymorphs for $Fe(C_2O_4)\cdot 2H_2O$ are shown alongside experimental data for a well ordered sample from a commercial supplier and a heavily disordered sample obtained by precipitation at pH 2. As the latter allows no assignment to any of the two known polymorphs an attempt using PDF was made to assign structural similarities to either polymorph, indicating a better agreement with the form in *Cccm*. Based on this, several stacking fault scenarios were simulated and a faulted structure model was optimized against the experimental data. However, surprisingly with a dominant stacking pattern that is yet unknown for the compound. Further, results on monometallic $Co(C_2O_4)\cdot 2H_2O$ and mixed metallic $(Fe_{1-x}Mg_x)(C_2O_4)\cdot 2H_2O$ will be presented.

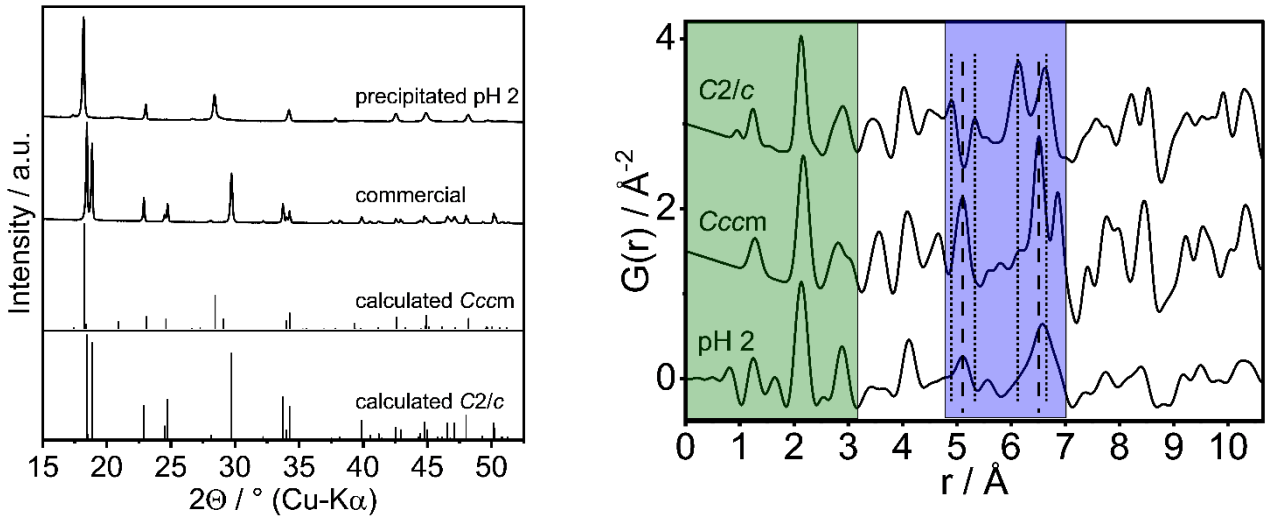


Figure 1. *XRPD (left) and PDF (right) data for selected samples alongside calculated data.*

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