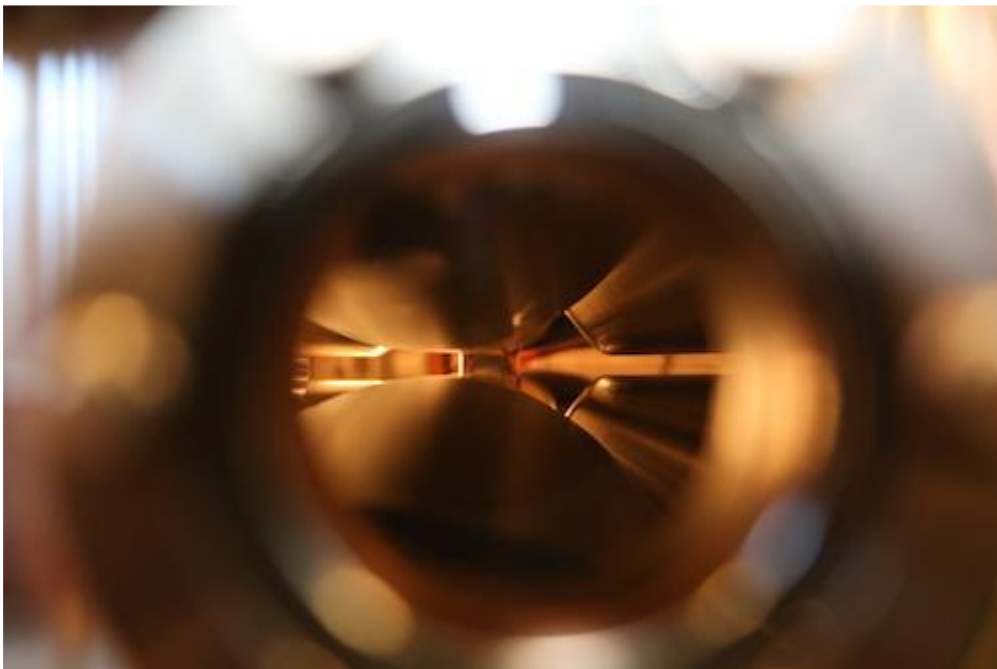


## **Max IV Lab Activity Report 2014-15**



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## Comparative structural study of layered double hydroxides prepared and intercalated by commonly as well as scarcely applied methods

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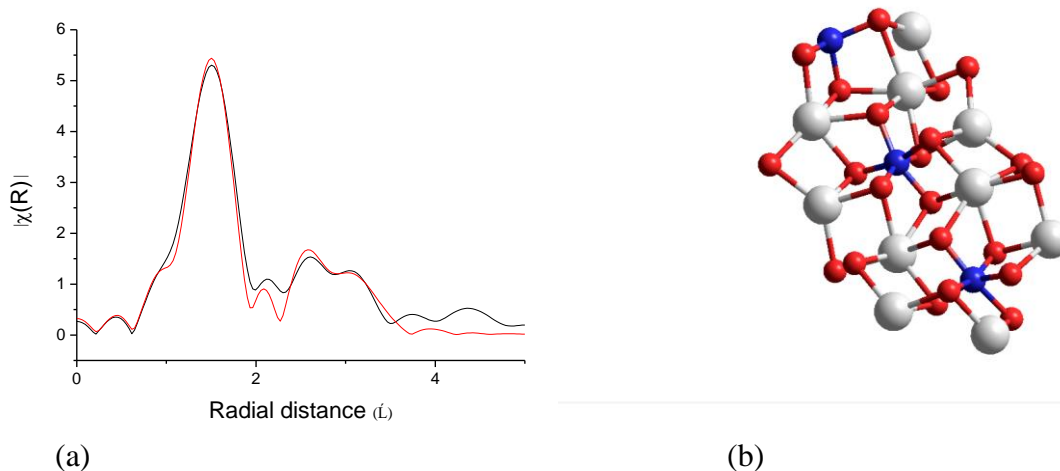
Layered double hydroxides (LDHs) can be prepared through a variety of ways. The synthetic methods applied influence the quality of the materials obtained, i.e., there are noticeable differences in their local structures, not easily approached by common characterization methods. XAS measurements at K-edge of iron can give information about these structural features in Ca(II)Fe(III)-LDHs and Ca(II)Al(III)Fe(III)-layered triple hydroxides (LTHs) and their amino acid intercalated varieties allowing a comparative study among those prepared by the most common co-precipitation and the less frequently applied mechanochemically-assisted as well as ultrasonically-enhanced methods.

Layered double hydroxides are also called anionic clays, and comprise a class of materials built up from positively charged layers (mainly) of bivalent- and trivalent metal hydroxides and negatively charged ions in-between. Many of their representatives are of natural origin; however, for use, they are usually synthesized. Several synthesis methods are available, and, usually, they are easy and produce, with some effort, phase-pure materials. The LDHs have structures with high regularity; however, the charge-compensating anions between the layers, can easily be altered through a large variety of methods. Through these methods, large inorganic, organic, inorganic-organic complex anions can be introduced, or as it is called in this field: intercalated, among the layers. Thus, the LDHs are flexible substances, they can be modified and functionalized easily; therefore, they have many uses. They may serve as catalysts or catalyst supports, nanoreactors providing confined space for reactants suitably close to each other, transporters of sensitive synthons to the place of the synthesis, containers of medicines, pesticides, fungicides providing their slow release, to mention just a few. For their syntheses many methods are available. The co-precipitation of the component cations by NaOH solution from the solution having both dissolved metal ions, is the most frequently used one. Other, more scarcely applied methods can also be used, e.g., we successfully applied mechanochemically-assisted synthesis for a variety of LDHs, among them for CaFe-LDHs; these materials and their ternary derivatives (for instance, CaAlFe-LTHs) could also be made by ultrasonically-enhanced method of synthesis. Moreover, these techniques could be applied for intercalating amino acid anions among the layers. To our surprise, the simple co-grinding of the component salts in a mortar with a pestle led to the formation of the LDHs too, and the intercalation of the amino acid anions was also successful in this way.

Characterization methods, commonly used in materials science laboratories (XRD, TG-DTG, SEM, SEM-EDX, TEM) revealed that there were structural differences among the materials depending on the way of preparation and intercalation. However, these methods are not able to provide with local structural information, which is much needed for a deeper understanding of these fine structural details. XAS measurements at the K-edge of Fe are expected to allow a detailed description of the local environment of the Fe(III) ion.

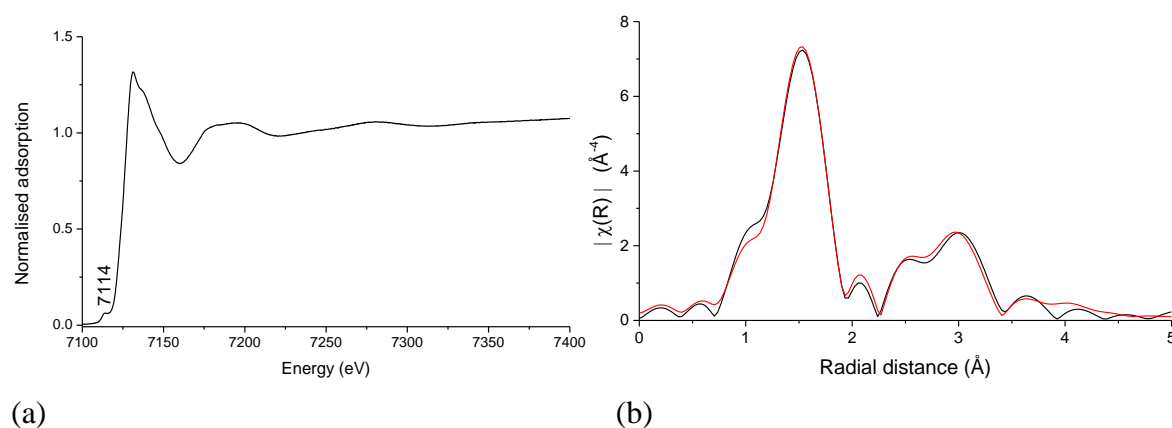
The Fourier-transformed NEXAFS/EXAFS spectrum of a Ca(II)Fe(III)-LDH sample prepared with the combination of dry and wet grinding is displayed in Fig. 1(a). In the first

coordination shell, there are six oxygen atoms, with a Fe–O interatomic distance of 1.99 Å. The second coordination sphere contains three Ca<sup>2+</sup> ions, where the Fe–Ca interatomic distance was fitted to be 3.12 Å and three other Ca<sup>2+</sup> ions, where the Fe–Ca interatomic distance was determined to be 3.55 Å. For easier visualization, a slab of a layer is depicted in Fig. 1(b).



**Fig. 1.** Mechanochemically prepared CaFe-LDH, (a) the Fourier-transformed NEXAFS/EXAFS spectrum (red line – fit, black line – experimental), (b) a slab of the CaFe-LDH layer deduced from the XAS measurement (Ca – white, Fe – blue, O – red; hydrogens are omitted for increasing clarity).

In the first coordination sphere CaAlFe-LTH prepared with the ultrasonically-enhanced mechanochemical method, there were six oxygen atoms at about 2 Å from the Fe(III) centre. In the second shell, the EXAFS data indicate a deformed system with two different Fe–Ca atomic distances. Two Ca atoms were placed closer to the Fe(III) ion (3.11–3.12 Å) and the other four were in the same position at 3.44–3.45 Å.



**Fig. 2.** The Fe K-edge X-ray absorption (a) and Fourier-transformed and fitted NEXAFS/EXAFS spectra (b) CaAlFe–CO<sub>3</sub><sup>2-</sup>-LTH. The black lines show the experimental data and the red ones denote the results of fitting.

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