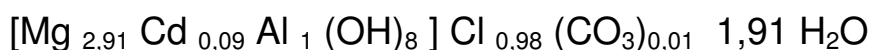
 ROBL-CRG	Experiment title: EXAFS investigations of Mg-Al layered double hydroxides containing Zr-IV, Hf-IV and Cd-II ions	Experiment number: 2001698
Beamline: BM 20	Date of experiment: from:21.01.2010 to: 23.01.2010	Date of report: 30.06.2010
Shifts:	Local contact(s): Dr. Andreas Scheinost	<i>Received at ROBL:</i>
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Report:**Reference Number of the proposal: 2001698**

The aim of the experiments was to give detail informations about the structural incorporation of different ions in the structure of Mg-Al layered double hydroxides. EXAFS investigations with Mg-Al layered double hydroxides containing Zr-IV, Hf-IV and Cd-II ions were performed. The samples were synthesised via the coprecipitation method and the following stoichiometries were obtained:



Prior to the EXAFS investigations results from XRD investigations showed that the LDHs were the only crystalline phases detected.

Layered double hydroxides of trivalent Al and either divalent Mg or 3d-metals are characterized by six-fold oxygen coordination of the metal, a nearest metal-metal distance in the range of 3.05 to 3.10 Å. The fit results are summarized in table 1.

In the **Zr-doped LDH** the Zirconium is in eight-fold oxygen coordination as supported by the coordination number of 7.6 and the distance of 2.14 Å. The DW of 0.0073 Å² shows a substantial structural disorder typical for eight-fold coordination. The second shell FT peak at about 3.25 Å is fitted by two Zr atoms at a distance of 3.57 Å. The observed k-wave amplitude distribution shows only one maximum at about 8.1 Å⁻¹, evidence that only heavier atoms like Zr can be present in this shell. In conclusion, first shell coordination, as well as distance and atomic nature of the second shell contradict incorporation of Zr into the crystal lattice of the MgAl-LDH.

As for the Zr-doped LDH the first-shell coordination number and distance suggest an 8-fold oxygen coordination for the **Hf-doped LDH** as well. A detailed wavelet analysis of the second shell shows backscattering from two

different types of atoms. The best fit was achieved by using two shells with Al and Hf. The Hf-Hf distance of 3.37 Å is similar to that in orthorhombic hafnia (HfO₂, 3.39 Å). The longer Hf-Al/Mg distance of 3.63 Å could point towards a (monodentate?) sorption complex at LDH edge sites.

For the **Cd-doped LDH** the coordination shell is split into two shells. The first peak is fit by about 5 oxygen atoms at a distance of 2.26 Å, the distance in line with a 6-fold oxygen coordination of Cd(II). The second peak is fit by about one chlorine atom at a distance of 2.62 Å, the distance in line with a 6-fold chlorine coordination (e.g. 2.64 Å in CdCl₂). The Cd-O shell and the Cd-Mg/Al shell would rather point to a sorption complex than to a isomorphic substitution in LDH.

Table 1: EXAFS fit results

Phase	Edge	Fit	coord				Metal				ΔE_0	χ_{res}	S_0^2
			E	CN	R	σ^2	E	CN	R	σ^2			
Zr-doped LDH	Zr	A	O	7.6	2.14	0.0073	Zr	1.9	3.57	0.0088	-0.3	11.9	0.9
Hf-doped LDH	Hf	A	O	7.7	2.12	0.0078	Hf	2.7	3.37	0.0074	11.8	6.2	0.9
							Mg/Al	1.4	3.63	0.0014			
							Mg/Al	2.3	3.57	0.0041	11.8	8.9	0.9
		C	O2	7.7	2.12	0.0078	Hf	4.9	3.42	0.0117	11.7	8.8	0.9
Cd-doped LDH	Cd	A	O	4.9	2.26	0.0087	Mg/Al	1.0	3.17	0.0016	8.4	8.1	0.9
			Cl	0.9	2.62	0.0070	Cd	2.0	3.86	0.0131			

Especially the EXAFS results for the Zr-doped LDH are contrary to results of recent XRD investigations. Different Zr-doped LDHs (molar exchange of Al by Zr in the range between 4 and 20 %) were synthesised and analysed. The expected increase in the a lattice parameter was observed clearly while increasing the Zr amount. More detail work is in progress.