



	Experiment title: Development of Eu ²⁺ doped Compounds for Novel Energy Saving LEDs	Experiment number: MA-916
Beamline: 26-A	Date of experiment: from: 10.11.2009 to: 13.11.2009	Date of report: 18.02.2010
Shifts: 9	Local contact(s): Sergey Nikitenko	<i>Received at ESRF:</i>
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Report:

In the context of energy saving one important challenge of solid state inorganic chemistry is the development of future materials for light emitting diodes (LEDs). For this purpose new phosphors have to be found in order to produce white light of high color quality by combination of blue, red, and green radiation. Eu(II) doped compounds are very interesting because of their extremely high luminescence efficiency, which leads to very bright luminescent materials. Coordination numbers and europium ligand distances are very important factors, which influence the crystal field splitting of the Eu(II) 5d-excited states and therefore the emission energy of europium ions. This structure property relationship which can be investigated with EXAFS and luminescence spectroscopy is, however, necessary in order to design novel phosphors.

Another goal of our studies is to determine the crystallographic position of Eu(II) in host lattices where two or more sites could be substituted. In our previous work we found red and green luminescent materials, especially when Eu²⁺ ions are expected to substitute Mg²⁺, which are very promising materials for applications in LEDs. Because of the large differences of the ionic radii of both ions, the substitution site was, however, not proved. Therefore, we investigated the compounds AMgCl₃ (A= Cs, Rb, K), where Eu²⁺ can enter either the alkaline metal or the magnesium site. Because of the completely different coordination spheres of both sites, this point can be very well investigated by EXAFS measurements.

For the EXAFS investigations powder samples were prepared by melting the binary chlorides in stoichiometric ratios. Doping was achieved by adding 3 mol% of EuCl₂. All steps were performed under inert gas conditions to avoid the oxidation of divalent europium. The presence of trivalent europium would disturb the oscillation in the EXAFS range and prevent the determination of the coordination numbers and bondlengths. In fact, no traces of Europium(III) could be detected. The EXAFS measurements were done at the L₃-edge of Europium in fluorescence mode at room temperature.

The following Eu^{2+} doped compounds were investigated: KMgCl_3 , RbMgCl_3 , CsMgCl_3 , KCaCl_3 , RbCaCl_3 , CsCaCl_3 and CsCdCl_3 . Fitting of the first coordination shell was successful for almost every host lattice and preliminary results could be obtained for the average Eu-Cl distances. Two examples are shown in figures 1 and 2. The EXAFS measurements revealed, that the theory describing the strong correlation between luminescence, bondlengths and coordination number cannot be applied to every system. The successful measurements on $\text{CsAlCl}_3:\text{Eu}^{2+}$ ($A = \text{Mg}, \text{Cd}, \text{Ca}$) which led to precise structural characterisation of bondlengths, coordination numbers and europium sites, encouraged us now to work on more complicated systems like $\text{KMgCl}_3:\text{Eu}^{2+}$ and $\text{RbMgCl}_3:\text{Eu}^{2+}$ where two sites seem to be occupied by europium. Investigations on further host lattices are mandatory in order to determine the influence of the second and third coordination spheres on the luminescence properties.

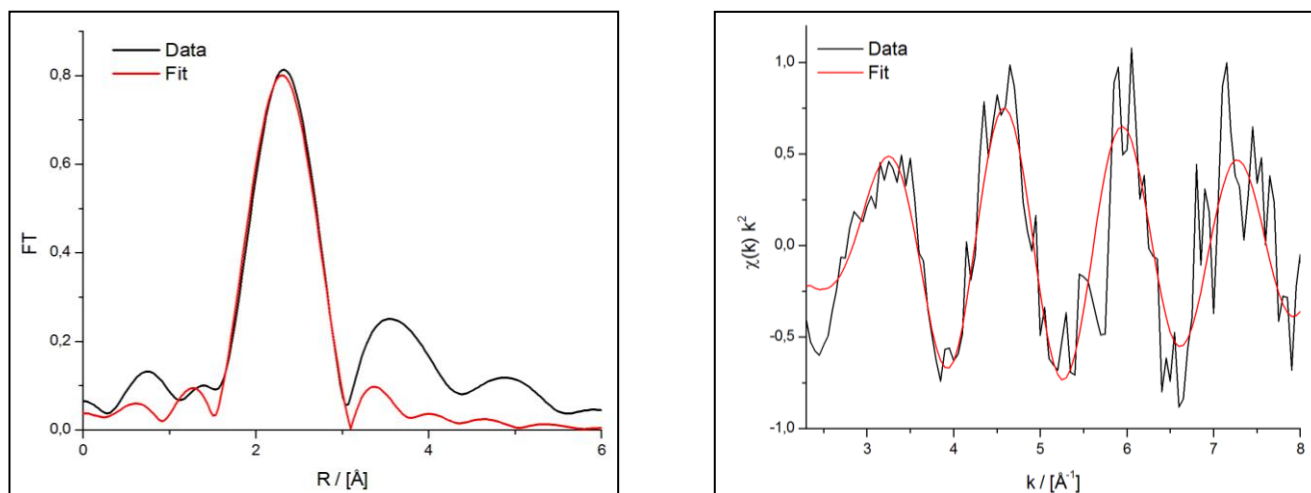


Figure 1 : Eu L_3 -edge k^2 -weighted EXAFS spectrum (right) and the corresponding Fourier transform (left) of CsCdCl_3 with 3% Eu^{2+} on the Cd^{2+} site

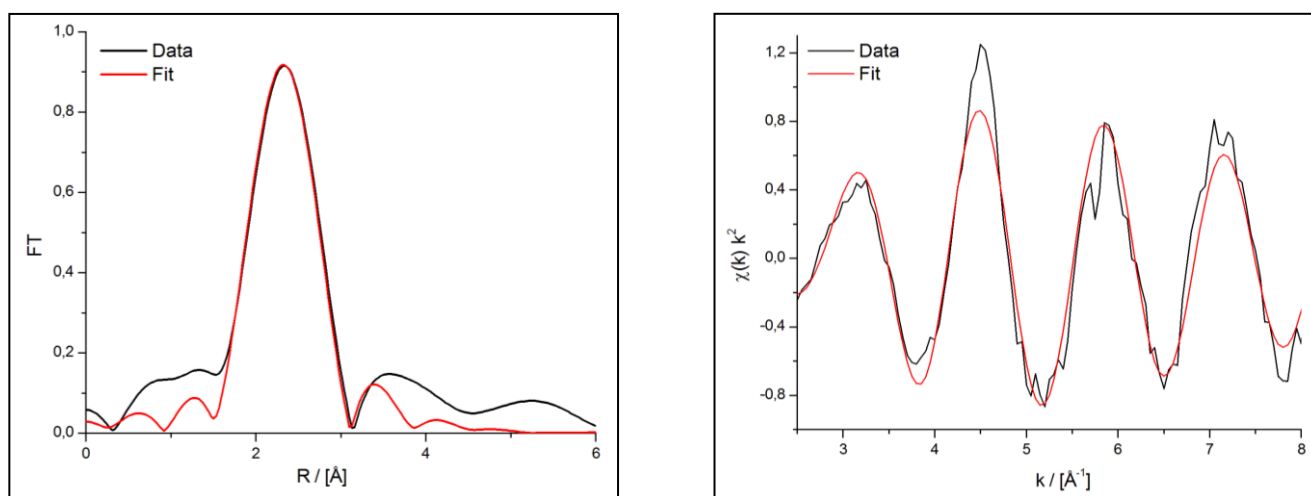


Figure 2: Eu L_3 -edge k^2 -weighted EXAFS spectrum (right) and the corresponding Fourier transform (left) of KCaCl_3 with 3% Eu^{2+} on the Ca^{2+} site