



## Experiment Report Form



	<b>Experiment title: XAS-XRD investigations on the effect of different synthetic routes and annealing conditions on the design of inorganic materials</b>	<b>Experiment number:</b> CH-6599
<b>Beamline:</b> BM23	<b>Date of experiment:</b> from: 12/07/2023                      to: 17/07/2023	<b>Date of report:</b> 13/09/2023
<b>Shifts:</b> 12	<b>Local contact(s):</b> Kirill Lomachenko	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> Prof. Silvia Gross (University of Padova, Italy) Federico Barbon (University of Padova, Italy) * Lucas Bemfert (Justus-Liebig-University Giessen, Germany) * Paolo Dolcet (Karlsruhe Institute of Technology, Germany) * Chiara Mazzariol (Justus-Liebig-University Giessen, Germany) *		

### Report:

#### Experimental details

XAS measurements were performed on Eu-doped calcium molybdate samples, obtained from two different synthetic methods (inverse miniemulsion and ball-milling syntheses), at Eu L<sub>3</sub>-edge (6977 eV) and at Mo K-edge (20000 eV). *In situ* experiments were performed using the Microtomo furnace, which allows to follow the evolution of the absorbing species during the annealing process up to 900 °C either in He flow, in vacuum or in air flow. The samples were heated from room temperature (RT) up to 900°C with a heating rate of 10 °C/min, holding the temperature for 2 h. Measurements at Eu L<sub>3</sub>-edge were performed in fluorescence mode, where EXAFS spectra were acquired in the range 6850-7550 eV at RT before and after annealing, and XANES spectra were measured in the range 6850-7200 eV while heating and cooling the sample (acquisition time per spectrum ca. 6 min, temperature step per spectrum ca. 65 °C). Measurements at Mo K-edge were performed in transmission mode in the range 19700-21700 eV. The evolution of gaseous species during the annealing process was followed *in situ* by mass spectrometer (MS). The samples were prepared as pure pellet, to avoid the interference of a binder (*e.g.* BN) during the annealing process. *Ex situ* experiments were performed at both edges collecting EXAFS spectra of reference and pre-treated pelletized samples. The original proposal aimed at collecting also XRD patterns, but due to technical problems the XRD detector was not available.

#### Results

The goal of this experiment was twofold: *i*) understand the transformation on the electronic and short-range structure of the doping ions and the matrix during the annealing process in inert atmosphere (He flow) and *ii*) to unravel the origin of the different behaviours of the samples during this process, arising from the different synthetic routes exploited to obtain the final product, *i.e.* inverse miniemulsion (wet chemistry) and ball-milling (solid-state chemistry). Eu-doped CaMoO<sub>4</sub> with 1 and 5 at. % (calculated as at. % Eu/Mo), from miniemulsion and ball-milling synthesis were tested. Considering the *in situ* experiments at the Eu L<sub>3</sub>-edge, the XANES spectra (Figure 1a,b) clearly show a partial reduction of Eu<sup>3+</sup> to Eu<sup>2+</sup> during the annealing process from RT to

900 °C in He flow for all samples investigated, namely samples with different Eu amount (1 and 5 at. %) and from different synthetic methods. Going more into details, considering the XANES spectra, the  $\text{Eu}^{3+}$  peak at 6983 eV decreases in intensity during annealing (RT to 900 °C) whereas the intensity of  $\text{Eu}^{2+}$  shoulder at 6876 eV increases. Upon cooling the system from 900 °C to RT, the  $\text{Eu}^{2+}$  shoulder decreases and the  $\text{Eu}^{3+}$  peak increases in intensity, meaning that part of the  $\text{Eu}^{2+}$  is re-oxidised to  $\text{Eu}^{3+}$  when lowering the temperature. However, the reduction and oxidation process of  $\text{Eu}^{3+}$  is not completely reversible, as a small quantity of  $\text{Eu}^{2+}$  is still present (presence of  $\text{Eu}^{2+}$  shoulder) even at RT after annealing and even after exposing the sample to air. The presence of  $\text{Eu}^{2+}$  in Eu-doped samples was also confirmed by *ex situ* measurements on samples previously annealed at home institution and exposed to air for days. In addition, samples after annealing in He flow appear of a black colour and no longer show the characteristic red luminescence of the  $\text{Eu}^{3+}$  upon excitation in the UV ( $\lambda_{\text{exc}}=254$  nm).

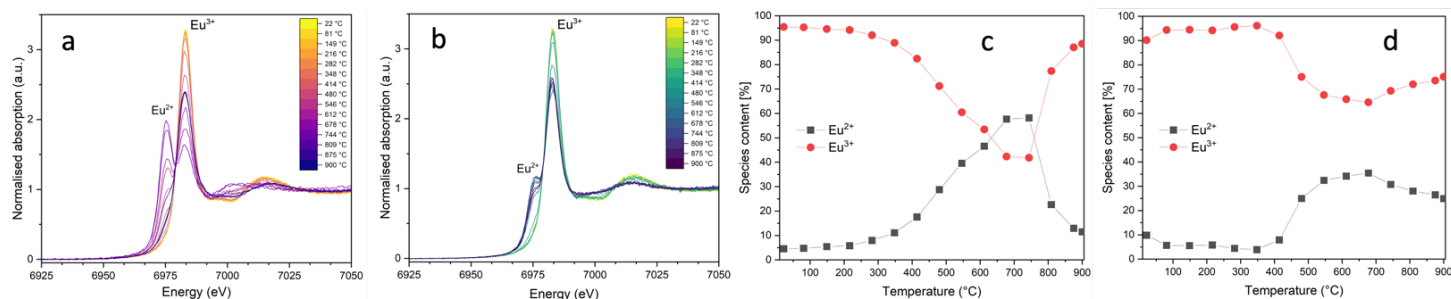


Figure 1 **a,b** *Eu L<sub>3</sub>-edge XANES spectra collected in situ during annealing in He flow from RT to 900 °C and c,d* quantification of the  $\text{Eu}^{3+}$  (red)/ $\text{Eu}^{2+}$  (grey) amount during this annealing process for 5 at. % doped miniemulsion (a,c) and ball milling (b,d) samples, respectively.

Moreover, a higher amount of  $\text{Eu}^{2+}$  is formed when heating in He flow samples with a higher Eu content, *i.e.* 5 at. % as compared to 1 at. % samples. However, even though the formation of  $\text{Eu}^{2+}$  during annealing in He flow was observed in all cases, some differences comparing the samples from the two synthetic approaches are worth to be highlighted, even though macroscopically (e.g., crystallite size) the samples are similar. Indeed, considering as an example the 5 at. % samples, the extent and the kinetic of the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  is significantly different. In particular, for miniemulsion sample (Figure 1c), the formation of  $\text{Eu}^{2+}$  starts at lower temperatures (300 °C) and the maximum amount of  $\text{Eu}^{2+}$  is higher (ca. 60 % of the total Eu content). On the other hand, the ball-milling sample (Figure 1d) shows a significant lower amount of  $\text{Eu}^{2+}$ , but a lower decrease in its content when heating from 700 to 900 °C.

During the heating, a strong increase in the absorption step was observed between 500-700 °C. We excluded the cause to be a displacement of the sample or a change in absorber concentration due to matrix evaporation, as it was also observed when measuring the samples at Mo K-edge. Therefore, this observation can be related to a possible structural change in the sample, both for ball-milling and miniemulsion samples.

*In situ* experiments at the Mo K-edge were performed on undoped and 5 at. % doped samples, obtained from both the synthetic methods. For all samples, changes in the XANES profile upon heating from RT to 900 °C in He were observed, even though in this case the transformations are reversible, as by cooling the system to RT the features in the XANES are restored. The detailed analysis of these changes is ongoing.

During all the *in situ* measurements, the evolution of gaseous species was followed by MS. At intermediate temperatures the formation of  $\text{H}_2$  was detected in He flow, and this can be correlated with the formation of  $\text{Eu}^{2+}$  and possible structural changes during the heating from 500 to 700 °C.

Further selected *in situ* experiments were performed in air or under vacuum. As expected, the annealing in air gives little to no reduction of  $\text{Eu}^{3+}$ .

### Conclusions and future work

The preliminary analysis of the data demonstrates that the annealing process in inert atmosphere (He flow) allows the partial reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$ , with different degree depending on the different synthetic methods. However, it is still not completely clear which is the driving force for this reduction mechanism and the stabilisation of  $\text{Eu}^{2+}$  in the crystal structure. Nonetheless, even though the data collected are very informative, they opened further questions on this investigation. Further experiments on samples with a higher Eu content (10 at. %) and combined *in situ* XAS-XRD measurements are crucial to clarify and fully understand the reduction mechanism and the transformations on the short- and long-range structure occurring during the annealing, especially in the temperature range 500-700 °C.