



	Experiment title: RIXS investigation of excitation processes in Eu-based phosphors	Experiment number: MA-2614
Beamline: ID26	Date of experiment: from: 08/04/2015 to: 14/04/2015	Date of report: 30/09/2015
Shifts: 12	Local contact(s): Lucia Amidani	<i>Received at ESRF:</i>
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Report:

We focused our investigation on Barium Magnesium Aluminate (BAM, $\text{BaMgAl}_{10}\text{O}_{17}$) singly doped with Mn and Eu and co-doped with both atomic species. A complete set of powder samples were synthesized in Lumilab laboratory (Ghent University): BAM:Eu, BAM:Mn, BAM:Eu,Mn. We also measured two efficient commercial powders of BAM:Eu and BAM:Eu,Mn. The experiment was divided in three parts: i) characterization of Mn and Eu local electronic structure in fresh samples, ii) investigation of the degradation induced by x-rays on the local structure of Eu and Mn while collecting luminescence spectra and iii) investigation of variations in the electronic structure of Mn during laser excitation at 405 nm, i.e. exciting Eu impurities.

i) Characterization of Mn and Eu local electronic structure in fresh samples:

We measured high resolution XANES at Mn K-edge monitoring Mn K α fluorescence photons and Eu L₃-edge monitoring Eu L α fluorescence. All samples, independently from doping and growing conditions, show the same lineshape in Mn K-edge XANES. On the contrary, Eu L₃-edge XANES is quite different from sample to sample: Eu is present in both 2+ and 3+ oxidation states, but the relative amount are very sample dependent, with the commercial BAM:Eu,Mn having the highest amount of Eu²⁺ (Figure 1).

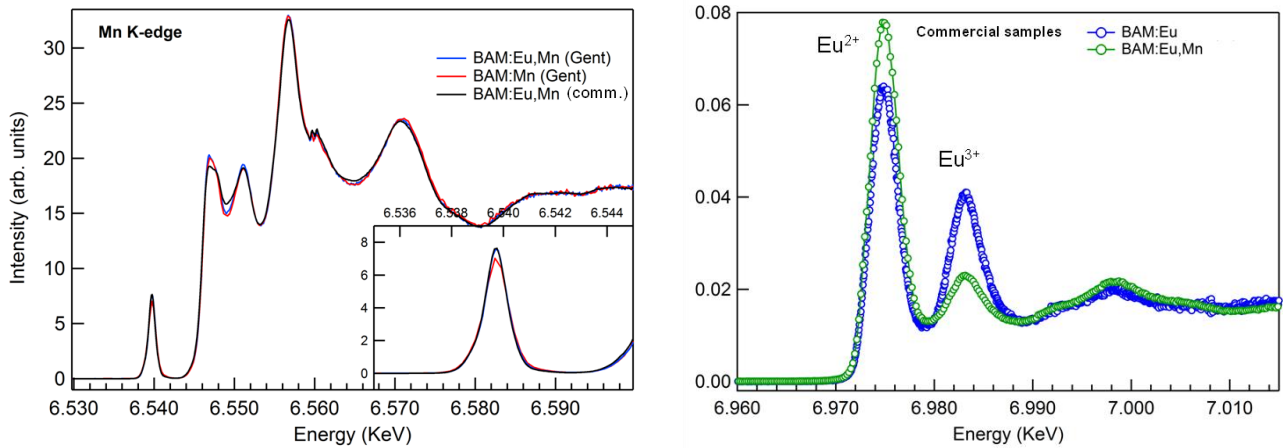


Figure 1: Left: Mn K-edge XANES of samples containing Mn. The same lineshape is observed in all samples, indicating a similar Mn local structure. Right: Eu L₃-edge of commercial sample, showing very different amount of Eu²⁺ and Eu³⁺.

ii) X-ray induced degradation:

BAM-based phosphors suffer from damage during VUV irradiation and this is the main drawback concerning their technological use as efficient blue phosphors. X-rays irradiation induces a very fast degradation of BAM samples which can have the same origin as VUV damage. We mounted a UV-vis portable spectrometer near the sample stage and by measuring fast XANES (2 s exploiting continuous scans) we were able to follow x-ray induced damage on the local structure of Mn and Eu impurities and on the UV-vis luminescence emitted by the samples under x-rays excitation. We clearly see that Mn electronic structure stays unchanged, while Eu undergoes a very fast oxidation to Eu³⁺. On the other hand, luminescence from Eu and Mn are both degraded.

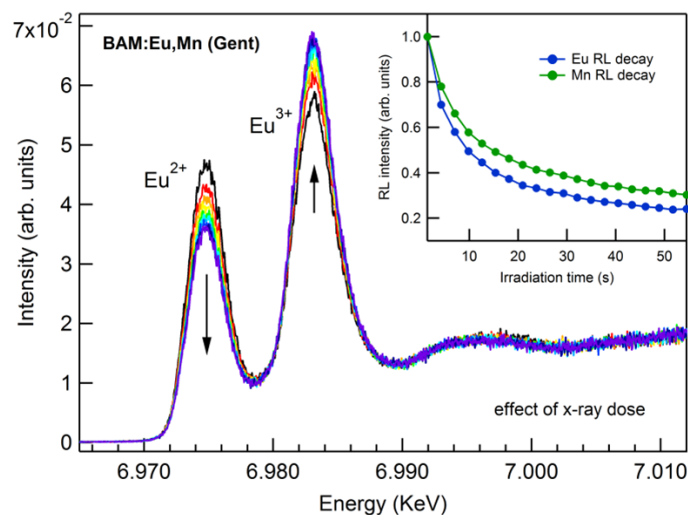


Figure 2: Eu L₃-edge fast XANES showing how the degradation of the sample is reflected on Eu local structure. The inset shows the parallel decrease of luminescence emission of Eu (blue) and Mn (green) impurities as measured by the UV-vis spectrometer.

iii) Mn local structure during Eu excitation:

We finally mounted two 405 nm lasers to excite Eu impurities and measured Mn K-edge XANES while alternating laser on/laser off cycles. Mn is efficiently excited through Eu excitation and it has a higher lifetime compared to Eu. We thus decided to monitor Mn K-edge to look for structural changes connected to the excited state. We optimized the set-up to focus as much as possible the excitation source and alternate laser on/laser off measurements

to minimize the effects of drifts, but we were not able to detect any spectral difference. Most probably a higher excitation power is needed to consistently excite Mn impurities. Moreover, the sample investigated had a very high amount of Mn (as indicated by laboratory characterization after the beamtime) making the observation of differences harder.

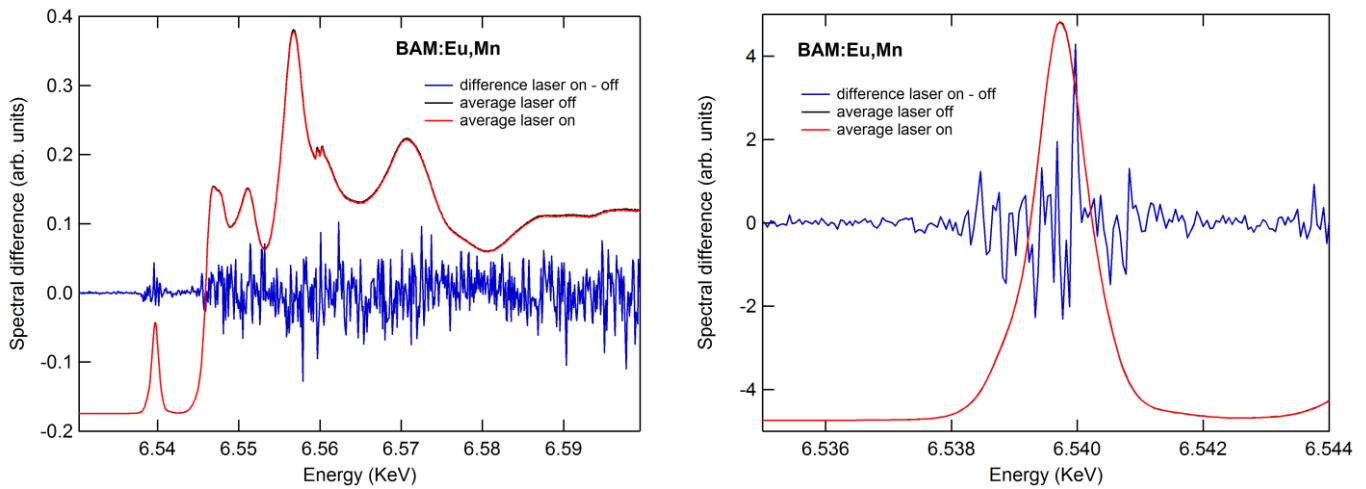


Figure 3: Left: Mn K-edge XANES with laser on (red) and laser off (black) and the relative difference. Right: a detail of the strong pre-edge feature. We were not able to detect any variation of Mn electronic structure upon excitation. The fast deexcitation process and the medium power of the 405 nm lasers made the observation of differences difficult.