ESRF	**Experiment title:** EXAFS measurements on Eu2+ in whitlockite dedicated to white diode	**Experiment number**: 30 02-940
Beamline: BM30B	**Date of experiment**: from: 22/07/2009 (8:00) to: 24/07/2009 (8:00)	**Date of report**: 11/12/2009
Shifts: 6	**Local contact(s)**: Proux Olivier	*Received at ESRF:*

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Report:

In the context of developing news phosphors materials for white light emitting display (LED), we did develop phosphate materials, based on rhomboedric whitlockite mineral, using divalent europium Eu^{2+} as phosphorous center. This initial formula of whitlockite is $Ca_3(PO_4)_2$, containing 6 metallic sites M1-M6 [2]. Three sites M1-M3 are occupied by Ca^{2+} in positions 18b, surrounded by eight oxygen atoms, forming distorted polyhedra. The M4 site surrounded by nine O atoms is 50% occupied by Ca^{2+} ions. The distorted octahedral M5 site is fully occupied by Ca^{2+} ions. The M6 site is vacant.

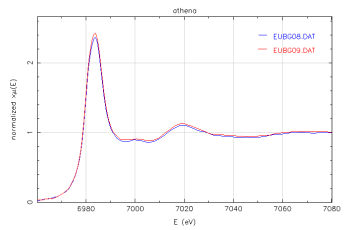
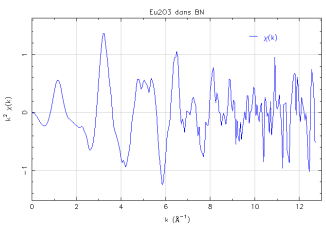
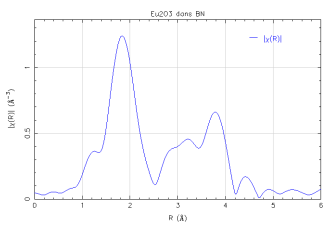
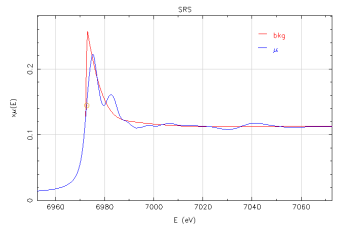
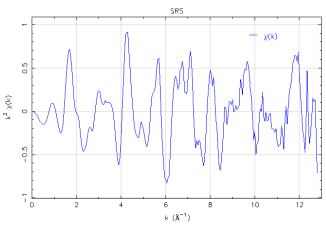
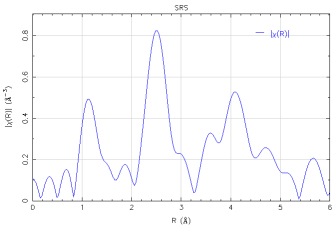
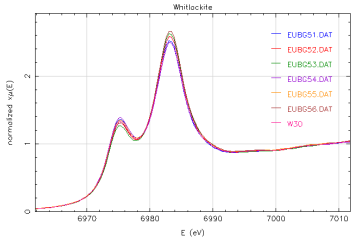
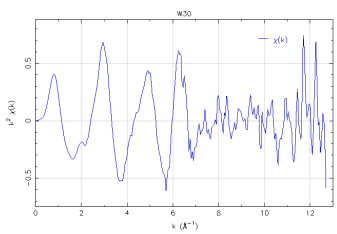
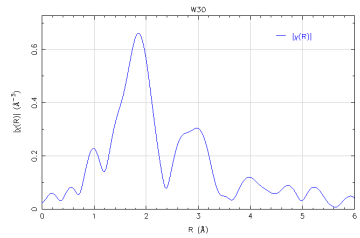
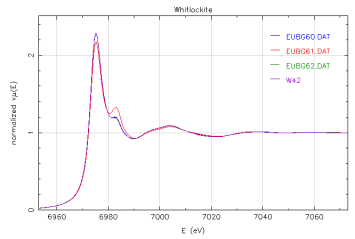
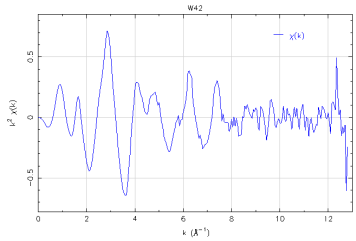
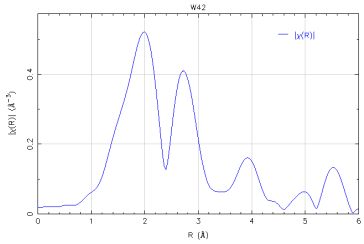
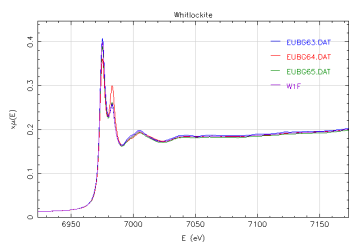
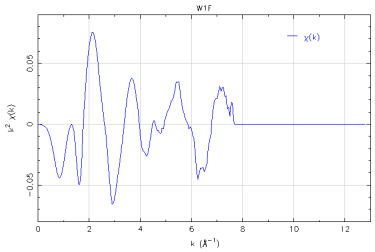
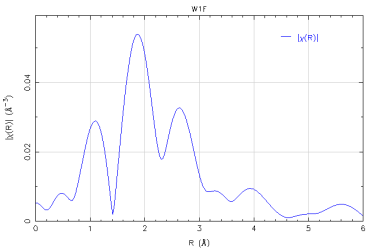
Some materials give really interesting and promising results, in term of optical properties and color rendering index, which are the necessary requested characteristics for developing phosphors. Those materials where composed basically on the whitlockite-like structure, with divalent europium substituting partially the calcium. In addition, calcium where additionally substituted by alkaline and rare earths (½ $Ca^{2+} \leftrightarrow M^{+}$ (M=Li, Na, K); $^3/2$ $Ca^{2+} \leftrightarrow Ln^{3+}$ (Ln= La, Gd, Y)).

The goal of the ESRF experiments was to identify, by EXAFS at the L_{III} edge (6977ev), the crystallographic position of europium, in order to determine the substitution process of calcium by europium, connect the luminescence characteristics of whitlockite with the position of europium in the structure, drive the luminescence properties, by adjusting the composition $(Ca_x,M_y,Ln_z)PO_4$ and the amount of Eu.

After optimizing the packing and the support of the powder (pellets encapsulated in kapton sheet), the first experiment where performed on reference samples: Eu_2O_3, $Sr_2GaS_4:Eu^{2+}$, and $SrS:Eu^{2+}$. The europium in the SrS compound gives relevant data, in order to identify the various parameters of trivalent and divalent europium.

Experiments were then performed on various samples: $Ca_{2.99}Eu_{0.01}(PO_4)_2$, $Ca_{2.97}Eu_{0.03}(PO_4)_2$, $Ca_{2.85}Eu_{0.15}(PO_4)_2$, $Ca_{2.7}Eu_{0.3}(PO_4)_2$, $Ca_{8.9}Eu_{0.1}La(PO_4)_7$, $Ca_8EuLa(PO_4)_7$, $Ca_{9.99}Eu_{0.01}K(PO_4)_7$, $Ca_{9.9}Eu_{0.1}K(PO_4)_7$, $Ca_9EuK(PO_4)_7$, $Ca_{10}Eu_{0.1}K_{0.8}(PO_4)_7$, $Ca_{7.9}Eu_{0.1}MgGd(PO_4)_7$,

Some examples of results are reported below

		
Eu_2O_3		
		
SrS:Eu		
		
$Ca_{9.99}Eu_{0.01}K(PO_4)_7$		
		
$Ca_8EuLa(PO_4)_7$		
		
$Ca_{7.9}Eu_{0.1}MgGd(PO_4)_7$		
Xanes and Exafs spectra, Exafs oscillations and radial structure function of Eu-L_{III} edge		

Various point were already revealed during the experiments. The presence of trivalent europium in some of our samples was evidenced, even if it was not revealed by regular x-ray experiments. After multipling experiments on a sample, the xanes signature of trivalent europium clearly increases under the beam irradiation. We, then, proceed to average 5 experiments on a sample. While the optical properties are relevant of trivalent europium, and the goal of our experiments is to localizz thess cristallographic position of divelent europium, the presence of trivalent europium has to be taken into account in the data analyses.

Preliminary results give some indications about the coordinance and the average Eu-O distance in our samples. By increasing the rate of europium, the coordination number clearly increased. Deep analyses have still to be performed. But it already seems difficult to perfectly identify the crystallographic position of europium, especially if this cation is located in multiple sites (what is the case of the most interesting samples, in an optical point of view). The quality of the signal is not relevant enough to distinguish quantitatively the characteristics of two (or more) crystallographic sites.

Those first results will be included, with careful attention paid to the assertion of data, on two future publications in progress. Those publications deal mainly with the optical properties. The exafs results will be mentioned as indications. In order to perfectly identify to crystallographic situation of divalent europium, a further request of beamtime will be submitted, at low temperature.