Eu L₂ XANES on CsBr:Eu needle image plates for X-ray radiography

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Introduction
Image plates based on the principle of X-ray storage phosphors are becoming more and more important in the field of medical imaging. When an X-ray photon is absorbed by the storage phosphor, electron-hole pairs are formed. These free charge carriers can be trapped in metastable lattice defects (anionic vacancy for electrons and activator ions for holes). After illumination of the screen with X-rays, the image can be read from the plate by exciting the charge carriers from the metastable levels towards the conduction band. Detection of the photons emitted during the subsequent de-excitation process gives an indirect way of recording the latent X-ray image.

CsBr doped with Eu²⁺ is a promising X-ray storage phosphor which can be grown in the form of needle crystals by vacuum deposition techniques [1]. The needle growth allows to obtain an improved lateral resolution comparison with commonly used BaFBr:Eu²⁺. The sensitivity of the photostimulated luminescence in the CsBr:Eu²⁺ depends strongly on the deposition conditions and on the thermal treatment after deposition. In order to examine the influence of these conditions on the mean Europium oxidation state in the CsBr:Eu plate, an Eu L₂ XANES study was performed.

Experimental
The Eu L₂ XANES spectra were recorded at beamline L of the DORIS III storage ring in fluorescence mode. The Eu L₂ edge was chosen, as the intense Cs L line series originating from the CsBr matrix overlaps with the Lα fluorescence radiation from the Eu L₃ edge.
An intense edge peak (‘white line’: WL) is present in Eu L₂ XANES spectra, whose position increases with the oxidation state of the Eu cation, see Figure 1. If both oxidation states are present, two well separated WL peaks can be observed. The area of the WL peaks for each oxidation state can in principle be used to determine the relative concentration of each oxidation state, after calibration of the fit method with a series of samples with known mean Europium oxidation state.

The shape of the XANES edge spectrum for one oxidation state can be seen as the combination of a step function and a WL peak. The step can be approximated by a tanh function and the WL by a Voigt function (= weighted sum of a Gauss and a Lorentzian). With these functions a non-linear least squares fit to the Eu L₂ XANES edge spectrum is possible. Figure 2 shows an example fit on the Eu L₂ XANES spectrum taken at the surface of a CsBr:Eu screen. In order to calibrate the fit procedure, a series of mixed EuOBr (Eu³⁺) and CsEuBr₂ (Eu²⁺) powder samples was used, the calibration curve is given in Figure 3.

**Eu oxidation state in CsBr:Eu plates as function of annealing status**

In CsBr:Eu²⁺ the intensities of photoluminescence (PL) and photostimulated luminescence (PSL) strongly depend on the annealing status of the samples. “As grown” image plates offer only poor PL and PSL output. When the image plates are annealed at temperatures around 450 K, the PL and PSL intensities can be increased by a factor of more than four, but when annealed at temperatures exceeding 470 K, the PL and PSL intensity is lowered again tremendously [1]. From the Eu L₂ XANES spectra for a CsBr:Eu screen after different heat treatments, shown in Figure 4, it is clear that annealing at too high temperatures almost completely oxidizes the Eu cations to the Eu³⁺ oxidation state, explaining the serious reduction in PL and PSL intensities for these temperatures.

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**References**