

Site selectivity of electron trapping in two Eu-activated phosphors for dosimetry

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In the search for new and improved materials for ionizing radiation detection, dosimetry and imaging at Lumilab, $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}$ and $\text{Ba}_2\text{SiO}_4:\text{Eu}$ have recently proven very promising. $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}$ can be applied as UV-radiation dosimeter featuring good erythral equivalence.¹ With $\text{Ba}_2\text{SiO}_4:\text{Eu}$ combined X-ray imaging and dosimetry is obtained.² Both materials are so-called photoluminescence (PL) dosimeters: the dose read-out is based on a change in the photoluminescence spectrum under UV light excitation. As opposed to thermoluminescence or optically stimulated luminescence dosimeter systems, the PL read-out does not erase the dose. The mechanism behind the change in PL spectrum is a valence state conversion in the dopant: $\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+}$. As can be seen in Figure 1, before exposure the phosphor only exhibits a multiline parity-forbidden intra-4f-shell luminescence spectrum of Eu^{3+} with wavelengths in the orange-red. Upon exposure, a broad $5d \rightarrow 4f$ luminescence band of Eu^{2+} grows in, which is situated in the violet-blue for $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}$, and in the green for $\text{Ba}_2\text{SiO}_4:\text{Eu}$. In both materials, only a limited fraction of the Eu dopant can undergo such valence state change. EPR spectroscopy is invoked to help elucidating the reasons for this limited dopant activity.

Combining PL and Q-band EPR (34 GHz) results, we could show that in both materials electron trapping at Eu^{3+} is site-selective. Both $\text{Ba}_3(\text{PO}_4)_2$ and Ba_2SiO_4 exhibit two crystallographically inequivalent Ba^{2+} sites, on which Eu substitution is expected. Eu^{3+} luminescence reveals that the dopant ions are incorporated on different sites. EPR demonstrates that stable electron trapping occurs at only one of the sites. Via estimates of the Eu^{2+} concentration from EPR spectra, we found that for $\text{Ba}_2\text{SiO}_4:\text{Eu}$ the site-selectivity is a dominant factor in the limited activity of the dopant. On the contrary, for $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}$ only a small fraction of the Eu^{3+} incorporated at the right site can be reduced by UV exposure. Further EPR and experiments are planned to solve the remaining mysteries.

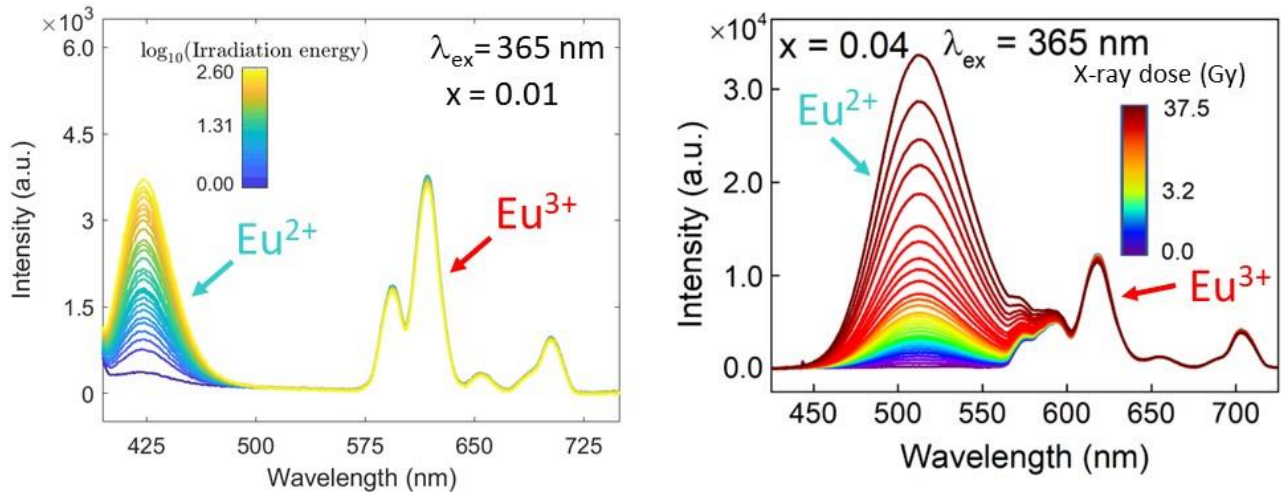


Figure 1: PL spectrum under UV light excitation for $\text{Ba}_3(\text{PO}_4)_2:\text{Eu}$ (left) and $\text{Ba}_2\text{SiO}_4:\text{Eu}$ (right). x indicates the fraction of Eu in the material $\text{Ba}_{3-x}\text{Eu}_x(\text{PO}_4)_2$ and $\text{Ba}_{2-x}\text{Eu}_x\text{SiO}_4:\text{Eu}$.

References

1. Z. Yang et al., *Advanced Optical Materials* (2023) DOI:10.1002/adom.202300733
2. Z. Yang et al., *Advanced Functional Materials* (2022), 32, 2201684 DOI:10.1002/lpor.202200809