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UNDERSTANDING THE DEGRADATION OF A BLUE PHOSPHOR AT THE ATOMIC LEVEL

The atomic modifications responsible for the degradation of one of the brightest blue phosphors used in technological applications have been studied. Using element-selective X-ray spectroscopy combined with a UV-vis probe it was found that irradiation induces oxidation of Eu^{2+} and the formation of killer centres that hamper remaining Eu^{2+} to emit.

White light emitting diodes (LEDs), plasma screens and fluorescent lamps are only some of the many daily-life objects exploiting inorganic phosphors to emit visible light. In this class of materials, light is emitted by luminescence centres – typically transition metal or rare-earth atoms incorporated in a transparent host crystal at concentrations of a few atomic percent. The electronic interactions in the partially filled d- and f-shell, and the influence of the nearest neighbouring atoms (via the ligand field), create a manifold of electronic states (multiplets) where the energy difference between the ground state and the first excited states is a few eV. When the luminescent centres are excited, directly or via energy transfer from the host crystal, visible light can be emitted in the de-excitation cascade.

The stability of the light emitted under working conditions is crucial in the technological use of phosphors [1]. Prolonged irradiation – LEDs are supposed to last for 50 000 hours – may induce modifications at the atomic level that degrade the luminescence efficiency. This is the case for one of the most employed blue phosphors, $\text{BaMgAl}_{10}\text{O}_{17}$ doped with Eu^{2+} (BAM:Eu), which sees its bright blue luminescence redshift and degrade after prolonged exposure to ultraviolet

excitation light. The alteration acting at the atomic level that is responsible for BAM:Eu degradation has been investigated before and explanations pointing to the degradation of the host crystal and of the energy transfer mechanism, as well as of the dopant itself, have been proposed [2, 3]. Nonetheless, a satisfactory explanation of the degradation process is still missing. Ideally, one would simultaneously probe the electronic structure of the luminescent centres and the luminescence efficiency while inducing progressive degradation. This investigation was recently performed on ID26, exploiting the X-rays as a probe of the local electronic structure, as excitation source for the luminescence and as an accelerated source of damage.

High-energy resolution fluorescence detected (HERFD) X-ray absorption near-edge structure (XANES) was measured at the Ba L_3 edge during X-ray irradiation and using a UV-vis spectrometer to simultaneously acquire emission spectra (Figure 104). The Ba XANES remained unchanged after an irradiation time that reduced the blue luminescence to less than 1% of the initial value, indicating that the structure of the host lattice was not degraded. Focusing on the Eu dopants, a series of fast HERFD XANES acquired at the Eu L_3

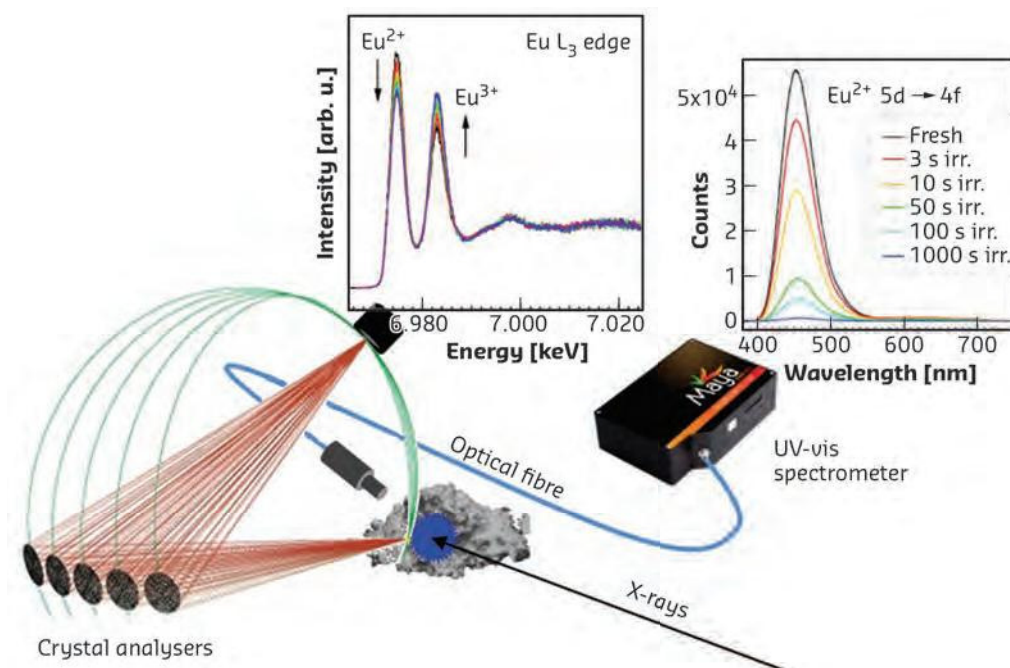


Fig. 104: Scheme of the experimental setup to collect the luminescence emitted by the sample during X-ray irradiation and the HERFD XANES at the same time. Eu^{2+} oxidation is observed in Eu L_3 edge HERFD XANES and degradation of blue luminescence is simultaneously measured with a UV-vis spectrometer.

edge revealed that irradiation rapidly oxidises Eu^{2+} to Eu^{3+} (Figure 104), suggesting that this could be the cause for luminescence degradation.

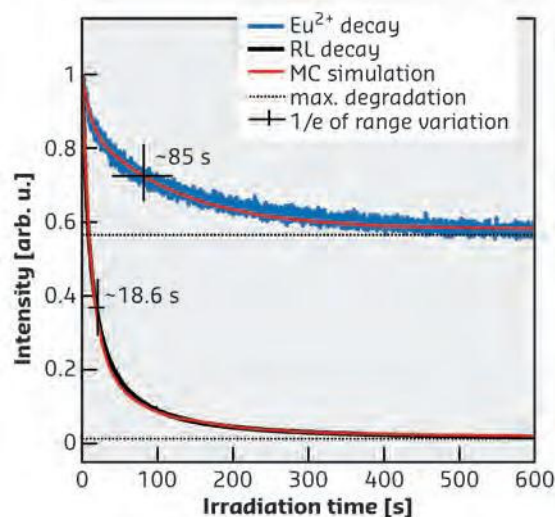
To correlate oxidation and degradation, the maximum of Eu^{2+} absorption and the luminescence during exposure to X-rays were sampled simultaneously. The comparison of the decay times of the luminescence intensity and of the oxidation of Eu^{2+} revealed that the luminescence decreases at a considerably faster rate. In addition, a fraction of Eu^{2+} dopants are

resistant to oxidation. Thus, potentially emitting Eu^{2+} centres are still present in the sample while luminescence is virtually zero. Oxidation is not solely responsible for the degradation and other processes are involved.

To clarify this point, a Monte Carlo simulation was performed that, in a first step, modelled the Eu^{2+} oxidation by random X-ray events hitting a sublattice of Ba and Eu atoms. Secondly, a quenching sphere centred on the newly formed Eu^{3+} was introduced to simulate the formation of a killer centre close to the Eu^{3+} that induces luminescence quenching of Eu^{2+} ions inside the sphere. The decay profiles of Eu^{2+} valence change and of blue luminescence were well reproduced by the simulation with a quenching radius of 24 \AA (Figure 105). This value is compatible with the Eu–Eu distance at which luminescence emission decreases because energy is exchanged between impurities rather than being emitted.

In conclusion, simultaneously measuring the electronic structure and the luminescence emission during progressive degradation has revealed that the degradation of this europium-doped phosphor is due to the partial oxidation of Eu^{2+} and to the simultaneous formation of killer centres that quench the remaining Eu^{2+} luminescence centres.

Fig. 105: The decay of Eu^{2+} XANES peak (blue) and of the integrated luminescence (black) during irradiation are compared to the results of the Monte Carlo simulation (red lines).



PRINCIPAL PUBLICATION AND AUTHORS

Oxidation and Luminescence Quenching of Europium in $\text{BaMgAl}_{10}\text{O}_{17}$ Blue Phosphors, L. Amidani (a), K. Korthout (b), J. J. Joos (b), M. van der Linden (a, c), H. F. Sijbom (b), A. Meijerink (d), D. Poelman (b), P. F. Smet (b) and P. Glatzel (a),

Chem. Mater. **29**, 10122–10129 (2017); doi: 10.1021/acs.chemmater.7b03918.

(a) ESRF

(b) Lumilab, Department of Solid State Sciences, Ghent University (Belgium)

(c) Inorganic Chemistry and Catalysis,

Debye Institute for Nanomaterials Science, Utrecht University (The Netherlands)

(d) Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University (The Netherlands)

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FERROELECTRIC AND ANTIFERROELECTRIC INSTABILITIES COMPETING IN Bi_2SiO_5

Bi_2SiO_5 has recently emerged as a promising ambient-temperature, lead-free ferroelectric. Here, the competition between ferroelectric and antiferroelectric instabilities is analysed by investigating the characteristic temperature-dependent phonon energies at the centre and edge of the Brillouin zone, respectively.

In the ferroelectric (FE) Bi_2SiO_5 (BSO), the ferroelectricity arises from the tilt of the quasi-one-dimensional (1D) chains formed by SiO_4 tetrahedral units (Figure 106, inset) [1], providing an alternative to perovskite-type FEs, such as in PbTiO_3 or BiFeO_3 , where the ferroelectricity arises from the cation off-centring. These findings

recently opened the way towards the engineering of new tetrahedra-based FEs.

The soft phonon mode in BSO, which drives the FE transition at T_C , corresponds to a torsion of the SiO_4 units along the 1D tetrahedral chains. The freezing of this phonon was evidenced at the