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Identification of Dy^{3+}/Dy^{2+} as electron trap in persistent phosphors

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Abstract

A long-standing issue in persistent luminescence is settled by providing direct evidence that Dy^{3+} is the main electron trap in $Sr_4Al_{14}O_{25}$:Eu,Dy by combining laser excitation with X-ray spectroscopy. A reversible electron transfer is demonstrated, controlled by light and showing the same kinetics as the persistent luminescence. Exposure to violet light induces charging by oxidation of the excited Eu^{2+} while Dy^{3+} is simultaneously reduced. Oppositely, detrapping of Dy^{2+} occurs at ambient temperature or by infrared illumination, yielding afterglow or optically stimulated luminescence, respectively.

Luminescent materials or phosphors are crucial for various technological applications, ranging from environmentally friendly lighting [1,2] to specialized applications in medicine and optoelectronics [3–7]. A subclass of luminescent materials are those that feature energy storage capabilities. For these compounds, not all of the energy absorbed upon excitation is immediately emitted as photoluminescence (PL). A fraction is used to transfer a charge carrier from the luminescent center to a so-called trap, generating a metastable state.

The lifetime of these metastable states can range over many orders of magnitude (quantified by the so-called trap depth), leading to very diverse applications. The long lifetimes of deep traps is exploited to date minerals or archeological artifacts, or for dosimeters, *e.g.* in medical imaging plates where red or infrared (IR) light is used to detrap charge carriers and induce the radiative decay of the luminescence activator, a process called optically stimulated luminescence (OSL) [8,9]. For luminescent materials with more shallow traps, ambient temperature can be sufficient to slowly thermally deplete the traps (in minutes to hours), giving rise to the process of long afterglow or persistent luminescence [10–13]. This process can be accelerated by heating the phosphor, giving rise to thermoluminescence (TL), the analysis of which allows to experimentally extract information on trap depths or trap depth distributions [14,15]. Afterglow materials hold the promise of new applications such as glow-in-the-dark traffic signalization [16], damage monitoring [17], radiation-free medical imaging [3,18], theranostics [19,20], cell characterization [21] or nanothermometry [22]. The storage capabilities need nevertheless to be improved in order to enable these advanced applications and important steps are yet to be taken in the optimization of existing materials and for the development of new ones [12,13].

In the 1990's it was found that some Eu^{2+} based phosphors acquire intense persistent luminescence upon codoping with a trivalent lanthanide ion (Ln^{3+}), often Dy^{3+} [23]. This triggered the discovery of a group of phosphors that, 25 years after the initial discovery, can still be regarded as state-of-the-art. Among them, the strontium aluminates ($SrAl_2O_4$:Eu^{2+},Dy^{3+} and $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+}) and the silicate $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} take the most prominent places [10,12]. As the trapping capacity is significantly increased upon Dy^{3+} addition, it is tempting to identify the trivalent codopant as a trap. To date, no hard evidence has however been found that confirms or rejects a valence state change for Dy^{3+}. The reason for this standstill is the difficulty to detect such transient phenomenon in common structural and optical experiments, and the intrinsic complexity of these materials, making theoretical studies scarce and hard to correlate with experiments such as TL [24,25].

TL experiments have suggested that distributions of trap depths are present, rather than one discrete trap [15,26]. However, TL does not infer the chemical nature of the traps, and the distribution can be due to multiple intrinsic defects that induce trapping [27], but equally well to multiple nonequivalent Dy^{3+} centers in the crystal [28] distributed at different distances from the Eu^{2+} activator [29]. Detailed experimental studies of $SrAl_2O_4$:Eu^{2+},Dy^{3+} suggest that trapping is local, *i.e.* close to the Eu^{2+} activator rather than a delocalization

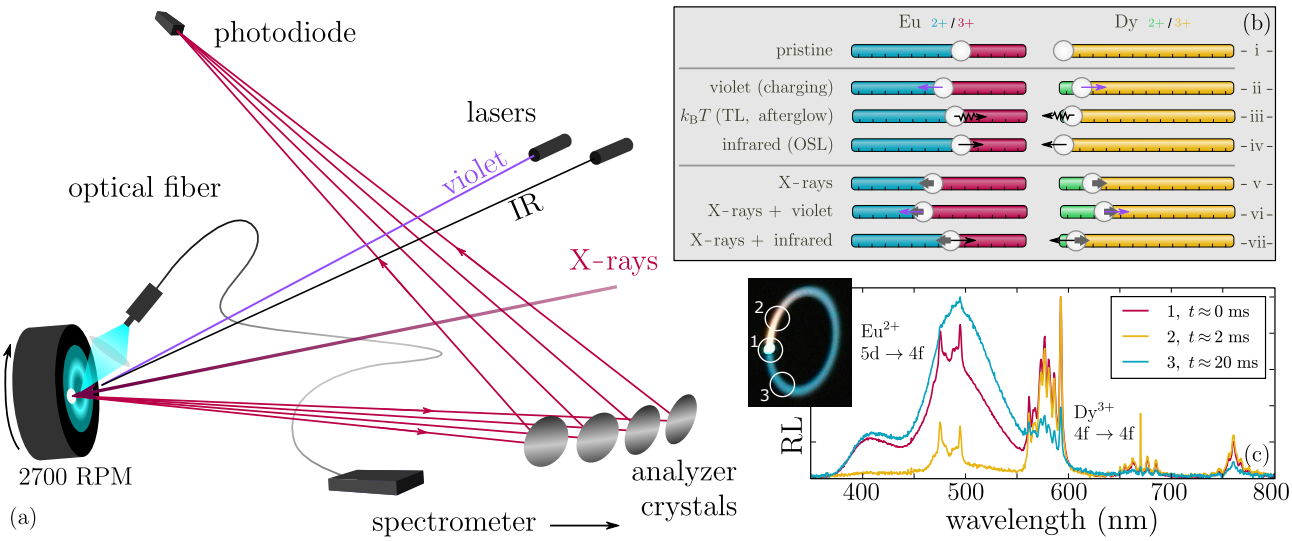

Figure 1 – Schematic representation of the experimental setup (a): monochromatic X-rays strike the rotating sample, the X-ray fluorescence is analyzed by a spectrometer in Rowland geometry, using an array of spherically bent crystal analyzers and an avalanche photodiode (APD). The sample is irradiated by violet or IR lasers and the radioluminescence (RL) is recorded. The schematic representation in (b) illustrates how light of different wavelengths, temperature and X-rays induce electron (e^-) transfer and hence affect the Eu^{2+}-Eu^{3+} (blue-red) and Dy^{2+}-Dy^{3+} (green-yellow) equilibria in the phosphor. Normalized radioluminescence spectra (c), measured on three different spots on the rotating sample are displayed, featuring Eu^{2+} $4f^6 5d^1 \rightarrow 4f^7$ broadband and Dy^{3+} $4f^9 \rightarrow 4f^9$ ($^4F_{9/2} \rightarrow {}^6H_J$ $(2J = 15, 13, 11, 9)$) line emissions.

of the electron towards the conduction band[26]. A limited number of X-ray absorption spectroscopy (XAS) studies have been performed on Eu^{2+}, Ln^{3+} codoped aluminates and silicates in the past[30–35]. Most studies failed to find reversible valence state changes, except for Korthout *et al.* who uncovered a partial oxidation of Eu^{2+} to Eu^{3+} in $SrAl_2O_4$:Eu^{2+},Dy^{3+}[34]. Exposure to X-rays does not only lead to radioluminescence (RL) from Eu^{2+} but also to charge trapping, as witnessed by the slow increase of RL intensity (the so-called charging) after switching on the X-ray beam and by the afterglow when switching off the X-ray beam. Thermal cleaning of traps was used to ensure that the electron transfer was reversible, *i.e.* that the observed oxidation was not due to a degradation process. This confirmed that indeed an electron is released from the Eu^{2+} ion during the charging (trapping) process, but no convincing information could be extracted on where it is trapped[34]. Carlson *et al.* recorded oxidation of Eu^{2+} in $Sr_2MgSi_2O_7$:Eu, but on a much longer timescale (hours) than the typical charging (seconds-minutes[26,34]), indicating that this was presumably caused by degradation, rather than the filling of traps[32].

In this letter, we report a novel experimental investigation where the valence state changes of both Eu and Dy in $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} persistent phosphors are recorded via Resonant Inelastic X-ray Scattering (RIXS, see Fig. 1(a)). It is found that a fraction of the Dy^{3+} is reduced to Dy^{2+} along with the oxidation of Eu^{2+} to Eu^{3+}, and that this reversible electron transfer is indeed responsible for the persistent luminescence.

The situation for a pristine Eu,Dy codoped persistent phosphor is represented in Fig. 1b(i), where Eu^{2+} and Eu^{3+} coexist with Dy^{3+}. Charging by blue to ultraviolet light (Fig. 1b(ii)) or X-rays (Fig. 1b(v)) causes a part of the Eu^{2+} to be oxidized, while the redox partner, Dy^{3+}or another defect, gets reduced. This metastable state is long-lived and is slowly depleted at room temperature in case of persistent phosphors (Fig. 1b(iii)), giving rise to afterglow or TL when the electron is transferred back to the Eu center. Infrared light has a similar effect by electronically exciting the trapped electron, giving rise to OSL (Fig. 1b(iv)).

When probing the sample with X-rays, the density of trapped charges can additionally be perturbed by illuminating the sample with violet or IR lasers as illustrated in Fig. 1. This gives rise to the situations represented schematically in Fig. 1b(vi and vii) where the effect of the lasers is superimposed on the effect of the X-rays. The use of the external light sources hence allowed us to affect a fraction of the charges and create a differential effect on top of the unavoidable charging induced by X-rays.

Additionally to laser illumination controlling the electron transfer, the sample was mounted on a rotating stage and spinned during the measurements. Rotating the sample allows to probe a larger sample volume and reduce the photon per unit volume per unit time. The main advantage is that when X-rays hit the sample, the time to reach a steady state (the equilibrium between the trapping effect of X-rays and the detrapping processes) is hugely enlarged, passing from a few ms to tens of seconds. As a consequence, the time evolution of the charging process as induced by X-rays becomes measurable. Finally, we were able to connect the X-ray measurements with the luminescence processes by collecting the RL emitted by the

sample under X-ray illumination. The parallel analysis of the two data sets was fundamental to ensure that the observation for Eu and Dy are indeed connected to the persistent luminescence process.

Our experiments were conducted on commercial $Sr_4Al_{14}O_{25}$:Eu,Dy powders at beamline ID26 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France[36,37]. The sample was diluted in boron nitride (BN), pressed to a pellet and mounted on a rotating sample stage (2700 RPM). The Ln L_{III} absorption edges were used to probe the oxidation states of Eu and Dy. The rotating sample was positioned in the X-ray beam (see Fig. 1). The incident photon energy was scanned across the Eu and Dy L_{III} edge. The maximum of the characteristic $L_{\alpha 1}$ emission was selected by an X-ray emission spectrometer based on Rowland geometry, resulting in High Energy Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES) spectra. For this experiment, the main advantage of using the HERFD mode to collect XANES is its superior energy resolution which increments the sensitivity of the technique to small spectral variations[38–40]. More technical details about the experimental setup are given in the *Supplementary Information*.

The spinning sample allows to record spectral changes on a ms timescale as shown by Fig. 1(c). The inset displays a picture of the clockwise rotating (16 °/ms) sample under continuous X-ray irradiation. The color of the luminescence changes, depending on the position, and hence on the time after irradiation. This is analyzed in detail by continuously recording the luminescence spectra. The figure shows spectra that were recorded at different positions (1, 2, 3) on the spinning pellet, corresponding to delays of 0 ms, 2 ms and 20 ms after irradiation, respectively. Upon X-ray irradiation (position 1), different spectral components are clearly visible: the blue-green broadband $4f^6 5d^1 \rightarrow 4f^7$ emissions from Eu^{2+} in $Sr_4Al_{14}O_{25}$ peaking around 495 nm[41,42] as well as characteristic Dy^{3+} inter-$4f^9$ transitions, predominantly in the yellow. The first few milliseconds after irradiation (position 2), the parity and spin-allowed Eu^{2+} emission already decayed (order of 1 μs) and the slow-decaying Dy^{3+} emission dominates the spectrum. The Dy^{3+} decay is clearly visible on the picture in Fig. 1. After 20 ms (position 3), also the excited Dy^{3+} ions have largely decayed and the afterglow remains, showing a dominant Eu^{2+} $4f^6 5d^1 \rightarrow 4f^7$ emission. It is hence clear that the X-rays are indeed able to excite the persistent luminescence.

Figure 2(a) shows HERFD-XANES spectra, measured at the Eu L_{III} edge. These spectra feature two relatively sharp peaks, so-called white lines, that correspond to the resonant $2p^6 4f^N \rightarrow 2p^5 4f^N 5d^1$ electronic transition of Eu^{2+} ($N = 7$, around 6.975 keV) and Eu^{3+} ($N = 6$, around 6.983 keV)[44,45]. The characteristic 7-8 eV separation between Eu^{2+} and Eu^{3+} white lines, and more generally between Ln^{2+} and Ln^{3+} white lines[43,46], is often used to acquire quantitative and qualitative information about the concurrence

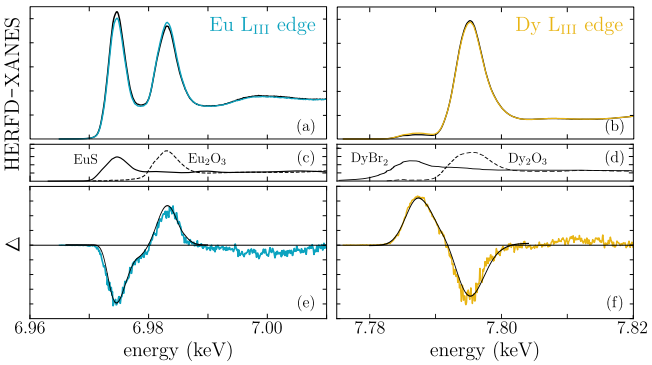

Figure 2 – High Energy Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES) spectra for the Eu (a) and Dy (b) L_{III} edges upon violet (colored line) or IR (black line) irradiation, compared to conventional XANES of reference spectra for (c) EuS (EuII) and Eu_2O_3 (EuIII) and (d) Dy_2O_3 (DyIII) and $DyBr_2$ (DyII, adapted from[43]), and the associated difference spectra, Δ, (colored lines) with their fit (black line) (e-f).

of lanthanide oxidation states[44,45].

It was previously found that Eu^{2+} oxidizes to Eu^{3+} in $SrAl_2O_4$:Eu,Dy upon X-ray irradiation on the same timescale as the charging of the persistent luminescence[34]. Therefore, it is clear that the X-rays, which are used as a probe for the lanthanide oxidation states, induce a net trapping effect, where a steady-state regime with a higher $[Eu^{3+}]$:$[Eu^{2+}]$ ratio, compared to a pristine sample, is established under irradiation (Fig. 1b(v)). In order to push this dynamic equilibrium in both directions, laser stimulation was applied on top of the X-ray irradiation: violet light to further increase $[Eu^{3+}]$:$[Eu^{2+}]$ (Fig. 1b(vi)) and IR light to provoke detrapping, counteracting the effect of the X-rays, thus lowering the $[Eu^{3+}]$:$[Eu^{2+}]$ ratio (Fig. 1b(vii)).

Figure 2(a) shows the effect of the laser stimulation. It is clear that the blue curve, for violet stimulation,

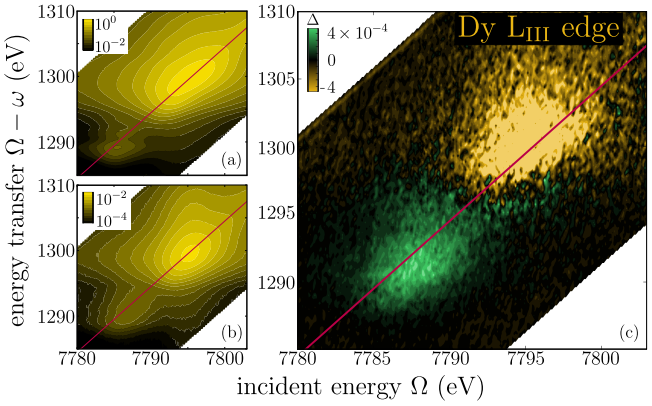

Figure 3 – RIXS planes of Dy_2O_3 (a) and $Sr_4Al_{14}O_{25}$:Eu,Dy (b), and the difference of RIXS planes of $Sr_4Al_{14}O_{25}$:Eu,Dy, measured upon violet and IR illumination (c). The red straight line corresponds to a scan of the incident energy at fixed emission energy (HERFD-XANES). All planes measured at the Dy L_{III} edge.

presents a higher $[Eu^{3+}]$:$[Eu^{2+}]$ ratio than the black curve, for IR stimulation. Interestingly, a similar but opposite effect on the same timescale was found for the same experiment, performed at the Dy L_{III} edge. Figure 2(b) indicates that the amount of Dy^{3+} goes slightly down upon violet stimulation (yellow curve), compared to IR stimulation (black curve). Concurrently, a small increase of the spectral intensity in the region where the Dy^{2+} white line is expected can be observed. Figures 2(e-f) display the differences between the HERFD-XANES spectra, measured upon violet and IR stimulation, more clearly illustrating the valence changes.

The Dy^{2+} white line lies at lower energy than the Dy^{3+} white line, in the region where the Dy^{3+} pre-edge features are also observed (see Fig. 2(d)). The latter, which typically show a richer fine structure, are due to weakly allowed $2p^6 4f^9 \rightarrow 2p^5 4f^{10}$ transitions[47–50]. In our experiment, both features have a comparably low intensity. In order to confirm that the changes below the Dy^{3+} white line are indeed due to the creation of Dy^{2+}, RIXS planes were measured under both illumination conditions and compared to RIXS planes of the pre-edge region (Fig. 3). The Dy^{3+} pre-edge structure is clearly seen in the RIXS plane of Dy_2O_3, but it is obscured for the phosphor sample . The difference of the violet and IR illuminated RIXS planes confirms that the spectral changes correspond to a decrease of the amount of Dy^{3+} and an increase of Dy^{2+}: two broad bands are found, consistent with the rise of a Dy^{2+} white line, rather than with changes in the Dy^{3+} pre-edge region. This explains why the Dy^{3+} pre-edge structure is obscured for the phosphor sample as the X-rays inevitably create some Dy^{2+} in the phosphor (see also Fig. 1(b)).

These observations clearly prove the existence of the following photoinduced electron transfer

$$Eu^{2+} + Dy^{3+} \underset{k_B T}{\overset{\text{violet}}{\underset{\text{IR}}{\overset{\text{X-rays}}{\rightleftharpoons}}}} Eu^{3+} + Dy^{2+} \qquad (1)$$

in accordance with the scheme in Fig 1(b). To obtain reliable estimates for the quantity of Eu and Dy that changes oxidation states, the HERFD-XANES spectra were fitted[51–53] with two Gaussians, one for each white line, and a smooth step function, representing the electronic transitions towards the dense set of unbound states, $2p^6 4f^N \rightarrow 2p^5 4f^N \phi^1$. Details about the fits are given in the *Supplementary Information* and the result for the difference spectra is shown in Figs. 2(e-f).

The area under the white line is associated with the concentration of Ln ions[43–45]. By exploiting that the total number of Ln ions remains constant throughout the experiment, it was verified that difference spectra of Fig. 2(e-f) correspond to 3% of all Eu and 2% of all Dy. Given the higher concentration of Dy in the phosphor (as verified by EDX[54], see *Supplementary Information*), quantitative agreement is found between the valence changes of Eu and Dy within the experimental uncertainties. This number is of the same order

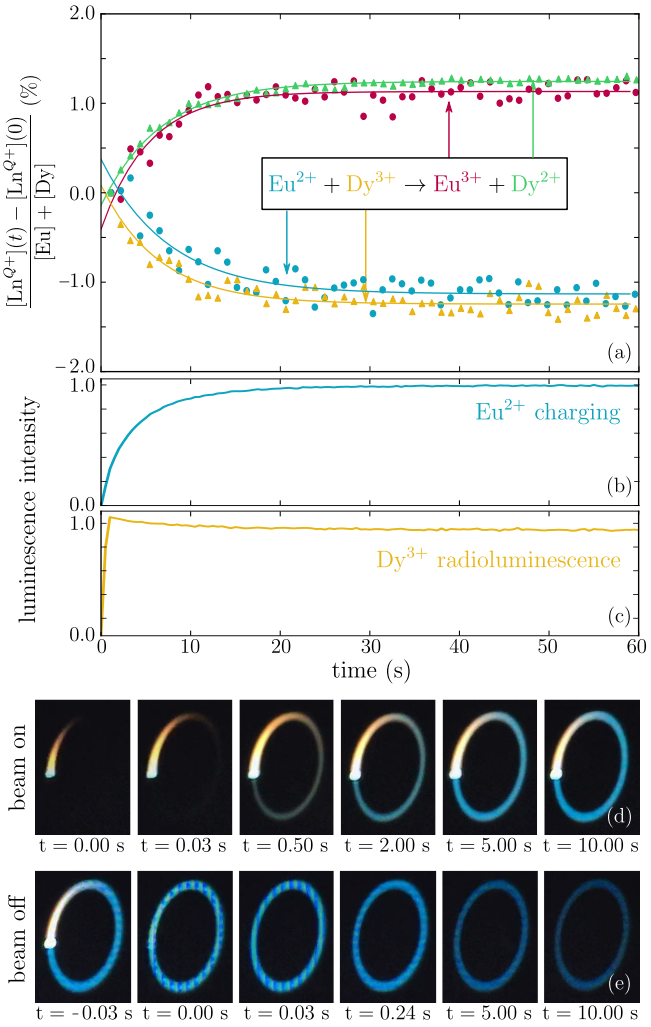

Figure 4 – Time evolution of the lanthanide oxidation states, relative to the total [Eu]+[Dy] content from HERFD-XANES (a). Time $t = 0$ corresponds to switching on of the X-ray beam. Simultaneously, the radioluminescence is probed for Eu^{2+} (broad band emission in 450-550 nm range) (b) and Dy^{3+} (line emission in 550-600 nm range) (c). Pictures of the rotating sample illustrate the charging and afterglow of the blue Eu^{2+} emission when the beam is switched on (d) and off (e), respectively.

of magnitude as a prior estimate for the number of Eu ions changing valence state, based on optical spectroscopy experiments on $SrAl_2O_4$:Eu,Dy [55], suggesting that the found electron transfer is indeed related to the persistent luminescence.

In order to further substantiate the connection between the electron transfer and the persistent luminescence, their time evolution was measured. The result is shown in Fig. 4, where an optically cleaned phosphor, *i.e.* for which all traps were first emptied by OSL, is irradiated by the X-ray beam by opening the fast shutter at $t = 0$. The oxidation states of the lanthanide ions are sampled every 100 ms from the HERFD-XANES intensity at a fixed energy, corresponding to the white line maximum. From Fig. 4(a), it is clear that the X-ray induced oxidation of Eu^{2+} and reduction of Dy^{3+} occur on the same time scale of about 20 s. After this, a dynamic equilibrium is reached where the forward and backward electron transfers, Eq. 1, occur at the same rate. It should be noted that this relatively long time scale is the consequence of the sample being mounted on a rotating stage. If not, the dynamic equilibrium would have been reached after 0.1 s, presumably explaining why no valence state changes were found in prior investigations [30–33,35].

Figure 4(b) shows that the charging of the persistent luminescence under the experimental irradiation conditions follows indeed the same temporal behavior as the electron transfer. In contrast, the Dy^{3+} radioluminescence (RL), shown in Fig. 4(c), grows fast, in the 0.1-0.5 ms range, corresponding to the intrinsic rate of the inter-$4f^9$ transitions [56,57]. In the same time frame of the charging, the Dy^{3+} RL intensity shows a small decrease, presumably due to the partial reduction of the Dy^{3+} ions.

The variations in luminescence are also visible in Fig. 4(d) showing the rotating sample at several time delays after switching on the X-ray beam. The coma shaped signature of the Dy^{3+} RL appears instantaneously, while the blue persistent luminescence builds up more slowly. Complementary, Fig. 4(e) displays how the Dy^{3+} RL disappears almost immediately after switching off the X-ray beam, leaving the blue afterglow visible for several hours. The first two frames of 4(e) confirm that the intensity of the blue Eu^{2+} luminescence that is probed during this experiment is due solely to the afterglow, *i.e.* the blue intensity along the rim of the pellet does not change abruptly when the excitation is switched off.

In summary, a dedicated RIXS study is performed on $Sr_4Al_{14}O_{25}$:Eu,Dy persistent luminescent materials in order to elucidate the electron transfer that underlies the energy storage in this persistent phosphor. While the X-rays allow to accurately probe the oxidation states of both dopants in real time, they unavoidably disturb the equilibrium electron occupation, prohibiting the unambiguous assessment of the persistent luminescence mechanism unless measures are taken to overcome the beam effect. A novel measurement approach is demonstrated, where illumination with visible and near-IR light are used to manipulate the electron occupations, in combination with an effective method to spread the applied X-ray dose by rapidly spinning the sample. Excitation by violet light induces trapping, creating metastable Eu^{3+}-Dy^{2+} centers, while IR light provokes detrapping, as described by Eq. 1. Quantitatively, 3% of the Eu ions and a corresponding number of Dy ions are affected, in agreement with the optically determined storage capacity. The characteristic time of the metastable Eu^{3+}-Dy^{2+} state coincides with the charging of the persistent luminescence. This is hence the first confirmation of the popular, yet debated, model where Dy^{3+} acts as the main electron trap in persistent phosphors.

Acknowledgements

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