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PII: S0022-2313(15)30431-2
DOI: <http://dx.doi.org/10.1016/j.jlumin.2015.10.035>
Reference: LUMIN13658

To appear in: *Journal of Luminescence*

Received date: 28 August 2015

Revised date: 15 October 2015

Accepted date: 16 October 2015

Cite this article as: H. Hagemann, D. Lovy, S. Yoon, S. Pokrant, N. Gartmann B. Walfort and J. Bierwagen, Wavelength dependent loading of traps in the persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$, *Journal of Luminescence* <http://dx.doi.org/10.1016/j.jlumin.2015.10.035>

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Wavelength dependent loading of traps in the persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$

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Abstract

The persistent phosphorescence and thermoluminescence of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ is reported for a variety of different excitation wavelengths and excitation temperatures, to provide new insights in the mechanism of the trapping and detrapping. These measurements reveal that the trapping is strongly dependent on the wavelength and temperature. First, with increasing loading temperature, the thermoluminescence peak shifts to lower temperatures which corresponds to a change of trap population. Secondly, the integrated thermoluminescent intensity increases with increasing loading temperature. All wavelength and temperature dependent experiments indicate that the loading of the traps is a thermally activated processes. Utilizing different wavelengths for loading, this effect can be enhanced or reduced. Furthermore excitation with UV-B-light reveals a tendency for detrapping the phosphor, reducing the resulting thermoluminescent intensity and changing the population of the traps.

Introduction

Materials with persistent phosphorescence attract increasing interests due to their wide application possibilities and their remarkable luminescent properties [1-10]. The persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ has been the subject of many investigations [3, 5-8, 10] due to its outstanding afterglow performance. According to these studies, both the Eu^{2+} - and Dy^{3+} -ions substitute for the Sr^{2+} in this host material. Two crystallographically nonequivalent Sr^{2+} sites are reported to be the origin of a blue (445 nm) and green (520 nm) emission originating from Eu^{2+} , as discussed in detail in [7]. The lifetime of the blue emission is significantly shorter and is associated in part with an energy transfer to

the green emitting phosphor [11, 12]. The blue emission is thermally quenched above 250 K, and as a result the intensity of the green emission at ambient temperature is less than half its intensity at 10 K [13]. The additions of Dy^{3+} and small amounts of boron have led to improved afterglow performance of this phosphor [4]. The mechanism of the long-lasting phosphorescence of the Eu^{2+} is not yet clear, but an electron trapping mechanism has been proposed either from the Dy^{3+} or oxygen vacancies in the surrounding of the Eu^{2+} [1, 5]. These findings are supported by XANES experiments, which show an increase of Eu^{3+} ions after excitation, implying an oxidation of Eu^{2+} while loading the traps [6, 14].

In a recent paper, Botterman et al [7] have studied in detail the trapping and detrapping in SrAl_2O_4 doped with Eu^{2+} and Dy^{3+} with thermoluminescence techniques. In this work, we use differently designed experiments, focusing on the wavelength dependency of the trapping and detrapping process. Our experimental results confirm the observations of Botterman et al.[7], and provide new information about the influence of exciting wavelength and irradiation temperature on the thermoluminescence. In particular, we study the thermoluminescence of a well characterized sample of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ at different irradiation temperatures (from 173K to 273 K) using five different excitation wavelengths (310, 375, 405, 445 and 455 nm). These experiments are completed by excitation and emission spectra at different temperatures, as well as afterglow experiments. These experiments reveal the presence of a complex trap distribution, which can be selectively populated by both temperature and excitation wavelength.

Experimental methods

Sample preparation

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} powders were synthesized by a solid-state reaction. Stoichiometric amounts of SrCO_3 and Al_2O_3 together with 1.5 mol % of Eu_2O_3 and 5 mol% Dy_2O_3 were thoroughly mixed with 0.9 wt. % of boric acid. The powder mixtures were then ground using a ball mill, heated to 1450 °C and annealed for 4 h under reducing condition at 1450 °C (5% H_2 in Ar). X-ray diffraction showed that the sample contains mainly SrAl_2O_4 (93.1%) with small amounts of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ (3.0 wt%) and other phases (DyAlO_3 3.4%, and $\text{Dy}_3\text{Al}_5\text{O}_{12}$: 0.5%, Fig. S9). The material shows very good afterglow performance, as seen in Fig. S1.

Thermoluminescence Setup

The following home-built thermoluminescence setup was used for our experiments (see scheme in the Supplementary Information). The sample (typically a 13 mm diameter and 1 mm thick pellet composed of 100 mg of phosphor with 300 mg KBr), is attached to a brass sample holder which can be cooled with a stream of cold nitrogen-gas from a liquid-nitrogen Dewar and heated with a heating cartridge (Omega, CSH-101100). The temperature was monitored with a temperature sensor (Omega, Type T) and controlled with a PID-controller (Omega, CN7523). The sample is illuminated with LED-Light (310 nm: Thorlabs M310L3 (approx. 30 mW), 375 nm: Thorlabs M375L3 (approx. 470 mW), 405 nm: Ultrafire WF 501B (approx. 1.2 W), 445 nm: HL-3WHPL-Roy445 (approx. 1.5 W), 455 nm: CR-XPE-ROY-D4 (approx. 1.5

W), respectively). Except for the 310 nm LED, appropriate band pass filters were set between LED source and the sample to make sure that only the desired wavelength reaches the sample. The emission path is equipped with a long pass filter (458 LP Edge Basic, AHF Analysentechnik). The thermoluminescence was collected with a custom-made 1:1 Telescope and detected with a PMT (Hamamatsu, R2949), equipped with a photon counting unit (Hamamatsu, C3863) attached to a custom-made high voltage supply. The entire setup (illumination, cooling, heating and detection) is controlled via a custom-made program, written in Pascal. Typically, the samples were first completely detrapped by heating them up to 523 K for 2 minutes. Then they were cooled to the appropriate temperature in the dark, and illuminated for 10 minutes with the suitable LED to load it completely at a defined temperature (compare Figure 7). After this illumination, the LED was switched off and the samples were heated with a rate of 10K/min up to 523 K. During the entire experiment, the light emission was monitored to follow both the loading curves and the subsequent thermoluminescence. With the aim to achieve an accurate comparison between the different excitation wavelengths, the detection path was not changed while exchanging the LED for excitation. This allows comparing quantitatively the thermoluminescence spectra after full loading with different excitation wavelengths. The intensity of the excitation light is monitored with a photodiode to correct the signal with drifting emission power.

Photoluminescence excitation and emission experiments and absolute quantum yield

The excitation and emission spectra were measured with a Fluorolog3-22 (Horiba Jobin Yvon), equipped with a water-cooled photo multiplier tube (PMT). Low temperature measurements were done using a closed cycle cryostat (Janis Research) which could be inserted into the sample chamber of the fluorometer. For measurement of the absolute quantum yield an integrating sphere (Quanta-phi, Horiba Jobin Yvon) was attached to the Fluospectrometer via an optical fibre bundle for excitation and emission.

Afterglow experiments

Afterglow was measured on a home-built Photometer, equipped with a Photomultiplier (R6233 SEL, Hamamatsu). 30 mg of the samples were mixed with 30 mg of on transparent acrylic varnish and placed onto a white coated aluminum sheet. The temperature was controlled with a Peltier element. After reaching the desired temperature the sample was illuminated with a UV-LED (365nm) for 10 min to reach full activation. After switching the LED off, the afterglow was measured for 2 h 45 min.

X-ray diffraction (XRD)

X-ray powder diffraction pattern was obtained using a PANalytical X'Pert PRO θ -2 θ scan system attached to a Johansson monochromator ($\text{Cu-K}\alpha_1$ radiation, 1.5406 Å) which was equipped with a X'Celerator linear detector. The diffraction patterns were recorded between 18° and 100° (2 θ) with an angular step interval of 0.0084°. To give information on the concentration of Eu and Dy, a phase analysis was performed by Rietveld refinement. The concentration of Dy and Eu in the SrAl_2O_4 phase was below the detection limit for SEM/EDX

Experimental results and discussion

Figure 1: a) Thermoluminescence spectra of SrAl₂O₄:Eu²⁺,Dy³⁺,B excited at 173 K, with different excitation light. - - - : 310 nm, — : 375 nm, : 405 nm, — · — : 445 nm, - - - : 455 nm. b) Thermoluminescence spectra of SrAl₂O₄:Eu²⁺,Dy³⁺,B excited at 248 K, with different excitation light. - - - : 310 nm, — : 375 nm, : 405 nm, — · — : 445 nm, - - - : 455 nm.

Figure 2: Normalized thermoluminescence of SrAl₂O₄:Eu²⁺,Dy³⁺,B excited at 173 K with 310 nm LED (dashed) and with 455 nm (continuous line). One should consider the difference of the peak-temperature, the change in shape and intensity (compare Figure 1). Fig. b: Temperature of maximum Luminescence as a function of the temperature of loading

The excitation and emission spectra at different temperatures agree with those reported in the literature [7, 11] (see Figure S2). It is interesting to note that with increasing temperature (from 6 to 250 K), the shape of the excitation spectra remains similar, but with broadened bands. At ambient temperature, the external quantum yield for the excitation wavelengths from 310 nm to 455 nm was found to be between 12 and 22 % (Table S1).

Figure 1 compares the observed thermoluminescence (TL) curves after excitation with 310 nm, 375 nm, 405 nm, 445 nm and 455 nm at 173 K (Fig. a) and 248 K (Fig. b). In agreement with previous results [7], all curves are rather broad (FWHM ca 100 K), indicating the presence of a wide trap distribution. Note that the afterglow curve (Fig. S1) does not follow exactly the 1/t behavior which was predicted for a uniform or wide Gaussian distribution of traps [15]. The shape of the TL curves is not symmetrical and

has a longer tail to higher temperatures, except the TL curves measured at 173 K, excited with 445 nm or 455 nm. The maximum of the TL peak shifts towards lower temperatures with increasing irradiation temperature for all excitation wavelengths (Figure 2b). This behavior stands in contrast to the measurements made with $\text{CaAl}_2\text{O}_4:\text{Eu},\text{Nd}$ [11], where the maximum shifts to higher temperatures when the sample is excited at higher temperatures, which is related to the thermal depletion of traps with increasing temperature. The behavior observed for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$, which was also reported in [7], indicates that the relative population of traps changes as a function of irradiation temperature. With increasing temperatures, more traps with a lower trap-depth can be filled, leading to a shift of the maximum TL peak towards lower temperatures.

This observation shows that for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ a thermal activation is needed to fill the traps. And it appears that this behavior especially applies for shallower traps, as they are easier filled at higher temperatures. Using different excitation wavelengths changes the shape of the TL curves, which means that, dependent on the wavelength different fractions of the trap distribution are filled. Especially at low temperatures the shape and intensity depends strongly on the excitation wavelength. Exciting the sample with 455 nm at 173 K leads to a typical single-trap-depth TL-curve as shown in Figure 2a. As can be seen in Figure 2b, the maximum of the TL curve is quite different for the 445 and 455 nm excitations at 173 K. At the excitation temperature above 260 K, the TL maximum is at a similar position (ca. 280 K) for all five different excitation wavelengths this comes probably due to an increasing thermal activated trapping. Summarizing the results, Table 1 shows the peak Temperature T_m for all ten measurements combined with the apparent trap-depth calculated with Urbach's approximation [16].

Excitation wavelength	T_m (173 K loading)	T_m (248 K loading)	Depth-Trap (173 K)	Depth-Trap (248 K)
310 nm	304 K	292 K	0.61 eV	0.58 eV
375 nm	310 K	294 K	0.62 eV	0.59 eV
405 nm	309 K	294 K	0.62 eV	0.59 eV
445 nm	364 K	306 K	0.73 eV	0.61 eV
455 nm	367 K	307 K	0.73 eV	0.61 eV

Table 1: Peak Temperature of TL curves and their correspondent apparent trap-depth, dependent on the excitation wavelength

Figure 3: Difference of the TL-Curves between excitation at 248 K and 173 K

Besides this, also more of the deeper traps are filled at higher irradiation temperature, but not with the same amount as the shallower traps. For a better visualization the difference of the TL-curves between the two loading temperatures are shown in Figure 3. The largest absolute increase of TL-intensity is seen with the excitation at 445 nm. Excitation with UV-light leads to a shift in the difference-TL curves to lower temperature. When the sample is excited with blue light the highest increase in thermoluminescence is found around 300 K in contrast to that UV-light leads to a pronounced increase around 265 K. All in all, the additional traps lead to a total increase of the TL intensity, as can be seen in Figure 1.

Figure 4: Integrated thermoluminescence intensity, dependent on the illumination temperature. The thermoluminescence was integrated starting from 0°C (273K) to the end of the Curve at 250°C (523 K).

Excitation wavelength [nm]	310	375	405	445	455
Ratio of integrated intensity [248K/173K]	1.65	1.93	2.23	10.8	12.4

Table 2: Ratio of the integrated luminescence, when loaded at -25°C and -100°C.

In order to estimate the relative amount of traps loaded at different temperatures, we have integrated the TL curves from 273 K to 523 K. The starting point at 273 K for the integration was chosen to allow loading experiments up to this temperature and still keep a significant amount of the integrated TL curves. If one considers the shift of the maximum of the TL curves to lower temperatures when charging at higher temperature (Figure 1), this analysis method will slightly underestimate the integrated intensity at higher charging temperatures. Nevertheless, if applied consistently, one can compare the integral of the TL curves with each other. These results are shown in Figure 4. For the five excitation wavelengths. At low temperatures the loading of the sample with 375 nm light leads to the highest TL intensity. This behavior changes at higher temperatures when enhanced thermally supported trapping takes place. The different increase in TL intensity could also be explained with possible detrapping due to harsh UV-light excitation, but one should consider the absorption cross-section at 310 nm and the low excitation intensity at this wavelength. Furthermore, the higher the loading temperature, the higher the total TL intensity for all loading wavelengths. The temperature dependence of the integrated TL-intensity and the peak intensity is reduced with UV light for excitation instead of blue light. This can be explained by an optical pumping of the electrons into the conduction band rather than into the excited 5d-levels of the Eu^{2+} . Using blue light at the edge of the excitation-spectrum does not provide enough energy to promote electrons into the conduction band, which is close to the excited 5d state and even overlaps partly with it [17].

The results of Figure 4 can be compared with Fig. 6 and 7 in Ref. [7] which show the combined afterglow and TL intensity after illumination at 370 and 435 nm as a function of the charging temperature. For the illumination at 435 nm, the intensity is almost equal to zero below 210 K (i.e. no charging of traps took place below this temperature at 435 nm), while in our case with 405 nm, the intensity is only about 10% less than for the excitation wavelength of 370 nm. Note that for all excitation wavelengths, the total afterglow and TL intensity increases up to the charging temperature of 273 K. Our experiment with the excitation wavelength of 445 and 455 nm reveals a weak thermoluminescence peak after excitation at 173 K. It should be also noted that in this case, the maximum of the TL curve is observed at ca. 365 K, which indicates that only the deeper traps are filled under these conditions. The temperature shift of this TL maximum is also much stronger than for higher activation energies (Table 1). Short UV-light irradiation has two effects on the loading behavior. First, it facilitates the trapping at low temperature, possibly due to an enhanced excitation into the conduction band even without thermal activation. Secondly, it also could enable optical detrapping. One possible explanation for this result is that the traps have a certain cross-section in the UV range, or due to a larger Stokes-shift between excitation photon and emission photon local heating around the Eu^{2+} -centers could appear, which also would lead to an increased release of the traps. These effects show similarities with the trapping of organic fluorescent dyes in certain embedding media used for high resolution microscopy[18].

Employing the model that the traps are in close proximity of the Eu^{2+} as suggested by Clabau et.al. [5], one can assume that the electron moves around after being excited. There are three possibilities, which

can be considered: First recombination with the Eu^{2+} -center to produce normal fluorescence, secondly interconversion or other non-luminescence processes such as thermal quenching, and thirdly being trapped in the surroundings of the Eu^{2+} -ions. Depending on the excess-energy of the electron after reaching the excited state it can move further away from the emission center. Applying this model to our system it appears that the trap-depth depends on the spatial distance to the Eu^{2+} centers, because utilizing blue light for excitation at low temperatures leads to high peak-temperatures in the TL curves, whereas excitation with UV-light shifts the peak-temperature of the TL curve to lower ones. Furthermore, it seems that UV-light depopulates favorably deeper-traps, which are close to the emission center, which can be seen in the differences of the TL curves of the excitation with 310 nm and 445 nm loaded at 248 K (Figure 1, Figure 3). These two TL curves do not differ much in intensity, but in the trap distribution. While the TL curve loaded with 310 nm peaks at 292 K, it peaks at 306 K when loaded with 445 nm, clearly showing a shift to deeper traps, when excited with blue light. This effect is probably even underestimated due to the fact that no correction for thermal quenching was applied as it was suggested in Ref. [19]. This result shows that one could charge different subsets of the traps, dependent on the temperature and excitation wavelength.

Figure 5: Normalized loading curve with different excitation wavelengths and at different temperatures in a logarithmic time scale. Excitation with 375 nm, 405 nm, 445 nm and 455 nm. Upper curves: Excitation at 173 K and lower curves excitation at 248 K.

Figure 5 shows the normalized loading curves at different temperatures and wavelengths, which correspond to the TL curves in Figure 1. The intensities are normalized to the initial intensity observed during the loading at 173 K. These curves resemble the loading curves reported in Ref. [6]. For clarity the excitation with 310 nm was excluded due to much lower excitation power (30 mW compared to 500-1500 mW). These experiments were performed with a 460 nm cut-off filter, and monitored thus only the green emission band. All our experiments showed that the loading reached a steady state after 10 minutes of irradiation, irrespective of the intensity. Of course, the shape of the loading curve is intensity dependent, as was reported previously [20]. The loading to the steady state ensures similar starting conditions between all excitation wavelengths. At low loading temperatures, the emission intensity

under constant illumination decreases with time and reaches a steady state after ca 2-3 minutes. This behavior reflects the trapping of some Eu^{2+} ions in a dark state, probably due to reversible oxidation, removing them thus from the potentially emitting species. This is illustrated in Figure 6 which compares the excitation spectrum (observed at 520 nm) before and after loading at 173 K. The intensity after the loading is weaker, in agreement with the loading curve in Figure 5. The spectra in Figure 5 show also that at 405 nm, the excitation intensity is more reduced as at 375 nm, which is also reflected in the relative steady state intensities in Figure 5. This observation shows that at low temperature, the Eu^{2+} on the green emitting site appears to be associated with trap states that can be populated, as their corresponding excitation spectral intensity decreases. However, this is not necessarily the case at ambient temperature. Preliminary experiments suggest that here the Eu^{2+} on the blue emitting site contributes to the trapped states. However, a similar experiment as the one shown in Figure 6, but at room temperature, is not obvious, as the afterglow adds signal to the measured spectra.

Figure 6 Excitation spectra before and after loading (at 173 K) continuous line: unloaded, dashed line: loaded sample. Excitation slit: 0.2 nm, Integration time 0.1 s, step width: 1 nm, Detection slit: 14 nm at 515 nm.

In this context it is also interesting to consider the observations by Botterman et. al. [7] for the excitation wavelength of 435 nm. Below 210 K, the charging curves are practically flat, suggesting that no charging takes place. With increasing temperature, some charging takes place and the intensity decreases as a function of time, similarly to the low temperature loading curves shown in Figure 6. At higher illumination temperatures (e.g. 248 K), the emission intensity increases with illumination time. This general behavior of the charging curves was also analyzed by Jia [20] with a 3-level model (ground state, excited state and trap state) and implies that the excited (light emitting) state is populated both by the optical pumping and by the depopulation of the trap states. It should be stressed that our experimental loading curves cannot be satisfactorily fitted with an equation of the type:

$$I = I_0(1 - A \cdot e^{-Bt})$$

and show that more parameters may come into play. The steady state emission intensity is lower at higher temperatures and reflects also the thermal quenching of the Eu^{2+} emission which has been reported previously [21]. The relative (high temperature vs low temperature) steady state emission under 375 nm illumination is stronger than the one under 405 nm illumination. This can be qualitatively explained by an optical detrapping of the traps with higher energy photons. It is important to note in this context that the reported onset of photoconductivity below 400 nm [17] could be related to the detrapping process.

Figure 7: Afterglow curves at different temperature

Figure 7 shows the afterglow curves measured at different temperatures from 278 to 328 K (5 °C to 55 °C). At higher temperatures, the initial emission intensity is high, however the decay is also significantly faster. For our sample studied, the integrated afterglow intensity from 2 min to 2 h 45 min is maximized at 288 K, but only a few percent less at 278 K and 298 K. At higher temperatures the integrated intensity decreases drastically, at 328 K it is about 73% of the intensity at 288 K. Botterman et. al. [5] observed for their commercial $\text{SrAl}_2\text{O}_4:\text{Eu},\text{Dy}$ sample a maximum of the combined “afterglow + TL” curves close to 273 K, while for the afterglow alone (measured for 30 min) the maximum was observed at 293 K. Comparing the afterglow curves at 278 K and 328 K, at all time-intervals, the decay is faster at 328 K, and the differences of the slopes become more pronounced at longer afterglow times. The competition between the population of low energy traps and depopulation of deep traps as a function of temperature leads to a relatively narrow (ca 30 K) temperature region in which the total TL intensity is maximum.

Conclusions

The present experiments confirm that the persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ possesses a great variety of traps. The population of traps depends on the charging wavelength and temperature. Starting from 173 K, we observed that with increasing temperature, more traps are populated. However, these new traps appear to be released with lower activation energies, leading to a shift of the TL maximum towards lower temperatures. The TL curves excited at 455 nm and 445 nm show a much weaker

thermoluminescence signal, which are shifted to higher temperatures (for this sample 367 K). But even after excitation at 173 K a TL curve was measurable, in contrast to the observation reported in [5]. The deep traps are associated with the green emitting Eu^{2+} , as only this ion can be excited at this wavelength. At higher temperatures, thermal- as well as light-induced detrapping (or a combination of both) depletes the trap population. But light induced detrapping reduces mainly deeper traps. In conjunction with the fact that the thermal quenching of the green emission does not change significantly between 280 and 370 K, this will lead to a maximum of the integrated TL emission as the result of the competition between increased trap filling as well as trap depletion and thermal quenching with increasing temperature. Temperature dependent afterglow curves allow determining the optimum afterglow temperature which may be tuned by minute chemical modifications.

Further it was shown, that $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ can be efficiently loaded with blue LED light, when excited at room-temperature. This shows, that this outstanding material is also applicable in areas, which are illuminated with LED-light and not with sunlight or mercury-lamps.

Acknowledgement

This work was supported by The Swiss Commission for Technology and Innovation (CTI) (project 15217.1 PFIW-IW) and by the Swiss National Science Foundation. The authors thank Sara Chahid for performing the quantum yield measurements under the guidance of J.B.

References

- [1] P. Dorenbos, Mechanism of Persistent Luminescence in Eu^{2+} and Dy^{3+} Codoped Aluminate and Silicate Compounds, *Journal of the Electrochemical Society*, 152 (2005) H107.
- [2] K. Van den Eeckhout, P.F. Smet, P. D., Persistent Luminescence in Eu^{2+} -Doped Compounds: A Review, *Materials*, 3 (2010) 31.
- [3] H. Takasaki, S. Tanabe, T. Hanada, Long-Lasting Afterglow Characteristics of Eu^{2+} , Dy^{3+} Codoped $\text{SrO-Al}_2\text{O}_3$ Phosphor, *Journal of the Ceramic society of Japan*, 104 (1996) 322-326.
- [4] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, A new long phosphorescent phosphor with high brightness, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$, *Journal of the Electrochemical Society*, 143 (1996) 2670-2673.
- [5] F. Clabau, X. Rocquefelte, S. Jobic, P. Deniard, M.-H. Whangbo, A. Garcia, T. Le Mercier, Mechanism of Phosphorescence Appropriate for the Long-Lasting Phosphors Eu^{2+} -Doped SrAl_2O_4 with Codopants Dy^{3+} and B^{3+} , *Chem. Mater.*, 17 (2005) 3904-3912.
- [6] K. Korthout, K. Van den Eeckhout, J. Botterman, S. Nikitenko, D. Poelman, P.F. Smet, Luminescence and x-ray absorption measurements of persistent $\text{SrAl}_2\text{O}_4:\text{Eu},\text{Dy}$ powders: Evidence for valence state changes, *Physical Review B*, 84 (2011).
- [7] J. Botterman, J.J. Joos, P.F. Smet, Trapping and detrapping in $\text{SrAl}_2\text{O}_4:\text{Eu},\text{Dy}$ persistent phosphors: Influence of excitation wavelength and temperature, *Physical Review B*, 90 (2014) 085147.
- [8] H. Shin, S. Ullah, K. Chung, Effect of nominal substitution of Dy^{3+} for host cations in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphor on phase evolution and long afterglow luminescence, *Journal of Alloys and Compounds*, 544 (2012) 181-187.
- [9] A. Nag, T.R.N. Kutty, The mechanism of long phosphorescence of $\text{SrAl}_{2-x}\text{B}_x\text{O}_4$ ($0 < x < 0.2$) and $\text{Sr}_4\text{Al}_{14-x}\text{B}_x\text{O}_{25}$ ($0.1 < x < 0.4$) co-doped with Eu^{2+} and Dy^{3+} , *Materials Research Bulletin*, 39 (2004) 331-342.

- [10] S. Yoon, J. Bierwagen, M. Trottmann, B. Walfort, N. Gartmann, A. Weidenkaff, H. Hagemann, S. Pokrant, The influence of boric acid on improved persistent luminescence and thermal oxidation resistance of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, *Journal of Luminescence*, 167 (2015) 126-131.
- [11] S.H.M. Poort, W.P. Blokpoel, G. Blasse, Luminescence of Eu^{2+} in Barium and Strontium Aluminate and Gallate, *Chem. Mater.*, 7 (1995) 1547-1551.
- [12] D. Wang, Q. Yin, Y. Li, M. Wang, Concentration quenching of Eu^{2+} in $\text{SrO} \cdot 6\text{Al}_2\text{O}_3 : \text{Eu}^{2+}$ phosphor, *Journal of Material Science*, 37 (2002) 3.
- [13] V. Chernov, T.M. Pitters, R. Meléndrez, W.M. Yen, E. Cruz-Zaragoza, M. Barboza-Flores, Photoluminescence, afterglow and thermoluminescence in irradiated with blue and UV light, *Radiation Measurements*, 42 (2007) 668-671.
- [14] S.K. Kandpal, B. Goundie, J. Wright, R.A. Pollock, M.D. Mason, R.W. Meulenberg, Investigation of the emission mechanism in milled $\text{SrAl}_2\text{O}_4:\text{Eu}$, *Dy* using optical and synchrotron X-ray spectroscopy, *ACS applied materials & interfaces*, 3 (2011) 3482-3486.
- [15] W.F. Hornyak, R. Chen, Thermoluminescence and Phosphorescence with a continuous Distribution of Activation Energies, *Journal of Luminescence*, 44 (1989) 73-81.
- [16] F. Urbach, Zur Lumineszenz der Alkalihalogenide: II. Messungsmethoden, *Sitzungsberichte Akademie der Wissenschaften in Wien*, 139 (1930) 363.
- [17] J. Ueda, T. Nakanishi, Y. Katayama, S. Tanabe, Optical and optoelectronic analysis of persistent luminescence in Eu^{2+} - Dy^{3+} codoped SrAl_2O_4 ceramic phosphor, *physica status solidi (c)*, 9 (2012) 2322-2325.
- [18] J. Fölling, M. Bossi, H. Bock, R. Medda, C.A. Wurm, B. Hein, S. Jakobs, C. Eggeling, S.W. Hell, Fluorescence nanoscopy by ground-state depletion and single-molecule return, *Nature Methods*, 5 (2008) 943-945.
- [19] K. Van den Eeckhout, A. Bos, D. Poelman, P. Smet, Revealing trap depth distributions in persistent phosphors, *Physical Review B*, 87 (2013).
- [20] D. Jia, Charging curves and excitation spectrum of long persistent phosphor $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} , *Optical Materials*, 22 (2003) 65-69.
- [21] E. Nakazawa, Y. Murazaki, S. Saito, Mechanism of the persistent phosphorescence in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}$ codoped with rare earth ions, *Journal of Applied Physics*, 100 (2006).