Thermal and concentration dependent energy transfer of Eu$^{2+}$ in SrAl$_2$O$_4$

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Abstract: SrAl$_2$O$_4$ doped with europium and dysprosium is a powerful and widely used afterglow material. Within this material strontium is found in two crystallographic different sites. Due to the similar ion radii and same charge, Eu$^{2+}$-ions can occupy both sites, resulting in two different Eu$^{2+}$-ions, one emitting in the blue and one in the green spectral range. The blue emission is thermally quenched at room temperature. In this paper we investigate the energy transfer between different Eu ions depending on the concentration and temperature using two different approaches: lifetime measurements and integrated intensity. We find an activation energy for the thermal quenching of the blue emission of 0.195 ± 0.023 eV and a critical radius for the energy transfer of 3.0 ± 0.5 nm. These results can help in designing better afterglow materials due to the fact that with energy transfer parts of the lost emission in the blue region at room temperature can be converted to the green site.

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1. Introduction

Afterglow materials have a high importance for many applications such as security signs, watches or road surface marking [1]. One of the most powerful afterglow materials is SrAl$_2$O$_4$:Eu:Dy. Nevertheless the precise mechanism of the afterglow is not known yet, but due to its spectral properties it is very well understood that the emission comes from the europium. The monoclinic crystal structure of SrAl$_2$O$_4$ contains two different sites for the strontium. When SrAl$_2$O$_4$ is doped with Eu$^{2+}$ the europium ions will substitute on the strontium sites, due to the very similar ion radius (146 pm and 147 pm respectively), hence the europium ions see two different chemical environments. Two emission bands of the 4f-5d transition of the Eu$^{2+}$ ions are observed. One in the blue region with a maximum around 450 nm and one in the green around 520 nm. Furthermore one can observe spectral overlap of the excitation and emission spectra, which leads to energy transfer from the blue to the green emission, depending on the concentration. Due to the fact, that the excited 5d-level of the blue emitting Eu$^{2+}$ ion is close to the conduction band one can observe also thermal quenching of the blue band at room temperature. Thus the spectrum of the SrAl$_2$O$_4$ doped with Eu$^{2+}$ is thermally as well as concentration dependent.

Aitasalo et al. [2] measured the lifetime of the green and blue emitting sites with 1.23 μs and 0.43 μs respectively at 20 K using a sample doped with 0.5 mol%. At this temperature the green emission showed a mono exponential decay. At room temperature (295 K) they found a multi exponential decay time of 0.73 μs for the green emission, whereas the blue emission was not detectable. Dutczak et al. [3] investigated a large variety of different strontium aluminates doped with Eu$^{2+}$. In SrAl$_2$O$_4$ doped with 1% Eu$^{2+}$ they found the lifetime of the blue and green emitting europium at 4 K at 0.4 μs and 1.2 μs respectively. At room temperature they measured the lifetime of the green emission with 0.7 μs [3]. Besides this they also measured the temperature dependence of the luminescence intensity of the blue and green emission between 4 and 500 K of sample doped with 0.1% Eu$^{2+}$. The T$_{1/2}$ value (Temperature at which the luminescence is reduced by 50% due to thermal quenching) of the blue and green luminescence was found at 230 K and 440 K respectively. This is in good correspondence to the findings of Poort et al. [4] (170 K and 440 K respectively). In a later paper by Poort et al. [5], a list of lifetimes and T$_{1/2}$ of Eu$^{2+}$ in different host lattices was reported. The lifetime of the Eu$^{2+}$-ions for the green and blue site were found at 1.7 and 0.7 μs respectively at 4.2 K. At room temperature a lifetime of 0.8 μs for the green emitting site using a sample doped with 1 mol% of europium was found [5].

Hölsä et al. [6] proposed the possibility of anomalous low-temperature luminescence, but the reported experimental data and theoretical calculations allow to conclude that the emission comes indeed from two different sites [4, 7]. Nakazawa et al. [8] observed the thermal quenching of SrAl$_2$O$_4$:Eu$^{2+}$ (doped with 1 mol%) but at much lower temperatures (100 K less) than all other publications. Wang et al. [9] have measured the concentration quenching of Eu$^{2+}$ in SrAl$_2$O$_4$. They started at concentrations beyond 1% and calculated a critical radius, which was found at 2.5 nm. Although SrAl$_2$O$_4$ doped with europium is an important luminescent ceramic, the energy transfer has to our knowledge not been studied quantitatively so far. In this paper we have studied the temperature dependence of luminescence intensity (up to 520 K) and the lifetimes of eight different SrAl$_2$O$_4$ samples doped with 0.01% up to 2% (from 3 to 300 K).

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2. Experimental methods

2.1 Synthesis

Single europium doped SrAl\(_2\)O\(_4\):Eu\(^{2+}\) powders were synthesized by a solid-state reaction. Stoichiometric amounts of SrCO\(_3\) and Al\(_2\)O\(_3\) together with different amounts of Eu\(_2\)O\(_3\) (0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00 and 2.00 mol\%) were thoroughly mixed using a ball mill. The ratio Al/(Sr + Eu) were always exact 2/1. The mixtures were then annealed for 6h under reducing condition at 1500 °C (5% H\(_2\) in Ar) in a tube furnace. For comparison reasons (afterglow pigments should show a similar grain size distribution) all sintered samples have been milled in a mortar and sieved to reach a final d50 and d90 value of ~25 and 45 micrometer respectively.

2.2 Excitation- emission spectra

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 fluorimeter.

2.3 Thermal dependent brightness measurements

For measuring the brightness of the samples, they were mounted in a home built thermoluminescent setup described elsewhere [10]. The samples (typically a 13 mm diameter and 1 mm thick pellet composed of 100 mg of phosphor with 300 mg KBr), were attached to a sample holder which can be cooled with a stream of cold nitrogen-gas and heated with a heating cartridge. The samples were initially heated rapidly up to 520 K and then cooled by 5K /min down to 170 K from where they were again heated to 520 K with a slope of 5 K/min. This procedure provides a cooling and a heating trace of the integrated intensity and its hysteresis. This was performed with a filter to collecting the total emission (CF-416/LP, AHF Tübingen). Excitation was performed with a UV-LED emitting at 375 nm (Thorlabs, M375L3).

2.4 Lifetime measurements

For measuring the fluorescent lifetime the samples were mounted in a closed cycle cryostat (Janis Research) and excited with a pulsed frequency tripled Nd:YAG Laser, running at 20 Hz (Quantel). The emitted light was collected with a telescope and refocused into fiber-bundle to direct the light to a monochromator (shamrock), equipped with a gated CCD-Camera (Andor).

2.5 XRD-measurements

X-ray powder diffraction pattern was obtained using a PANalytical X’Pert PRO 0-20 scan system attached to a Johansson monochromator (Cu-K\(_{\alpha}\) radiation, 1.5406 Å) which was equipped with an X'Celerator linear detector. The diffraction patterns were recorded between 18° and 100° (2\(\theta\)) with an angular step interval of 0.0084°. Phase analysis were performed by Rietveld refinement. The concentration Eu\(^{2+}\) in the SrAl\(_2\)O\(_4\) phase was below the detection limit for SEM/EDX

3. Results

The XRD-measurements of our SrAl\(_2\)O\(_4\):Eu\(^{2+}\) samples with different concentrations of europium ions show that they were synthesized in high purity of 98-99%. Only traces of Sr\(_2\)Al\(_2\)O\(_6\) were detected (0.01 mol\% Eu\(^{2+}\): 1.85wt%, 0.02 mol\% Eu\(^{2+}\): 1.40wt%, 0.05 mol \% Eu\(^{2+}\): 1.20wt%, 0.10 mol\% Eu\(^{2+}\): 1.20wt%, 0.20 mol\% Eu\(^{2+}\): 1.62wt%, 0.50 mol\% Eu\(^{2+}\): 2.04wt%, 1.00 mol\% Eu\(^{2+}\): 2.20wt% and 2.00 mol\% Eu\(^{2+}\): 2.58wt%). The diffraction patterns correspond to the published monoclinic structure [11].
The emission and excitation spectra at different temperatures are shown in Fig. 1. The excitation spectra of the blue and the green site overlap and an efficient excitation of both sites is provided between 330 and 380 nm. Since the blue emission is nearly completely quenched at room temperature, its excitation spectrum at 300 K is very weak. Probably due to spectral broadening at higher temperatures the excitation probability increases with increasing temperature for both sites, until the quenching effect reduces the blue emission. Our data treatment procedure is illustrated below for the sample SrAl$_2$O$_4$:Eu$^{2+}$ doped with 0.01 mol%.

Emission spectra at different temperatures between 10 and 300 K were collected for all samples (Fig. 2). These spectra were analyzed in two different ways: first a deconvolution routine was used (Fig. 3) and secondly the two peaks were separated with a cut-off filter at 460 nm. Further, the spectral dependent lifetimes of the two europium ions were measured over the temperature range between 3 and 300 K. With a custom made analysis script the decay curves, measured on every pixel of the gated CCD camera, were fitted mono (Fig. 4), and bi-exponentially (Appendix Fig. 10). The lifetime of the blue and the green emission was extracted by averaging the calculated lifetimes over a spectral range (410-445 for blue and 510-570 nm for green respectively).

These values from the mono exponential fit were used for a quantitative analysis described below. The results of the bi-exponential fits are not presented because at low temperatures the decay curves were very nicely single exponential and could not be fitted with a double exponential function (Fig. 11 in the Appendix).
Fig. 3. Thermal quench curves calculated from emission spectra of SrAl$_2$O$_4$:Eu$^{2+}$ doped with 0.01 mol% from 10 to 300 K. The small increase in total luminescence at 290 and 300 K comes from experimental inaccuracy.

Fig. 4. Spectral dependent mono-exponential fit of the lifetime of SrAl$_2$O$_4$:Eu$^{2+}$ doped with 0.01 mol% at 3 K (left) and 300 K (right). The black curves represent the integrated luminescence.

At higher temperature instabilities of the algorithm due to very weak amplitudes and very fast decays often resulted in jumps and large errors of the calculated lifetimes. However, the experimental data shows that the deviations from the mono exponential decay increase with increasing temperature. To estimate the quenching temperature of the green emission the total luminescence was measured up to 520 K (Fig. 5). Regard that here the normalized intensity is in respect of the added intensity of the blue and the green emission. As an example the results of the measurements at 3 K can be found in Table 1.

Table 1. Lifetime of the europium ions at 3 K

| Eu$^{2+}$ Conc. | $\tau_1$ (blue) | $\tau_2$ (green) |
|-----------------|-----------------|-----------------|
| 0.01%           | 795             | 1180            |
| 0.02%           | 739             | 1122            |
| 0.05%           | 774             | 1204            |
| 0.10%           | 681             | 1130            |
| 0.20%           | 624             | 1221            |
| 0.50%           | 481             | 1192            |
| 1.00%           | 361             | 1219            |
| 2.00%           | 252             | 1125            |
4. Discussion

4.1 Kinetic model

A schematic diagram of the energy transfer model is shown in Fig. 6. The band gap of SrAl$_2$O$_4$ is 6.6 eV [12]. The positions of the ground states can be estimated by the Dorenbos model [13], as it was done in [7] or it can be measured [14]. The europium ions in the two sites can be excited with UV-light. Due to a slightly lower excitation energy at the green emitting site, it can also be excited with blue light. The lower position of the excited level of the green emitting Eu$^{2+}$ affects also the quenching probability, because this band is further away from the conduction band of the SrAl$_2$O$_4$. Due to the spectral overlap between the excitation band of the green site and the emission band of the blue band energy transfer occurs.

To describe this system with a simple model, one assumes only single exponential decays for the luminescence and the thermal quenching. The energy transfer would follow the Dexter mechanism [15]. This leads to following decay rates for the green (1) and the blue (2) emission:

$$k_{\text{green}} = k_{\beta_g} + k_{\delta_g} \quad (1)$$
$$k_{\text{blue}} = k_{\beta_b} + k_{\delta_b} + k_{ET} \quad (2)$$
Here \( k_{\text{green}} \) and \( k_{\text{blue}} \) are the decay rates of the two Eu\(^{2+}\) ions \( k_{\text{flu}} \) and \( k_{\text{flq}} \) stand for the fluorescence rate of the green and blue emission and \( k_{\text{qfl}} \) and \( k_{\text{qgreen}} \) are the quenching rates, whereas \( k_{\text{ET}} \) expresses the rate of energy transfer. Correspondent to this, one can also establish the normalized luminescence of the blue and the green emission. In this case normalized brightness means that the emission is 1 if neither energy transfer nor quenching occurs:

\[
I_{\text{green}}(r, T) \propto \frac{k_{\text{flu}} + k_{\text{flq}} \ast k_{\text{ET}}}{k_{\text{flu}} + k_{\text{flq}} + k_{\text{qgreen}} + k_{\text{ET}}} \tag{3}
\]

\[
I_{\text{blue}}(r, T) \propto \frac{k_{\text{flq}}}{k_{\text{flq}} + k_{\text{qblue}} + k_{\text{ET}}} \tag{4}
\]

Here \( I_{\text{blue}}(r, T) \) and \( I_{\text{green}}(r, T) \) represent the normalized luminescence of the blue and green peak. Furthermore for the quenching we assume an Arrhenius-type behavior and for the energy transfer a Dexter-mechanism, which results for the blue emission:

\[
I_{\text{blue}}(r, T) \propto \frac{k_{\text{flq}}}{k_{\text{flq}} + A_{\text{b}} \ast e^{-E_{\text{un}}/k_{\text{B}}T} + J \ast e^{-2r/c}} \tag{5}
\]

Here \( A_{\text{b}} \) is a pre-exponential frequency-factor representing the quenching rate at infinite temperature (attempt rate). \( E_{\text{un}} \) is the activation energy needed for thermal quenching of the blue emission. Furthermore \( J \) is a pre-factor for the energy transfer, representing the spectral overlap and \( r \) is the average distance between two inequivalent Eu\(^{2+}\) ions and \( r_c \) is the critical radius, at which only the transition probability is (1-1/e). The average distance between two inequivalent Eu\(^{2+}\) ions was calculated according to Eq. (6). The volume \( V \) of the unit-cell of SrAl\(_2\)O\(_4\) is 0.384 nm\(^3\). Within this volume \( n = 2 \) formula units are incorporated and the structure has \( m = 2 \) inequivalent Sr sites. Assuming an even distribution of the Eu\(^{2+}\), regardless the doping concentration \( c \), within the samples and between the two sites the mean distance \( r \) between two inequivalent Eu\(^{2+}\) ions is given by this equation:

\[
r(\text{Eu}^{2+}) = \frac{3V}{\sqrt{c / m \ast n}} \tag{6}
\]

In Figure 8 the measured lifetimes were plotted against the temperature (left) and average distance between the ions (right). To summarize the model one can say, at low temperature and low Eu\(^{2+}\) concentrations, neither thermal quenching nor energy transfer occurs. When the temperature increases and the concentration increases thermal quenching and energy transfer takes place according the Eq. (5). In this simple model both effects are not coupled. As a result of these considerations one can estimate values for the critical radius for the energy transfer and thermal quenching, by measuring the brightness and the lifetime thermally and concentration dependent. The measured lifetimes were plotted against the temperature (left) and average distance between the ions (right). This procedure was also performed for the thermal dependent luminescence spectra. Figure 9 shows the results from the deconvolution method (for the cut-off method see Fig. 11). Out of these data sets it was possible to calculate the quenching temperature of the blue emission and the critical radius of the energy transfer in this compound, applying Eq. (5). Doing so gives the fitting results represented in Table 2. The fits show overall a relatively low variation in the fitting results, but a structural difference between the two methods (lifetime and luminescence). Neglecting the upper and lower
outliers one finds the following values: \( E_a = 0.212 \pm 0.015 \) eV and \( r_c = 2.6 \pm 0.3 \) nm for the luminescence method and \( E_a = 0.179 \pm 0.013 \) eV and \( r_c = 3.4 \pm 0.7 \) nm for the lifetime method. The values for the attempt rate \( A_g \) showed a large variation. The mean for \( A_g \) was \( 1.5 \pm 1.3 \cdot 10^{11} \) Hz which is considerably smaller than for \( A_g \). Fig. 7 shows the smoothed emission spectra of the eight samples at 10 K, excited at 370 nm. The integrals under the spectra were normalized. One can clearly see the energy transfer from the blue site to the green, since the blue emission decreases and in the same way the green emission increases.

To derive the activation energy of the thermal quenching of the green emission, the total luminescence curves shown in Fig. 5 were used. Follow the model presented above the function to approximate the curves in Fig. 5 contains seven parameters, five for the blue emission and two for the green. Applying this function, the activation energy of the thermal quenching of the green emission is \( E_a = 0.683 \pm 0.098 \) eV. The attempt rate \( A_g \) is found to be \( 2.0 \pm 1.0 \cdot 10^{13} \) Hz. This is in agreement with previously reported values [16]. The difference between the two pre-factors of the blue and the green site could come from variations in the local phononic environment around the emission centers. Both methods, the lifetime and luminescence measurements, for estimating the critical radius and quenching temperature have their advantages and drawback. The lifetime method is independent on the different excitation cross-sections of the two sites at a certain wavelength. Due to this the strong chromatic aberration in the detection path due to large aspheric but not chromatic corrected lenses had no influence on the lifetime (but on the relative amplitudes) (compare Fig. 2 with Fig. 4).

But the difference in excitation probability could have influence on the luminescence measurements, also it was taken care that the probability is even. A second reason for errors could be the uneven distribution of \( \text{Eu}^{2+} \) between the two sites and within the sample, but due to the near perfect match of the radii of \( \text{Sr}^{2+} \) and \( \text{Eu}^{2+} \) there seems to be no driving force to build up dimers or other clusters. Additionally the relatively low concentration of the dopant makes the appearance of clusters or dimers unlikely. Due to this the bi-exponential decay seen at higher concentrations and temperatures (compare Fig. 11) is probably not due to this dimers. One plausible explanation is the more pronounced surface effect or the effect of oxygen vacancies which are present in the sample. In a more sophisticated model one could add a thermal dependency of the energy transfer due to spectral broadening. Furthermore it would be possible to do a Monte Carlo Modelling of the energy transfer to incorporate the statistical distribution of the two inequivalent \( \text{Eu}^{2+} \) ions and calculate out of the distribution of the distances an inhomogeneous energy-transfer function [17].

Fig. 7. Emission spectra of the eight different samples at 10 K. The integral under the spectra were normalized.
5. Conclusion

We have presented a thorough study of the thermal quenching and energy transfer of the two inequivalent Eu$^{2+}$ ions in SrAl$_2$O$_4$. Using two complementary methods, by employing luminescence and lifetime measurements it was possible to find similar values with independent methods. These findings provide a better understanding of the material, giving hints for an increased quantum efficiency at higher concentrations due to an efficient energy transfer, rescuing the blue emission from quenching by transferring it to the green site. Nevertheless double exponential behavior at higher temperatures gives hints of anomalous
quenching effects resulting potentially from vacancies or surfaces, splitting the Eu$^{2+}$ ions in sub-groups.

Appendix: Plots

Fig. 10. Spectral dependent bi-exponential fit of the lifetime of SrAl$_2$O$_4$:Eu$^{2+}$ doped with 0.01 mol% at 300 K.

The bi-exponential fit in Fig. 10 shows two components in the decay, the slower one (black) is in the range of the expected lifetime, but much longer than the lifetime derived with a single-exponential function. The fast component (red) is has similar the slow decay a spectral dependent shift in the lifetime, but the ratio of the blue and green emission amplitudes are different. In the fast component the amplitude in the blue range is nearly as high as in the green range whereas it is much weaker for the slower component. One has to consider that the calculated lifetime of the fast component in the blue region is at the edge of the instrumental resolution.

The results with the cut-off luminescence curves (Fig. 12.) are similar with the once found with the deconvolution method. Overall the blue emission is found to be a weaker compared to the deconvolution method and residual ‘blue’ emission is larger than with the other method. Both contributes to a gentler transition, but this has only minor influence to the estimated activation energies for quenching and the critical radius for energy transfer (Table 3).

Fig. 11. Decay of luminescence at 3 K (left) and 300 K (right) respectively of SrAl$_2$O$_4$:Eu$^{2+}$ doped with 0.01 mol% at 446 nm, fitted with mono and double exponential functions.
Fig. 12. (Left) thermal dependent intensity of the blue emission of the eight components, calculated by a cut-off filter at 460 nm. Drawn lines are the fitted curves. (Right) concentration (Mean-distance) dependent lifetime at eight different temperatures. Drawn lines are the fitted curves.

### Table 3. Fitting results found with the cut-off method

| Eu²⁺ Conc. | Eₐ/eV | Temp. | rₑ/nm |
|------------|-------|-------|-------|
| 0.01%      | 0.206 | 10 K  | 2.3   |
| 0.02%      | 0.185 | 100 K | 2.6   |
| 0.05%      | 0.218 | 150 K | 2.3   |
| 0.10%      | 0.182 | 180 K | 2.3   |
| 0.20%      | 0.262 | 200 K | 2.2   |
| 0.50%      | 0.163 | 220 K | 2.2   |
| 1.00%      | 0.212 | 250 K | 3.1   |
| 2.00%      | 0.195 | 300 K | 1.1   |

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