APPLICATION NOTE

KINETICS OF PERSISTENT LUMINESCENCE PHOSPHORS

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EDINBURGH INSTRUMENTS

INTRODUCTION

Persistent luminescence, or commonly called afterglow, is characterised by long-lasting visible emission over several hours after ultraviolet excitation. This finds wide application in glow-in-the-dark signage and in-vivo imaging for disease diagnosis and treatment. Biological tissue, however, allows transmission of near-infrared (NIR) light shorter than 1400 nm due to absorption by water and lipids[1]. The majority of bio-imaging applications utilises the 700 nm-950 nm window[2–4].

FLS1000 Spectrometer

Moreover, with persistent luminescence, auto-fluorescence of the tissue is circumvented under continuous illumination. Lanthanides and transition metals such as Eu/Dy/Mn[5], Eu/Pr/Dy[6], Mn/Cr/Pr[7,8] have been used as the active centres in silicate[5], diopside[6], gallate and germanate[7,8] hosts. However, silicate and aluminate hosts have seen wider application with Eu[9] and non-Eu ions[10]. In this note, the persistent luminescence kinetics of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} are characterised by optical spectroscopy.

METHODS & MATERIALS

Excitation and emission spectra, as well as decays were measured in a FLS1000 Fluorescence Spectrometer equipped with a 450 W Xe source and double monochromators. A 250 nm blazed grating was used at the excitation and a 400 nm blazed grating at the emission arm. Luminescence was detected with a photomultiplier tube detector (Hamamatsu, R928P), while higher diffraction orders were filtered by integrated long wave-pass filters in the FLS1000.

$SrAl_2O_4$: Eu^{2+}, Dy^{3+} micro-crystalline powder phosphor (Glotech International) was used for all measurements as received. To obtain the persistent luminescence decay of the phosphor, the sample was illuminated for 5 min by a Xe source with the monochromator set between 300 nm – 350 nm. Consequently, illumination was blocked via software-controlled shutters and the luminescence decay was monitored for 1 h with 1 s resolution.

This resolution was adequate to monitor the persistent luminescence kinetics of this phosphor, however, for more complex kinetics and decays as long as 277 h, a resolution of 100 s can be used.

The decays (results not shown) were also acquired in an FS5 Spectrofluorometer equipped with a 150 W Xe source and resulting in similar kinetics.

RESULTS - DISCUSSION

$SrAl_2O_4$: Eu^{2+}, Dy^{3+} is one of the first and most widely studied persistent luminescence phosphors. It's been widely applied mainly due its long duration, despite some degradation that has been reported after two years in water[11,12].

The excitation and emission spectra of $SrAl_2O^4$: Eu^{2+}, Dy^{3+} are shown in Figure 1. The emission peak around 520 nm is a $4f^65d^1$ to $4f^7$ Eu transition[13] leading to the phosphor's persistent luminescence. It can be excited in the ultraviolet between 300 nm - 500 nm, however, vacuum ultraviolet studies of doped and pure $SrAl_2O_4$ have shown that the excitation onset starts at 200 nm matching the peak of the afterglow excitation spectrum[14].

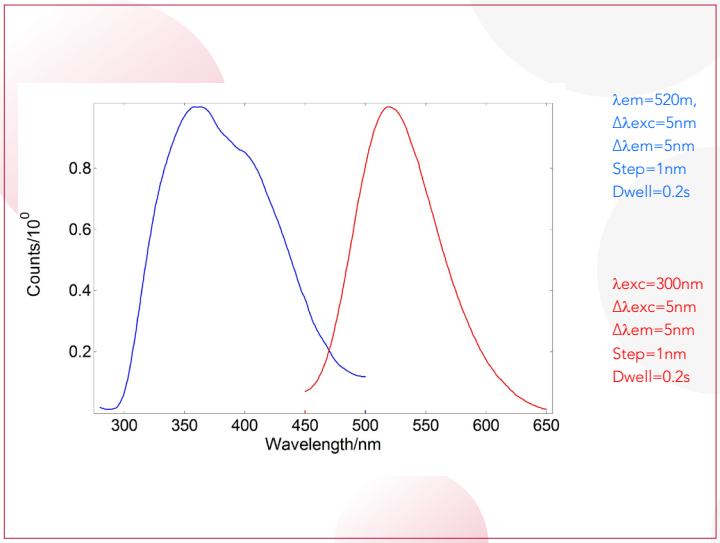

Figure 1: Excitation and emission spectra of $SrAl_2O_4$:Eu^{2+}, Dy^{3+}

The kinetics of the afterglow have been further monitored for 1 h after 5 min excitation. Figure 2 shows characteristic evidence of competition between photoluminescence and energy storage in trap states. Several trap states placed as low as 0.19 eV[15] and up to 1.47 eV[16] were reported, while the optimum energy value has been found around 0.65 eV[17].

It can be seen that the initial charging phase is excitation dependent. However, this is reduced after correcting for the excitation intensity as shown in a logarithmic scale in the inset and agreeing with normalised excitation and afterglow studies[18]. A similar behaviour is observed for the decay phase, which has been reported previously[19] and correlated with the behaviour of thermo-luminescence. In fact a good agreement of the integrated intensity was reported between the persistent luminescence and the thermo-luminescence curves, exposing the application of the phosphor to radiation dosimetry.

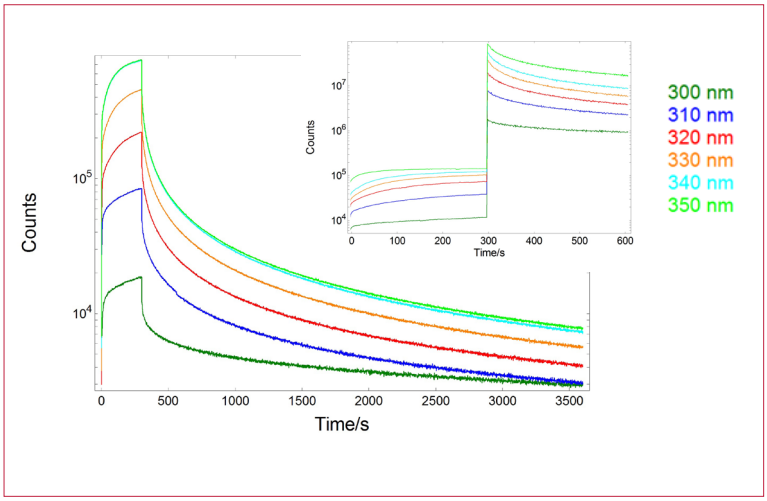

Figure 2: Persistent luminescence decays of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} at 520 nm, excited for 5 min between 300 nm - 350 nm. The decays corrected for the excitation intensity are shown in the inset in logarithmic scales.

The decays have been fitted into four exponential models of the form:

$$\Sigma[A+B_i e^{(-t/\tau_i)}],\ i=1\ldots4.$$

The derived lifetimes are presented in Table 1 along with the corresponding χ^2 and average lifetimes. Several models such as the stretched exponential[20] or even the stretched or compressed hyperbola[21] were reported for the afterglow kinetics of persistent luminescence phosphors. A good fit has been obtained with the aforementioned equation and four exponentials. The three exponential models result in χ^2 higher than 3, however the lifetimes are similar to these previously reported at 400 nm excitation[16].

Table 1: Lifetimes of the persistent luminescence kinetics in $SrAl_2O_4$:Eu^{2+}, Dy^{3+} excited from 300 nm to 350 nm.

λ_{exc} (nm)	τ_1 (s)	τ_2 (s)	τ_3 (s)	τ_4 (s)	χ^2	<τ> (s)
300	1.29	29.27	221.10	1955.00	1.16	1776.99
310	0.94	26.66	172.60	1089.00	1.53	849.53
320	5.32	48.04	221.00	1137.00	1.66	803.19
330	10.47	57.52	240.90	1170.00	1.53	773.17
340	9.75	54.38	229.30	1115.00	1.88	719.85
350	11.58	59.84	243.60	1167.00	1.66	757.25

Several models have been proposed for the mechanism of persistent luminescence including traps close to the valence band[17]. However, electronic band calculations place the Eu^{2+} levels below the conduction band in agreement with XPS measurements placing it 3 eV above the valence band[22]. Moreover, combined radio-luminescence and x-ray absorption spectroscopy confirmed the ionisation of Eu^{2+} to Eu^{3+}, albeit ionisation of Dy^{2+} to Dy^{3+} was not detected[23], which indicates a low probability of existing trap states just above the valence band. The depth of traps can be further studied via thermo-luminescence emission[24,25] as well as excitation mapping[10,18] to obtain direct information about trap filling states.

CONCLUSION

The persistent luminescence kinetics of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, were presented in this application note. Standard configuration FLS1000 and FS5 Fluorescence Spectrometers were used to characterise excitation spectra in the UV, emission spectra, as well as the persistent luminescence decays of the phosphor. The afterglow peak at 520 nm was monitored for 1 h after 5 min excitation between 300 nm - 350 nm. The afterglow decays showed a limited excitation-dependence and after fitting into four exponential models, average lifetimes ranging from 750 s to 1780 s were obtained, depending on the excitation wavelength.

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