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Thermal quenching and luminescence lifetime of saturated green $Sr_{1-x}Eu_xGa_2S_4$ phosphors

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ABSTRACT

Due to the lack of efficient green emitting solid state light sources, conversion phosphors emitting saturated green emission are highly interesting, both for display and signalling applications. In this work, we study the luminescence properties of $Sr_{1-x}Eu_xGa_2S_4$ phosphors over a wide dopant concentration range (x = 0.01–0.3), as function of temperature. The phosphors show a saturated green emission over the entire studied range, with a typical peak wavelength around 536 nm and a FWHM of 50 nm. The internal quantum efficiency is 71% for x = 0.04. For this concentration, the emission intensity at 400 K is still 90% of the intensity at room temperature. By measuring both decay and thermal quenching profiles as a function of europium concentration, we were able to explain the emission properties on the basis of the local environment of the europium ions in the lattice.

1. Introduction

Research into photoluminescent (PL) inorganic materials, or phosphors, has (re)gained tremendous research interest in the past decade, due to their use as colour or wavelength conversion materials in light-emitting diodes (LEDs) [1–4]. Commonly, white LEDs are based on the partial conversion of the blue emission of an (In,Ga)N LED by one or more phosphor materials, which are typically oxides (e.g. $Y_3Al_5O_{12}$:Ce [5]), nitrides (e.g. $CaSiAlN_3$:Eu [6] or $Sr_2Si_5N_8$:Eu [7]) or oxynitrides (e.g. β-SiAlON:Eu [8]).

Instead of blue or violet LEDs, also near-ultraviolet LEDs can be used as primary light sources. In that case, all the emission of the LED chip should be converted to visible light to optimise the light output of the device. In any case, these conversion phosphors should fulfil six main requirements, as recently outlined [2]. These include an appropriate emission spectrum (e.g. to yield white light with a certain colour temperature and with high colour rendering) and excitation spectrum (i.e. to possess a strong absorption of the LED's emission). Third, the conversion process should have high quantum efficiency (QE). Fourth, the emission spectrum and intensity should be stable as function of temperature, as high brightness LEDs can reach fairly high operating temperature. Fifth, the phosphor should be (photo) chemically stable to allow a long operational lifetime. Finally, the luminescence emission should be fast (or, alternatively, have a short decay time) to avoid saturation effects and colour shifts as a function of excitation intensity.

In general, one will aim for phosphors with a relatively broad emission band to increase the colour rendering of white LEDs, in the case of lighting applications [2]. When conversion phosphors are used for display and imaging applications however, it is beneficial to use phosphors with rather narrow emission bands, which show saturated (primary) colours. The typical ions incorporated in phosphors for fluorescent lamps (i.e. Tb^{3+} and Eu^{3+} for green and red, respectively) cannot be used in combination with blue LEDs, due to their narrow excitation lines with low absorption strength in the visible. The broad band emitting rare earth ions Eu^{2+} and Ce^{3+} do not have this excitation disadvantage, and in combination with a short decay time, thus avoiding saturation, they are currently the prime choices as dopant ions. For narrow emission bands, Eu^{2+} doped phosphors are preferred, as Eu^{2+} has only a single terminating ground state level, while Ce^{3+} always shows two emitting transitions (separated by about 2000 cm^{-1}). Recently reported green phosphors which are excitable with blue LEDs and have relatively narrow emission bands are $SrBaSiO_4$:Eu^{2+} (peak emission wavelength of 525 nm (FWHM of 70 nm), [9]), $SrSi_2O_2N_2$:Eu^{2+} (537 nm (80 nm), [10]), $Ba_3Si_6O_{12}N_2$:Eu^{2+} (530 nm (70 nm), [11]), $Sr_3Si_{13}Al_3O_2N_{21}$:Eu^{2+} (520 nm (65 nm), [12]), α-SiAlON:Yb^{2+} (549 nm (80 nm), [13]), β-SiAlON:Eu^{2+} (536 nm (60 nm), [3]).

In this work we will focus on a green phosphor with a narrow emission spectrum, which can be used for display and imaging

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applications. The number of saturated green Eu^{2+}-based phosphors is rather limited, because several phosphors have multiple lattice sites with clearly different coordination, which can lead to emission bands with different peak positions. A good candidate for green emission is strontium thiogallate doped with europium ($SrGa_2S_4$:Eu). This phosphor is well known to the phosphor community in the framework of electroluminescent thin film displays [14,15] or as (cathodoluminescent) phosphor for field emission displays (FED) [16–19]. The use of strontium thiogallate phosphors for LEDs was described by Mueller-Mach et al. [20]. Recently, mixed alkaline earth thiogallate phosphors have been studied as LED conversion phosphor [21–24]. However, the behaviour of $SrGa_2S_4$:Eu as PL conversion phosphor has not been completely studied before and absolute data on QEs and thermal quenching are relatively scarce. Chartier et al. studied the fundamental PL properties of $SrGa_2S_4$:Eu with very low dopant concentration (0.1% of the Sr ions substituted by Eu) [25]. Reported key parameters (at room temperature) are an emission band at 534 nm (FWHM of 50 nm), a decay time at room temperature of 480 ns and a thermal quenching temperature $T_{0.5}$ of 460 K ± 10 K ($T_{0.5}$ is the temperature at which the emission intensity has dropped to half of the emission intensity at low temperature). Motivated by the fact that the stoichiometric phosphor $EuGa_2S_4$ (in which all alkaline earth ions are substituted by europium) is still luminescent at room temperature with an emission peak at 549 nm (FWHM = 44 nm, [26]) [27], Hidaka and Takizawa studied the optical and structural properties of the mixed compound $Sr_{1-x}Eu_xGa_2S_4$ [28]. They found that $EuGa_2S_4$ and $SrGa_2S_4$ form a solid solution at any given Sr:Eu ratio. The highest emission intensity was found for $Sr_{0.9}Eu_{0.1}Ga_2S_4$. The QE for this compound was estimated in an indirect way, and supposed to be about 75% [28]. This was partially based on the assumption by Iida et al. that the QE should be close to 100% for $EuGa_2S_4$ at low temperature [27]. This uncertainty justifies more detailed measurements on the conversion efficiency of $Sr_{1-x}Eu_xGa_2S_4$ phosphors.

In view of colour conversion applications, we studied a series of $Sr_{1-x}Eu_xGa_2S_4$ phosphors with x ranging from 0.01 to 0.30. In the analysis we focused on the following aspects of $SrGa_2S_4$:Eu. First, it is useful to know both the internal (η_{int}) and external (η_{ext}) QE of the phosphors. While the former only considers the efficiency of the luminescence process once the photon needed for the excitation is absorbed, the latter takes also the absorption (A) at this excitation wavelength into account. This can be expressed as follows, with N_{em} the number of photons emitted by the phosphor, N_{inc} the number of incident photons and N_{abs} the number of absorbed photons,

$$\eta_{ext} = \frac{N_{em}}{N_{inc}}, \quad \eta_{int} = \frac{N_{em}}{N_{abs}}, \quad \eta_{ext} = \eta_{int} \cdot A$$

Depending on the application type, η_{int} or η_{ext} needs to be optimised. Indeed, the internal quantum efficiency is often constant up to a certain critical dopant concentration, after which it starts to decrease due to the combination of energy transfer between dopant ions and non-radiative decay paths, the so-called concentration quenching. On the other hand, the absorption in general increases upon higher dopant concentration. Therefore, η_{ext} can reach its maximum for higher dopant concentrations than η_{int}.

A second part of this paper deals with a study of the thermal quenching behaviour, taking both the colour shift and emission efficiency into account, as function of the dopant concentration. To interpret the results, luminescence decay measurements are undertaken as a function of dopant concentration and measurement temperature. Finally, this phosphor is critically evaluated against the six requirements mentioned above.

2. Experimental setup

$Sr_{1-x}Eu_xGa_2S_4$ powders with x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.15, 0.20 and 0.30 were prepared by solid state synthesis. Appropriate amounts of SrS (Alfa Aesar, 99.9%), Ga_2S_3 (Alfa Aesar, 99.99%) and EuF_3 (Alfa Aesar, 99.5%) were weighed, mixed in an agate mortar and put into an alumina crucible. Then the powders were heat treated under a flow of H_2S at 900 °C for 2 h. Powders were allowed to cool naturally. After recuperation they were lightly ground.

Structural information was obtained using standard powder X-ray diffraction (XRD), using Cu Kα radiation on a Bruker D5000 diffractometer. Luminescence emission and excitation spectra were performed on an Edinburgh FS920 fluorescence spectrometer. Decay times were collected using a pulsed LED as an excitation source (peak wavelength of 400 nm, repetition rate of 5 kHz) in combination with an Andor intensified CCD. Temperature dependent measurements were performed by using an Oxford Optistat CF cryostat.

Internal and external QEs were obtained by exciting the phosphor samples with a blue LED (peak wavelength of 460 nm), and measuring simultaneously the reflected blue light and the green luminescence. After measurement of a white reflective standard, all relevant parameters could be calculated. The method was validated by using the same procedure for phosphors with known QEs.

3. Results and discussion

3.1. Structural characterisation

From the X-ray diffraction patterns (not shown) of the synthesised $Sr_{1-x}Eu_xGa_2S_4$ phosphors, it was observed that crystalline powders were obtained, without the presence of impurity phases. The similarity between all diffraction patterns confirms the solid solubility of $SrGa_2S_4$ and $EuGa_2S_4$, as described earlier by Hidaka and Takizawa [28]. Both lattices are isostructural and have similar lattice constants, differing only 0.58% [28], which results in only a small shift of the position of the diffraction peaks when increasing the Eu concentration from 1% to 30%.

3.2. Photoluminescence emission and excitation

The PL emission and excitation spectra for $Sr_{1-x}Eu_xGa_2S_4$ at room temperature are shown in Fig. 1. Both the width and the position of the emission spectrum (Table 1) are stable over the

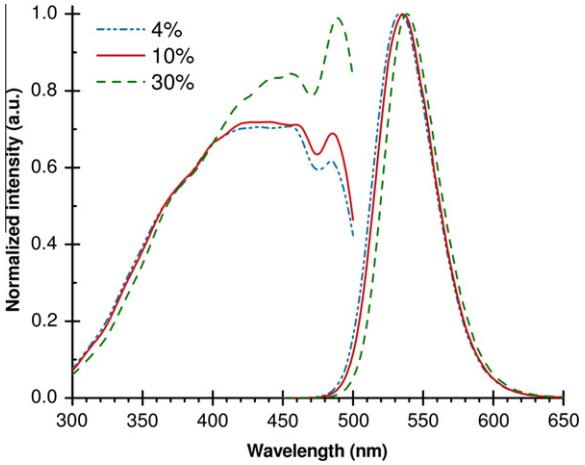

Fig. 1. Normalized PL emission and excitation spectra for $Sr_{1-x}Eu_xGa_2S_4$ powders obtained at room temperature, by excitation at 400 nm and monitoring at 532 nm, respectively. The dip in the excitation spectra around 470 nm is an artefact.