Journal of Luminescence 129 (2009) 1140–1143

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Persistent luminescence in rare-earth codoped $Ca_2Si_5N_8$:Eu^{2+}

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ARTICLE INFO

Article history:
Received 22 January 2009
Received in revised form
6 May 2009
Accepted 13 May 2009
Available online 21 May 2009

PACS:
78.55.−m
78.60.Kn

Keywords:
Nitrides
Persistent luminescence
Europium
Thermoluminescence
Rare earth

ABSTRACT

The luminescence properties of $Ca_2Si_5N_8$:Eu, M (with M = Nd, Sm, Dy, Ho or Tm) are reported. $Ca_2Si_5N_8$:Eu without codopants shows a relatively weak afterglow. $Ca_2Si_5N_8$:Eu,Tm shows the highest persistent emission intensity, with an orange emission color due to a broad emission band peaking at 620 nm. The persistence emission spectrum is red-shifted by about 10 nm compared to the steady state photoluminescence. Based on thermoluminescence measurements, it is shown that the addition of Nd, Dy and Ho to $Ca_2Si_5N_8$:Eu introduces trap states which are too shallow for considerable enhancement of the persistent luminescence. The persistent luminescence in $Ca_2Si_5N_8$:Eu, Tm is efficiently excited in the visible part of the spectrum.

1. Introduction

Nowadays more and more attention is being paid to reducing energy consumption and CO_2 emission when developing new products. In this paper persistent phosphor materials, needing no other energy than ambient light, are reported. They could provide the perfect alternative to traditional emergency illumination in case of electric power failures [1]. $SrAl_2O_4$:Eu, Dy (green, [2]), $CaAl_2O_4$:Eu, Nd (violet, [3]) and $Sr_2MgSi_2O_7$:Eu, Dy (blue, [4]) all show a long afterglow with high initial brightness. However, efficient materials emitting in the orange-to-red region of the visible spectrum, which would allow to make visually more prominent products, are relatively scarce [5]. Y_2O_2S:Eu, Ti, Mg has a relatively long, intense and reddish afterglow [6,7], although the decay is considerably faster than $SrAl_2O_4$:Eu, Dy. This material has the major disadvantage of ultraviolet light being required to efficiently charge the phosphor, which limits its field of applications.

The lack of orange-to-red persistent phosphors which can still be perceived many hours after the excitation mainly relates to the following two problems:

- Most of the currently used persistent materials are based on oxides, with Eu^{2+} as an emitting ion. However, in oxides it is very difficult to have a sufficiently large crystal field to obtain orange or red Eu^{2+} emission [8].
- The eye sensitivity is much lower in the long wavelength range when the eye enters the mesopic and scotopic vision region (already for intensities below 500 mcd/m^2), typical for persistent phosphor applications [1].

The first problem can be tackled by turning to other host materials for the Eu^{2+}, such as the thiosilicates or the nitrides. We recently showed that persistence luminescence (with an emission peaking at 650 nm) can be obtained in Ca_2SiS_4:Eu, Nd [5]. Unfortunately, ultraviolet light ($\lambda \leqslant 360$ nm) is required for the excitation and the emission is actually too far into the red to make it visible to the human eye for a sufficiently long time.

Hence we turned to other, recently reported host materials for orange-to-red Eu^{2+} emission, namely the nitrides. This large class of materials is actively studied for use as color conversion material in white light emitting diodes (LEDs) [9]. Its main advantages are a high thermal and chemical stability, and a high quantum efficiency for several hosts. For instance, $M_2Si_5N_8$:Eu^{2+} with M = Ca, Sr or Ba, have a broad emission peaking at 605, 610 and 570 nm, respectively (for low europium concentrations) [10]. In this work we report on the persistent luminescence of $Ca_2Si_5N_8$:Eu and the influence of codoping with the rare-earth ions neodymium, samarium, dysprosium, holmium and thulium.

2. Experimental

$Ca_2Si_5N_8$:Eu, RE powders were prepared from appropriate mixtures of Ca_3N_2 (99%, Alfa Aesar), Si_3N_4 (99.85%, Alfa Aesar),

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doi:10.1016/j.jlumin.2009.05.007

EuF_3 (99.5%, Alfa Aesar) and RE_2O_3 (RE = Nd, Sm, Dy, Ho or Tm, typically 99.9%). Unless otherwise mentioned, the powders were prepared with 1 mol% of Eu^{2+} (i.e. 1% substitution of the Ca ions) and 0.5 mol% of RE^{3+} ions. All materials were weighed, ground and mixed under a protective Ar atmosphere. Then the powders were heated for 1 h under a reducing atmosphere (90% nitrogen, 10% hydrogen) at 1300 °C. After natural cooling of the furnace, the powders were recuperated and slightly ground.

The photoluminescence and the persistence decay of the powders were studied with a fluorescence spectrometer (FS920, Edinburgh Instruments). Thermoluminescence measurements were recorded using a contact gas cryostat (Optistat CF, Oxford Instruments) and the same spectrometer. Scanning electron microscopy (SEM) was performed using a FEI Quanta 200, equiped with EDX (energy dispersive X-ray analysis, EDAX Genesys 4000). The cathodoluminescence was monitored using the low energy channels of the EDX detector [12].

3. Results

Fig. 1 shows the steady state photoluminescence emission and excitation spectra for $Ca_2Si_5N_8$:Eu. The emission spectrum, peaking at 609 nm is relatively broad (FWHM of 110 nm). The excitation spectrum spans a broad wavelength range, limited on the short wavelength side by the host absorption [13], which appears not to be very efficient. The emission and excitation behavior is in good correspondence with literature data [10]. Li et al. reported an emission maximum at 605 nm for $Ca_2Si_5N_8$:Eu with low europium concentration. Increasing the europium concentration shifts the steady state emission spectrum to 615 nm for a maximum Eu solubility of 7% [10]. The emission spectrum for the persistent luminescence in $Ca_2Si_5N_8$:Eu, Tm (Fig. 1) peaks at 620 nm, which is red-shifted by about 10 nm compared to the steady state emission. We observed no changes in the emission spectrum during the decay of the persistent luminescence. Furthermore, the excitation spectrum for the persistent luminescence (i.e. the wavelengths which are suitable to induce the persistent luminescence) appears to be similar to the steady state excitation spectrum, although it is difficult to measure this accurately [5]. It was verified that both ultraviolet and blue-to-green visible light are suitable to charge the phosphors, which makes the persistent luminescence efficient for applications where charging is performed by artificial light sources or ambient daylight.

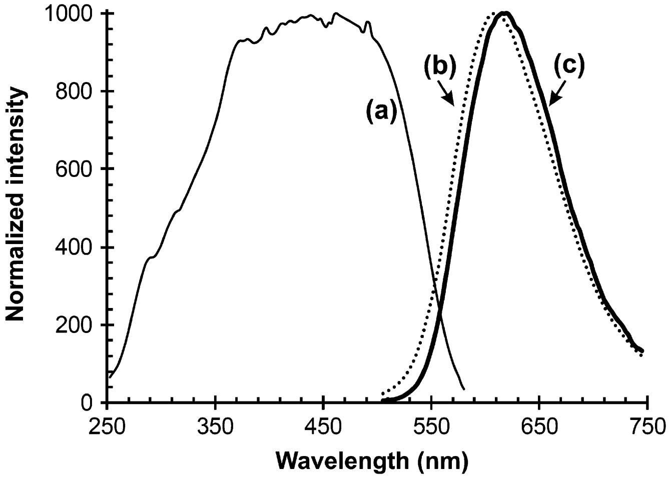

Fig. 1. (a) Steady state excitation spectrum for $Ca_2Si_5N_8$:Eu[1%] by monitoring the emission at 610 nm. (b) Steady state emission spectrum for $Ca_2Si_5N_8$:Eu[1%] upon excitation at 400 nm. (c) Persistent emission spectrum for $Ca_2Si_5N_8$:Eu [1%], Tm[0.5%].

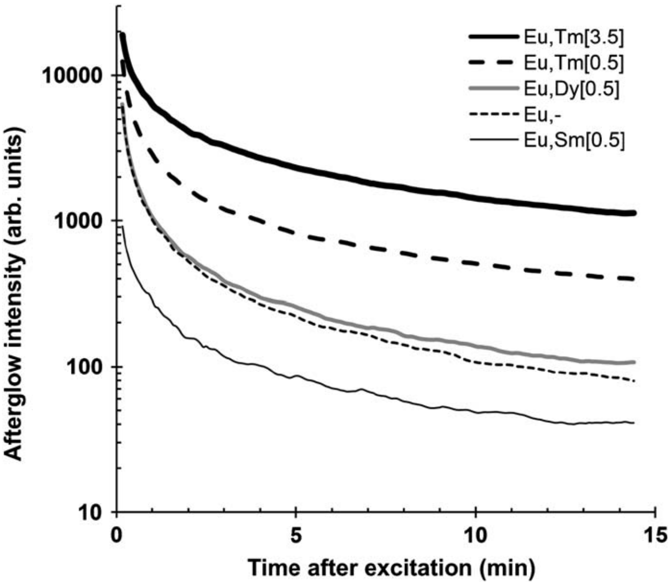

Fig. 2. Decay profiles for the persistent luminescence of $Ca_2Si_5N_8$:Eu[1%] with and without codopants. The powders were excited at 400 nm.

In Fig. 2 the decay profiles for the persistent emission are shown for several $Ca_2Si_5N_8$:Eu, RE powders after excitation at 400 nm.

The intensity of the persistent luminescence is plotted in Fig. 3 for all the powders studied, measured 20 s and 10 min after the excitation had stopped. In this way, one can distinguish between the 'fast' and the 'slow' components in the decay profiles. Clearly all powders, including $Ca_2Si_5N_8$:Eu, possess a significant afterglow. The addition of Nd, Dy or Ho hardly alters the decay profile or the intensity of the afterglow. Adding Sm has a detrimental effect, especially shortly after the excitation. Adding 0.5%Tm to $Ca_2Si_5N_8$:Eu[1%], only moderately increases the afterglow intensity in the beginning of the decay curve. The main effect is an enhancement of the 'slow' component (approximately an increase by a factor of 4 compared to $Ca_2Si_5N_8$:Eu[1%] 15 min after the excitation).

For the studied $Ca_2Si_5N_8$:Eu[1%], RE[0.5%] powders, codoping with Tm is clearly the best option. Then the concentration of Eu and Tm was changed, to assess their influence on the intensity of the persistent luminescence. Increasing the europium concentration (while keeping [Tm] fixed at 0.5%), enhances the 'fast' component while the effect on the 'slow' component is very limited. For an europium concentration of 1%, increasing the Tm concentration intensifies the afterglow considerably, especially the 'slow' component.

To elucidate the observed effects of the rare earth codoping on the persistence behavior, thermoluminescence glow curves were recorded (Fig. 4). The powders were first cooled to 10 K and excited at 400 nm. Then the thermoluminescence intensity was measured upon heating the powders with a constant rate of 6.6 K/min up to 475 K.

The TL glow curve of $Ca_2Si_5N_8$:Eu (without codopants) is characterized by three major peaks (Fig. 4). The main one is situated at about 100 K, although its shape suggests multiple components. A second peak, extending beyond room temperature, peaks at 200–220 K. Beyond 450 K, a third glow peak emerges, although this peak could not be fully recorded due to the temperature limitation of the cryostat. The addition of codopants