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Luminescence in Eu^{2+} -doped $\text{Ba}_2\text{Si}_5\text{N}_8$: fluorescence, thermoluminescence, and upconversion

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Abstract

Fluorescence emission was investigated in a series of $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ compounds. Two maxima corresponding to the two crystallographic Eu^{2+} sites are observed. Excitation with intense laser light at $1.047\ \mu\text{m}$ reveals strong fluorescence emission at $\sim 600\ \text{nm}$ due to two-photon-excitation. In $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ the long lasting luminescence was studied. The emission peaking at about $590\ \text{nm}$ has been observed in the dark with the naked eye even 15 min after removal of the activating lamp. This effect is due to the recombination of holes and traps consisting of nitrogen vacancies formed by reducing synthesis conditions. The maximum emission was observed at -7°C . © 2000 Elsevier Science Ltd. Open access under [CC BY-NC-ND license](#).

Keywords: B. Chemical synthesis; C. X-ray diffraction; D. Luminescence

1. Introduction

Materials exhibiting long lasting luminescence cover a large scope of applications including luminescent paints or optical data storage media. Some of these materials are also used for X-ray dosimetry. Most of these compounds contain rare earth metal ions. The luminescence of europium, for example, has been intensively studied during the last decades and several applications have been reported [1]. As a specific fact europium is able to occur both, as divalent and trivalent ion and both of them are of practical interest: BaFBr:Eu^{2+} is an important X-ray storage phosphor in image plate detection systems and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is used in the display technology. Blue light emitting $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ is a very efficient lamp phosphor.

Most of the luminescence studies of europium in solids were carried out on compounds where europium is coordinated by fluorine, chlorine, bromine and/or oxygen. Recently, luminescence of materials containing europium coordinated by nitrogen has been reported [2].

In some cases it is quite difficult to stabilise Eu^{2+} because

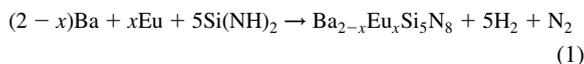
of its lower stability compared with Eu^{3+} [3]. This requires at least smoothly reducing conditions during the synthesis.

Recently, several investigations on Eu-doped compounds showing long lasting luminescence were presented (for example in Eu-doped aluminosilicate glasses [4]).

We present here a study on the luminescence observed on a Eu^{2+} -doped crystalline nitridosilicate phase. These compounds have been proven to be high-temperature stable and chemically almost inert [5].

2. Experimental

The synthesis of $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ was performed in a radiofrequency furnace (type IG 10/200 Hy, frequency: 200 kHz, electrical output: 0–12 kW, Hüttinger, Freiburg) according to Eq. (1).



Under argon a mixture of 116 mg (2.00 mmol) silicon diimide [6], 171 mg (1.25 mmol) barium and 17 mg (0.11 mmol) europium metal were mixed and transferred into a tungsten crucible. The crucible was then heated under nitrogen to 800°C within 30 min in the water-cooled

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Fig. 1. Colour photo of the phases $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ ($x = 0.14, 0.29, 0.40, 0.52, 0.81, 1.16$).

quartz-reactor of the radiofrequency furnace. After 1 h the crucible was heated to 1600°C within 25 h and maintained at this temperature for 40 h. Further heating to 1650°C within 2 h and quenching to room temperature in 30 min yielded single phase $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$. Excess metal evaporated out of the reaction mixture and condensed on the inner surface of the water-cooled quartz-reactor. $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ was obtained as a coarsely crystalline, bright orange powder (Fig. 1).

The crystal structure was checked by X-ray powder diffraction using $\text{CuK}\alpha_1$ radiation. $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ crystallises isotypically with $\text{M}_2\text{Si}_5\text{N}_8$ ($\text{M} = \text{Sr}, \text{Ba}$ [7], Eu [5]: space group: $\text{Pmn}2_1$, $Z = 2$, $a = 577.38(3)$, $b = 694.73(4)$, $c = 937.73(4)$ pm). The crystal structure is based on a network of corner sharing SiN_4 tetrahedra. In this network half of the nitrogen atoms connect two ($\text{N}^{[2]}$), and the other ones three Si atoms ($\text{N}^{[3]}$). The metal ions (Ba^{2+} , Eu^{2+}) occupy two different sites in the channels running along [100], which are formed by Si_6N_6 rings (Fig. 2). They are

predominantly coordinated by the $\text{N}^{[2]}$ atoms with coordination numbers of 8 and 10, respectively.

The composition of $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ was derived on the basis of the lattice constants of $\text{Ba}_2\text{Si}_5\text{N}_8$ ($a = 578.2(3)$, $b = 695.4(3)$, $c = 939.5(8)$ pm, [7]) and $\text{Eu}_2\text{Si}_5\text{N}_8$ ($a = 570.94(4)$, $b = 682.07(4)$, $c = 932.91(6)$ pm, [5]), respectively, by linear interpolation using Vegard's rule [8]. Furthermore the analytical results have been confirmed by energy dispersive X-ray microanalysis (Jeol, JSM-6400).

The crucial details of the spectrofluorometer, which has been used for the spectroscopic measurements, are a xenon lamp (XBO 450 W, Zeiss, Oberkochen), two monochromators (MM12 and M20, Zeiss) and a photomultiplier (RCA C7164R, Zeiss).

First the sample was cooled down under argon to -100°C using liquid nitrogen. Then the xenon lamp was turned on and the sample was illuminated for 30 min. After the initial luminescence had been relaxed the thermoluminescence curve (Fig. 7) was measured by heating the sample with a rate of $5^\circ\text{C}/\text{min}$ starting at -100°C .

The upconversion experiments were performed with a diode-laser pumped picosecond Nd:YLF laser ($\lambda = 1.047 \mu\text{m}$) which generates a $4 \mu\text{s}$ long train of 400 pulses of 7 ps duration and 150 nJ energy [9]. After frequency doubling by a BBO crystal pulses of ~ 1 nJ energy at 523 nm are available. The fluorescence emission of the samples was collected by an ellipsoidal mirror.

3. Results and discussion

The energy level scheme of Eu^{2+} has been known for long [10]. In the emission spectra either sharp 4f–4f transitions or very broad band emission due to 5d–4f transitions

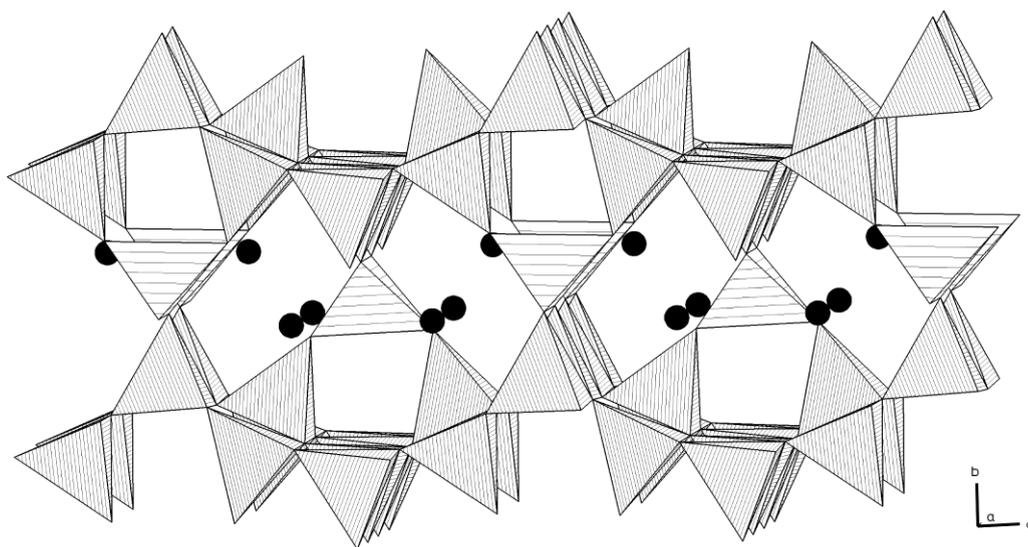


Fig. 2. Structure of $\text{Ba}_2\text{Si}_5\text{N}_8$, view along [100], the black spheres represent the metal atoms situated in channels built up by SiN_4 tetrahedra.

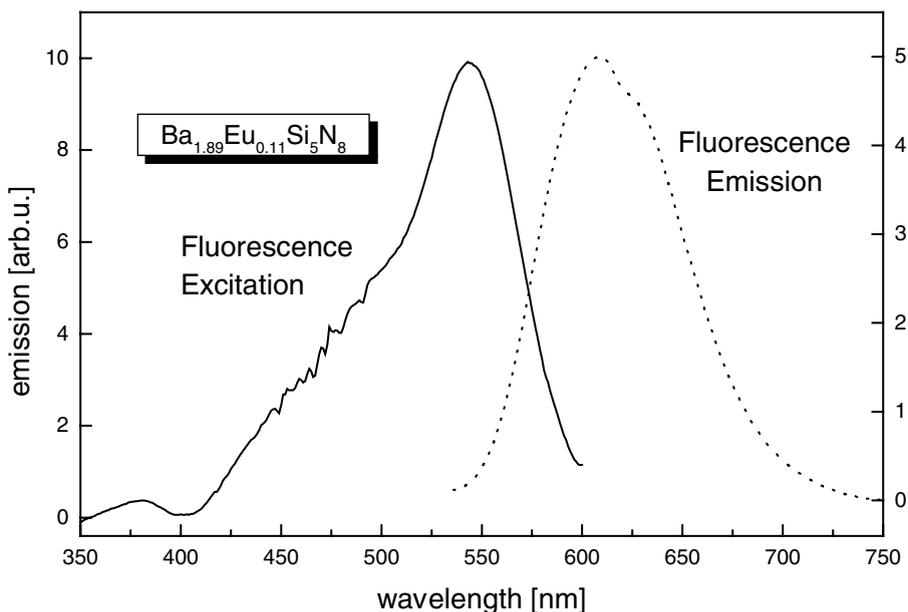


Fig. 3. Fluorescence excitation and emission spectrum of $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$.

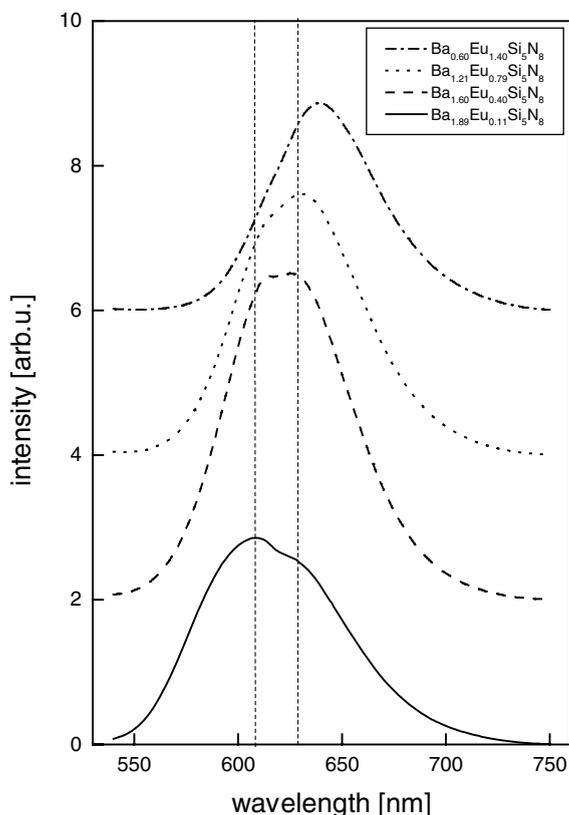


Fig. 4. Comparison of fluorescence spectra of $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ samples with different Eu-contents ($x = 1.40, 0.79, 0.40, 0.11$).

are observed depending on the fact how large the ligand-field splitting of the 5d-levels is (the 4f levels remain unaffected) [11]. Therefore, the lowest excited state either belongs to the $5d^14f^6$ configuration or to the $4f^7$ configuration. Broad band emission is thus assigned to the $5d^14f^6 \rightarrow 4f^7$ transition.

3.1. Fluorescence and upconversion

Fig. 3 shows a fluorescence excitation and a fluorescence emission spectrum of $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$. Both spectra consist of very broad bands: the absorption peaks at ~ 540 nm and the emission peaks at ~ 600 nm. Even after cooling down to -190°C the same emission spectrum is obtained. This is characteristic for the mentioned 5d–4f transitions. Furthermore, no indications for Eu^{3+} -emission (sharp line emission) were found. The emission curves are additionally broadened by the fact that two slightly differing europium emission bands at 610 and 630 nm exist which clearly show up in Fig. 3. They are caused by two overlaying crystallographic Eu^{2+} sites.

The observed emission occurs at fairly long wavelengths. Usually Eu^{2+} shows emission from about 300 nm in doped alkaline earth fluorides [12,13] up to 550 nm in doped alkaline earth oxosilicates [14]. Exceptions are 625 nm in $\text{SrO}:\text{Eu}^{2+}$ [15] or even 733 nm in $\text{CaO}:\text{Eu}^{2+}$ [16]. Some authors suggest that the preferential orientation of a d-orbital [17] or low lying states of the conduction band [13] shift the emission to longer wavelengths. Because of the higher formal charge of N^{3-} compared with O^{2-} on the one hand and the nephelauxetic effect on the other hand the ligand-field splitting of the 5d-levels should be larger and the centre

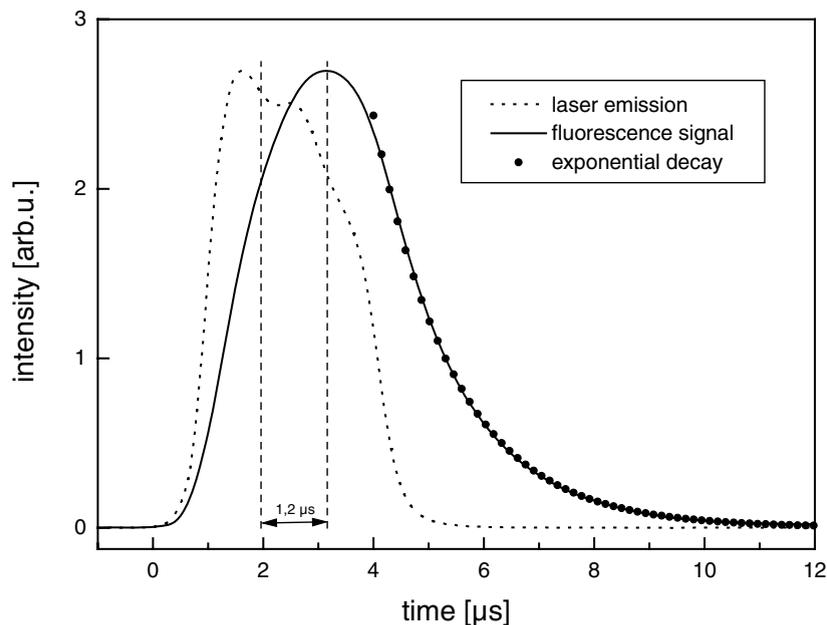


Fig. 5. Fluorescence decay time measured in $\text{Sr}_{1.45}\text{Eu}_{0.55}\text{Si}_5\text{N}_8$. Solid line: fluorescence signal, Broken line: emission of the exciting laser. The dots represent an exponentially decaying function with a time constant of $1.5 \mu\text{s}$.

of gravity of the 5d-states should occur at lower energies than in an analogous oxygen environment. Recently this has been convincingly shown for Ce^{3+} -doped Y–Si–O–N compounds [18] and it also seems to be confirmed with reference to the similar coordination distances in Eu-doped Ba_2SiO_4 or $\text{BaMg}_2\text{Si}_2\text{O}_7:\text{Eu}^{2+}$, Mn^{2+} [19–21].

Fluorescence spectra of $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ samples with different Eu content are shown in Fig. 4. The fluorescence intensity increases with x and reaches a maximum at $x \sim 0.5$. For $x > 0.5$ a shift of the emission to longer wavelengths is observed. The same behaviour is found in the

$\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ and $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ system. The blue fluorescence band is dominating in compounds with an Eu-content $x < 0.1$; the red-shifted band only rises at higher x -values. From this observation one may conclude that the Eu atoms prefer the blue-emitting crystallographic sites. However, there is no indication that this observation can be explained by a different size of the two sites as discussed in Ref. [22]. The same behaviour is observed in $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, $\text{Sr}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$, and $\text{Ca}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ despite the fact that the ionic radius of Eu^{2+} is larger than that of Ca^{2+} and Sr^{2+} and smaller than that of Ba^{2+} . We believe that reabsorption

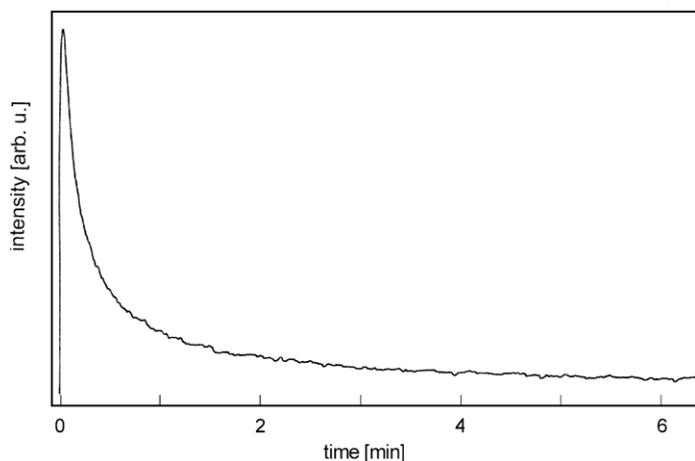


Fig. 6. Decay curve monitored at 588 nm (room temperature) after an illumination by the Xe lamp for 30 min.

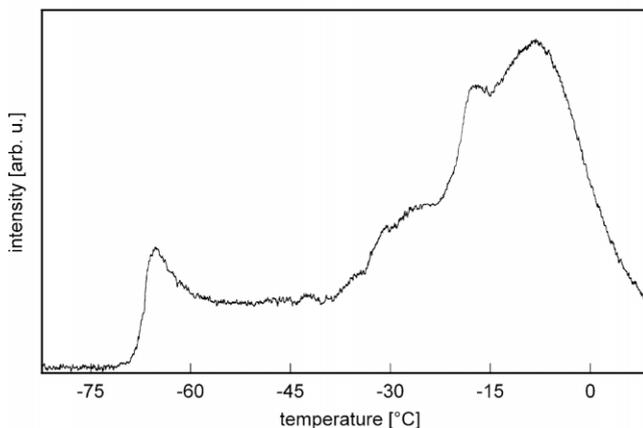


Fig. 7. Thermoluminescence curve (heating rate: 5°C/min) after illumination by the Xe lamp for 30 min at -100°C .

plays an important role in compounds with high Eu-content. With increasing x the Eu-absorption becomes quite strong, reabsorption begins to reduce the emission at the blue wing, and the second red-shifted fluorescence band gains intensity. For $x > 0.8$ the exciting light is completely absorbed by the powder, but the reabsorption is still rising. Consequently the emission signal decreases and the wavelength of the maximum is red-shifted as observed in Fig. 4.

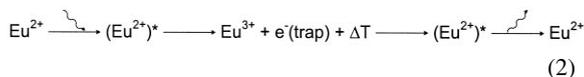
$\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ does not only show a strong fluorescence emission, but also a relatively strong two-photon absorption which can be used for upconversion. Excitation of the samples with intense ultrashort pulses from a Nd:YLF laser (wavelength 1.047 μm , 7 ps duration) generates a fluorescence emission around 600 nm which amounts to roughly 10^{-7} of the fluorescence emission after excitation at 523 nm by the frequency doubled laser. Such an efficiency achieved with a relatively low excitation intensity of $\sim 1 \text{ MW}/\text{cm}^2$ is an indication of a fairly high two-photon absorption cross section.

Moreover, the Nd:YLF laser allows us to measure the fluorescence lifetime. The frequency doubled laser emits a pulse train of $\sim 4 \mu\text{s}$ length at 523 nm with steeply rising wings. The envelope of the pulse train together with the fluorescence signal of $\text{Sr}_{1.45}\text{Eu}_{0.55}\text{Si}_5\text{N}_8$ is shown in Fig. 5 as a function of time. The emitted fluorescence signal is delayed by 1.2 μs and exhibits an exponential decay with a time constant of 1.5 μs which directly represents the fluorescence lifetime.

3.2. Thermoluminescence

The less doped phases $\text{Ba}_{2-x}\text{Eu}_x\text{Si}_5\text{N}_8$ ($x < 0.5$) exhibit long lasting luminescence and for $x = 0.11$ this effect reaches its maximum afterglow length. Surprisingly this afterglow does not relax following 1st order kinetics, but continues after a short period of quick decay for a rather long time (Fig. 6). After illumination for 30 min with an ambient fluorescent lamp (MinUVIS analysis lamp 230 V,

DESAGA) at room temperature one can observe the luminescence in the dark with the naked eye for 15 min. As mentioned above, no indications for Eu^{3+} were found and the emission maximum of the long lasting luminescence is monitored at the same wavelength as the fluorescence emission (588 nm). Therefore, we suggest the following trap-hole-recombination mechanism for the observed long lasting luminescence (Eq. (2)):



Initially the electron is excited and afterwards trapped creating a hole Eu^{3+} . Before relaxation to the ground state ($4f^7$) and light emission occurs, the electron is thermally released to the excited Eu^{2+} -state ($5d^14f^6$)*. This is identical to a recombination of the hole and the trap. Here it is indispensable that both the reduced and the oxidised valence state of the phosphorescent ion are fairly stable.

Up to now the nature of the trap state is unclear. Recently, phosphors of various rare earth doped systems like $\text{SrAlO}_4:\text{Eu}^{2+}:\text{Dy}^{3+}$ were examined for their long lasting luminescence [23]. Here the long lasting luminescence is explained by the presence of a second rare earth ion in the sample and its role in the delayed emission process. In the case of Eu-doped glasses several ideas to explain the long lasting luminescence were presented. The first one ascribed this effect to shallow traps in the glass matrix [24]. The latter one dealt with oxygen vacancies formed during the synthesis, which was carried out in a reducing atmosphere [25]. Our doped samples were synthesised in a rather reducing atmosphere, too. Therefore, it is imaginable that analogous to the oxo-compounds mentioned previously nitrogen vacancies were created. Furthermore, the reducing conditions provide the formation of Eu^{2+} . In addition the nitrogen atoms are neighbouring the Eu^{2+} . The thermoluminescence curve (Fig. 7) peaking at about -7°C consists of several maxima. This supports the latter aspect, because around

the europium sites there are six different nitrogen sites. If vacant each may offer a slightly different trap depth resulting in different releasing temperatures ΔT . The proposed mechanism also considers the fact that no evidence for Eu^{3+} has been detected.

4. Conclusions

In this study on Eu-doped nitridosilicates, fluorescence emission at two neighbouring wavelengths at 600 nm is observed. Changes in the spectra with the Eu-content are believed to be mainly due to reabsorption processes. The relatively efficient two-photon absorption is of considerable interest in possible applications of the material for upconverting infrared light. In the Eu-doped barium nitridosilicate $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ long lasting phosphorescence peaking at 588 nm was found. We suggest a hole-trap-recombination mechanism. The traps are ascribed to nitrogen vacancies and the trapped electrons can be thermally released below room temperature. The temperature of maximum emission was determined at -7°C . Therefore, this new phosphor could be used as a bright orange luminescent paint or for energy saving displays. As suggested elsewhere [4], these compounds might be useful for the enhancement of the conversion efficiency of solar cells. Furthermore all these compounds are high-temperature stable and are stable against almost all chemicals.

Acknowledgements

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