Spectroscopic properties and energy level location of Eu$^{2+}$ in Sr$_2$Si$_5$N$_8$ phosphor

Agata Lazarowska$^{a, *}$, Sebastian Mahlik$^a$, Marek Grinberg$^a$, Chiao-Wen Yeh$^b$, Ru-Shi Liu$^{b,*}$

$^a$Institute of Experimental Physics, University of Gdańsk, Wita Stwosza 57, 80-952 Gdańsk, Poland
$^b$Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

**Article info**

Article history:
Received 1 May 2014
Received in revised form 29 August 2014
Accepted 1 September 2014
Available online 3 October 2014

**Keywords:**
Nitridosilicate
Europium
Luminescence
Anharmonicity of potential
Impurity trapped exciton (ITE)
Nephelauxetic effect

**Abstract**

In this contribution luminescence properties of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ ($x$ = 0.02 and 0.1) at temperatures from 10 to 600 K are presented. Both materials exhibit broad band red emission assigned to the parity allowed 4f$^5$5d$^1$ → 4f$^6$ transitions in Eu$^{2+}$ ions occupying two different crystallographic sites labeled as Eu(Sr1) and Eu(Sr2). For low concentration of dopants only Sr1 site is occupied, whereas for higher concentration both Sr1 and Sr2 sites are occupied. Optical data are used to construct configurational coordination diagrams of the Eu(Sr1) and Eu(Sr2) centers in Sr$_2$Si$_5$N$_8$ lattice. Effects of temperature luminescence quenching and luminescence lifetime shortening were related to ionization of Eu$^{2+}$ ions and anharmonicity of adiabatic lattice potential. Effect of non-homogeneity of the Eu$^{2+}$ occupation between the Sr1 and Sr2 sites is discussed by considering the energies of the ground states of Eu(Sr1) and Eu(Sr2) in respect to the valance and conduction bands.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Recently, nitridosilicates doped with lanthanide ions have received interest due to high chemical stability, high hardness, excellent luminescence and thermo-mechanical properties. Among nitridosilicates, Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ is a promising red phosphor for light emitting diodes (LEDs) due to very efficient emission after UV or blue light excitation [1–5]. Moreover Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ can be synthesized under ambient pressure and therefore have the lower production cost in comparison to high pressure synthesized nitridosilicates [6]. Luminescence of Eu$^{2+}$ in Sr$_2$Si$_5$N$_8$ is related to the parity allowed 4f$^5$5d$^1$ → 4f$^6$ transitions. The relatively long wavelength of the Eu$^{2+}$ emission is attributed to high covalence of the lattice bonds and a large crystal field splitting of the 4f$^5$5d electronic configuration of the Eu$^{2+}$ coordinated by nitrogen ions [7].

The Sr$_2$Si$_5$N$_8$ crystallizes as orthorhombic lattice described by the space group of Pnam [6,8]. In the Sr$_2$Si$_5$N$_8$ lattice, Eu$^{2+}$ ions can replace Sr$^{2+}$ at two different crystallographic sites, tenfold coordinated site with mean distance of Sr1–N equal to 0.2928(7) nm and eightfold coordinated site with mean distance of Sr2–N equal to 0.2865(6) nm [3]. The luminescence of Sr$_2$Si$_5$N$_8$:Eu$^{2+}$ varies from orange to red, depending on the Eu$^{2+}$ concentration [3,9,10]. This effect has been explained by several mechanisms. Piao et al. [3] have argued that the red shift of emission band caused by increasing of Eu$^{2+}$ concentration is associated with the uneven distribution of the Eu$^{2+}$ in Sr1 and Sr2 positions. Sohn et al. [10] have assumed that Eu$^{2+}$ activators are evenly distributed to both Sr$^{2+}$ sites regardless of the Eu$^{2+}$ concentration and the red shift is associated with an energy transfer mechanism from Eu$^{2+}$ site with the higher emission energy to the site with the lower emission energy that increase for the higher Eu$^{2+}$ concentration. Additionally, decrease of unit cell volume of Sr$_2$Si$_5$N$_8$ due to increase of incorporation of Eu$^{2+}$ ions in the lattice is observed. Since Eu$^{2+}$ ions are smaller than Sr$^{2+}$ the size of Eu–N polyhedron is reduced in comparison to Sr–N polyhedron which increase the crystal field strength and eventually lead to the red shift of emission.

Lie et al. [9] have claim that with increase of Eu$^{2+}$ concentration the reabsorption process starts to have impact, giving rise to the observed red shift of the emission. Numerous investigations have been dedicated to thermal quenching of Eu$^{2+}$ luminescence in Sr$_2$Si$_5$N$_8$ [3,6]. There are two proposal that have been used to explain thermal quenching of the Eu$^{2+}$ emission. The first is related to thermally activated electron in the excited state, that crosses the intersection of the lowest 4f$^5$5d excited state and the 4f ground state, and reaches the ground state nonradiatively [3,6,11]. The second assumes thermally activated ionization (autoionization) from the 4f$^5$5d$^1$ excited state to the conduction band [12–14].
Autoionization of the Eu$^{2+}$ creates Eu$^{3+}$ and an electron in the conduction band. However, the mechanism of the non-radiative recombination process of thermally excited e$_{cb}$ electrons in the conduction band at Eu$^{3+}$ ions was not discussed in the literature.

Time-resolved spectroscopy is essential method to distinguish different optical active centers, especially when the large spectral overlap between excitation and emission spectra of these centers is observed. In this paper we performed the systematic study of temperature dependence of the Eu$^{2+}$ luminescence, for the range from 10 K to 600 K. We have measured time-resolved luminescence of the Sr$_{1.9}$Si$_5$N$_8$:Eu$^{2+}$ phosphor with two concentration of dopants (2 at.%, 10 at.%). Time evolution of the luminescence width and maximum as well as luminescence decay at different part of the spectrum were examined. Using these data we discussed the mechanisms of thermal luminescence quenching.

2. Experiment

Sr$_{2-x}$Si$_x$N$_8$:Eu$^{2+}$ ($x=0.02, 0.1$) that corresponds to 2 at.% and 10 at.% were synthesized by the solid-state reaction from Sr$_3$N$_2$, Si$_x$N$_4$ and EuN. The mixture of substrates were fired at 1400 °C for 16 h under flowing 90% N$_2$ – 10% H$_2$ atmosphere in a tube furnace. The sintered products were ground again, yielding crystalline powder.

The obtained compounds have a orthorhombic crystal structure with a space group Pmn2$_1$. The unit cell parameters are $a=5.7138(4)$ Å, $b=6.8211(1)$ Å, $c=9.3963(4)$ Å for Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.02}$ and $a=5.7110(3)$ Å, $b=6.8299(4)$ Å, $c=9.3298(4)$ Å for Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.1}$. More details on preparation and structural investigations are described in the paper Yeh et al. [6].

Room temperature luminescence excitation spectra were measured using a spectrofluorimeter FluoroMax-4P TCCPC produced by Horiba. The excitation source in this system was a 150 W Xenon lamp emitting in the 220–850 nm range. Fluorescence intensity was measured using a monochromator and a photomultiplier R928 Side-on. The experimental setup for luminescence kinetics and time resolved emission spectra consists of YAG:Nd laser of PL 2143 A/SS type and the parametric optical generator PG 401/ SH (OPG) [15]. The laser generated pulses of the 355 nm wavelength with frequency 10 Hz and pump PG generator which could produce light pulses with wavelength ranging from 220 nm to 2200 nm. The halfwidth of the time profile of the light pulse produced by an excitation source under experimental conditions is 44 ps and includes the half time of the light pulse duration produced by the OPG coupled to the YAG:Nd laser and the time response of the detector. Emission signal was analyzed by the spectrometer 2501S (Bruker Optics) and a Hamamatsu Streak Camera model C4334-01 with a final spectral resolution of about 0.47 nm. Time resolved luminescence spectra were obtained by integration of streak camera images over time intervals, whereas luminescence decays were obtained by the integration of streak camera images over the wavelength intervals. Sample were cooled by an ADP Cryogenics closed-cycle DE-202 optical cryostat, which allows to vary temperature between 10 K and 600 K.

3. Results and discussion

The luminescence and luminescence excitation spectra of the Sr$_{2-x}$Si$_x$N$_8$:Eu$^{2+}$ ($x=0.02, 0.1$) obtained at room temperature are presented in Fig. 1a and b. The emission spectra obtained under blue excitation at 460 nm consist of broad band attributed to the 4$f^5$5d$^1$ → 4$f^6$ transitions of Eu$^{2+}$ ions, with maximum at 615 nm for Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.02}$ and at 639 nm for Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.1}$. For both samples the luminescence excitation spectra consist of several overlapping broad bands that are almost independent of the monitored wavelength and Eu$^{2+}$ concentration. The emission band with higher energy is expected for the Eu$^{2+}$ in ten-fold coordinated Sr1 site with mean distance Sr1–N of 2.928(7) Å and the emission band with lower energy is expected for the Eu$^{2+}$ in the eight-fold coordinated Sr2 site with mean distance Sr2–N of 2.865(6) Å [3]. When Eu$^{2+}$ concentration increases from 2 at.% to 10 at.% the strong red shift of the emission band (equal to 658 cm$^{-1}$) and broadening of the bandwidth (equal to 292 cm$^{-1}$) are observed. These effects can be explained assuming uneven occupation of the Eu$^{2+}$ in Sr1 and Sr2 positions. The Eu$^{2+}$ ions occupy mainly Sr1 sites in the sample with 2 at.% Eu$^{2+}$ concentration (Fig. 1a), while for the larger concentration of Eu$^{2+}$ (10 at.%), dopant ions occupy both: Sr1 and Sr2 sites (Fig. 1b). The emission spectrum of Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.02}$ (Fig. 1b) was decomposed into two Gaussian bands – the first with maximum at 15,905 cm$^{-1}$ (629 nm) corresponding to Eu$^{2+}$ located in the Sr1 position and the second with maximum at 14,959 cm$^{-1}$ (669 nm) corresponding to Eu$^{2+}$ in the Sr2 site. One notices that maximum of the Eu(Sr1) luminescence is slightly shifted to the red (by 355 cm$^{-1}$) in the sample with 10 at.% of Eu$^{2+}$ compared to the sample with 2 at.% of Eu$^{2+}$. The Eu$^{3+}$ ion is slightly smaller than Sr$^{2+}$ ion and thus the increase of concentration of Eu$^{3+}$ ions in Sr$_{3-x}$Si$_x$N$_8$ reduces the Eu–N average distance. This causes the increase of crystal field strength and splitting of the 4$f^5$5d electronic manifold.

For more detailed consideration of two different sites in Sr$_{3-x}$Si$_x$N$_8$:Eu$^{2+}$ the time-resolved luminescence spectra were measured. The main advantage of time resolved technique is the possibility to observe changes of the spectrum line-shape in time. Fig 2a and b present time resolved luminescence spectra obtained under 460 nm pulse excitation at 10 K temperature for Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.02}$ and Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.1}$, respectively. Shape and maximum of the Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.02}$ emission (Fig. 2a) does not change over the time, which suggests that only one the Eu(Sr1) luminescence center contributes to this emission. The time evolution of the Sr$_{1.98}$Si$_{5-x}$N$_8$:Eu$^{2+}$$_{0.1}$ luminescence is different, namely the emission band shifts toward the longer wavelengths with the time after excitation. The luminescence maximum observed at 630 nm for acquisition time 0–0.5 µs is shifted to 670 nm for acquisition time 6–10 µs. This suggests that two luminescence centers with different decay times contribute to the emission spectrum of Sr$_{3-x}$Si$_x$N$_8$:Eu$^{2+}$ and the decay of the short-wavelength component of the spectrum is faster than the long-wavelength one.

Fig. 2c and d shows the decays profiles of luminescence measured at 10 K, monitored at 580 nm and 660 nm for
and monitored at 600 nm and 710 nm for emission. We have used hyper-C22 luminescence have been decomposed into two Gaussian bands is in good agreement with Eu(Sr1) bandwidth system). The existence of the fast component can be regarded as a radiative decay time of the Eu

This causes the red shift of the emission spectrum and elongation of the short wavelength part of the Eu

The decay of the Sr1.98Si5N8:Eu2+ emission in Sr1.9

Solving for $S$ yields:

$$S = \frac{\sqrt{\frac{\hbar \omega}{2k_B T}}}{\coth \frac{\hbar \omega}{2k_B T}}$$

where $\hbar \omega$ is the effective phonon frequency and $S$ is Huang–Rhys factor. Quantity $\hbar \omega$ is the energy of the lattice relaxation.

The temperature dependence of the FWHM-s presented in Fig. 3 has been fitted to the relation (1). The best fits (represented by solid curves) were obtained for $\hbar \omega = 454$ cm$^{-1}$ and $S = 3$ for Eu(Sr1) in the Sr1.98Si5N8:Eu0.02, while for Eu(Sr1) in the Sr1.98Si5N8:Eu0.02 for $S = 3$ and $\hbar \omega = 459$ cm$^{-1}$. The Best fit for Eu(Sr2) was obtained for $S = 5$ and $\hbar \omega = 476$ cm$^{-1}$. Obtained parameters allow to construct one dimensional configurational coordinate diagrams representing the ground state and the excited 4f$^5$d$^1$ states of the Eu(Sr1) and Eu(Sr2).

One noticed that luminescence of the Eu(Sr2) is shifted to the lower energy with respect to the Eu(Sr1) emission by quantity of $946$ cm$^{-1}$. Since this difference is approximately equal to the difference between electron lattice coupling of the 4f$^5$d$^1$ state of Eu(Sr2) (which is equal to 2380 cm$^{-1}$) and Eu(Sr1) (which is equal
to 1377 cm\(^{-1}\)) the minimum energy of the lowest 4f\(^{6}\)5d\(^{1}\) state, considered as the energy of the zero phonon line, is approximately the same in Eu(Sr2) and Eu(Sr1) sites. It means that the sum of the centroid shift and the crystal field splitting of the 4f\(^{6}\)5d\(^{1}\) state is approximately the same in both sites.

The calculated Eu(Sr1) and Eu(Sr2) luminescence decay times at different temperatures are presented in Fig. 4. Decay times are constant below 400 K and 200 K, for Eu(Sr1) and Eu(Sr2) respectively, while for higher temperatures the decay times become shorter with increasing temperature. Luminescence decays of Eu(Sr1) observed for 10 at.% Eu\(^{2+}\) sample are non-exponential and are faster than the decays of Eu(Sr1) luminescence observed for 2 at.% Eu\(^{2+}\) sample. The luminescence decays of Eu(Sr1) observed for 10 at.% Eu\(^{2+}\) were considered as a superposition of two exponents and temperature dependence of the longer one is presented in Fig. 4.

In order to analyze the temperature shortening of the emission decay time \(\tau\) for both sites we discussed the data presented in Fig. 4 considering formula [17]:

\[
\tau = \frac{1}{\tau_r} + \frac{1}{\tau} \sum P_i \exp \left( \frac{E_i}{\tau_r} \right)
\]

in which \(\tau_r\) is photoluminescence radiative lifetime, \(E_i\) are the activation energies and \(P_i\) are the probabilities of the non-radiative depopulations for \(i\)-th nonradiative pathway.

Fitting relation (2) to the experimental data we have estimated single nonradiative pathway for Eu(Sr1) center in Sr\(_{1.98}\)Si\(_5\)N\(_8\):Eu\(^{2+}\) characterized by activation energy \(E_a = 3388\) cm\(^{-1}\) and probability \(P_1 = 3 \times 10^8\) s\(^{-1}\). For Eu(Sr2) in Sr\(_{1.95}\)Si\(_5\)N\(_8\):Eu\(^{2+}\) we had to use fitting double nonradiative pathways: the first characterized by probability \(P_2 = 3 \times 10^8\) s\(^{-1}\) and energy \(E_a = 2739\) cm\(^{-1}\) and the second characterized by the energy \(E_a = 507\) cm\(^{-1}\) and probability \(P = 8 \times 10^8\) s\(^{-1}\).

The pathways of the Eu(Sr1) and Eu(Sr2) luminescence quenching, characterized by probability \(P_1 = P_2 = 3 \times 10^8\) s\(^{-1}\) and activation energies equal to 3388 cm\(^{-1}\) and 2739 cm\(^{-1}\), respectively, can be related to autoionization of the Eu\(^{2+}\) excited to the 4f\(^{6}\)5d\(^{1}\) state, considered as transition from the 4f\(^{6}\)5d\(^{1}\) to the conduction band. Autoionization of the Eu\(^{2+}\) creates Eu\(^{3+}\) and an electron in the conduction band that can be described as Eu\(^{2+}\) → Eu\(^{3+}\) + e\(_{cb}\) transition. Since there is a Coulomb attraction between Eu\(^{2+}\) and e\(_{cb}\) the system can exist in the bound state – Europium Trapped Exciton (ETE) state [18,19] which is energetically is located below the conduction band. Therefore finally one can consider autoionization also as the transition from the 4f\(^{6}\)5d\(^{1}\) to ETE state.

The second nonradiative pathway describing the quenching of the Eu(Sr2) emission, characterized by energy \(E_a = 507\) cm\(^{-1}\) and probability \(P = 8 \times 10^8\) s\(^{-1}\) can be attributed to the nonradiative energy transfer from the Eu(Sr2) to Eu(Sr1) centers. Probability of such transfer \(P\) is almost equal to probability of radiative transition in the Eu(Sr1) center. Transfer of energy from the Eu(Sr2) to Eu(Sr1) needs the activation energy \(E_a\) since this energy is necessary to overlap between the Eu(Sr2) emission and the Eu(Sr1) absorption.

For more detailed analysis of the non-radiative intersystem crossing we have constructed configurational coordinate diagrams describing the luminescence properties of the Eu(Sr1) and Eu(Sr2) sites (Fig. 5a and b). In the first approximation we have assumed that all electronic configurations can be represented by harmonic potentials that yield parabolas in configurational coordinate diagrams. Using the data obtained from the luminescence spectra and calculated quantity of Sh\(_{00}\) the diagrams representing the ground states 4f\(^{7}\)\((S_{7/2})\) and the first excited states 4f\(^{6}\)5d\(^{1}\) in both sites have been constructed and presented in Fig. 5a and b. One notices that in both cases energy of crossing of the 4f\(^{7}\)\((S_{7/2})\) and 4f\(^{6}\)5d\(^{1}\) states are too high to allow the temperature activated the intersystem crossing 4f\(^{6}\)\((S_{7/2})\) – 4f\(^{5}\)d\(^{1}\). As the next step to explain the thermal quenching of Eu\(^{2+}\) luminescence in Sr\(_{3}\)Si\(_5\)N\(_8\) we considered the existence of auto-ionization. From the analysis presented in Ref. [12] it is known that energy of the lowest 4f\(^{6}\)5d\(^{1}\) state of Eu(Sr1) is about 4000 cm\(^{-1}\) below the bottom of the conduction band in Sr\(_{3}\)Si\(_5\)N\(_8\). We assumed that this distance is similar in the case of Eu(Sr2) system. Using these data we have presented in Fig. 5a and b the curves labeled as Eu\(^{2+}\) + e\(_{cb}\) representing the “conduction band” (actually representing the ionized Eu\(^{2+}\) (Eu\(^{3+}\)) and electron in the conduction band). We considered further that the ETE state exists with energy higher than the 4f\(^{6}\)5d\(^{1}\) and lower than energy of the Eu\(^{2+}\) + e\(_{cb}\) system. To not influence the luminescence, the minimum energy of the ETE electronic manifold should be placed significantly above the minimum energy of the 4f\(^{6}\)5d\(^{1}\) electronic manifold. Since we have not the certain information about this energy we made arbitrary but reasonably assumption that ETE is placed more than 3000 cm\(^{-1}\) above the minimum energy of the 4f\(^{6}\)5d\(^{1}\) electronic manifold. This assumption yields that the bounding energy of the ETE is at most 3000 cm\(^{-1}\). Thus the ETE is placed more than 3000 cm\(^{-1}\) below the conduction band (Eu\(^{2+}\) + e\(_{cb}\)) state.

The (Eu\(^{2+}\) + e\(_{cb}\)) state and ETE state are characterized by much larger coupling with lattice than the 4f\(^{6}\)5d\(^{1}\) state thus electron–lattice coupling energy is estimated to be Sh\(_{00}\) = 5000–7000 cm\(^{-1}\). We considered that respective Sh\(_{00}\) is equal to 6400 cm\(^{-1}\) and is the same for ETE state and for (Eu\(^{2+}\) + e\(_{cb}\)) state.
Considering above assumptions we present the ETE states on configuration coordination diagrams by dashed parabolas labeled as ETE in Fig. 5(a) and (b). One can consider that after autoionization the relaxation takes place first to the ETE state and then finally to the ground state, due to the intersystem crossing between ETE and \(4f^65d^1\). The activation energies for the intersystem \(4f^6(S_{7/2}) - ETE\) crossing for Eu(Sr1) and Eu(Sr2) obtain using diagram are marked as \(E_1\) in Fig. 5(a) and \(E_2\) in Fig. 5(b). One notices that still these activation energies are much larger then calculated from formula (2).

The cases when temperature luminescence quenching yields the activation energy much smaller than one can obtained from configurational coordinate diagrams has been already studied [17,20]. Proposed solution is based on the fact that ions motion in solids is confined. As the result, the electronic energy increase faster than in harmonic approximation. Specifically this effect influences of the ground state. To visualize the problem and to perform qualitative calculations the model potential has been used:

\[
V(Q) = 0.5[\alpha(x - 1)]^{1/2}\tan^2[Q(x(x - 1))]^{-1/4}
\]

where coordinate \(Q\) is related to ions displacement \(R, Q = R(q)/[\alpha(x - 1)]^{1/4}\). Coefficients \(x, A\) is the strength constant and size of confinement, respectively. Coefficients \(\alpha\) and \(A\) are mutually dependent,

\[
\sqrt{\alpha(x - 1)} = \frac{kA^2}{\pi\hbar\omega}
\]

where \(\hbar\omega\) and \(k\) are phonon energy and elastic constant of the matrix, respectively.

Potential (3) yields the discrete energy spectrum [17,20]:

\[
E_n = [\alpha(x - 1)]^{-1/2}\left[\frac{n^2}{2} + x\left(n + \frac{1}{2}\right)\right]
\]

Assuming that displacement cannot be greater than ion-ion distance (\(\approx 5\ \text{Å}\)) we end up with estimation of \(x \approx 10^4\). For these quantities energies of a few lowest vibronic states are almost the same as those of the harmonic potential \(V_0 = \frac{1}{2}Q\). However for quantum number \(n\) larger than 20, the energy spectrum differs from the harmonic one. The distance between neighboring vibronic levels increases with increasing \(n\).

In Fig. 5(a) and (b) anharmonic potentials representing the ground electronic manifolds of Eu(Sr1) and Eu(Sr2) states are represented by dotted curves. One notices that anharmonicity of the system diminishes significantly the activation energy for intersystem \(ETE - 4f^6(S_{7/2})\) crossing, and thus explains the observed temperature luminescence quenching. These energies are shown in Fig. 5(a) and in Fig. 5(b) as \(E_{10}\) and \(E_{20}\), respectively.

Considering spectroscopic data of \(Sr_2Si_3N_6:Eu^{2+}\) we can also make prediction concerning the energies of the ground states of \(Eu^{2+}\) ions (in both sites) in relation to the bands edges. As it has been mentioned Sr–N average distance in the Sr2 site is smaller than respective distance in the Sr1 site. According to the existing models [19,21] energy of the ground state of the \(Eu^{2+}\) should be higher when the distance between \(Eu^{2+}\) and ligands is smaller. Therefore the ground state energy of \(Eu^{2+}\) in Sr2 site should be higher than the energy of the ground state of \(Eu^{2+}\) in the Sr1 site. This conclusion is in full accordance with the results of this paper. We noticed that the Sr2 site is not occupied for low \(Eu^{2+}\) concentration and become occupied when \(Eu^{2+}\) concentration is sufficiently large. Such effect can take place when energy of the Eu(Sr2) system is higher than energy of the Eu(Sr1) system.

4. Conclusions

The \(Eu^{2+}\) ions in \(Sr_2Si_3N_6\) can occupy the two available Sr\(^{2+}\) sites: tenfold coordinated Sr1 sites and eightfold coordinated Sr2 sites. Since Eu\(^{2+}\) in Sr1 site is tenfold coordinated thus it is characterized by lower crystal field splitting and electron–lattice coupling strength than Eu\(^{2+}\) in eight fold coordinated Sr2 site thus the energy of the emission related to the \(4f^65d^1 - 4f^7\) transition is higher in the case of Eu(Sr1) site.

Considering the spectroscopic data we concluded that the ground state energy of the Eu\(^{2+}\) in Sr2 site should be higher than the ground state energy of Eu\(^{2+}\) in the Sr1 site. This explains uneven distribution of Eu\(^{2+}\) ions in Sr1 and Sr2 positions at different level of Eu\(^{2+}\) doping in \(Sr_2Si_3N_6\) lattice. For low concentration of Eu\(^{2+}\) only Sr1 site is occupied, whereas for higher concentration both Sr1 and Sr2 sites are occupied. The experiments performed at temperatures above 10 K show that the luminescence intensity and decay time decreases with increasing temperatures, however the decrease of the Eu(Sr2) luminescence decay and intensity takes place at lower temperatures than Eu(Sr1) luminescence.

To describe the thermal luminescence quenching and lifetime diminishing we considered thermally activated ionization of Eu\(^{2+}\) ions. After autoionization the system can exist in the ETE state.
which energetically is located between the lowest 4f6d1 and the conduction band. Therefore one can consider that the relaxation after autoionization takes place first to the ETE state and then finally to the ground state, due to the intersystem crossing between ETE and 4f(5/2). If one uses the standard model of harmonic potential with linear electron–lattice coupling parameterized to be consistent with the spectroscopic data, one cannot reproduce the experimental temperature dependence of the emission decay time. We have considered anharmonic model potential which assume that the ion motion in a crystal is confined. Since the confined potential is steeper, it results in the decrease of the energy barrier of nonradiative process and thus explains the observed temperature luminescence quenching.

Acknowledgements

This study has been funded by the European Social Found and by POIG.01.01.02-02-006/09 project “New efficient phosphors for lighting and solar concentrators”. The contribution of A.L. was supported within the International PhD Project “Physics of future quantum-based information technologies”: grant MPD/2009-3/4 from Foundation for Polish Science and by the project “InnoDoktorant – Scholarships for PhD students, Vth edition” co-financed by the European Union in the frame of the European Social Fund. R.S. Liu would like to thank the support from National Science Council with the contract number of NSC101-2113-M-002-014-MY3.

References