

Characterization of various Eu^{2+} sites in $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ by high-pressure spectroscopy*

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Photoluminescence of Ba_2SiO_4 and Ca_2SiO_4 activated with Eu^{2+} was investigated at various temperatures (from 10 K to 300 K) and pressures (from ambient to 200 kbar). At ambient pressure and room temperature, under UV excitation both phosphors yielded a green emission band with maxima at 505 nm and 510 nm for Ba_2SiO_4 and Ca_2SiO_4 , respectively. The energies of these bands depended on pressure; the pressure shifts were $-12.55 \text{ cm}^{-1}/\text{kbar}$ for $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$; and $-5.59 \text{ cm}^{-1}/\text{kbar}$ for $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$. In the case of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$, we observed additional broadband emission at lower energies with a maximum at 610 nm (orange band). The orange and green emission in $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ had different excitation spectra: the green band could be excited at wavelengths shorter than 470 nm, whereas the orange band – at wavelengths shorter than 520 nm. The pressure caused a red shift of orange emission of $7.83 \text{ cm}^{-1}/\text{kbar}$. The emission peaked at 510 nm was attributed to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} in the β - $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ phase, whereas the emission peaked at 610 nm – to the γ - $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ phase. The emission of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ peaked at 505 nm was attributed to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition of Eu^{2+} in the β - Ba_2SiO_4 phase.

Keywords: *high pressure spectroscopy, Eu^{2+} , silicates*

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1. Introduction

Alkali orthosilicates M_2SiO_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) doped with Eu^{2+} are widely investigated as potential materials for the production of phosphors that convert UV light of InGaN light-emitting diodes (LEDs) into white light [1–3]. The structure of Ca_2SiO_4 has been investigated due to applications of this material in concrete and cement. Five different phases of Ca_2SiO_4 , viz. α , α'_H , α'_L , β and γ have been reported [4].

The Eu^{2+} ion contains seven electrons in the unfilled $4f^7$ and $4f^65d$ electronic shells. The ground state of Eu^{2+} ($^8S_{7/2}$) belongs to the ground electronic configuration $4f^7$. The first excited state in the same configuration ($^6P_{7/2}$) has an energy of about 28000 cm^{-1} above the ground state [5]. Therefore, in many materials the first

excited state of Eu^{2+} is the lowest state of the excited electronic configuration $4f^65d$. It is the $4f^65d(t)$ state for O_h symmetry (octahedral sixfold coordination) or the $4f^65d(e)$ state for T_d symmetry (tetrahedral fourfold coordination) as well as O symmetry (cubic eightfold coordination). In the first approximation, the splitting between the $4f^65d(t)$ and $4f^65d(e)$ states is proportional to the crystal field strength (Dq). In the crystal-field point-charge model, this parameter depends on R^{-5} , where R is the ion-ligand distance [6].

The energies of the excited electronic configuration $4f^65d$ in different materials depend on the coordination number, bond lengths and crystal field strength (see [7]). In alkali orthosilicates, the absorption band related to the parity-allowed $4f^7(^8S_{7/2}) \rightarrow 4f^65d$ transition is in the spectral range of 350 nm – 410 nm and overlaps with the emission band of nitride-based LEDs. The emission corresponding to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition peaks is in the visible region, between 440 nm and 640 nm [8].

*The paper was presented at the 8th Functional and Nanostructured Materials in Szczecin (Poland) hold on 6-9 September 2011

The crystal field causes the splitting between $4f^65d(t)$ and $4f^65d(e)$ states and further lowers the energy of the lower state. A customary way of varying the crystal-field strength is to alter the chemical composition of the host lattice. A series of chemically nonequivalent isostructural host lattices represents a set of discrete points along the crystal-field strength and band structure continua. Pressure compresses the materials and reduces the distance between Eu^{2+} and the oxygen ligands. Therefore, an important feature of high pressure is its ability to continuously vary the crystal-field strength. As a result, high pressure studies offer a meaningful complement to host lattice studies because of the finer resolution of crystal-field strength that they provide. In addition, other variables, such as covalence, are much less sensitive to pressure than to chemical composition.

In this paper, we present a detailed study on the luminescence, luminescence kinetics and high-pressure spectroscopy of Eu^{2+} -doped Ba_2SiO_4 and Ca_2SiO_4 . The purpose of our research was to identify the luminescence bands and their assignment to the specific sites of Eu^{2+} in various crystal phases.

2. Experimental

In order to study luminescence under pressure, we excited the system with a CW He-Cd laser with a wavelength of 325 nm and an Ar laser with a wavelength of 488 nm. Luminescence excitation spectra and luminescence spectra under different excitation conditions were measured using a Xe lamp (450 W), two SPM2 monochromators (one in the excitation, the other in the detection line) and two photomultipliers (the first for luminescence and the second for the detection of the reference signal). All spectra were corrected for instrumental response.

To analyze the time evolution of the luminescence spectra, the crystals were excited with an optical parametric generator (OPG) PG401/SH pumped by a pulsed triple-wavelength Nd:YAG laser which yielded 30-ps pulses. The luminescence was spectrally analyzed with a

Bruker Optics 2501S model spectrometer and the luminescence kinetics was measured using a Hamamatsu C4334-01 model streak camera. The streak camera provides a three-dimensional picture, where the luminescence intensity is plotted along the vertical z-axis, versus the wavelength (or energy) along the x-axis and time along the y-axis. The luminescence spectra were obtained by integrating the streak camera picture over time, whereas the luminescence decays were obtained by integrating the streak camera picture over the wavelength.

High hydrostatic pressure was applied in a diamond anvil cell (DAC). The sample was placed in a hole drilled in an Inconel X 750 steel gasket between two parallel diamond anvils. Polydimethylsiloxane oil (Dow Corning Corporation 200 fluid) was used as a pressure-transmitting medium and a ruby crystal was used as a pressure monitor. Pressure was estimated with an accuracy of about 2 kbar.

3. Results and discussion

3.1. Ambient pressure results

The luminescence spectra of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ consist of broad bands corresponding to the $4f^65d \rightarrow 4f^7(^8\text{S}_{7/2})$ transition at various sites. In the case of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$, it is a single band peaked at 505 nm, whereas the luminescence spectrum of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ is multiband and depends on the excitation wavelength. The luminescence spectra of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ obtained under different excitations are presented in Fig. 1, panel a and b, respectively. The excitation spectra of these emissions are presented in Fig 1, panel c. The excitation spectrum of the luminescence of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ is denoted by a thick black curve and can be attributed to an absorption band corresponding to the $^8\text{S}_{7/2} \rightarrow 4f^65d$ transition, peaked at 355 nm. The observed emission spectra and excitation spectra of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ are consistent with spectra previously obtained for this material [9, 10]. The small asymmetry in the emission peak was attributed to the existence of

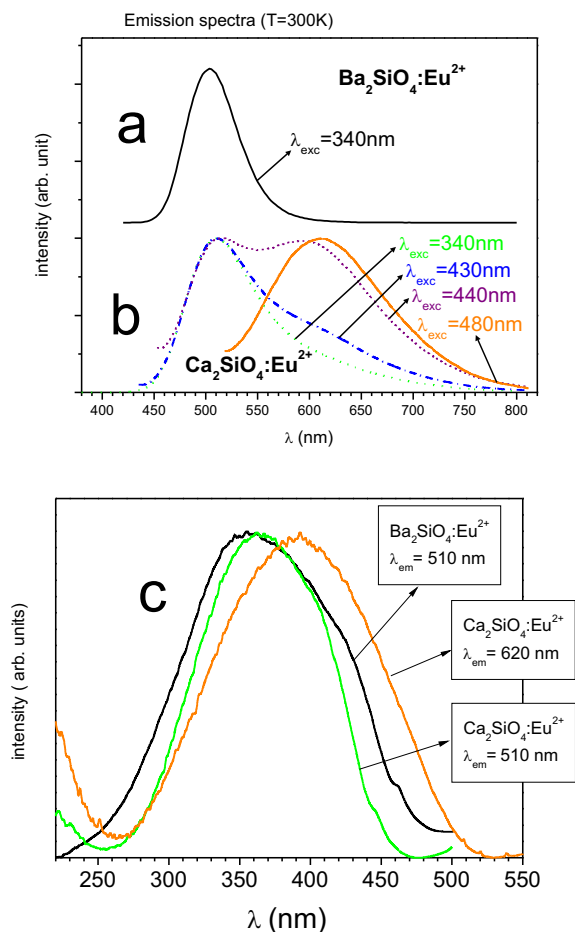


Fig. 1. a) Emission spectrum of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ under excitation with 340 nm. b) Emission spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ under different excitations (labeled in the figure). c) Luminescence excitation spectra of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$.

two Eu^{2+} sites in the orthorhombic β phase of Ba_2SiO_4 [9], which were responsible for the two emission peaks at 505 nm and 520 nm. The actual spectrum was considered as a superposition of these two bands.

The emission spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ depended on the excitation wavelength (see Fig. 1, panel b). Under excitation with 340 nm, the broad-band emission, peaked at 510 nm was very similar to the luminescence of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$. On the other hand, under excitation with 480 nm, the emission showed a broad-band peak at 610 nm.

For excitations under intermediate wavelengths, such as 440 nm, both bands were observed. The luminescence excitation spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ are presented in Fig. 1, panel c. The excitation spectrum of the emission of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ monitored at 510 nm was very similar to the excitation spectrum of the luminescence of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$, however, it was slightly narrower and shifted towards the red, with a peak at 365 nm. The excitation spectrum of the emission monitored at 620 nm had a peak at 395 nm.

Broad-band luminescence with a peak at around 615 nm has also been observed in alkali orthosilicates co-doped with Mn^{2+} [11]. To verify the hypothesis on the presence of uncontrolled Mn^{2+} , we measured the luminescence kinetics of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$. The luminescence decays were almost single-exponential. The fitted lifetime constants, luminescence lifetimes of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ and $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ obtained at 297 K and 77 K are presented in Table 1. In all cases, the emission decay had a lifetime below 1 μs . The kinetics of the green luminescence (bands peaked at 505 nm and 510 nm) was almost identical at 297 K and 77 K. In the case of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$, the lifetimes we measured were identical with those reported by Poort *et al.* [12] for 4.2 K, implying that the luminescence lifetime is independent of temperature over a broad temperature region. The luminescence lifetime of the emission peaked at 610 nm increased with a decrease in temperature. The decrease in the luminescence lifetime with an increase in temperature can be attributed to an increase in the probability of occurrence of non-radiative processes. The lifetime of the 610 nm emission was far shorter than expected for Mn^{2+} luminescence. Therefore, the 610 nm emission should be attributed to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ luminescence of the Eu^{2+} ion in the sites with the crystal field higher than that for Eu^{2+} in the sites yielding the emission peaked at 510 nm.

A similar situation has been observed in Eu^{2+} -doped Ca_2SiS_4 , where for the concentrations of Eu^{2+} higher than 0.5% [13], two luminescence bands peaked at 564 nm and 660 nm have been

Table 1. Luminescence lifetimes

sample	$T(\text{K})$	λ_{em} (nm)	τ (μs)
$\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$	300	510	0.65(5)
$\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$	77	510	0.64(5)
$\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$	300	510	0.53(5)
$\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$	77	510	0.57(5)
$\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$	300	610	0.52(5)
$\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$	77	610	0.83(5)

observed – both bands have been related to Eu^{2+} ions. Specifically, the emission peaked at 660 nm was attributed to Eu^{2+} in the monoclinic phase, isostructural with Eu_2SiS_4 . Five different phases (α , α'_H , α'_L , β and γ) have been reported for Ca_2SiO_4 [4]. Therefore, we conclude that our Ca_2SiO_4 sample must consist of a mixture of different phases, for instance, of phases β and γ . The details of different Ca sites that can be occupied by Eu^{2+} in the β and γ phases are listed in Table 2. Tentatively, we attributed the emission peaked at 510 nm to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition in Eu^{2+} , which occupies Ca sites in the β - Ca_2SiO_4 phase, whereas the emission peak at 610 nm – to the γ - Ca_2SiO_4 phase.

3.2. High-pressure spectra

The luminescence spectra of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ obtained at different pressures at room temperature under excitation at 325 nm are presented in Fig. 2, panel a. The emission peak is shifted towards lower energies with increasing pressure. The position of the energy peak versus pressure is presented in Fig. 2, panel b. The pressure reduced the energy of the emission with a constant rate of $-12.55 \text{ cm}^{-1}/\text{kbar}$.

The luminescence spectra of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ obtained at different pressures under excitation at 325 nm and 488 nm are presented in Fig. 3, panel a and Fig. 3, panel b, respectively. In both cases, pressure caused red shifts of the emission. Respective pressure rates were smaller than in the case of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ luminescence and equal to $-5.59 \text{ cm}^{-1}/\text{kbar}$ for the band peaked at 510 nm excited with a wavelength of 325 nm and

Table 2. Bond lengths in β and γ dicalcium silicate at room temperature. Accuracy is given in brackets.

Bond lengths in β dicalcium silicate [14]			
Ca(1)-O	Å	Ca(2)-O	Å
	2.2287(15)		2.4367(18)
	–		2.6575(18)
	2.4869(18)		2.3907(20)
	2.8818(18)		2.3855(19)
	2.5426(18)		2.6542(21)
	2.4281(18)		2.3852(17)
	2.6415(18)		2.6209(20)
	2.3582(18)		2.4493(18)
Average	2.5105		2.4975
Bond lengths in γ dicalcium silicate [15]			
Ca(1)-O	Å	Ca(2)-O	Å
	2.367(7)		2.470(10)
	2.367(7)		2.321(10)
	2.295(6)		2.436(7)
	2.295(6)		2.436(7)
	2.390(7)		2.395(7)
	2.390(7)		2.395(7)
Average	2.351		2.343

$-7.83 \text{ cm}^{-1}/\text{kbar}$ for the band peaked at 610 nm excited with a wavelength of 488 nm. The pressure compressed the crystal leading to an increase in the energy splitting of the $4f^65d(t)$ and $4f^65d(e)$ states. In the case of the β phase, the lower state was $4f^65d(e)$, whereas in the case of the γ phase, the lowest excited state was $4f^65d(t)$. A negative pressure shift of all the luminescence bands in $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ supports the assumption that all of them correspond to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition in Eu^{2+} ions in different sites.

In order to assess the influence of the Eu^{2+} occupation site on the luminescence shift due to pressure, we consider the relation between the energetic structure of an isolated ion and an ion in a crystal. The energy of the lowest state of the excited electronic configuration $4f^65d$ in a crystal is lower than the energy of an isolated ion, due to the centroid energy corresponding to the reaction of the lattice to the transition of an electron from an “f”

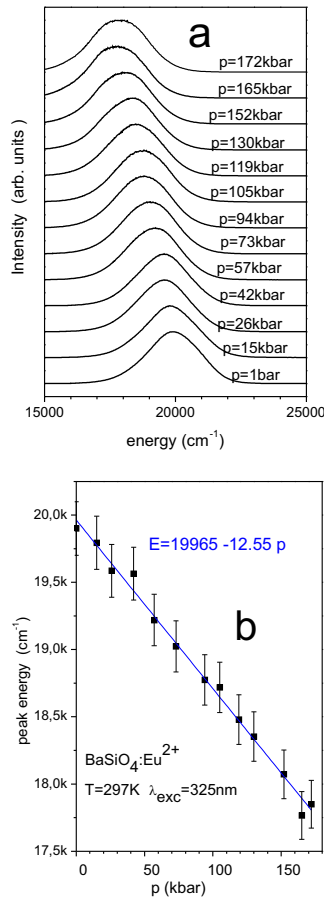


Fig. 2. a) Emission spectra of $\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$ at different pressures at a temperature of 297 K under excitation with 325 nm. b) Energies of the emission peak versus pressure.

to a “d” orbital and the energy of the crystal-field splitting of the “d” level [16]. The pressure-induced red shifts of the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ luminescence of Eu^{2+} can be expressed as follows [17]:

$$\frac{dE_{em}}{dp} = -\frac{n'\Delta E_{cen} + n\Delta E_{c-f}}{3B}, \quad (1)$$

where ΔE_{cen} and ΔE_{c-f} are the centroid and crystal-field splitting energies; n' and n are the exponents describing the dependence of the respective energies on the distance between the central ion and the ligand; and B is the bulk modulus of the material.

For $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$, the distances between the Eu^{2+} ion and the O^{2-} ligands were significantly smaller for the γ phase than for the β phase

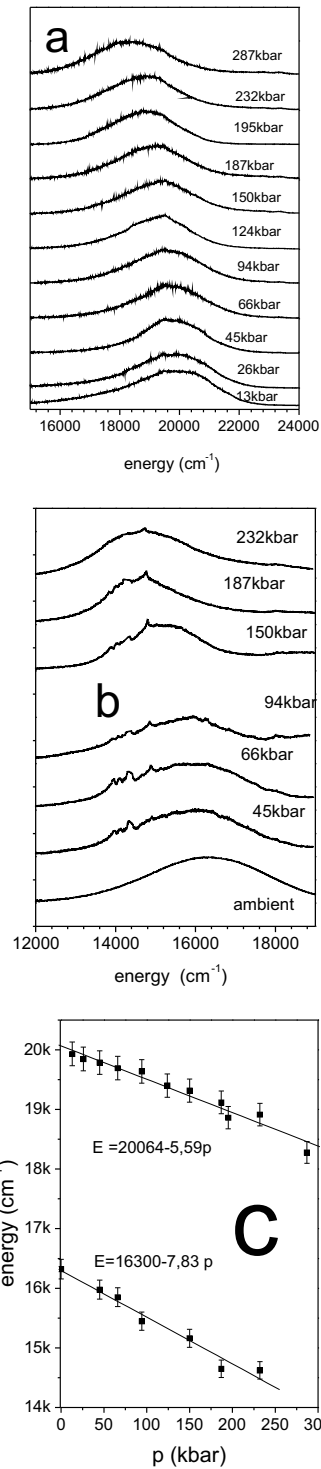


Fig. 3. a) Emission spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ at different pressures at a temperature of 297 K under excitation with 325 nm. b) Emission spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{2+}$ at different pressures at a temperature of 297 K under excitation with 488 nm. c) Energies of the emission peaks versus pressure.

(see Table 2). As a result, E_{cen} and E_{c-f} were larger in the γ phase. Thus, the band peaked at 510 nm probably corresponded to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition in Eu^{2+} in the β phase of Ca_2SiO_4 , whereas the emission peaked at 610 nm – to the γ phase of Ca_2SiO_4 . The pressure shift in the Eu^{2+} emission in $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ was larger than in the case of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$. This does not prevent assigning the $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ luminescence to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition in two Eu^{2+} sites in the β - Ba_2SiO_4 phase. The bulk modulus of β - Ca_2SiO_4 has been reported to be equal to 1400(80) kbar [18]. We did not find the corresponding data for γ - Ca_2SiO_4 or β - Ba_2SiO_4 , however, we expect the value of the bulk modulus for β - Ba_2SiO_4 to be smaller than for β - Ca_2SiO_4 due to a larger ionic radius of the Ba^{2+} ion. Should this be the case, the larger pressure shift of the Eu^{2+} emission in β - Ba_2SiO_4 compared to β - Ca_2SiO_4 would be a direct consequence of eq. (1). Assuming further that the value of the bulk modulus is similar for β - Ca_2SiO_4 and for γ - Ca_2SiO_4 , it follows from eq. (1) that the pressure shift of the band peaked at 16300 cm^{-1} should be smaller than for the band peaked at 20064 cm^{-1} (see Fig. 3, panel c).

4. Conclusions

The measurements of high-pressure luminescence of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ indicated the presence of one phase (the β phase) in the case of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$, and of two phases (β and γ) in the case of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$. In the case of $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ a single emission band was observed. In the case of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$, we observed two emission bands with different excitation spectra. The band peaked at 510 nm is related to the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition in Eu^{2+} in the β phase of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$, which is characterized by longer Eu-O bond lengths and, therefore, smaller crystal fields and a smaller crystal field splitting of the $4f^65d$ electronic manifold. Tentatively, we related the emission peaked at 610 nm to the γ phase of $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$, which is characterized by a larger splitting due to shorter Eu-O bond lengths.

Acknowledgements

This work was supported by the Polish National Center for Research and Development under grant no. NR 15 02906 and

the Polish Ministry of Science and Higher Education under grants active in years 2008–2011. The authors would like to thank Dr. Richard Meltzer from the University of Georgia, Athens, USA for the $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ and $\text{Ca}_2\text{SiO}_4\text{:Eu}^{2+}$ samples and for critical discussion of the results.

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Received 2011-12-23

Accepted 2012-01-17