

Photoluminescence of Eu^{2+} in SrGa_2S_4

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Abstract

A photoluminescence (PL) study of the green-emitting $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor is reported. Diffuse reflectance, excitation, and emission spectra were examined with the aim to enlarge the fundamental knowledge about the emission of the Eu^{2+} ion in this lattice. The thermal dependence of the radiative properties was investigated. In particular, the Stokes shift, the crystal field splitting and the activation energy of the thermal quenching were determined. By combining these results with the information presented in literature, we discussed the location of the Eu^{2+} levels relative to the valence and conduction bands of SrGa_2S_4 .

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1. Introduction

Inorganic compounds doped with rare earth ions form an important class of phosphors for many luminescence applications. The ternary compounds $\text{II-III}_2(\text{S,Se})_4$ doped with Eu^{2+} and Ce^{3+} ions are very attractive for lighting and display applications [1–6]. The Eu^{2+} -doped SrGa_2S_4 compound is well known as an efficient green-emitting phosphor, with excellent colour coordinates ($x = 0.26$, $y = 0.69$), high lumen equivalent (560 lm/W) [1] and luminescence decay

of 480 ns [2]. The low saturation effects of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ make it very advantageous for applications where high beam currents are required to achieve the wanted brightness levels like Field Emission Display (FED) [1,3,4]. Furthermore, this phosphor allows efficient acceleration of charge carriers up to optical energies under high electric fields leading to high electroluminescent efficiency in inorganic Thin Film Electroluminescent (iTDEL) devices [5]. Besides $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ is used in phosphor converted light emitting diodes (pc-LED) for Solid State Lighting (SSL) [6]. High-quality powders or films are required for all these device applications.

In order to improve the phosphor properties in powder or thin film form, it is necessary to enlarge

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the fundamental understanding of the mechanisms involved in the luminescence process. In particular, the knowledge of the precise location of the ion–electronic levels relative to the conduction and valence bands of the host matrix is of great interest and very helpful to predict the energy transfer between the lattice and the luminescent centres and to identify the loss mechanisms responsible for the decreasing luminescence efficiency.

In this work, a photoluminescence (PL) study of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor is reported. The diffuse reflectance, excitation and emission spectra were analysed and the influence of the temperature on the luminescence process was investigated.

2. Experimental procedure

Eu^{2+} -doped- SrGa_2S_4 powder was prepared by solid-state reactions between strontium carbonate (SrCO_3 , 99.999%), gallium oxide (Ga_2O_3 , 99.999%) and europium oxide (Eu_2O_3 , 99.99%). The powders were mixed and treated at 900 °C for 4 h under a H_2S stream, then ground and retreated at 1000 °C under similar conditions. The good crystalline properties of the powder were checked by XRD measurements. The powder consisted of 10–50 μm grains. Powders with different Eu^{2+} concentration (from 0.1% to 10%) were analysed.

Diffuse reflectance spectra were obtained using a Cary 50 spectrophotometer equipped with an integrated sphere accessory coated with PTFE (Poly Tetra Fluoro Ethylene) white material. The photonic excitation at 420 nm was obtained by using a dye laser (Laser Photonics LN102, Coumarine 420) pumped by a pulsed N_2 laser (Laser Photonics LN 1000, 1.4 mJ per pulse, pulse width 0.6 ns). The emission was collected by an optical fiber and analysed by a Jobin–Yvon Spectrometer HR460 and a multichannel CCD detector. PL decay measurements were performed with the same excitation laser with a repetition rate of about 1 Hz. The decays were analysed with a PM Hamamatsu R5600U and a Tektronix TDS 784A scope with a time constant of the order of 1 ns. Excitation spectra were recorded with a Jobin–Yvon spectrophotometer Fluorolog-3 using a Xenon lamp (450 W). Thermal dependence of the

emission was analysed from 77 to 500 K using a cold finger cryostat JANIS ST-100 under vacuum.

3. Results

3.1. Emission spectrum

The emission spectrum of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder at 77 K presents a broad band centred at 537 nm with a full width at half-maximum (FWHM) of 35 nm (Fig. 1). This emission is ascribed to the dipole-allowed transition from the lower $4f^6(^7F)5d$ state to the $4f^7(^8S_{7/2})$ fundamental state of the Eu^{2+} ions [1].

The band shape is characteristic of a phonon-broadened emission that can be described by using the single configuration coordinate model. The emission band is considered to be composed of vibronic transitions, i.e. transitions from the vibrational level of the excited electronic state characterized by the quantum number m to the vibrational level of the fundamental electronic state characterized by the quantum number n . In first approximation, we suppose that only the fundamental vibration level ($m = 0$) of the excited electronic state is occupied at 77 K. Using this

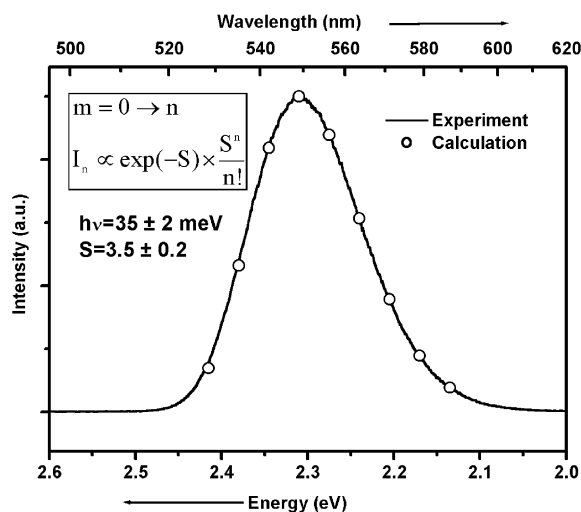


Fig. 1. Experimental (black line) and calculated (open circles) emission spectrum of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder at 77 K under excitation at 420 nm.

hypothesis, the intensity of the vibronic transition $m = 0 \rightarrow n$ is proportional to the expression [7]

$$\exp(-S) \times \frac{S^n}{n!},$$

where S is the Huang–Rhys parameter and measures the interaction between the luminescent centre and the vibrating lattice. The energy gap between two vibronic peaks is equal to the quantity $h\nu_g$, the mean lattice phonon energy for the $4f^7(^8S_{7/2})$ ground electronic state. The fit of the emission band, presented in Fig. 1, was performed with $S = 3.5 \pm 0.2$ and $h\nu_g = 35 \pm 2$ meV. This S value corresponds to an intermediate electron–phonon coupling and can be linked to the slight asymmetry of the emission band. By supposing that the ground state parabola of the configuration coordinate model presents the same curvature as the excited state parabola i.e. the mean phonon energy is the same for the $4f^7(^8S_{7/2})$ ground state as for the $4f^6(^7F)5d$ excited state $h\nu_g = h\nu_e = h\nu$, we can determine the Stokes shift (ΔS). ΔS is related to the offset of the parabolas in the configuration coordinate diagram. ΔS is equal to $(2S-1)h\nu = 0.21 \pm 0.03$ eV (1700 ± 200 cm⁻¹). These values are in good agreement with those presented in the literature [2,8].

3.2. Absorption and excitation spectrum

Absorption spectrum of SrGa₂S₄:Eu²⁺ (10%) at 300 K is shown in Fig. 2. It is obtained from diffuse reflectance spectrum by using the Kubelka–Munk formula [9]. The absorption factor K is linked to the diffuse reflectance rate R and to the diffusion factor S_{sca} :

$$\frac{K}{S_{\text{sca}}} = \frac{(1-R)^2}{2R}.$$

We can neglect the spectral dependence of the diffusion factor because the grain size of the powder is larger than the wavelength in the UV–visible range [7]. So the ratio K/S_{sca} versus wavelength is a good representation of the absorption spectrum of the compound. The absorption below about 300 nm (above about 4.1 eV) is due to the absorption of the SrGa₂S₄ host matrix. This energy value can be compared

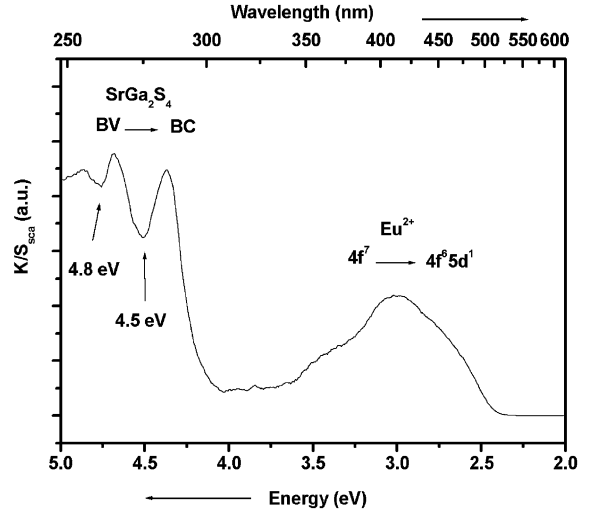


Fig. 2. Spectral variation of the ratio between the absorption coefficient and the scattering coefficient (determined from the Kubelka–Munk method) for the SrGa₂S₄:Eu²⁺ (0.1%) powder at 300 K.

with the energy gap evaluated at 4.4 eV by optical measurements for CaGa₂S₄ monocrystal [10]. The large band located between 320 and 550 nm is ascribed to the absorption of the Eu²⁺ ions. This strong absorption in the near UV and blue range is responsible for the yellow colour of the powder sample.

In the band of the host absorption, we observe two dips located at 258 nm (4.8 eV) and 275 nm (4.5 eV). Such a structure was already found for polycrystalline SrS compound where five dips were observed and ascribed to excitonic transitions; the lowest energy dips (at 4.8 and 4.9 eV) were assigned to direct exciton transitions at the X point in the Brillouin zone of the host crystal and the highest energy dips (at 5.2 and 5.4 eV) were associated to the direct transitions at the Γ point [11]. Few data concerning the band structure of SrGa₂S₄ exist, consequently, the results cannot be interpreted with certitude. Additional measurements on high-quality monocrystals would be necessary to provide an accurate analysis.

The excitation spectrum of SrGa₂S₄:Eu²⁺ (0.1%) for the emission at 537 nm at 77 K is presented in Fig. 3. Although it is coherent with those presented by Peters et al. [1] and Eichenauer

et al. [2], our spectrum allows to distinguish with less ambiguity the different excitation bands. It is composed of three large bands in the UV–visible range:

- The excitation band (A) (maximum at 265 nm) is ascribed to the transitions between the valence band and the conduction band of the SrGa_2S_4 host matrix.
- The two excitation bands (B) and (C) are ascribed to the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F)5d$ transitions in Eu^{2+} electronic levels.

In the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ compound, the Sr^{2+} ions are substituted by the Eu^{2+} ions. They occupy three different sites with C_2 and D_2 symmetry [12]. In first approximation, they are located at the centre of square anti-prisms formed by the 8 S^{2-} anions. In this D_{4d} symmetry, the 5d orbitals are split in three levels as illustrated in Fig. 4. The band (C) is ascribed to the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F)5d$ (a_1) transitions and the band (B) to the $4f^7(^8S_{7/2}) \rightarrow 4f^6(^7F)5d$ (e_2) transitions. By evaluating the energy gap between the (B) and (C) bands to 8000 cm^{-1} (1 eV), the crystal field strength, $\Delta_{a-p} = 8.9 D_q$, can be estimated at about $16,000\text{ cm}^{-1}$ (2 eV).

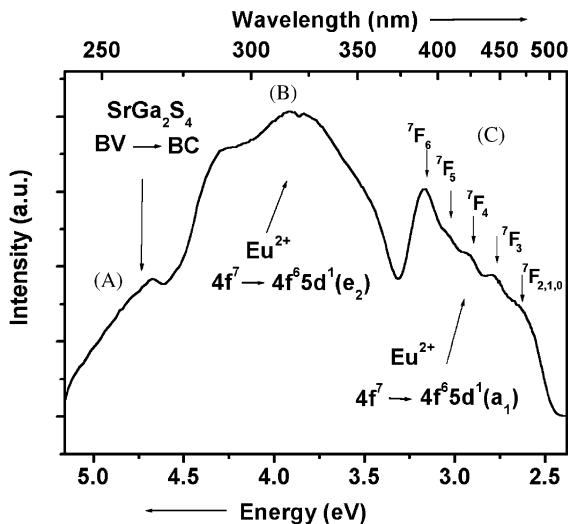


Fig. 3. Excitation spectrum of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder at 77 K for the emission at 537 nm.

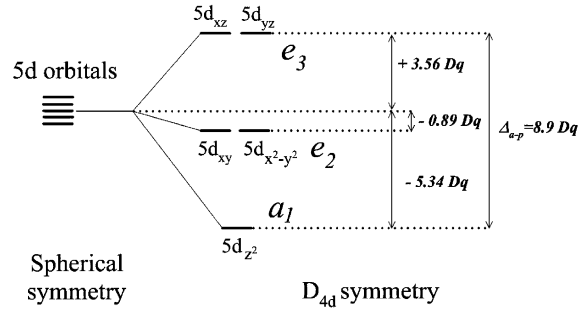


Fig. 4. Splitting of the five 5d orbitals in a square antiprismatic (D_{4d}) symmetry.

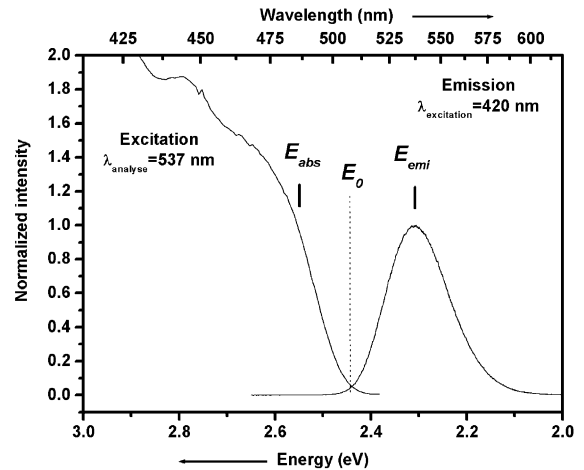


Fig. 5. Comparison of the low-energy excitation spectrum and the emission spectrum illustrating the almost mirror-image relationship and providing the values of E_{abs} and E_{emi} at 77 K.

An almost mirror-image relationship seems to hold between the emission and the excitation spectra in the energy region between the two maxima (Fig. 5). This relation is characteristic of a phonon-broadened emission and confirms the hypothesis we made previously; it suggests that the mean phonon energy $h\nu$ is the same for the $4f^7(^8S_{7/2})$ ground state as for the $4f^6(^7F)5d$ (a_1) excited state. We can determine the energy of the zero-phonon line E_0 at the intersection of the emission and excitation spectra. From Fig. 5, we found $E_0 = 2.44\text{ eV}$, which corresponds to a wavelength of 508 nm (comparable with that given by Eichenauer et al. [2]).

The (C) band presents the characteristic “staircase” structure of the $\text{Eu}^{2+} f \rightarrow d$ absorption. This structure is due to the spin–orbit coupling in the $4f^6$ configuration leading to the splitting of the ^7F levels in seven levels: ^7F_J with $J = 0-6$. The different steps of the structure are indicated by an arrow in Fig. 3. We observe 5 maxima instead of 7, because the energies of the first maxima corresponding to the $4f^7 (^8S_{7/2}) \rightarrow 4f^6 (^7F_{0,1,2})5d (a_1)$ transitions are very closed. The energy differences between the 5 maxima ($\Delta E \approx 0.1$ eV) are in good agreement with those of the ^7F_J levels derived from the $4f^6$ configuration of the free Eu^{3+} ion [13]. The energy E_{abs} of the $f \rightarrow d$ transition from the ground state to the lowest level of the $4f^6 5d (a_1)$, i.e. the $^7F_0$ level, corresponds to the energy of the first step of the “staircase” structure. Since the step is not resolved, we can only give an estimation of E_{abs} . By using the mirror–image relationship between the emission and the excitation spectra, we have found $E_{\text{abs}} = 2.55 \pm 0.05$ eV (Fig. 5).

The energy of the transition from the $4f^7 (^8S_{7/2})$ ground state to the $4f^6 (^7F_0)5d$ excited state is lowered from the free ion value when the Eu^{2+} ion is brought into a crystal environment. The energy of the $f \rightarrow d$ absorption and of the $d \rightarrow f$ emission can be written according to the formalism of P. Dorenbos [14]

$$E_{\text{abs}} = E_{\text{free}} - D \text{ and } E_{\text{emi}} = E_{\text{free}} - D - \Delta S,$$

where E_{free} is the energy difference between the lowest $4f^7$ level and the $4f^6 (^7F_0)5d$ level for the free or gaseous ion, D is the energy lowering also called redshift and ΔS the Stokes shift. The redshift energy depends on the crystal environment and can be represented by a term, called the centroid shift, concerning the shift of the average of the five $5d$ levels relative to the free ion value, and a second term associated to the crystal field splitting. For Eu^{2+} , E_{free} is equal to 4.19 eV [13]. The emission and excitation spectra provide the values of absorption and emission energies, $E_{\text{abs}} = 2.55 \pm 0.05$ eV and $E_{\text{emi}} = 2.31$ eV. The Stokes shift is then $\Delta S = E_{\text{abs}} - E_{\text{emi}} \approx 0.24 \pm 0.05$ eV ($2000 \pm 400 \text{ cm}^{-1}$) and the redshift $D = E_{\text{free}} - E_{\text{abs}} = 1.64 \pm 0.05$ eV ($13\,000 \pm 400 \text{ cm}^{-1}$). The value of the Stokes shift is comparable with this previously obtained

by fitting the band emission: 0.21 ± 0.03 eV ($1700 \pm 200 \text{ cm}^{-1}$).

3.3. Influence of the temperature

The emission spectra of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder are presented as a function of the temperature from 77 to 500 K in Fig. 6. The wavelength of the emission maximum decreases from 537 to 532 nm with the increasing temperature. The energy shift of the band is associated to the increase of the energy for the most occupied vibration level of the emitting electronic state. The FWHM of the band rises from 35 to 62 nm with the temperature due to the increase of the number of $m \rightarrow n$ vibronic transitions. At room temperature, the emission band peaks at 534 nm, and its FWHM is equal to 50 nm.

The temperature variation of the FWHM can be described by using the configuration coordinate model and the Boltzmann distribution according to the following equation proposed in [15]:

$$\text{FWHM}(T) = \sqrt{8 \ln 2} \times h\nu \times \sqrt{S} \times \sqrt{\coth\left(\frac{h\nu}{2kT}\right)},$$

where $h\nu$ is the mean phonon energy, S the Huang–Rhys parameter and k the Boltzmann

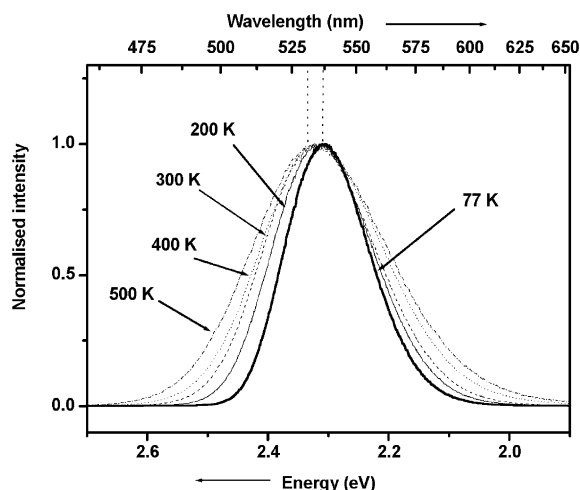


Fig. 6. Emission spectra of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder at different temperatures from 77 to 500 K with excitation at 420 nm.

constant. This equation can be used only when the parabolas of the ground state and the excited state have the same curvature: the best fit was obtained with $S = 3.8 \pm 0.2$ and $h\nu = 36 \pm 1$ meV (Fig. 7). These values enable to evaluate the Stokes shift at 0.24 ± 0.02 eV (2000 ± 200 cm⁻¹), which is coherent with those determined by other methods in the first and second points. However, this third method provides the most accurate values, hence we will use in the following text, the values $S = 3.8 \pm 0.2$, $h\nu = 36 \pm 1$ meV and $\Delta S = 0.24 \pm 0.02$ eV (2000 ± 200 cm⁻¹).

Fig. 8 represents the integrated intensity as a function of the inverse of the temperature for excitation wavelength at 420 nm (excitation within the band C, in the 4f⁶5d (a₁) level). From 350 K, the integrated PL intensity decreases with increasing temperature due to strong thermal quenching. The quenching temperature, for which the intensity is half of the maximum intensity, can be evaluated at 470 K. The slow increase of the intensity from 250 to 350 K can be explained by the trapping effect. The kinetic study of the luminescence has enabled us to characterize the thermal quenching process. Fig. 9 shows the luminescent decay curves for the emission at 535 nm and an excitation at 420 nm for different temperatures between 77 and 500 K. At 77 K, the

luminescent decay is represented by an exponential curve over three decades with a time constant equal to 480 ± 20 ns. At higher temperatures, the decay curves are composed of a short first non-exponential part, due to thermally enhanced energy transfer to defects, followed by an exponential one. The decay time $\tau(T)$ of the exponential part remains constant at 480 ns up to 350 K, then decreases to 150 ns at 500 K (Fig. 8). The temperature dependence of the decay time is the same whatever the Eu²⁺ concentration from 0.1% up to 10%. By considering that the non radiative processes are negligible from 77 up to 350 K, we can estimate that the value of 480 ns corresponds to the radiative decay time τ_0 of the Eu²⁺ ions in SrGa₂S₄. This value is coherent with those given in literature [2]. Beyond 350 K, the strong decrease of the decay time means that non-radiative processes dominate. The decay time $\tau(T)$ is given by

$$\frac{1}{\tau(T)} = \frac{1}{\tau_0} + \frac{1}{\tau_{nr}(T)},$$

where τ_0 and τ_{nr} are, respectively, the radiative and non-radiative decay times.

The insert in Fig. 8 illustrates the temperature variation of the non-radiative decay rate ($W_{nr} = 1/\tau_{nr}$). The fit was done assuming that the non-radiative decay rate varies following an Arrhenius law:

$$W_{nr} = A \exp\left(-\frac{\Delta E}{kT}\right),$$

where k is the Boltzmann constant, ΔE the activation energy of the thermal quenching and A a constant. The best fit was obtained for $\Delta E = 0.6 \pm 0.1$ eV. This value can be compared with the thermal activation energy of the CaGa₂S₄:Eu²⁺ phosphor [16]. An approximate value of 0.2 eV was obtained by supposing that $1/\tau \approx 1/\tau_{nr} \gg 1/\tau_{rad}$ at high temperatures but a more accurate value (about 0.5 eV) may be found by considering the temperature dependence of $1/\tau_{nr}$.

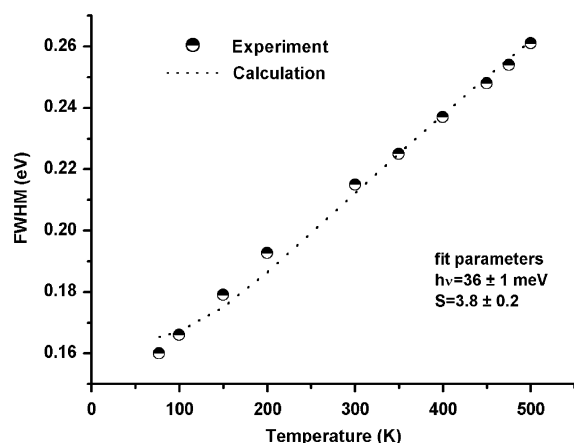


Fig. 7. Experimental (circles) and calculated (broken line) temperature dependence of the FWHM of the emission band measured under excitation at 420 nm for the SrGa₂S₄:Eu²⁺ (0.1%) powder.

4. Discussion

In this study, we have determined some radiative properties very useful to describe the main

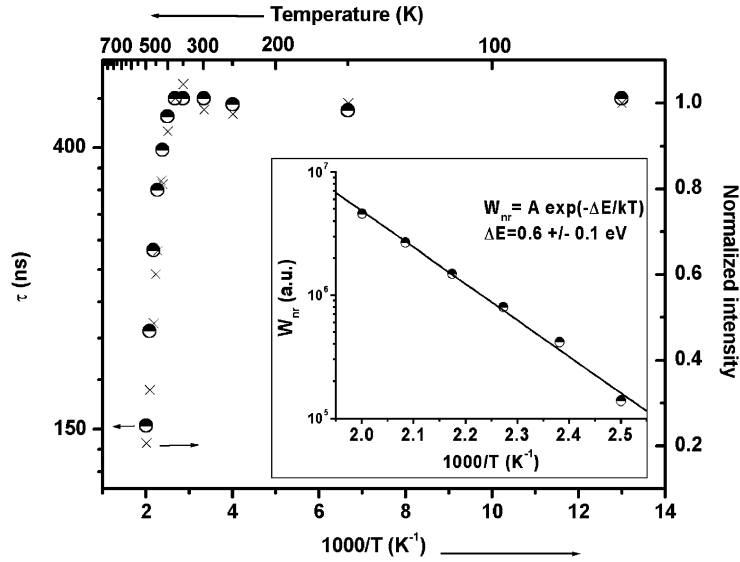


Fig. 8. Temperature dependence of the integrated emission intensity, normalized at the 77 K value (cross) and of the decay time $\tau(T)$ (circles) in the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder under excitation at 420 nm. The insert represents the temperature variation (circles) of the non radiative decay rate W_{nr} . The fit (line) was obtained using an Arrhenius law.

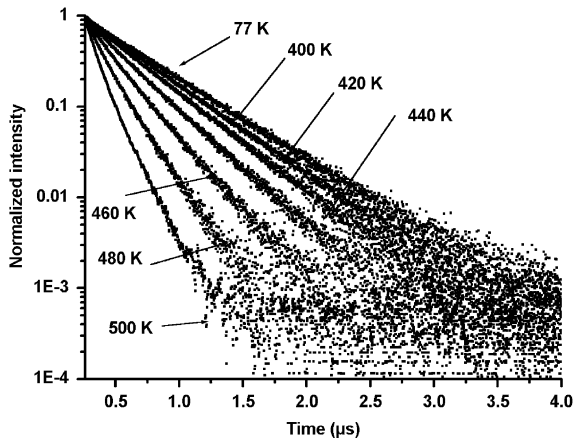


Fig. 9. Influence of the temperature on the PL decay curves for the emission at 535 nm of the $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ (0.1%) powder under excitation at 420 nm.

characteristics of the Eu^{2+} emission in SrGa_2S_4 : the energies of the $f \rightarrow d$ and $d \rightarrow f$ transitions, the crystal field splitting, the redshift, the influence of the lattice vibration properties (electron–phonon coupling, host mean phonon energy), the thermal quenching of the luminescence. In the

discussion, we propose to analyse and compare the results obtained in this work with those presented elsewhere concerning $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ or other $\text{II-Ga}_2\text{S}_4:\text{Eu}^{2+}$ compounds. Results are also used to determine the location of the activator energy levels relative to the host energy levels.

4.1. The redshift and the crystal field splitting

The redshift for the Eu^{2+} transitions in SrGa_2S_4 was estimated at $1.64 \pm 0.05 \text{ eV}$ ($13\,000 \pm 400 \text{ cm}^{-1}$). It is associated to two combined effects: the crystal field which splits the 5d levels and the nephelauxetic effect (or centroid shift) which tends to lower the energy of the 5d levels.

In this work, the crystal field splitting for $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ was estimated at about $16\,000 \text{ cm}^{-1}$. No value concerning the other sulphur ternary compounds exist in literature. For $\text{SrS}:\text{Eu}^{2+}$ [17] and $\text{CaS}:\text{Eu}^{2+}$ [18], the values of $17\,300$ and $18\,750 \text{ cm}^{-1}$, were respectively, reported. The higher crystal field splitting in the binary compounds than in the ternary phosphors nicely demonstrates the effect of the first anion coordination polyhedron symmetry. In SrS , the Eu^{2+} ions are located at the centre of an

octahedron formed by six anions whereas in SrGa_2S_4 coordination is eight-fold with the D_{4d} symmetry. It is known that the splitting of octahedron crystal field Δ_o is larger than this of square anti-prismatic one Δ_{a-p} [19]. The values of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ and $\text{SrS}:\text{Eu}^{2+}$ satisfy the relation: $\Delta_{a-p}=8/9\Delta_o$. The crystal field splitting is higher in CaS than in SrS due to the smaller size of the Ca^{2+} cation and then to the shortest Ca–S bond lengths. From the relation $\Delta_{a-p}=8/9\Delta_o$ and the crystal field splitting in $\text{CaS}:\text{Eu}^{2+}$, we can estimate the crystal field splitting for the yellow emitting $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor at about $\Delta_{a-p} = 16\,700\text{ cm}^{-1}$.

4.2. The Stokes shift and the mean phonon energy

Among the non-radiative transition mechanisms a multiphonon process is often observed between 4f excited levels of rare-earth ions. The non-radiative multiphonon transition probability is dependent on the energy difference between the electronic states ΔE and n , the number of phonons necessary to fill the energy gap. This probability is increasing with the frequency of the high-energy phonons of the lattice. In the case of inorganic ElectroLuminescent (iEL) materials, the cooling of the “hot” electrons is dominated by the electron–phonon coupling. The scattering rate is lower for iEL phosphors presenting low-frequency phonons. For cathodoluminescent (CL) materials the luminescence efficiency is controlled by electron–phonon interaction and decreases with increasing phonon energy [20]. As a consequence, the knowledge of the phonon frequencies and of the electron–phonon coupling (i.e. the value of ΔS) for a given compound is of great interest in order to evaluate the PL, CL or iEL efficiency of Eu^{2+} in this lattice.

We have evaluated the Stokes shift ΔS of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ at $2000 \pm 200\text{ cm}^{-1}$. The value ΔS of the $\text{II-Ga}_2\text{S}_4:\text{Eu}^{2+}$ thiogallate compounds is influenced by the nature of the II cation. It tends to increase with the increasing size of the divalent cation II^{2+} (in the following order Ca, Sr, Ba) from about 2000 cm^{-1} for $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ [1,21,22], $2000 \pm 200\text{ cm}^{-1}$ for $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ [this work] to 2800 cm^{-1} for $\text{BaGa}_2\text{S}_4:\text{Eu}^{2+}$ [1].

We have evaluated the mean phonon energy of SrGa_2S_4 by optical methods; the value $36 \pm 1\text{ meV}$

was found. It is coherent with the results obtained by Raman spectroscopy [23]. In this previous study, the most intense Raman mode of the SrGa_2S_4 spectrum was found at 34.5 meV . In this work, the vibration properties of five orthorhombic $\text{II-Ga}_2\text{S}_4$ compounds (PbGa_2S_4 , SrGa_2S_4 , EuGa_2S_4 , YbGa_2S_4 and CaGa_2S_4) were determined by Raman spectroscopy. We had observed that the effect of the divalent cation mass on the phonon frequencies of orthorhombic thiogallate compounds is negligible and that the vibrations are essentially influenced by the size of the II cation. The phonon energy increases slightly with the decreasing size of the divalent cation in the order Pb, Sr, Eu, Yb and Ca.

4.3. The thermal quenching

Thermal quenching processes of the luminescence can be explained by three different mechanisms: energy transfer up to impurities, non radiative $5d \rightarrow 4f$ recombination and electron or hole transfer between the activator states and the band structure of the lattice:

- (1) Increased energy migration among Eu^{2+} ions up to defects or “killer” centres is a concentration dependent mechanism. Results indicate that the Eu^{2+} concentration up to 10% has no influence on the quenching behaviour. Thus, we conclude that energy transfer until defects is not the preponderant mechanism involved in thermal quenching.
- (2) The thermal quenching cannot be due to internal conversion, i.e. the relaxation to the ground state in a non-radiative manner via the crossing between the fundamental and excited parabolas. Assuming that the mean phonon energy is the same in the two states and using the parameters found previously ($S = 3.8 \pm 0.1$, $E_0 = 2.44\text{ eV}$ and $h\nu = 36 \pm 1\text{ meV}$), we have estimated the cross-point location at about 10 eV above the bottom of the excited state. This high value can be related to the weak Stokes shift. This value is considerably higher than the experimentally obtained value of the thermal quenching activation energy (0.6 eV).

(3) The remaining process to be considered involves the electronic states of the host lattice. Electron or hole transfer between Eu^{2+} levels and matrix bands was already reported to explain the thermal quenching of Eu^{2+} emission in binary or ternary sulphides [8,16]. Two mechanisms of ionisation can be distinguished: the thermal activation of an electron from the Eu^{2+} excited state to the conduction band (mechanism (a)) or the thermal activation of a hole from the Eu^{2+} ground state to the valence band (mechanism (b)). Both models were proposed elsewhere for the thermal quenching of Eu^{2+} in thiogallate. Najafov et al. ascribed the thermal quenching of the Eu^{2+} emission in CaGa_2S_4 to the hole transfer from activator ground state level to the host valence band [16]. Davolos et al. [8] have reported the thermal activation of an electron from 5d level to the conduction band for the Ba-thiogallates. In Ca, Sr or BaS:Eu^{2+} , the thermal quenching was ascribed to the thermal release of an electron from Eu^{2+} to the host conduction band [24]. The actual mechanism depends on the location of the Eu^{2+} electronic levels relative to the valence and conduction bands of the lattice but few data concerning the Eu^{2+} energy levels in the thiogallate compounds exist. In order to find the genuine mechanism of thermal quenching, we have combined some results presented elsewhere with those obtained in this study.

Previous studies concerning the properties of iTFEL devices based on the $\text{SrGa}_2\text{S}_4\text{:Eu}^{2+}$ phosphors can be used to evaluate the location of the first 5d level of the Eu^{2+} ions relative to the conduction band. In EL, distinct mechanisms of excitation are distinguished: direct impact excitation, impact ionisation of the lattice or of the emitting centres. In the latter case, the excited luminescent centres are ionised under high electronic field by delocalisation of the electrons from excited levels to the conduction band. The impact ionisation mechanism is often described by a two-step process: the luminescent centre is excited by impact with hot electrons and subsequently field ionised. The impact ionisation mechanism requires

the proximity in energy of the luminescent centre levels and the conduction band of the lattice. This mechanism was experimentally shown for the Ce^{3+} or Eu^{2+} -doped alkaline earth sulphides (BaS , SrS , CaS) [25] by the observation of two main emission peaks under pulsed electric excitation. The first one appears at the leading edge of the electric pulse and the second at the trailing edge of the voltage pulse. At the end of the voltage pulse, the electrons can move on the opposite direction due to the residual polarisation field (causing the second current peak) and recombine with the ionised emitting centres. The de-excitation of these excited ions leads to the trailing edge emission.

Unlike rare earth-doped alkaline earth sulfides, no second current peak or second emission was observed for SrGa_2S_4 doped with Eu^{2+} or Ce^{3+} [5], which suggests that the excitation is not achieved by impact ionisation. In order to get a deeper understanding of the excitation mechanism, experiments of photonic excitation under an electric field were performed on SrS:Ce^{3+} [26] and on $\text{SrGa}_2\text{S}_4\text{:Eu}^{2+}$ electroluminescent devices [27]. For SrS:Ce^{3+} , photoexcitation in the lower absorption band of the emitting centre at voltage below the EL threshold is followed by a tunnelling delocalisation of the electron in the conduction band: this ionisation leads to a decrease of the PL intensity. On the contrary, no decrease of the emission intensity was observed for $\text{SrGa}_2\text{S}_4\text{:Eu}^{2+}$ even after increasing the applied voltage suggesting that the excited Eu^{2+} ions are not field ionised. The occurrence of field ionisation depends on the position of the excited level with respect to the conduction band. In SrS:Ce^{3+} , the location of the lowest 5d level of Ce^{3+} was evaluated at about 30–50 meV below the conduction band of SrS [28]: the excited level is then little localised and hardly bound so it can release electron to the host conduction band. Attributing the thermal quenching of $\text{SrGa}_2\text{S}_4\text{:Eu}^{2+}$ to the mechanism (a) would mean that the energy difference of 0.6 eV between the first 5d level and the conduction band would be large enough to avoid the excitation by field ionisation. To confirm the mechanism (a), it would be necessary to know the energy value required to prevent 5d electrons from being released and

delocalised under electronic field. By considering the mechanism (b), the first 5d level is located at about 1.5 eV below the conduction band (Fig. 11), hence the excited level is strongly localised. This energy difference is high enough to avoid field ionisation of excited Eu^{2+} ions in SrGa_2S_4 .

Let us now consider the energy of the hot electrons to understand the excitation mechanism in $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$. It was recently shown that the hot electron distribution in $\text{SrS}:\text{Cu},\text{Ag}$ -emitting layers, peaks at energies corresponding to UV range (energy > 3.2 eV) [29]. Assuming that hot electron energies are equivalent in SrGa_2S_4 , the Eu^{2+} thermal quenching mechanism (a) may be rejected. Actually, the mechanism (a) would imply that the Eu^{2+} ground state lies at $2.3 + 0.6 = 2.9$ eV below the SrGa_2S_4 conduction band. Thus, impact excitation with electrons of more than 3 eV should be followed by field delocalisation because electrons are energetic enough to promote Eu^{2+} ions into excited levels located within the conduction band. Only the mechanism (b) can explain the fact that no field ionisation occurs. Assuming that the ground state is located at 0.6 eV above the valence band, the energy difference between the ground state and the conduction band is equal to about $E_g - 0.6 = 3.8$ eV (gap energy $E_g = 4.4$ eV). Energies of hot electrons may be too weak to promote Eu^{2+} ions by impact electrons into excited levels located within the conduction band. Let us consider the electronic structure of $\text{ZnS}:\text{Mn}$ to illustrate this point. The Mn^{2+} ground state is located at about 0.9 eV below the top of the valence band and consequently at $E_g + 0.9 = 4.6$ eV (gap energy $E_g = 3.7$ eV) below the conduction band [30]. This high value compared to hot electron energies explains why the Mn^{2+} ions in ZnS are not excited by ionisation mechanism but by direct impact mechanism. It is highly probable that the energy of 3.8 eV for $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ may be also high enough to explain why no field ionisation occurs under high electronic field.

These EL results may receive arguments to reject the mechanism (a) which are more consistent with the mechanism (b). The mechanism (b) was already reported for the thermal quenching of the yellow-emitting $\text{CaGa}_2\text{S}_4:\text{Eu}^{2+}$ phosphor [16]. However, the quenching mechanism (b) implies

the formation of the Eu^+ ion (Fig. 10) and does not match with the fact that the Eu^{2+} ion is generally described as a hole trap rather than an electron trap. Although the existence of monovalent Eu has been reported for long persistent phosphors such as $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [31] or $\text{CaS}:\text{Eu}^{2+}$, Dy^{3+} [32], the possibility of Eu^+ creation in these compounds was contested by more recent publications [33]. The persistent luminescence of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ was described by a mechanism involving a valence band-assisted transfer of a hole from deep trapping levels to the Eu^{2+} ions via an electron–hole recombination process between intermediate levels provided by lattice defects. The electron and hole traps were identified respectively as oxygen and calcium vacancies. This model may be adapted to explain the thermal quenching of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$.

At this step of the discussion, the results suggest that the model (b) is the most likely mechanism to interpret the thermal quenching in $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$. However, the available information do not enable to confirm this mechanism with certitude. Which means that the question is still open and that further studies are necessary to solve it, for instance photoconductivity measurements on $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ monocrystals.

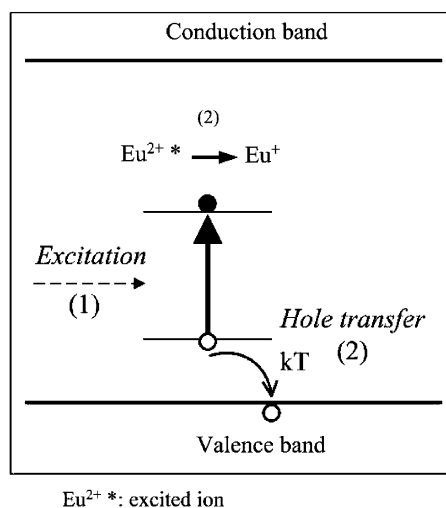


Fig. 10. Illustration of the thermal quenching mechanism involving a thermally activated hole transfer from Eu^{2+} ground state to the SrGa_2S_4 valence band.

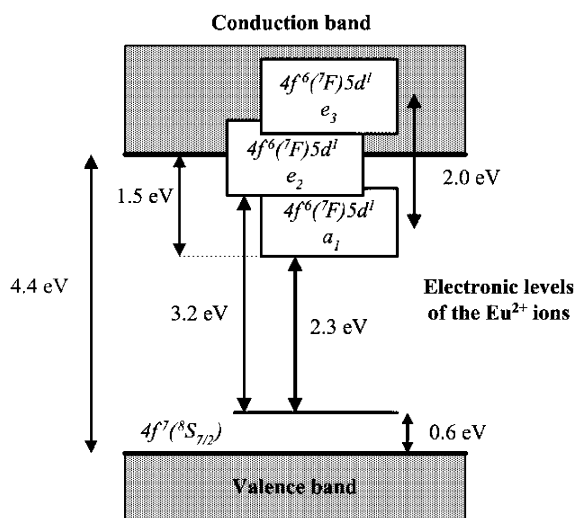


Fig. 11. Energetic scheme representing the location of the Eu^{2+} electronic levels relative with the SrGa_2S_4 valence and conduction band.

Considering the proposed mechanism (b) we can evaluate the energy difference between the $4f^7$ ground level and the top of the valence band to about 0.6 eV, corresponding to the thermal quenching activation energy. From the energy of the excitation and emission bands, the location of the Eu^{2+} electronic levels in relation with the valence and conduction bands of the SrGa_2S_4 host matrix can be determined. We propose the energetic scheme given in Fig. 11. The bottom of the first $4f^65d$ level (a_1) is located at about 1.5 eV below the bottom of the conduction band and the second $4f^65d$ level (e_2) is in part in the bandgap, the other part being located in the conduction band. Thanks to the determination of the crystal field strength, we can evaluate the energy gap between the lower $4f^65d$ level (a_1) and the upper $4f^65d$ level (e_3) to about 2 eV. Thus the upper $5d$ level lies entirely above the bottom of the conduction band.

5. Conclusion

The PL study of $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ was achieved in order to enlarge the understanding of the radiative processes. The crystal field splitting was evaluated

at $16\,000\text{ cm}^{-1}$ (2 eV), the Stokes shift at about 2000 cm^{-1} (0.24 eV) and the activation energy of the thermal quenching at 0.6 eV. Luminescence efficiency of Eu^{2+} -doped SrGa_2S_4 is little affected by thermal quenching: the quenching temperature has been estimated at 470 K. The thermal quenching is described by a mechanism based on the energy transfer between the Eu^{2+} levels and the band structure of the lattice. Considering the results of the recent EL studies in $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$, we propose to explain the thermal quenching of the mechanism involving a thermally activated hole transfer from the Eu^{2+} ground state to the host valence band. An energetic scheme with the location of the Eu^{2+} levels with respect to host lattice bands is given. This information is very useful to preview the energy transfer between the Eu^{2+} ions and the host lattice.

This study confirms that $\text{SrGa}_2\text{S}_4:\text{Eu}^{2+}$ is a well suitable phosphor in lighting and display devices especially for applications where heat effects are expected (FED, TV-projection, SSL).

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