Luminescent characterization of CaAl$_2$S$_4$:Eu powder

J.E. Van Haecke*, P.F. Smet, D. Poelman

Department of Solid State Sciences, Ghent University (UGent), Krijgslaan 281-S1, B-9000 Ghent, Belgium

Received 29 October 2005; received in revised form 8 June 2006; accepted 2 October 2006

Available online 13 November 2006

Abstract

The photoluminescent (PL) emission and excitation behaviour of green-emitting CaAl$_2$S$_4$:Eu$^{2+}$ powder phosphor is reported in detail. CaAl$_2$S$_4$:Eu$^{2+}$ emission provides good CIE colour coordinates ($x = 0.141; y = 0.721$) for the green component in display applications. Powder with a dopant concentration of 8.5 mol% shows the highest luminescence efficiency. Temperature dependence of the radiative properties, such as luminescence intensity and decay time, was investigated. In particular, the Stokes shift, the mean phonon energy, the redshift, the energy of the f→d and d→f transition and the crystal field splitting of the CaAl$_2$S$_4$:Eu$^{2+}$ emission were determined. The thermal quenching of the emission was examined.

© 2006 Elsevier B.V. All rights reserved.

PACS: 71.70.d; 78.40.Fy; 78.55.−m

Keywords: Luminescence; Europium; Ternary compounds

1. Introduction

Inorganic electroluminescence (iEL) is a very promising technique for full-colour flat panel display applications. iEL devices present many attractive features, such as ruggedness, wide-viewing angles, a large operating temperature range, fast response time and scalability [1]. However, to obtain a full-colour display, red, green and blue-emitting phosphors with suitable colour coordinates are necessary. Owing to the lack of a satisfying blue-emitting phosphor, the commercial breakthrough of full-colour devices was postponed for several years. In 1999, Miura introduced a ternary inorganic compound, BaAl$_2$S$_4$:Eu, as a bright and saturated blue-emitting phosphor for full-colour EL devices [2]. This enormous progress of the blue phosphor even led to the development of the ‘colour-by-blue’ (CBB) technique proposed by iFire Company [3]. CBB has further simplified the already simple manufacturing process of thick dielectric electroluminescent (TDEL) displays and also accelerated iFire’s development of the world’s first full-colour 34-inch inorganic electroluminescent television screen. Nevertheless, many lighting applications require green, red and/or blue-emitting phosphor materials. As a blue-emitting phosphor, BaAl$_2$S$_4$:Eu has demonstrated sufficient stability and luminance. CaS:Eu has been investigated as saturated red-emitting phosphor [4]. For the green emission, CaAl$_2$S$_4$:Eu is a promising material. In this way, the three phosphors red, blue and green, needed for full-colour applications, can be obtained by changing only the host.

The ternary compounds II-III$_2$S$_4$ doped with rare-earth ions have been studied for several years and were found to be very attractive for lighting and display applications, such as field emission display (FED) [5], wavelength converters in phosphor-converted light-emitting diodes (LEDs) for solid-state lighting [6] and most importantly iEL [7–9]. Le Thi et al. [10] investigated different MS-Al$_2$S$_3$ systems (M = Ca, Sr, Ba) and described some luminescence properties of Eu$^{2+}$ as dopant in these thioulanates. The II-III$_2$-(S,Se)$_4$ ternary compounds were introduced as phosphors for thin-film electroluminescence (TFEL) by Benalloul et al. [11]. In particular, thiogallates doped with rare-earth ions, such as Ce$^{3+}$ and Eu$^{2+}$, have been studied for full-colour TFEL displays [9,12–14].
Aim of this paper is to investigate in detail CaAl$_2$S$_4$:Eu as a green-emitting phosphor. Eisenmann reported that CaAl$_2$S$_4$ exhibits an orthorhombic crystal structure with space group Fddd and lattice constants $a = 2016.3$ pm, $b = 2005.2$ pm and $c = 1202.6$ pm [15]. The Ca$^{2+}$ ions occupy three different sites, two with symmetry $D_2$ and one with symmetry $C_2$. The Ca–S distances of the former are in a similar range with an average of 298 pm, while the Ca–S distances of the latter are slightly longer (306 pm on average). Although different Ca sites are present, only one emission band has been reported by Le Thi et al. [10]. This characteristic has been observed for other homologous thioaluminate [16] and thiogallate phosphors [7] as well. CaAl$_2$S$_4$:Eu has been reported as a promising green-emitting thin film phosphor for EL applications with excellent colour coordinates [7]. The CaAl$_2$S$_4$:Eu EL emitting thin film phosphor for EL applications with more, the optimal europium concentration in CaAl$_2$S$_4$ was discussed. The influence of the temperature on the coupling (i.e. the value of the phonon frequencies and of the electron–phonon symmetry $C_2$. The Ca–S distances of the former are in a similar range with an average of 298 pm, while the Ca–S distances of the latter are slightly longer (306 pm on average). Although different Ca sites are present, only one emission band has been reported by Le Thi et al. [10]. This characteristic has been observed for other homologous thioaluminate [16] and thiogallate phosphors [7] as well. CaAl$_2$S$_4$:Eu has been reported as a promising green-emitting thin film phosphor for EL applications with excellent colour coordinates [7]. The CaAl$_2$S$_4$:Eu EL devices showed high luminance of 3041 cd/m$^2$ at a driving frequency of 1 kHz and exhibited a broad emission peak with its maximum at about 518 nm [17].

While CaAl$_2$S$_4$:Eu is a very good green-emitting phosphor material, relatively little fundamental information about this phosphor is available. To enlarge the fundamental understanding of the mechanisms involved in the luminescence process, the emission wavelength, the Stokes shift $\Delta S$ and the redshift $D$ related to the Eu$^{2+}$ emission in CaAl$_2$S$_4$:Eu powder are determined in the present paper, based on the single configuration coordinate model [18]. Knowledge of the phonon frequencies and of the electron–phonon coupling (i.e. the value of $\Delta S$) is of great interest in order to model and evaluate the EL efficiency of Eu$^{2+}$ in this lattice. In the case of iEL materials, the cooling of ‘hot’ electrons is dominated by the electron–phonon coupling to the high-frequency modes. The scattering rate is lower for iEL phosphors presenting low-frequency phonons [9,19].

In this paper, the excitation spectrum, the emission spectrum and the PL decay curves of the CaAl$_2$S$_4$:Eu$^{2+}$ powder were analysed. The influence of the temperature on the luminescence characteristics was investigated. Furthermore, the optimal europium concentration in CaAl$_2$S$_4$ was determined. By comparing these results with data available in literature, the radiative properties of CaAl$_2$S$_4$:Eu$^{2+}$ are discussed.

2. Experimental procedure

To obtain polycrystalline CaAl$_2$S$_4$:Eu powder, stoichiometric amounts of commercially available CaS (Cerac, 99.999%), Al$_2$S$_3$ (Cerac, 99.9%) and EuF$_3$ (Alfa Aesar, 99.5%) were thoroughly mixed in a mortar under protective nitrogen atmosphere, to maintain the purity of the highly reactive aluminium sulphide powder. The mixture was sintered in an alumina crucible in a tube furnace under continuous flow of H$_2$S [16]. The powders were kept at 1000 °C during 2 h. If a second sintering was required, the powders were recuperated and ground under a protective nitrogen ambient before the second sintering.

This preparation method is different from that reported by Le Thi et al. [10], who used carbonates or sulphates, Eu$_2$O$_3$ and Al$_2$S$_3$ as starting materials to prepare thioaluminate powders. The sulphides were obtained by heating the carbonate or the sulphate in a H$_2$S or H$_2$ stream at 1000 °C. Eu$_2$O$_3$ was converted to EuS by H$_2$S at 900 °C. It was not mentioned whether calcium carbonate or calcium sulphate was used to prepare CaAl$_2$S$_4$:Eu powder. The synthesis reactions were performed in silica tubes sealed under vacuum. Oh et al. [20] prepared CaAl$_2$S$_4$ single crystals by a chemical transport reaction method in a closed system using high-purity iodine as a transport agent. Sealed quartz ampules, containing the starting materials under vacuum, were placed in a furnace for a process of 12 days to obtain single crystals. The method used in the present work provides powders with good crystalline properties as shown by X-ray diffraction (XRD) measurements and avoids the complication of using sealed quartz tubes.

Several techniques were used to evaluate the properties of the powder phosphors. The crystal structure of the powders was determined by $\theta$–20 XRD (Siemens D5000, CuK$\alpha$ radiation) measurements. Photoluminescent (PL) excitation and emission spectra were recorded with a steady-state fluorescence spectrometer (Edinburgh Instruments FS920). Emission characteristics at low temperature were studied by using a cold-finger cryostat using liquid nitrogen. Time-resolved emission measurements were obtained with an intensified CCD (Andor Instruments) attached to a Jarrell-Ash 0.5 m Ebert-monochromator. PL decay measurements were performed using a pulsed nitrogen laser (337 nm, pulse length of 800 ps).

3. Results

3.1. Structural characterization

The XRD spectrum of the sintered powder (Fig. 1) shows the orthorhombic structure of CaAl$_2$S$_4$. This result corresponds with earlier data on the structure of CaAl$_2$S$_4$ [7,10,15]. When the mole ratio of CaS and Al$_2$S$_3$ differs from 1, the starting binary sulphides can be present as a separate phase in the resulting powder. In the XRD spectrum of CaAl$_2$S$_4$, sintered in a H$_2$S atmosphere for 2 h at 1000 °C, we notice that trace amounts of CaS and Al$_2$O$_3$ are left. Small amount of CaS:Eu in the sintered powder has an negligible emission, as it has a low efficiency at Eu concentration higher than 0.2 mol% [21].

Presence of Al$_2$O$_3$ is most probably due to oxidation of a small part of the aluminium sulphide in the starting material. Aluminium sulphide is extremely sensitive to moisture. Even a short exposure to air leads to a noticeable deterioration of the powder. The aluminium oxide phase is very stable. So, when sulphur is substituted by oxygen, it is practically irreversible under the used sintering conditions. Re-sintering of the powder did not result in a better stoichiometry. However, the presence of a small amount of
Al₂O₃ in the powder has no influence on the PL emission characteristics. Al₂O₃:Eu powder is characterized by Eu³⁺ emission lines, which were not seen in the emission spectra [18].

No notable shifts of the diffraction lines of CaAl₂S₄ powder were observed, indicating that no significant substitution of sulphur ions by oxygen ions occurs. As CaAl₂O₄ has a monoclinic crystal structure, it is difficult to predict, using Vegard’s law, how partial substitution of sulphur by oxygen in CaAl₂S₄ would influence the position of the XRD peaks.

### 3.2. Luminescence characteristics: emission spectrum

The emission spectrum of CaAl₂S₄:Eu powder (1 mol% Eu) at 70 K presents a broad emission band centred at 520 nm (2.38 eV) with a full-width at half-maximum (FWHM) of 27 nm (Fig. 2). The emission spectrum confirms the absence of CaS:Eu in the powder, as no emission peak is seen at 650 nm. CaAl₂S₄:Eu emission is ascribed to the dipole-allowed transition from the lower 4f⁶ (7F) 5d¹ state to the 4f⁷ (8S⁷/₂) ground state of the Eu²⁺ ions [22].

As explained in the introduction, the Ca²⁺ ions occupy three different sites, one with symmetry C₂ and two with symmetry D₂, the latter having very similar Ca–S distances. For these different sites of the Ca²⁺ ions, a different crystal field splitting might be expected. Nevertheless, CaAl₂S₄:Eu powder shows only one emission band. When the excitation wavelength was varied, no shift of the emission band was observed. This behaviour has been observed for other homologous thioaluminate [10,16] and thiogallate phosphors [7] as well. It could be an indication that the Eu²⁺ ions preferentially substitute one Ca²⁺ ion site.

The shape of the emission spectrum is characteristic of a phonon-broadened emission that can be described by using the single configuration coordinate model [18]. The emission band is considered to be composed of vibronic transitions, i.e. transitions from the vibrational level of the excited electronic state (m) to the vibrational level of the ground electronic state (n). In first approximation, we assume that only the ground vibrational level of the excited electronic state (m = 0) is occupied at 70 K. If m = 0, the transition probability is given by the relation [18]

\[ W_{n0} = S^n e^{-S/n!} \]

The emission intensity of CaAl₂S₄:Eu powder is proportional to this transition probability \( W_{n0} \). The Huang–Rhys parameter, \( S \), measures the number of emitted phonons accompanying the optical transition \( m = 0 \to n \). The energy gap between two vibronic levels is equal to the phonon energy \( h \nu \). If we assume that the phonon energy is the same for the 4f⁷ (8S⁷/₂) ground state as for the 4f⁶ (7F) 5d¹ excited state, we can determine the Stokes shift \( \Delta S \) from the emission peak shape. This method has been used previously for other phosphor materials [12,13]. It is known that the emission peak is located at an energy corresponding to \( n \geq S \) [18]. The fit of the emission spectrum was performed with \( S = 4.5 \pm 1 \) and \( h \nu = 25 \pm 4 \text{ meV} \). This \( S \) value corresponds to an intermediate electron–phonon coupling and can be linked to the slight asymmetry of the emission band. The Stokes shift is the difference between the absorption and emission energy and can be calculated from the above values as \( \Delta S = (2S-1)h \nu = 0.20 \pm 0.06 \text{ eV} \).

![Fig. 1. (a) The calculated XRD pattern of CaAl₂S₄ (ASTM file 01-077-1186) and (b) the experimental XRD spectrum of CaAl₂S₄, sintered in a H₂S atmosphere for 2 h at 1000 °C. The expected positions of XRD lines of Al₂O₃ and CaS are indicated by dots and squares, respectively.](image)

![Fig. 2. Emission spectrum of CaAl₂S₄:Eu powder (1 mol% Eu) at an excitation wavelength of 400 nm, measured at room temperature (293 K) and at 70 K.](image)
3.3. Luminescent characteristics: excitation spectrum

The excitation spectrum of CaAl<sub>2</sub>S<sub>4</sub>:Eu powder for the emission at 520 nm at 70 K is presented in Fig. 3. The centre of the first excitation band in the visible part of the spectrum is located at about 426 nm (2.89 eV). A second excitation band is at about 347 nm (3.57 eV). Both excitation bands are due to the 4f<sup>7</sup> (8S<sub>7/2</sub>) → 4f<sup>6</sup> (7F) 5d<sup>1</sup> transitions in Eu<sup>2+</sup> electronic levels.

In the CaAl<sub>2</sub>S<sub>4</sub>:Eu compound, part of the Ca<sup>2+</sup> ions is substituted by Eu<sup>2+</sup> ions. The Ca<sup>2+</sup> ions occupy three slightly different sites with C<sub>2</sub> and D<sub>2</sub> symmetry as mentioned in the introduction [23,24]. These low-symmetric sites can be approximated as centres of square anti-prismatic sites formed by the eight S<sub>2</sub>/C<sub>0</sub> anions, with D<sub>4d</sub> symmetry. In this D<sub>4d</sub> symmetry, the 5d orbitals of the Eu<sup>2+</sup> ions are split in three levels (Fig. 4) [25]. Transitions to the lowest Eu<sup>2+</sup> levels give rise to the first (a<sub>1</sub>) and second (e<sub>2</sub>) excitation bands in CaAl<sub>2</sub>S<sub>4</sub>:Eu powder (Fig. 3). By evaluating the energy gap between the excitation bands (a<sub>1</sub>) and (e<sub>2</sub>) as 0.7 eV, the crystal field strength Δ<sub>a1-e2</sub> = 8.9D<sub>q</sub> can be estimated at 1.4 eV (Fig. 4). This crystal field strength is weaker than in CaS (2.3 eV) due to the presence of trivalent ions [26]. This is confirmed by the higher Ca–S mean value bond lengths in CaAl<sub>2</sub>S<sub>4</sub>:Eu (0.302 nm) than in CaS:Eu (0.284 nm). The crystal field strength of 1.4 eV implies that the centre of the third excitation band (e<sub>3</sub>) is located at about 4.3 eV. However, these transitions are partly masked by transitions between the valence band and the conduction band of the CaAl<sub>2</sub>S<sub>4</sub>:Eu host. This band gap excitation has a low efficiency for CaAl<sub>2</sub>S<sub>4</sub>:Eu powder. Furthermore, mixing of the highest Eu<sup>2+</sup> excitation levels with the conduction band levels will reduce the excitation efficiency.

In the first excitation band, a characteristic ‘staircase’ structure of the Eu<sup>2+</sup> absorption is present. This structure is due to spin–orbit coupling in the 4f<sup>6</sup> configuration leading to the splitting of the 7F level in seven levels: 7F<sub>J</sub> with J = 0–6. In the excitation spectrum (Fig. 3), we observe only 6 maxima instead of 7. The energy differences between the maxima, which are not equidistant, are in good agreement with those of the 7F<sub>J</sub> levels derived from the 4f<sup>6</sup> configuration of the free Eu<sup>3+</sup> ion [27]. The energy difference between two successive 7F<sub>J</sub> levels is approximately 0.12 eV, except for the first maxima (J = 0, 1), where it is equal to about 0.05 eV. Therefore, these two maxima are not observed separately in the excitation spectrum.

By using the mirror–image relationship between the emission and the excitation spectrum (Fig. 3), we can estimate the position of the lowest excited level of the 4f<sup>6</sup> 5d<sup>1</sup> state (7F<sub>0</sub> level). This relationship is characteristic of a phonon-broadened emission with the same phonon energy for both the ground and excited states [18]. The mirror–image of the emission spectrum fits the low-energy side of the excitation spectrum. The energy of the zero-phonon line E<sub>0</sub> at the intersection of the emission and excitation spectrum can be determined as 2.46 eV. As the emission spectrum peaks at 520 nm (2.38 eV), we found from the mirror–image relationship absorption energy of 484 nm (2.54 eV). This absorption energy E<sub>abs</sub> of the f → d transition corresponds to the energy of the first step of the ‘staircase’ structure.

The energy between the lowest 4f<sup>7</sup> (8S<sub>7/2</sub>) level and the first 4f<sup>6</sup> (7F<sub>0</sub>) 5d<sup>1</sup> level is lowered from the free electron value when the Eu<sup>2+</sup> ion is brought into a crystal environment. The effect of the host crystal on this energy difference is expressed by the redshift Δ and the Stokes...
shift $\Delta S$. The energy of $f \rightarrow d$ absorption and of the $d \rightarrow f$ emission can be written respectively, as [28]

$$E_{\text{abs}} = E_{\text{free}} - D \quad \text{and} \quad E_{\text{em}} = E_{\text{free}} - D - \Delta S.$$  

$E_{\text{free}}(\text{Eu}^{2+}) = 4.19 \text{eV}$ [29] is the energy of the $f \rightarrow d$ transition for free (gaseous) Eu$^{2+}$ ions. The emission spectrum of CaAl$_2$S$_4$:Eu powder provides the value of the emission energy, $E_{\text{em}} = 2.38 \text{eV}$. Using the mirror–image relationship, we found absorption energy $E_{\text{abs}}$ of 2.54 eV. The Stokes shift can be calculated as $\Delta S = E_{\text{abs}} - E_{\text{em}} = 0.16 \text{eV}$. Using the first equation, we determined the value of the redshift as $D = 1.65 \text{eV}$. When we compare this calculated value with the redshift of the Eu$^{2+}$ emission in other earth alkaline thioualuminates such as SrAl$_2$S$_4$ ($D = 1.58 \text{eV}$) and BaAl$_2$S$_4$ ($D = 1.29 \text{eV}$), we notice that the value of the redshift is influenced by the nature of the II-cation. It tends to decrease with increasing size of the cation (Ca $<$ Sr $<$ Ba) [28]. The redshift is associated with two effects: the crystal field that splits the 5d levels and the nephelauxetic effect, which tends to lower the energy of the 5d levels. The effect of the host matrix on the Eu$^{2+}$ PL emission is clearly seen when we compare the emission spectra of these three compounds [10].

### 3.4. Influence of the temperature

With increasing temperature, we notice a shift of the emission spectrum to shorter wavelengths due to the nephelauxetic effect, as seen in Fig. 5. This effect implies that when the temperature rises, the vibration of the ions increases, resulting in a lower crystal field. Owing to the dependency of the 4f$^0$ (1$F$) 5d$^1$ excited state of the Eu$^{2+}$ ions on the surrounding crystal field, the emission spectrum shifts to shorter wavelengths [4,7]. As the temperature rises from 70 to 310 K, the wavelength of the peak emission decreases from 520 (2.38 eV) to 515 nm (2.39 eV) under excitation at 400 nm and the FWHM increases from 27 to 40 nm due to an increase of $m \rightarrow n$ vibronic transitions.

At room temperature (293 K), CaAl$_2$S$_4$:Eu emission has an emission maximum at 516 nm (2.39 eV) and the FWHM of the emission band is equal to 39 nm (Fig. 2). The CIE colour coordinates (Commission Internationale de l’Eclairage, 1931) are (0.14; 0.721), which comes down to pure green emission.

The temperature dependence of the FWHM of the emission spectrum of the CaAl$_2$S$_4$:Eu powder can be described by using the single configuration coordinate model and the Boltzmann distribution according to the following equation proposed in [28]

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

The FWHM is related to the mean phonon energy $h \nu$, the Huang–Rhys parameter $S$, the absolute temperature $T$ and the Boltzmann constant $k$. This equation only holds for the case that the phonons in the ground state and the excited have the same angular frequency as supposed earlier. The best fit was obtained with $S = 4.8 \pm 0.5$ and $h \nu = 24 \pm 1 \text{meV}$, leading to a Stokes shift of 0.21 ± 0.02 eV. This value of the Stokes shift is comparable with the one previously obtained by fitting the emission spectrum; however, the method used here is a more accurate method. By using the mirror–image relationship, we obtained a Stokes shift of about 0.16 eV, which is somewhat lower than the other two values. The Stokes shift of BaAl$_2$S$_4$:Eu is 0.32 eV, determined by Barthou et al. [30] using a similar method. This value is higher compared to the Stokes shift of CaAl$_2$S$_4$:Eu, which is comparable to the behaviour of the thiogallates, showing an increase of the Stokes shift with increasing size of the II-cation.

The value of the phonon energy is in the same range as the one calculated previously from the fit of the emission spectrum of CaAl$_2$S$_4$:Eu. Barthou et al. [30] determined the phonon energy of BaAl$_2$S$_4$ using two separate methods, namely optical methods and Raman spectroscopy. With optical methods, similar to ours, a value of 31 ± 2 meV was obtained. In the Raman spectrum, two vibration lines at very close similar energy (∓ 40 meV) dominated the spectrum.

In the inset of Fig. 5, the integrated PL emission intensity as a function of the inverse of the temperature is presented. The emission intensity only slightly decreases with increasing temperature. At 310 K, the integrated PL emission intensity still reaches 97% of the maximum intensity. According to Le Thi et al. [10], the quenching temperature, for which the intensity is half of the maximum intensity, was evaluated at about 350 K. They reported a thermal quenching in the order of 20% at 310 K, which is stronger compared to the thermal quenching of 3% of our powder at the same temperature. In our set-up, it was not possible to reach temperatures higher than 310 K.

The CaAl$_2$S$_4$:Eu powder (0.2 mol% Eu) was excited at 337 nm, provided by a pulsed nitrogen laser. The change of the emission intensity of the powder was measured with the
intensified CCD after excitation with the laser pulse. The decay profile of the CaAl$_2$S$_4$:Eu powder is only slightly influenced by the temperature (Fig. 6). The main part of the decay curve is characterized by a single exponential decay, with a time constant of 0.40 μs. During the first 0.3 μs after excitation, the decay is slightly faster, an effect which is enhanced at room temperature. The main decay constant of 0.40 μs is comparable to other Eu-doped thiogallates and thioaluminates [30].

3.5. Influence of the europium concentration

The influence of the europium concentration on the luminescence process was investigated and the optimum concentration of europium in CaAl$_2$S$_4$ was determined. The europium concentration was varied from 0.2 to 10 mol%. The PL emission intensity was the highest for CaAl$_2$S$_4$ doped with 8.5 mol% Eu (Fig. 7). Both the FWHM of the emission spectra (about 39 ± 1 nm for all the spectra recorded) and the position of the emission maxima are not influenced by the Eu concentration. At room temperature (293 K), the PL decay curves are characterized by a single exponential decay, with a decay constant of 0.40 μs, independent of the Eu concentration. At the beginning of the decay curves, a fast decay component is present. These data indicate no influence of non-radiative transitions on the decay of Eu$^{2+}$ in CaAl$_2$S$_4$. The observed concentration quenching is comparable to the results found in literature. Djazovski reported an optimum Eu concentration of about 2 mol% in BaAl$_2$S$_4$:Eu [26]. Le Thi reported an Eu concentration of 12 and 10 mol% for SrAl$_2$S$_4$:Eu and CaAl$_2$S$_4$:Eu, respectively [10]. The low self-quenching for the calcium and strontium phases was related to the fact that these materials are isostructural with EuAl$_2$S$_4$.

The quantum efficiency of the CaAl$_2$S$_4$:Eu powder with 8.5 mol% Eu was estimated to be about 10%. This is somewhat lower than the efficiencies of 8% and 24% for, respectively, 1 mol% Eu and 12 mol% Eu, as published by Le Thi et al. [10]. However, the luminescence intensity of the powder decreases upon exposure to air, which is a known effect for thioaluminates. Therefore, if one wants to prepare stable CaAl$_2$S$_4$:Eu powders or thin films, encapsulation will be necessary to prevent reaction with moisture.

4. Conclusions and perspectives

A PL study of the green-emitting CaAl$_2$S$_4$:Eu phosphor was made. Excitation and emission spectra were examined with the aim to enlarge the knowledge about the Eu$^{2+}$ emission in CaAl$_2$S$_4$:Eu powder phosphor. By applying the single configuration coordinate model, we determined several radiative properties of the Eu$^{2+}$ emission in CaAl$_2$S$_4$, such as the Stokes shift, the mean phonon energy, the redshift, the energy of the f→d and d→f transition and the crystal field splitting.

The crystal field splitting of Eu$^{2+}$ in CaAl$_2$S$_4$:Eu was estimated at about 1.4 eV. The Huang–Rhys parameters $S$ was determined as $S = 4.8 ± 0.5$, corresponding to an intermediate electron–phonon coupling regime. We have evaluated the mean phonon energy for CaAl$_2$S$_4$ compound at about 24 ± 1 meV. This study allowed comparison of the properties of this green phosphor with other ternary sulphide compounds doped with Eu$^{2+}$ ions recently studied.

We obtained green-emitting CaAl$_2$S$_4$:Eu with a simple and cheap preparation method. The next step would be to
prepare CaAl$_2$S$_4$:Eu thin films, which could be incorporated and studied in EL devices.

Acknowledgements

PFS is a post-doctoral researcher for the BOF-UGent. JVH is a doctoral researcher for the BOF-UGent. This research is partially sponsored by FWO-Vlaanderen.

References


