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Structure and luminescence of Eu-doped $(\text{Ca,Sr})_2\text{SiS}_4$ phosphors

Structure and luminescence of $(\text{Ca,Sr})_2\text{SiS}_4\text{:Eu}^{2+}$ phosphors

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$\text{Sr}_2\text{SiS}_4\text{:Eu}^{2+}$, $\text{Ca}_2\text{SiS}_4\text{:Eu}^{2+}$ and the solid solution of both, europium-doped $(\text{Ca,Sr})_2\text{SiS}_4$, were investigated as UV-VIS excitable green to red powder phosphors. $\text{Sr}_2\text{SiS}_4\text{:Eu}^{2+}$ shows two emission bands, peaking at 480 nm and 550 nm. By changing the ratio between Ca^{2+} and Sr^{2+} , the photoluminescent emission spectrum can be tuned. Using X-ray diffraction, the phase composition and lattice parameters of the thiosilicate compounds were determined. The material forms a single, monoclinic Sr_2SiS_4 -like phase up to 40% substitution of Sr^{2+} by Ca^{2+} . From 50% to 90% of substitution by Ca^{2+} , phase separation was observed, leading to more complex emission spectra. These spectra were studied in detail using photoluminescence spectroscopy, cathodoluminescence microscopy and temperature dependent optical measurements. The thermal quenching temperature decreases from 470 K in $\text{Ca}_2\text{SiS}_4\text{:Eu}^{2+}$ to 380 K in $\text{Sr}_2\text{SiS}_4\text{:Eu}^{2+}$ upon increasing substitution of Ca^{2+} by Sr^{2+} . The possibilities of these materials as wavelength converters for white LEDs were evaluated.

Keywords: thiosilicates, europium, light-emitting diodes

1 Introduction

The possible energy savings associated with the replacement of incandescent light bulbs (and even fluorescent tubes) by light emitting diodes (LEDs) have triggered new efforts in phosphor research [1]. The appropriate combination of a blue or near-UV LED with a single phosphor or a mixture of phosphors should lead to energy efficient lighting devices, with good colour rendering and wide colour temperature range. Europium doped sulfide phosphors have gained renewed attention as alternatives for oxide phosphors, because they are more suited to obtain saturated red emission [2]. The thiosilicate materials Ba_2SiS_4 [3] and Ca_2SiS_4 [3, 4] were recently investigated for use as phosphor hosts in white phosphor

converted LEDs (pcLEDs). A third phosphor in this series, Sr₂SiS₄, has not been studied since the work on cathodoluminescence of thiosilicate materials by Avella [5] and Olivier-Fourcade [6] in the early 19-seventies. Because the recent studies on the other thiosilicates shed a substantially new light on the photoluminescent (PL) behaviour of these materials, it seems suited to reconsider Sr₂SiS₄ as well. As the results on (Ca,Eu)-thiosilicates [4] point out the very interesting possibility of tuning the PL characteristics by changing the composition, in the current work, a series of europium-doped (Ca,Sr)-thiosilicates are prepared and investigated. Phase compositions and lattice parameters are investigated and optimized using Rietveld refinement. Photoluminescence excitation and emission spectra are recorded, and sample homogeneity is studied using cathodoluminescence spectroscopy in a scanning electron microscope (SEM-CL). Finally, the thermal quenching behaviour of the luminescence is investigated, as this is an important criterion when phosphors are to be used as wavelength convertors for white light LEDs.

2 Experimental

All powders are synthesized by sintering a homogeneous mixture of stoichiometric amounts of SrS (Alfa Aesar, 99.9%), CaS (CERAC 99.99%), EuF₃ (Alfa Aesar, 99.5%) and Si (Alfa Aesar, 99.9%) in a continuous H₂S-flow at 875°C for 1 hour. Hydrogen sulfide is used as a source of extra sulfur needed to form the thiosilicate. As suggested in [4], a slight surplus of Si (5%) is used. After cooling, the samples are manually ground with a mortar and pestle in order to get a fine powder. Except for the sintering, the processing of the samples is done in ambient air. Samples are prepared with a composition ranging from Sr₂SiS₄ to Ca₂SiS₄, in steps of 10% Sr²⁺-substitution by Ca²⁺. Unless stated otherwise, all samples are doped with 4% Eu²⁺, meaning that 4% of the alkaline earth ions are replaced by Eu²⁺-ions. E.g., a 20% substitution of Sr²⁺ by Ca²⁺ is written as Ca_{0.4}Sr_{1.6}SiS₄:Eu²⁺, implying a doping with Eu²⁺ of 4%.

X-ray diffraction (XRD) measurements are collected with a Bruker D5000 θ -2 θ diffractometer, using Cu-K α radiation. Lattice constants are estimated using a spreadsheet solver and refined with the Rietveld structure refinement program FullProf [7]. The goodness of fit was evaluated graphically [8]. Neither the atomic positions nor the thermal expansion factor were further refined, as this typically requires higher quality XRD spectra. The initial parameters were based on the data available for the similar compounds Ca₂GeS₄ [9] and Eu₂SiS₄ [10].

Photoluminescence spectra are collected using a FS920 fluorescence spectrometer (Edinburgh Instruments). Variation of the measurement temperature (70 K - 475 K) is obtained by an Optistat CF helium cryostat (Oxford Instruments).

Spectrally resolved SEM-CL (cathodoluminescence in a scanning electron microscope) measurements at 10 K were performed in a JSM6400 (Jeol) scanning electron microscope equipped with a helium cryostat.

CL emission spectra were not corrected for the detector sensitivity. Details of the SEM-CL setup can be found here [11].

3 Results

3.1 Sr_2SiS_4

Sr_2SiS_4 was found to be monoclinic with space group $\text{P2}_1/\text{m}$ (11) by Dumail [12]. XRD-measurements (Figure 1) on our undoped samples are consistent with this space group, and the lattice parameters found

Figure 1: XRD pattern of monoclinic Sr_2SiS_4 without Eu^{2+} -doping.

are in good agreement with the ones recorded by Dumail [12] (See **table 1** for an overview of lattice

Table 1: Lattice parameters for Sr_2SiS_4 . The numbers between brackets represent errors on the last digit.

	a (pm)	b (pm)	c (pm)	β (°)
This work (no Eu^{2+})	655.0(1)	664.1(1)	824.8(1)	108.4(1)
This work (4% Eu^{2+})	654.8(1)	663.9(1)	824.6(1)	108.4(1)
Dumail et al. [12]	655.6	664.0	824.8	108.6

parameters for Sr_2SiS_4). As the reflections observed are also compatible with space group $P2_1$ (4), a refinement of the XRD results using this model was performed, and an equally acceptable fit was found. Thus, from the data collected, the possibility of space group $P2_1$ (4) cannot be excluded. Nevertheless, it seems unlikely that Sr_2SiS_4 has a different space group than the group $P2_1/m$ (11) reported by Dumail [12]. Johrendt reports that there is no temperature dependent $P2_1/m$ (11) to $P2_1$ (4) transition in Eu_2SiS_4 [13]. Given that Eu^{2+} is similar in size to Sr^{2+} , the same behaviour is probably the case for Sr_2SiS_4 . Furthermore Tampier states that the similar compound Sr_2GeS_4 is also $P2_1/m$ (11) [14].

As the concentration of Eu^{2+} in the samples is very small (typically 1% to 4% substitution) it is not expected to have a large impact on the crystallographic structure. To verify this, the lattice constants were determined for a sample of Sr_2SiS_4 with 4% Eu^{2+} . As expected, this substitution affected the lattice parameters only slightly (numerical values are also given in **table 1**). In the following discussion on the structure of $(\text{Ca,Sr})_2\text{SiS}_4$ we will therefore not mention the Eu^{2+} -doping explicitly.

Avella [5] as well as Olivier-Fourcade [6] reported for Sr_2SiS_4 an emission wavelength of 545 nm, both measured on samples with low Eu^{2+} -concentration (<0.5%). The PL measurements carried out at room temperature on our Sr_2SiS_4 samples show a similar value of 548 nm, irrespective of the excitation wavelength. The shape of the emission curve published by Olivier-Fourcade suggests a second emission center at lower wavelength (450-500 nm). This shoulder can also be seen, especially at short exciting wavelengths, in the emission spectra of our Sr_2SiS_4 samples (**figure 2a, room temperature**). In order to examine this more

Figure 2: PL spectra of Sr₂SiS₄:Eu²⁺ (a) Emission spectra at room temperature, for different excitation wavelengths: low wavelength reveals extra peak. (b) Emission spectrum spectra for 4% Eu²⁺ substitution at low temperature (70 K), excitation wavelength 375 nm.

thoroughly, a low temperature measurement (**figure 2b**, 75K,) was carried out, yielding two emission peaks: a main emission peak at 556 nm, and an additional emission peak at 486 nm. These values were found by fitting a superposition of two Gaussian distributions to the measured emission curve for Sr₂SiS₄ when drawn on an energy scale.

The occurrence of two emission peaks can be explained by pointing out that there are two distinct Sr²⁺-sites which can be occupied by Eu²⁺, as is the case for the similar compounds Eu₂SiS₄ [13] and Sr₂GeS₄ [9]. Although the coordination in both sites is rather similar, the orientation of the 5d orbitals of the substituting Eu²⁺-ion can be different, leading to two clearly different emission energies. The same effect was observed by Smet et al. [4] in Ca₂SiS₄:Eu²⁺. The intensity ratio between both emission bands can then be influenced by energy transfer from the center with higher emission energy to the lower one. The study of this process, which is affected by the dopant concentration, is the subject of future research. We determined the external quantum efficiency of Sr₂SiS₄ at about 30%, This is slightly lower than the quantum efficiency of Ca₂SiS₄ [4]. Although this is lower than other values reported for some other conversion phosphors in the yellow-to-red region of the spectrum [15], there is still significant room for improvement by fine-tuning the synthesis conditions.

3.2 (Ca,Sr)₂SiS₄

3.2.1 Structure

Upon substitution of Sr²⁺ by Ca²⁺, the samples remain monoclinic up to 40% Sr²⁺ substituted by Ca²⁺, with reflections monotonically shifting towards larger angles (**figure 3**). This suggests the presence of a

Figure 3: Pattern of (Ca,Sr)₂SiS₄ as a function of Ca²⁺-concentration. The large box emphasizes the monoclinic signature of the S- phase. The three smaller boxes designate the orthorhombic C- phase.

Sr₂SiS₄-like phase with gradually larger substitution of Sr²⁺ by the smaller Ca²⁺. Upon larger substitutions, diffraction peaks become less intense with increasing Ca²⁺-concentration, but remain visible until the almost fully substituted composition. This can be easily seen in **figure 3** by inspecting the reflections around e.g. 31°, 34°, 36° (larger box in the figure) which are typical for the monoclinic phase.

For Ca²⁺-concentrations between 50% and 90%, additional reflections appear in the XRD pattern, e.g. 24-25°, 29-30°, 38-39° (three smaller boxes in **figure 3**), which are typical for an orthorhombic phase, isostructural with Ca₂SiS₄. This suggests that for Ca²⁺ concentrations between 50% and 90%, the samples contain two distinct phases, one monoclinic and isostructural with Sr₂SiS₄ (which is called the S-phase hereafter) and the other orthorhombic and isostructural with Ca₂SiS₄ (the C-phase).

It is interesting to notice that for Ca²⁺-concentrations between 50% and 90%, the reflections typical for the monoclinic phase do not shift as outspokenly on adding more Ca²⁺ as for Ca²⁺-concentrations up to 50%. This means that for Ca²⁺-concentrations above 50%, the monoclinic lattice hardly shrinks upon adding more Ca²⁺, suggesting that once half of the Sr²⁺-ions is substituted by Ca²⁺-ions, it becomes difficult to force additional Ca²⁺ into the monoclinic phase. Not coincidentally, at this Ca²⁺-concentration, the orthorhombic C-phase starts to appear, accommodating the surplus of Ca²⁺-ions that cannot be fitted into the monoclinic phase. Further research could show if the suggestion –supported by the PL characteristics– that the Ca²⁺-ions only substitute substantially for one of the two Sr²⁺-sites, is confirmed.

The results of the Rietveld refinement for the lattice parameters of the (Ca,Sr)₂SiS₄-series are given in **table 2**.

Table 2: Lattice parameters of (Ca,Sr)₂SiS₄ in function of Ca²⁺-concentration. If a sample contains 2 phases, the refined lattice parameters of both phases are shown in the table.

% Ca ²⁺	Space Group	a (pm)	b (pm)	c (pm)	β (°)
0	P2 ₁ /m (11)	655	664	825	108.4
10	P2 ₁ /m (11)	654	664	819	108.3
20	P2 ₁ /m (11)	652	663	814	108.2
30	P2 ₁ /m (11)	652	663	809	108.1
40	P2 ₁ /m (11)	650	662	803	108.0
50	P2 ₁ /m (11)	650	663	802	107.8
	Pnma (62)	1357	824	622	
60	P2 ₁ /m (11)	649	663	799	107.9
	Pnma (62)	1356	824	621	
70	P2 ₁ /m (11)	649	663	798	107.8
	Pnma (62)	1356	823	621	
80	P2 ₁ /m (11)	649	662	798	107.9
	Pnma (62)	1356	823	621	
90	P2 ₁ /m (11)	648	661	796	107.8
	Pnma (62)	1352	821	620	
100	Pnma (62)	1352	819	621	

One clearly notices a shrinking c-axis (0% to 40% Ca²⁺ in **table 2**) for the monoclinic S-phase, while the a- and b-axis are relatively unaffected. An explanation for the anisotropic shrinking could be found in the position of one in two Sr²⁺-atoms in Sr₂SiS₄, which form a plane with the c-axis perpendicular to it (similar to the case of Eu₂SiS₄, as explained by Hartenbach [10]). As a Ca²⁺ substitutes for one of these Sr²⁺, the dimensions will shrink along the c-axis, but as the dimensions along the a- and b-axis are mainly determined by atoms other than the alkaline earths, these will not change much.

Like most sulfide materials, the (Ca,Sr) -thiosilicate phosphors suffer from decomposition upon contact to ambient air due to their hygroscopic nature. After exposure to ambient air for several weeks, some degradation of the phosphor material can be observed. Although the stability is slightly less than that for the binary sulfides like CaS and SrS , the (Ca,Sr) -thiosilicate phosphors are much more stable than the similar thioaluminate compounds, like CaAl_2S_4 or SrAl_2S_4 [16, 17].

3.2.2 PL – Emission Room Temperature

The body colour of the samples with 4% Eu^{2+} ranges from grass green (0-10% Ca^{2+}) over whitish-yellow (20-30% Ca^{2+}) and orange-yellow (40-80% Ca^{2+}) to orange (90-100% Ca^{2+}). Small changes in Eu^{2+} -concentration (1-4% Eu^{2+}) do not affect the body colour of the samples significantly. The body colour of a sample without any Eu^{2+} is grayish-white and does not exhibit any luminescence, which confirms that only the Eu^{2+} -ion is activating the luminescence.

Figure 4: PL emission of $(\text{Ca,Sr})_2\text{SiS}_4:\text{Eu}^{2+}$ as a function of Ca^{2+} -concentration, upon excitation at 400 nm.

Figure 4 shows the emission spectra (excitation at 400 nm) for (Ca,Sr)₂SiS₄:Eu²⁺ as a function of Ca²⁺-concentration. The main emission peak at 548 nm for pure Sr₂SiS₄ shifts towards longer wavelengths as more Ca²⁺-ions are introduced into the initial mixture. This can be related to the structural properties of the S-phase with an increasing fraction of Ca²⁺: the shrinking crystal lattice causes a stronger crystal field and thus a longer emission wavelength. At around 50% Sr²⁺-substitution by Ca²⁺, the main emission peak shifts back towards the shorter wavelengths. This is explained by the contribution to the emission spectrum of the C-phase that emerges at Ca²⁺-concentrations of 50% or more. Depending on the Ca²⁺-concentration, the second emission peak of the S-phase at shorter wavelength (495 nm) and the second emission peak of the C-phase at longer wavelength (650 nm) are less or more noticeable when excited at 400nm. In particular, the sample with 70% Ca²⁺-concentration, is clearly a mixture of two phases (confirmed by the XRD results), as it exhibits both the 495 nm peak characteristic for a S-phase and the 650 nm peak characteristic for the C-phase. The series ends with the emission spectrum of pure Ca₂SiS₄. The hypothesis of two phases (S-phase and C-phase), each causing two distinct emission peaks, will be amplified in both the section on SEM-CL results and the section on low temperature photoluminescence measurements. We will use the following abbreviations: the S1-peak (short wavelength) and S2-peak (longer wavelength) for the emission maxima of the S-phase; the C1-peak (short wavelength) and the C2-peak (longer wavelength) for the emission maxima of the C-phase.

The percentage Eu²⁺ that substitutes for (Ca,Sr)²⁺ does not heavily influence the structure of the phosphor, but it does have a substantial impact on the photoluminescence of the material. A limited number of samples were prepared with different Eu²⁺-concentration. One finds that the Eu²⁺ concentration does not affect the position of the emission peaks much, but that it does have an impact on the relative intensity of the peaks (figure 5). A deeper investigation of the (Sr,Eu)₂SiS₄-series is necessary to confirm if this behaviour is analogous to what was found for (Ca,Eu)₂SiS₄ in [4].

Figure 5: Normalized emission spectrum of SrCaSiS_4 as a function of Eu^{2+} -concentration (measured at 75 K).

3.2.3 PL – Excitation

All $(\text{Ca,Sr})_2\text{SiS}_4$ -compositions have a broad and relatively featureless excitation spectrum (**figure 6**) at room temperature. The main excitation band is situated from 350 to 475 nm, which means that all phosphors can be used in combination with both the standard near-UV-LEDs (390 to 400nm) and the standard blue LEDs (460 to 470nm) commercially available. Host excitation, which is situated at 4.9eV for Ca_2SiS_4 [18] is not very efficient.

Figure 6: Excitation spectra for different compositions of $(\text{Ca,Sr})_2\text{SiS}_4:\text{Eu}^{2+}$ monitored at the emission maxima. The curves are shifted vertically for clarity. (a) Ca_2SiS_4 (b) $\text{Ca}_{1.6}\text{Sr}_{0.4}\text{SiS}_4$ (c) $\text{Ca}_{1.2}\text{Sr}_{0.8}\text{SiS}_4$ (d) $\text{Ca}_{0.8}\text{Sr}_{1.2}\text{SiS}_4$ (e) $\text{Ca}_{0.4}\text{Sr}_{1.6}\text{SiS}_4$ (f) Sr_2SiS_4 .

3.2.4 SEM-CL results

To explain the luminescence behaviour of the $(\text{Ca,Sr})_2\text{SiS}_4:\text{Eu}^{2+}$ powders as function of the composition and to relate this to the XRD results, SEM-CL measurements on $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiS}_4:\text{Eu}^{2+}$ powder were performed. CL maps from an area of about $22\ \mu\text{m}$ by $35\ \mu\text{m}$ were measured. The measurement temperature was lowered to 10K, which reduced the width of the emission bands and enabled to distinguish different emission features more easily. The CL spectrum averaged over the measured area clearly shows the contribution of at least 4 emission bands. Evaluation of the individual CL emission spectra clearly reveals strongly different emission spectra over the measured area. By carefully choosing the spectral windows for monochromatic maps (**figure 7**), A (460-525nm) and C (610-625nm) on the one hand, and B (530-555nm) and D (660-750nm) on the other hand show a striking similarity in intensity distribution, while both sets of maps are each other's inverse. **Figure 7 (top)** shows the CL emission spectra integrated over two selected areas, as indicated in the CL maps A to D. Clearly two

Figure 7: SEM-CL measurement at 10K of $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{SiS}_4:\text{Eu}^{2+}$. (bottom) secondary electron image and CL emission spectrum integrated over the entire measurement area, (center) CL intensity maps in selected wavelength ranges relative to the total CL intensity. A: 460-525nm, B: 530-550nm, C: 610-625nm, D: 660-750nm, (top) local CL emission spectra from the areas indicated in the CL maps, along with the wavelength ranges used for the CL maps. (colour online)

distinct sets of spectra are obtained, one set with emission bands peaking at 485 and 585nm and one peaking at 560 and 660nm. Based on this luminescence signature and on the X-ray diffraction results, the former set can be related to the S-phase, with about 50% of the Sr^{2+} -ions replaced by Ca^{2+} . The latter one

can be related to the C-phase, with limited substitution of Ca^{2+} by Sr^{2+} . The brighter area in the centre of intensity map D could be related to a trace of CaS:Eu^{2+} , or to a $\text{Ca}_2\text{SiS}_4\text{:Eu}^{2+}$ -like phase with higher europium concentration.

3.2.5 PL – Emission Low Temperature

At room temperature, the emission spectra of several $(\text{Ca,Sr})_2\text{SiS}_4$ -compositions show interesting substructure, but due to thermal broadening this cannot easily be resolved. Therefore, in this paragraph, the results of paragraph 3.2.2 (PL at room temperature) are completed with the results of low temperature measurements on the samples with 0%, 20%, 50%, 70%, 80% and 100% Sr^{2+} substituted by Ca^{2+} . Also, all PL emission spectra are interpreted in terms of the model developed in the paragraphs on structure and on SEM-CL results. An overview of the experimental results can be found in table 3.

Table 3: Emission maxima as a function of Ca^{2+} -concentration in $(\text{Ca,Sr})_2\text{SiS}_4\text{:Eu}^{2+}$. Main values are emission peaks of the samples at room temperature. Values between brackets are the emission peaks of the samples measured at low temperature (75 K). Values with an asterisk (*) have a larger error, because the associated peak in the emission is small and/or broad, and thus cannot be easily resolved.

% Ca^{2+}	$2+2\text{SiS}_4$ -like		Ca_2SiS_4 -like	
	S1	S2	C1	C2
0	478 (486)	548 (556)	-	-
10	479	559	-	-
20	482 (489)	570 (574)	-	-
30	484	581	-	-
40	487	584	-	-
50	489 (493)	584 (592)	-	-
60	489	585	-	-
70	496* (496)	590 (590)	556 (557)	660* (658)
80	489* (496)	591 (591)	560 (559)	664* (665)
90	-	-	573	659*
100	-	-	569 (565)	668 (665)

For the S-phase (0-40% Ca^{2+}) the emission spectrum can be modeled as a sum of two Gaussian peaks, the S1-peak and the S2-peak. The S2-peak shifts from 550 nm to about 590 nm as the Ca^{2+} -concentration is

increased. The S1-peak is much weaker, and shifts from 480 nm to about 490 nm. For both peaks, the shift towards longer wavelengths is explained by the shrinking lattice, as this causes a stronger crystal field and thus longer wavelength emission. The strength of the emission shift is strongly different for both emission centers (S1 hardly shifts while S2 shows a 40nm shift for 50% substitution). This again points at a possibly preferential lattice site for the Ca²⁺ ions upon substitution in the S-phase.

For the two-phase compositions (50-90% Ca²⁺), one can try to fit the emission spectra to a sum of four Gaussian distributions. For the samples with little C- phase (50-60% Ca²⁺), this is not feasible because the intensity of C-phase peaks is too low. The powders with more C- phase (70-90% Ca²⁺) can be fitted very well, as is illustrated in **figure 8** for Sr_{0.4}Ca_{1.6}SiS₄.

Figure 8: The emission spectrum (measured at 75 K) of Sr_{0.4}Ca_{1.6}SiS₄:Eu²⁺ consists of 4 separate peaks: 2 (solid lines) originating in the S- phase, and 2 (dashed lines) originating in the C- phase.

3.2.6 Thermal Quenching

The use of phosphor materials in white-light emitting diodes is seriously hampered if thermal quenching occurs at relatively low temperatures. For high-power LEDs, the LED chip can reach temperatures of 450K [19]. Unless a remote phosphor approach is used, both the emission colour and the quantum efficiency should remain stable at this elevated temperature. The thermal quenching behaviour was determined from 70 to 470K, for a selected number of phosphor materials (i.e. Ca₂SiS₄:Eu²⁺, CaSrSiS₄:Eu²⁺ and Sr₂SiS₄:Eu²⁺). Powder samples were illuminated from outside the cryostat by a single

400nm-LED (operated at 20mA). **Figure 9** shows the total emission intensity as function of temperature. $\text{Ca}_2\text{SiS}_4:\text{Eu}^{2+}$ clearly has the most

Figure 9: Normalized PL intensity as a function of temperature, with indication of $T_{0.5}$ for (a) $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ (b) $\text{CaSrSiS}_4:\text{Eu}^{2+}$ and (c) $\text{Ca}_2\text{SiS}_4:\text{Eu}^{2+}$. The powders were excited by a 400nm-LED.

favorable thermal quenching behaviour, with $T_{0.5} = 467\text{K}$ (i.e. the temperature at which the emission intensity has dropped to half its value at low temperature), which is in line with earlier reports. $\text{Sr}_2\text{SiS}_4:\text{Eu}^{2+}$ has a much lower $T_{0.5}$ value of 380K, pointing at the excited Eu^{2+} 5d state being closer to the bottom of the conduction band [20]. Partial substitution of Sr^{2+} by Ca^{2+} leads to an increase in $T_{0.5}$ value. Additional detailed investigations are required to explain the thermal quenching behaviour, based on an accurate energy level scheme incorporating the $(\text{Ca,Sr})_2\text{SiS}_4$ band structure and the Eu^{2+} 4f and 5d energy levels.

4 Conclusions

The (Ca,Sr) - thiosilicate phosphors have interesting features. First, as the excitation spectrum is very broad, they can readily be excited by commercially available LEDs, both near-UV and blue. Secondly, the emission peaks can be shifted by changing the $\text{Sr}^{2+}/\text{Ca}^{2+}$ concentration. Thirdly, the sintering temperatures used in the preparation are relatively low as compared to e.g. nitride phosphors. The europium-doped (Ca,Sr) -thiosilicate phosphors have a relatively high emission efficiency, which could be further improved by tuning the synthesis conditions, such as the sintering temperature and duration, the dopant concentration and the $(\text{Ca,SrS}): \text{Si}$ ratio. A drawback of the (Ca,Sr) -thiosilicates is their degradation upon contact with moisture. Preparing and processing in inert conditions and encapsulating the particles with an Al_2O_3 -coating as in [21] could eliminate this drawback. Nevertheless, the thermal quenching temperature

T_{0.5} decreases upon increasing substitution of Ca²⁺ by Sr²⁺. Although Sr₂SiS₄:Eu²⁺ appears not very favourable for application as colour conversion material in LEDs (due to the onset of the thermal quenching near room temperature), the intermediate compositions have a sufficiently high thermal quenching temperature, certainly if a remote phosphor approach is used.

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