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Structural and Luminescent Properties of Eu^{2+}-doped Aluminates Prepared by the Sol-gel Method

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Abstract

Alkaline earth aluminates with the overall nominal compositions $Mg_{0.5}Sr_{0.5}Al_2O_4$ (MSA), $Ca_{0.5}Sr_{0.5}Al_2O_4$ (CSA) and $Ca_{0.5}Mg_{0.5}Al_2O_4$ (CMA) doped with 0.5 or 1 mol% of Eu^{2+} ions were obtained by a modified aqueous sol-gel method and annealed in a reductive atmosphere at 900, 1000, 1100 and 1300 °C. The sample compositions and their structures were studied by XRD employing the Rietveld method. Solid solubility was confirmed in CSA only, due to the similar ionic radii of Ca^{2+} and Sr^{2+}. UV excited luminescence was observed in the blue region (λ = 440 nm) in samples of CSA and CMA containing the monoclinic phase of $CaAl_2O_4$ and in the green region (λ = 512 nm) in samples of MSA containing hexagonal or monoclinic phases of $SrAl_2O_4$.

Keywords: Sol-gel, aluminates, europium, persistent luminescence, Rietveld refinement, solid solubility

1. Introduction

Materials that possess persistent luminescence can emit in visible several hours after ceasing the irradiation,[1,2] therefore are successfully used in various applications, e.g. luminous paints for buildings, airports and highways, textile products, display technology, lighting, etc. The desired properties for these materials are good chemical stability, high quantum efficiency and long-lived afterglow.[1–3]

Among others, the alkaline earth aluminates MAl_2O_4 (M = Ca, Mg, Sr) doped with the europium(2+) ion,[4–8] or co-doped with other rare earth ions (Nd^{3+}, Dy^{3+}, Er^{3+})[9–14] are potential persistent luminescent materials, displaying luminescence in the blue/green region. In order to achieve the longest and intense afterglow typical concentrations between 0.5 and 1 mol% of Eu^{2+} ions are suggested.[1,4,9,10,12,13] The luminescence properties of these materials depend crucially upon their chemical homogeneity and microstructure. Most frequently they are prepared by solid state reactions, with long reaction times and at high calcining temperatures up to 1600 °C.[4,10,12,13,15] Alternatively, the sol-gel technique is a more convenient method to achieve chemical homogeneity in such materials with smaller grain size particles, obtained at lower annealing temperatures (850–1250 °C).[5,7,8,14]

As previously reported, the structure of these compounds depends on their preparation route.[5,8,16] The hexagonal form of $CaAl_2O_4$ was prepared through the sol-gel method by calcining the xerogel at 850 °C, whereas the monoclinic phase was formed at 1200 °C[5] or by a conventional solid state reaction at 1250 °C.[16] The UV excited luminescence of monoclinic $CaAl_2O_4$ was observed in the blue region, peaking at approximately 440 nm, while the hexagonal phase had a peak maximum at a slightly higher wavelength.[16] $SrAl_2O_4$ exists in two crystallographic forms; the monoclinic (space group $P2_1$) and the hexagonal (space group $P6_322$).[17] Most frequently monoclinic $SrAl_2O_4$ was prepared by conventional solid state reaction at high temperatures 1200–1650 °C.[11,18] The coexistence of the monoclinic and the hexagonal polymorphs of $SrAl_2O_4$ was demonstrated, when it was prepared by the sol-gel method with a boron content of 1 mol% and annealed at temperatures of about 1000–1100 °C.[19] When these aluminates were doped with Eu^{2+} ions, a strong broad band centred at 520 nm was observed under UV-excitation.[6,10,18] $MgAl_2O_4$ doped with Eu^{3+}/Eu^{2+} and Dy^{3+} ions, prepared by the citrate sol-gel method and annealed in air had a cubic spinel structure (space group *F*d-3m, PDF No. 21-1152).[14] Its emission spectra showed broad bands at 480 and 579 nm. Aluminates with

formulae $M_xSr_{1-x}Al_2O_4$ (M: Ca, Ba; x = 0 to 1) and $Mg_xSr_{1-x}Al_2O_4$ (x = 0.05 to 0.25) doped with Eu^{2+} and Nd^{3+} ions were prepared by conventional solid state reactions with the aim of investigating their structural properties in relation to their luminescent abilities.[15,20,21] In some cases Ca/Sr or Mg/Sr replacement enhanced the persistence of their luminescence. Solid solubility of $Ca_{1-x}Sr_xAl_2O_4$ was expected since the Sr^{2+} ion is only 11% larger than the Ca^{2+} ion and both parent compounds have similar tridymite-type structures.[20,22]

In this work, we studied alkaline earth aluminates with the overall nominal compositions $Mg_{0.5}Sr_{0.5}Al_2O_4$ (MSA), $Ca_{0.5}Sr_{0.5}Al_2O_4$ (CSA) and $Ca_{0.5}Mg_{0.5}Al_2O_4$ (CMA) doped with Eu^{2+} ions, obtained by a modified aqueous sol-gel method. The influence of annealing temperature on structure and consequently on the luminescent properties was investigated.

2. Experimental

2. 1. Sample Preparation

The sol-gel technique is a convenient method of achieving chemically homogeneous materials. The alkoxy sol-gel route[5,8,16,23] using hydrolysis and condensation of metal alkoxides, or Pechini's gel methods[19] using chelate polyesterification of hydrocarbonic acids containing at least one hydroxyl group with a polyfunctional alcohol and metal ions, were most often applied. Among the aqueous sol-gel methods, only the citrate sol-gel process was used to prepare ultrafine powders of pure $MgAl_2O_4$.[24] However, this method is not convenient for the preparation of materials in a reductive atmosphere, which is needed to obtain Eu^{2+} ions as luminescent centres. Furthermore, in a reductive atmosphere a residue of carbon arises from the citric acid. We modified the preparation of boehmite sols employing the aqueous sol-gel route by using nitric acid as peptizing agent, as has been reported in detail elsewere.[25]

All starting chemicals ($Al(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$ and Eu_2O_3) were analytical grade reagents purchased from Aldrich.

The polycrystalline aluminates MSA, CSA and CMA doped with 0.5 or 1 mol% of Eu^{2+} (in mol% of the total alkaline earth metals amount), were prepared by the sol-gel method. Gaseous ammonia was introduced into a 0.05 M aqueous solution of $Al(NO_3)_3$ to precipitate $Al(OH)_3$ at pH 9; this was filtered and washed with deionised water. Then a transparent sol was prepared by peptizing $Al(OH)_3$ with 1 M HNO_3, admixing appropriate amounts of solutions of Ca^{2+}, Mg^{2+}, Sr^{2+} and Eu^{3+} ions and heating at 80 °C for 4 hours. The xerogel was obtained by heating the sol in a Petri dish at 80 °C. Portions were then annealed in a tubular oven in a reductive atmosphere (Ar/H_2–5%) at various temperatures (900, 1000, 1100, 1300 °C) for 3 hours.[26]

2. 2. Instrumental Methods

The phase composition of the calcined materials was determined by the Rietveld method from their X-ray powder diffraction patterns, collected using a PANalytical X´Pert PRO diffractometer with CuK_α radiation (λ = 1.5406 Å) in the range of $2\theta = 5°– 80°$ in steps of 0.034° with a total integration time of 100 s per step (the full range of the 128 channel linear RTMS detector was used, so that each channel integrated the intensity for about 0.78 s at each step). Total collection time was 28.8 min.

The same patterns were first used for phase identification by Crystallographica Search Match[27] using the PDF-4 database.[28]

Rietveld refinement was performed using the TOPAS 4.1 software.[29] The structural data were taken from the ICSD database,[30] refining only the unit cell parameters, scale factors and profile and background parameters. Any amorphous phase possibly present was not considered, so that the results represent only the relative amounts of identified crystalline phases. In order to estimate errors, some measurements were repeated.

The luminescence spectra were measured at room temperature using a Perkin Elmer LS-5 spectrometer in the range of 400–650 nm using a powder sample holder. 25 mg of the sample was distributed on the surface of the holder with a surface area of 1 cm^2. The excitation and emission slits widths were set to 5 nm and 8 nm, respectively. The excitation wavelength was 350 nm.

Persistent luminescence spectra were measured with a Mettler Toledo HP DSC827^e analyser equipped with a PCO SensiCam at room temperature after exposure to an Hg lamp for 5 min. The delay between the initial irradiation and the afterglow measurements was 3 min. 8 mg of the sample was distributed in a 40 μL aluminium holder with a surface area of approximately 28 mm^2. During measurement the camera shutter was set to f/0.95 and the exposure time was 3 seconds. Sampling utilized a 12 bit DAC (digital to analogue converter), therefore sample values range between 0 and 4095 in arbitrary units.

3. Results and Discussion

The structure and consequent luminescence properties of these materials depend on their thermal treatment. Various phases of the material with different luminescent properties were obtained by dynamic TG and DSC measurements of the xerogels up to 1100 °C, and by their isothermal heat treatment in a reductive atmosphere for 3 hours at 900, 1000 and 1100 °C as reported.[26] In order to explain such behaviour, investigation of their structures at the quantitative level was necessary.

3. 1. Phase Compositions

All samples of MSA, CSA and CMA doped with 0.5 or 1 mol% of Eu^{2+} annealed at the temperatures mentio-

ned above, contained up to four of the following phases: monoclinic $CaAl_2O_4$ (PDF No. 23-1036, ICSD No. 241240), cubic $Ca_3Al_2O_6$ (PDF No. 38-1429, ICSD No. 151369), hexagonal $SrAl_2O_4$ (PDF No. 31-1336, ICSD No. 160300), monoclinic $SrAl_2O_4$ (PDF No. 34-379, ICSD No. 160297), cubic $MgAl_2O_4$ (PDF No. 75-1796, ICSD No. 91379), hexagonal $SrMgAl_{10}O_{17}$ (PDF No. 26-0879) or $SrMg_{0.94}Al_{10.06}O_{17}$ (ICSD No. 155527) and orthorhombic phase isostructural with orthorhombic $Ca_{20}Al_{26}Mg_3Si_3O_{68}$ (PDF No. 35-133, ICSD No. 26353). The formulae of the phases, listed in the databases are given for clarity, although it is known that in some systems (especially Ca-Sr aluminates) solid solutions are formed.[22]

The Rietveld refinement was performed for all samples and acceptable fits for quantitative analysis were achieved. *Rp* and *Rwp* values are listed in Table 1. Somewhat higher values of the reliability indices in the CSA samples are probably due to preferred orientation of both major phases, however, the quantitative mass ratios are not significantly affected as the intensity mismatch is compensated using the whole profile. The phase compositions obtained are presented in Table 1. The results are given in terms of wt.%; possibly present amorphous phase was not considered and the formulae are given for pure compounds for clarity. The relative errors, estimated from some repeated measurements, are about 5% when the phase concentration is high (above 20%) and increase at lower phase concentrations.

As shown in Table 1, beside the cubic phase of $MgAl_2O_4$, the hexagonal phase of $SrAl_2O_4$ is present in the samples of **MSA** annealed at 900, 1000 and 1100 °C, while its monoclinic phase appears and its amount increases when they are annealed at 1000 and 1100 °C. Finally, only the monoclinic phase was identified in the samples annealed at 1300 °C. The fact that the phase mass ratio of $MgAl_2O_4$ versus $SrAl_2O_4$ almost perfectly reaches its theoretical value (41:59) at high temperatures confirms that the solid solubility between these two phases is very

Table 1. Selected results of Rietveld refinement.

Temperature Sample	900 °C	1000 °C	1100 °C	1300 °C
MSA:0.5Eu^{2+}	$SrAl_2O_4$ **hexagonal** 44% $MgAl_2O_4$ **cubic** 56% *Rp* = 6.04 *Rwp* = 8.44	$SrAl_2O_4$ **hexagonal** 24% $SrAl_2O_4$ **monoclinic** 28% $MgAl_2O_4$ **cubic** 48% *Rp* = 9.85 *Rwp* = 12.42	$SrAl_2O_4$ **hexagonal** 24% $SrAl_2O_4$ **monoclinic** 32% $MgAl_2O_4$ **cubic** 44% *Rp* = 10.45 *Rwp* = 13.29	$SrAl_2O_4$ **monoclinic** 60% $MgAl_2O_4$ **cubic** 40% $SrMg_{0.94}Al_{10.06}O_{17}$ **hexagonal** < 1% *Rp* = 12.36 *Rwp* = 16.30
MSA:1Eu^{2+}	$SrAl_2O_4$ **hexagonal** 41% $MgAl_2O_4$ **cubic** 59% *Rp* = 8.79 *Rwp* = 11.24	$SrAl_2O_4$ **hexagonal** 25% $SrAl_2O_4$ **monoclinic** 26% $MgAl_2O_4$ **cubic** 50% *Rp* = 8.11 *Rwp* = 10.12	$SrAl_2O_4$ **hexagonal** 22% $SrAl_2O_4$ **monoclinic** 35% $MgAl_2O_4$ **cubic** 43% *Rp* = 11.18 *Rwp* = 14.25	$SrAl_2O_4$ **monoclinic** 63% $MgAl_2O_4$ **cubic** 36% $SrMg_{0.94}Al_{10.06}O_{17}$ **hexagonal** < 2% *Rp* = 10.84 *Rwp* = 13.70
CSA:0.5Eu^{2+}	$CaAl_2O_4$ **monoclinic** 42% $SrAl_2O_4$ **hexagonal** 45% $SrAl_2O_4$ **monoclinic** 5% $Ca_3Al_2O_6$ **cubic** 8% *Rp* = 11.56 *Rwp* = 15.20	$CaAl_2O_4$ **monoclinic** 48% $SrAl_2O_4$ **hexagonal** 42% $SrAl_2O_4$ **monoclinic** 3% $Ca_3Al_2O_6$ **cubic** 7% *Rp* = 14.10 *Rwp* = 18.28	$CaAl_2O_4$ **monoclinic** 53% $SrAl_2O_4$ **hexagonal** 40% $SrAl_2O_4$ **monoclinic** 3% $Ca_3Al_2O_6$ **cubic** 4% *Rp* = 15.39 *Rwp* = 20.91	$CaAl_2O_4$ **monoclinic** 66% $SrAl_2O_4$ **hexagonal** 18% $SrAl_2O_4$ **monoclinic** 13% $Ca_3Al_2O_6$ **cubic** 4% *Rp* = 12.81 *Rwp* = 16.76
CSA:1Eu^{2+}	$CaAl_2O_4$ **monoclinic** 48% $SrAl_2O_4$ **hexagonal** 41% $SrAl_2O_4$ **monoclinic** 7% $Ca_3Al_2O_6$ **cubic** 4% *Rp* = 12.35 *Rwp* = 16.14	$CaAl_2O_4$ **monoclinic** 51% $SrAl_2O_4$ **hexagonal** 39% $SrAl_2O_4$ **monoclinic** 5% $Ca_3Al_2O_6$ **cubic** 5% *Rp* = 14.19 *Rwp* = 18.69	$CaAl_2O_4$ **monoclinic** 65% $SrAl_2O_4$ **hexagonal** 33% $Ca_3Al_2O_6$ **cubic** < 2% *Rp* = 17.16 *Rwp* = 23.72	$CaAl_2O_4$ **monoclinic** 78% $SrAl_2O_4$ **hexagonal** 20% $Ca_3Al_2O_6$ **cubic** < 2% *Rp* = 17.25 *Rwp* = 23.81
CMA:0.5Eu^{2+}	Poorly crystalline phase of $MgAl_2O_4$ could be seen only	Poorly crystalline phase of $MgAl_2O_4$ could be seen only	$MgAl_2O_4$ **cubic** 63% $CaAl_2O_4$ **monoclinic** 37% *Rp* = 11.84 *Rwp* = 16.01	$MgAl_2O_4$ **cubic** 50% $CaAl_2O_4$ **monoclinic** 50% *Rp* = 12.85 *Rwp* = 17.33
CMA:1Eu^{2+}	Poorly crystalline phase of $MgAl_2O_4$ could be seen only	Poorly crystalline phase of $MgAl_2O_4$ could be seen only	$MgAl_2O_4$ **cubic** 48% $CaAl_2O_4$ **monoclinic** 40% $Ca_{20}Al_{26}Mg_3Si_3O_{68}$ **orthorhombic** 12% *Rp = 10.58* *Rwp = 13.58*	$MgAl_2O_4$ **cubic** 41% $CaAl_2O_4$ **monoclinic** 48% $Ca_{20}Al_{26}Mg_3Si_3O_{68}$ **orthorhombic** 11% *Rp = 11.86* *Rwp = 16.02*

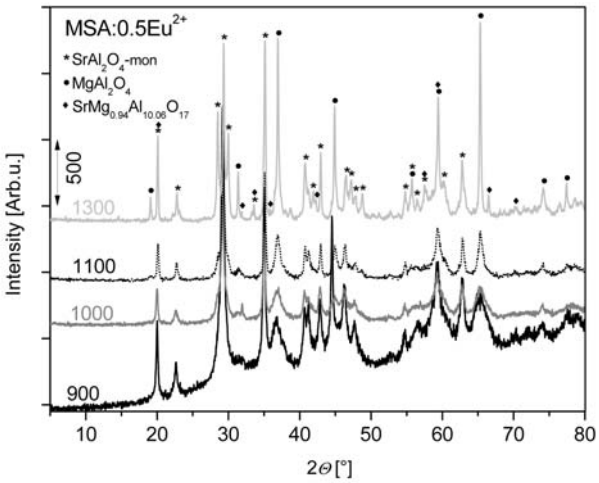

Figure 1. Crystallization and phase development with increasing temperature in a typical sample of MSA:0.5Eu^{2+} as shown by XRD. Peaks of individual phases are marked by symbols according to the legend.

small. This is also confirmed by comparison of the refined unit cells of the present phases. The unit cell parameters of the present phases are nearly equal in all samples and very close to the reference values from PDF and ICSD. The maximum difference in the unit cell volumes of the phases is less than 0.5%. Fig. 1 shows the increase of crystallinity and phase development with increasing temperature of a typical sample of MSA.

In the samples of **CSA** the hexagonal and monoclinic phases of $SrAl_2O_4$ were identified in all samples except CSA:1Eu^{2+} annealed at 1100 and 1300 °C (Table 1, Fig. 2). The hexagonal phase of $SrAl_2O_4$, was also found when preparing these aluminates by conventional solid state reactions at 1200 and 1250 °C.[20,21] It was accompanied by two calcium aluminates present in all samples of this composition: monoclinic $CaAl_2O_4$ and cubic $Ca_3Al_2O_6$. The amount of monoclinic $CaAl_2O_4$ was high in all samples of this composition, especially in the samples annealed at 1300 °C (the theoretical mass ratio between $CaAl_2O_4$ and $SrAl_2O_4$ if they were pure would be 43:57) (Fig. 2). This indicates that a substantial amount of Sr is in fact incorporated into the crystal lattice of a monoclinic $CaAl_2O_4$ forming a solid solution; this has also been reported elsewhere.[22] Solid solubility was also confirmed by comparing the refined unit cells of the present phases. Table 2 shows the unit cells with maximal and minimal refined volume, compared to the PDF and ICSD references. It is seen that the differences among the samples are small (differences in the unit cell volume are within 1%), which means that the maximum solid solubility is similar at all studied temperatures. Significant increase of the unit cells of the calcium phases with respect to the PDF and ICSD (unit cell volume differs for up to 3.7%) confirms inclusion of Sr into the Ca sites in these phases. Unit cells of the strontium phases are smaller than that of the reference PDF and ICSD ones, which mean that Ca is included into the Sr sites in these phases (maximum difference is 7%). However, it has to be noted, that the reference data themselves also differ by 2% between the PDF and ICSD data, so that it is not possible to draw very decisive conclusions from these comparisons.

The samples of **CMA** remain amorphous when annealed at 900 °C. The cubic phase of $MgAl_2O_4$ first appears at 1000 °C as shown in Fig. 3 in contrast to samples of **MSA** which display this phase after annealing at 900 °C. The monoclinic phase of $CaAl_2O_4$ crystallizes not earlier than at 1100 °C in the samples of this composition. However, its crystallization is probably complete at 1300 °C, while the proportions of the two phases achieve their theoretical mass ratio (53:47) in the samples with 0.5 mol% of Eu^{2+} (Table 1), confirming that solid solubility in

Table 2. Unit cells with maximal and minimal refined volume, compared to the PDF and ICSD references for CSA:Eu^{2+} samples.

Phase	Sample/Reference	a [Å]	b [Å]	c [Å]	β [°]	Volume [Å^3]
$SrAl_2O_4$_hex	CSA:1Eu^{2+}–900	5.0839(4)		8.2345(8)		184.31(4)
	CSA:1Eu^{2+}–1300	5.0822(5)		8.213(2)		183.70(4)
	PDF No. 31–1336	5.1400		8.462		193.61
	ICSD No. 160300	5.1666(1)		8.5485(3)		197.62
$Ca_3Al_2O_6$_cub	CSA:0.5Eu^{2+}–1300	7.668(2)				450.8(3)
	CSA:0.5Eu^{2+}–900	7.681(3)				453.2(4)
	PDF No. 38–1429	15.2631				444.5
	ICSD No. 151369	7.624				443.1
$CaAl_2O_4$_mon	CSA:1Eu^{2+}–900	8.778(2)	8.212(0)	15.313(3)	89.87(2)	1103.9(5)
	CSA:0.5Eu^{2+}–1300	8.809(3)	8.245(3)	15.280(5)	89.94(9)	1109.7(6)
	PDF No. 23–1036	8.698	8.092	15.208	90.14	1070.4
	ICSD No. 241240	8.6942(2)	8.09299(19)	15.20965(32)	90.1665(19)	1070.2
$SrAl_2O_4$_mon	CSA:0.5Eu^{2+}–1100	8.42(1)	8.80(1)	5.223(5)	92.1(1)	387.1(7)
	CSA:1Eu^{2+}–1000	8.406(6)	8.790(5)	5.295(6)	91.6(2)	391.1(6)
	PDF No. 34–379	8.4424	8.822	5.1607	93.415	383.7
	ICSD No. 160297	8.5066(5)	8.8898(5)	5.1732(3)	92.875(4)	393.4

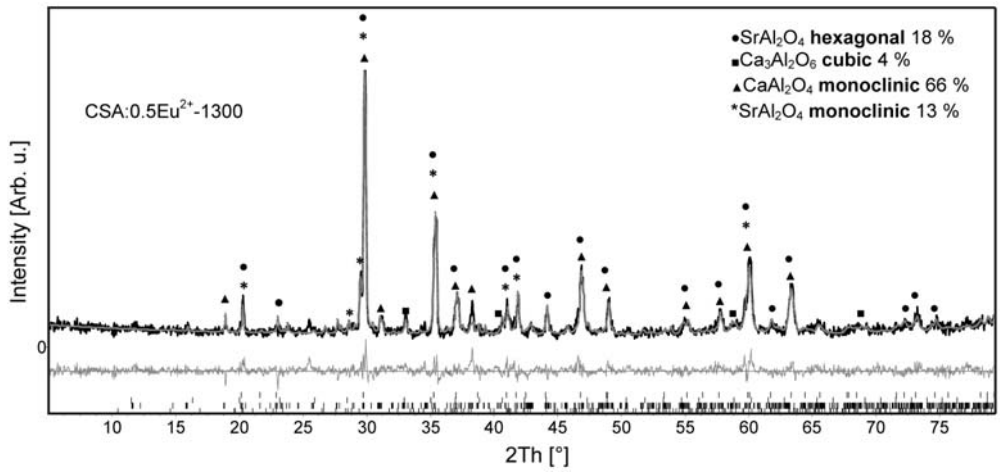

Figure 2. Rietveld plot of CSA:0.5 mol% Eu^{2+}–1300. The *black* pattern is measured, the *grey* calculated; the *grey* line below is the difference and the vertical bars at the bottom are the reflection positions of the phases observed (see legend). Strongest peaks of individual phases are marked by symbols in the legend.

this system is very small. Like in the case of **MSA**, this was confirmed by the unit cell volumes. The unit cells of the present phases are nearly equal in all samples and very close to the reference values from PDF and ICSD. The maximum difference in the unit cell parameters of the phases is less than 0.4%.

When 1 mol% of Eu^{2+} is added to samples of **CMA** an unexpected phase was identified at high temperatures (1100 and 1300 °C). In the PDF database it is described as orthorhombic $Ca_{20}Al_{26}Mg_3Si_3O_{68}$ (PDF No. 35-133). The synthesis and analyses of these samples were double-checked and are highly reproducible, and show that there is no Si present in the samples. Rietveld refinement, on the other hand, confirmed the structural model, so that the most probable explanation is that Eu stabilizes the phase isostructural with $Ca_{20}Al_{26}Mg_3Si_3O_{68}$ where Si is replaced by Al and charge balance is likely achieved by oxidisation of Eu^{3+} or by oxygen vacancies ($Ca_{17}Eu_3Al_{29}Mg_3O_{68}$, $Ca_{20}Al_{29}Mg_3O_{66.5}$), or a combination of the two. The first possibility was checked by UV excited fluorescence, but it was found that oxidation to Eu^{3+} is very limited and insufficient to cover the charge balance by itself, so that the second effect probably takes place. For the purpose of phase quantity estimation, the formula and structure of this phase were left as containing Si, as the scattering factors of Si and Al are so similar that this does not cause any significant error in the Rietveld refinement.

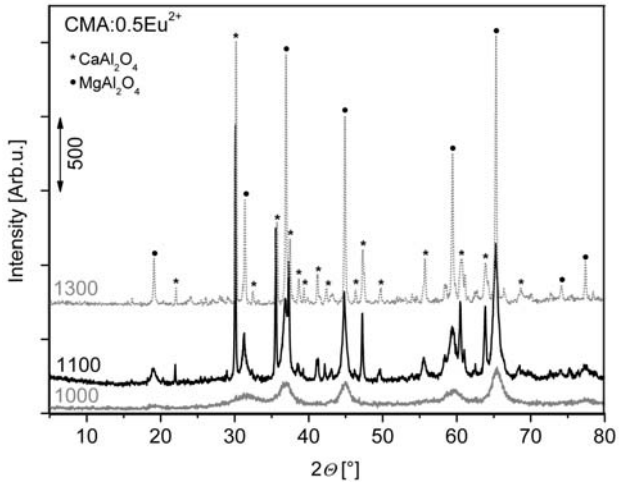

Figure 3. Crystallization and phase development with increasing temperature in a typical sample of CMA:Eu^{2+} as shown by XRD. Peaks of individual phases are marked by symbols according to the legend.

3. 2. UV Excited and Persistent Luminescence

The luminescence properties of these materials depend on their crystal structures and frequently on the quantity of Eu^{2+} (Table 1). The luminescence of the Eu^{2+} ion arises from transitions between the $4f^6 5d^1$ and $4f^7$ configurations. A shift in the luminescence band position for the

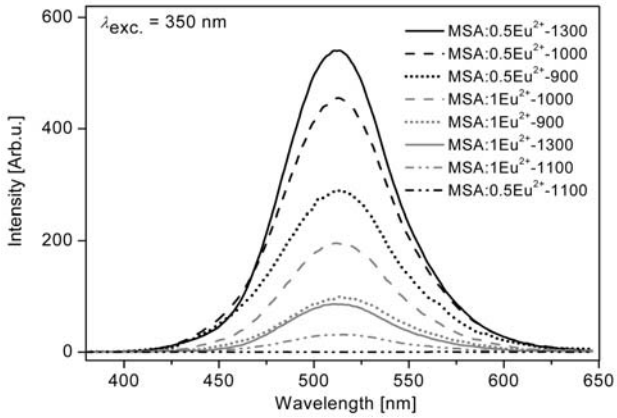

Figure 4. UV excited ($\lambda_{exc.}$ = 350 nm) luminescence spectra of MSA:Eu^{2+} (0.5 mol% or 1 mol% of Eu^{2+}) annealed at various temperatures, measured at room temperature. The curves legend is ordered by appearance.

different host lattices can be explained by a change in the crystal field effect on the Eu^{2+} ion.[16,31] Therefore the structure of the host lattice affects the luminescent properties of the material.

The host lattice for Eu^{2+} ions (0.5 and 1 mol%) in **MSA** is one of the phases of $SrAl_2O_4$ (hexagonal or monoclinic), since only the characteristic band of pure $SrAl_2O_4$ observed in the green region (λ_{max} ~ 512 nm) appears in the UV excited luminescent spectra,[15,18] as shown in Fig. 4.

The lifetime of persistent luminescence depends on quantity of Eu^{2+} ions and the annealing temperature. Luminescence was measured at room temperature as long as it could be perceived by the naked eye.

Appropriate initial persistent luminescence intensities and afterglow lifetimes were obtained when the samples of **MSA** doped with 0.5 mol% Eu^{2+} were heated at 900 or 1300 °C (Fig. 5). Both samples contained pure phases of $SrAl_2O_4$, the hexagonal phase when the sample was annealed at 900 °C, and the monoclinic phase when it was annealed at 1300 °C (Table 1).

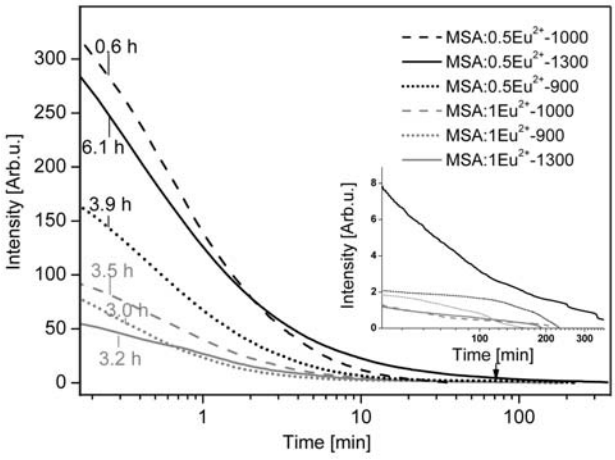

Figure 5. Persistent luminescence lifetimes of samples with nominal formula MSA:Eu^{2+}, measured at room temperature. The inset graph represents magnification of curves tails. The curves legend is ordered by appearance.

Annealing the samples at 1000 °C caused weakening of the initial persistent luminescence intensity, together with shortening of the afterglow lifetime (sample with 1 mol% of Eu^{2+}) as well as quick quenching of the persistent luminescence with initial high intensity (sample with 0.5 mol% of Eu^{2+}). The luminescent properties practically disappeared in the samples heated at 1100 °C (Fig. 4). The reason for this behaviour could be explained by the presence of the two phases of $SrAl_2O_4$ (hexagonal and monoclinic) in the samples annealed at 1000 or 1100 °C and at the ratio in the amounts of these two phases, which decrease or even quench the luminescent behaviour of these materials (Table 1).

UV excited luminescence of **CSA** and **CMA** doped with 0.5 or 1 mol% Eu^{2+} was observed in the blue

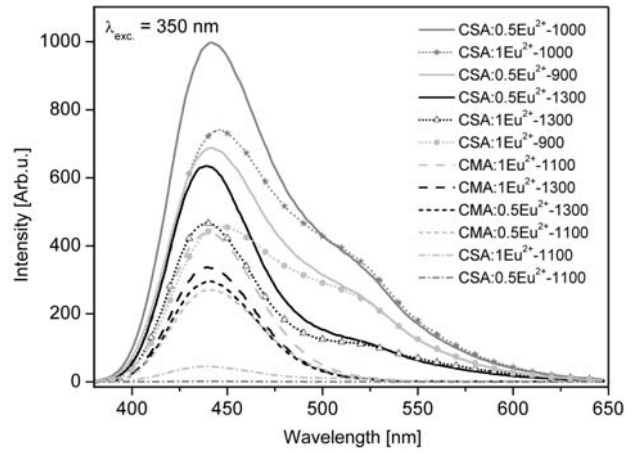

Figure 6. UV excited ($\lambda_{exc.}$ = 350 nm) luminescence spectra of CSA:Eu^{2+} and CMA:Eu^{2+} (0.5 mol% or 1.0 mol% of Eu^{2+}) annealed at various temperatures, measured at room temperature. The curves legend is ordered by appearance.

region (λ_{max} ~ 440 nm), as shown in Fig. 6. These aluminates contain the monoclinic phase of $CaAl_2O_4$, indicating that this phase is mostly responsible for the luminescent properties of the material.[8,10] In **MSA** (0.5 and 1 mol% Eu^{2+}) luminescence is observed in the green region (λ_{max} ~ 512 nm) corresponding to that of pure $SrAl_2O_4$. But the Eu^{2+} ions seem to prefer the $CaAl_2O_4$ host lattice in those aluminates which contain it, since only the single band characteristic of pure $CaAl_2O_4$ is present in the UV excited luminescence spectra of **CMA**. This band is also dominant in the UV excited luminescent spectra of **CSA**, with a prolonged shoulder indicating that the $SrAl_2O_4$ phase causes some luminescent activity in the green region, which is manifested as a bright cyan colour, especially in the samples annealed at 900 and 1000 °C. This also confirms the structural results (Table 1), indicating the existence of some pure $SrAl_2O_4$ phases beside a solid solution of strontium in the $CaAl_2O_4$ phase. The luminescence properties disappear when the samples of **CSA** are annealed at 1100 °C (Fig. 6). The reason for this behaviour could be explained by change in the amounts of phases at various annealing temperatures (Table 1).

The lifetime of **CSA** samples persistent luminescence depends on quantity of Eu^{2+} ions and the annealing temperature (Fig. 7). In **CSA** samples annealed at 1000 °C, 1 mol% of Eu^{2+} ions provided nearly nine hours of luminescence activity. The initial afterglow from the sample doped with 0.5 mol% of Eu^{2+} was stronger than that from doped with 1 mol% of Eu^{2+}, but its afterglow lifetime was shorter by almost four times. Several shorter lifetimes were achieved in the samples doped with 0.5 mol% of Eu^{2+} annealed at 1300 °C (7.5 hours). The sample doped with 1 mol% of Eu^{2+} annealed at this temperature had a low initial persistent luminescence with a short lifetime (2.7 hours).

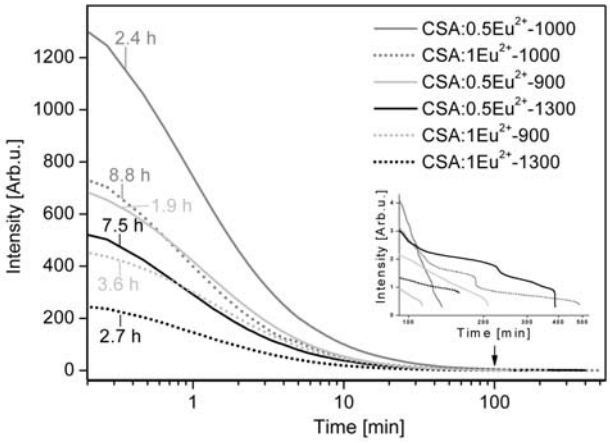

Figure 7. Persistent luminescence lifetimes of CSA:Eu^{2+} materials, measured at room temperature. The inset graph represents magnification of curves tails. The curves legend is ordered by appearance.

Samples of **CMA** acquire luminescent properties on annealing them at 1100 or 1300 °C, when the monoclinic phase of $CaAl_2O_4$ is formed (Table 1). As shown in Fig. 8, the samples doped with 1 mol% of Eu^{2+} display longer afterglow lifetimes irrespective of annealing temperature, with a higher initial intensity in the sample annealed at 1100 °C. It seems that the orthorhombic phase (Table 1), which appears in the samples doped with 1 mol% of Eu^{2+}, enhances their luminescent properties. The samples doped with 0.5 mol% of Eu^{2+} and annealed at 1300 °C have very short afterglow lifetimes (17 min), although the initial afterglow is stronger than those annealed at 1100 °C.

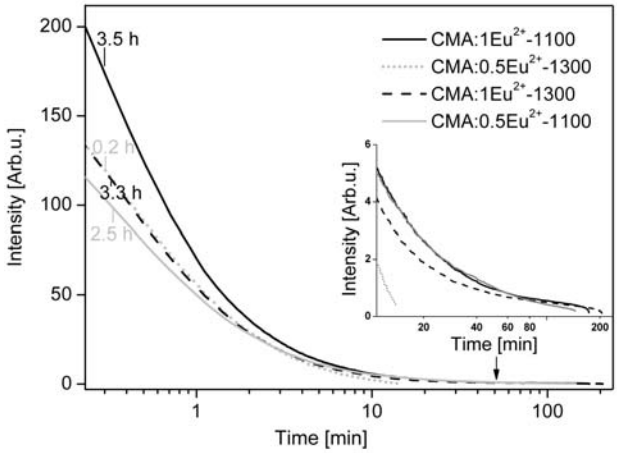

Figure 8. Persistent luminescence lifetimes of CMA:Eu^{2+} materials, measured at room temperature. The inset graph represents magnification of curves tails. The curves legend is ordered by appearance.

4. Conclusions

A modified preparation of boehmite sols by the aqueous sol-gel route using nitric acid as peptizing agent was employed to obtain the xerogels as precursors of alkaline earth aluminates doped with Eu^{2+} ions, thus enabling preparation of the materials in a reductive atmosphere without a carbon residue.

Structural studies showed the presence of various phases obtained at different annealing temperatures. They confirmed the solid solubility of strontium in the monoclinic phase of $CaAl_2O_4$ in CSA at all annealing temperatures, beside some pure phases (hexagonal and monoclinic) of $SrAl_2O_4$. Solid solubility was not observed in CMA and MSA. In CMA the presence of magnesium somewhat hindered the crystallization process of the material up to 1100 °C and an additional orthorhombic phase (beside monoclinic $CaAl_2O_4$ and cubic $MgAl_2O_4$) appeared in the samples doped with 1 mol% of Eu^{2+}. Nevertheless, pure phases of $SrAl_2O_4$ (hexagonal at 900 °C and monoclinic at 1300 °C), or mixtures of both phases (at 1000 or 1100 °C), were identified in MSA.

Appropriate luminescent properties could be achieved at annealing temperatures lower than those required in conventional solid state reactions.

UV excited luminescence was observed in the blue region (λ = 440 nm) in CSA and CMA containing the monoclinic phase of $CaAl_2O_4$, indicating that this phase primarily defined the luminescent properties of the materials. However, in CSA the luminescence turned out to be a bright cyan colour, corresponding to the presence of some pure phases of $SrAl_2O_4$, which caused additional UV excited luminescence in the green region (λ = 520 nm). In MSA only UV excited luminescence in the green region with a maximum at ~512 nm was observed, corresponding to that of pure $SrAl_2O_4$.

The best materials CSA:1Eu^{2+} annealed at 1000 °C provided nearly nine hours of cyan luminescence activity, CSA:0.5Eu^{2+} annealed at 1300 °C 7.5 hours and MSA:0.5Eu^{2+} prepared at 1300 °C exhibited bright and green luminescence in darkness for more than six hours, which makes them suitable for application in various optoelectronic devices.

5. Acknowledgements

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Povzetek

Z modificirano sol-gel metodo smo pripravili zemeljskoalkalijske aluminate z nominalno sestavo $Mg_{0,5}Sr_{0,5}Al_2O_4$ (**MSA**), $Ca_{0,5}Sr_{0,5}Al_2O_4$ (**CSA**), $Ca_{0,5}Mg_{0,5}Al_2O_4$ (**CMA**), dopirane z 0,5 ali 1 mol% Eu^{2+} ionov, ki smo jih žgali pri 900, 1000, 1100 in 1300 °C. Sestavo vzorcev in njihovo strukturo smo proučevali z XRD analizo s pomočjo Rietveldove metode. Trdno topnost, ki je posledica podobnih ionskih radijev, smo potrdili v vzorcih CSA. V CSA in CMA vzorcih, ki vsebujejo monoklinsko fazo $CaAl_2O_4$, smo UV vzbujeno luminiscenco opazili v modrem območju (λ = 440 nm), v vzorcih MSA, ki vsebujejo heksagonalno ali monoklinsko fazo $SrAl_2O_4$ pa v zelenem območju (λ = 512 nm).