Novel fatty-acid assisted co-precipitation method for the synthesis of $SrAl_2O_4:Eu^{2+}$, Sm^{3+} storage phosphor nanoparticles

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ABSTRACT

In this work $SrAl_2O_4$ doped with Eu^{2+} and Sm^{3+} were successfully synthesized using a novel fatty acid assisted co-precipitation method. The main focus was laid on (1) finding a suitable synthesis procedure to reproducibly obtain nanosized $SrAl_2O_4$ doped with Europium and Samarium of high purity (2) optimizing the Eu^{2+} concentration for nano scaled Strontium Aluminate and finally (3) optimizing the co-doping amount of Sm^{3+} to obtain a high intensity photostimulated luminesence (PSL). As a last step the dependence of the PSL signal to the write-in and read-out wavelengths of the stimulating light was determined.

Keywords: $SrAl_2O_4$, phosphor, photostimulated luminescence, co-precipitation,

1 INTRODUCTION

Optical imaging is a steadily developing field of medical diagnostics, which provides more cost efficient and harmless to the patient as well as an simpler setup – superior to other imaging techniques like microCT, ultraound or positron emission tomography. However, optical imaging is still limited by some factors.

When organic tissue is irradiated with blue or UV light it exhibits autofluorescence, which hinders the detection of biomarkers based on luminescence. Thus using conventional luminescence is limited to surface near imaging.

Using materials that show a long afterglow can bypass the problem of organic autofluorescence. By irradiating the phosphor particles prior to injection the phosphorescence (PP) can still be detected in the organic tissue without simultanious stimulation with UV light. For this method the time of afterglow is the limiting factor

Photostimulated luminescence occurs due to trapping the charge carriers in deep traps in the material.

Those electrons can be freed by stimulating with long wavelength light, not able to excite the autofluorescence, enabling the background-free detection of luminescence .

Another important issue is cytotoxicity. Core-shell particles that are or are proposed to be used for photoluminescence imaging often contain elements Se, Cd, Zn, Te, Hg and Pb.[1] Rare-earth-doped oxide particles have the potential to provide nontoxic water-stable photostimulable markers .

In recent years strontium aluminates doped with Europium and other rare earth ions, have gained more and more interest. In 2013 Dong et al. reported that the photostimulated luminescence intensity and the storage capacity of $Sr_3Al_2O_5Cl_2:Eu^{2+}$ could be enhanced by factors of 441 and 91 respectively by co-doping the aluminate with Tm^{3+}. Dong et al. used the commonly used solid state reaction to synthesize the phosphor. After irradiating the phosphor with UV or blue light the sample exhibited PSL after stimulation. [2] In 2015 Manashirov et al. expanded this research and reported a new strontium-aluminate based phosphor that showed long persistent photostimulated luminescence afterglow. By triple doping $Sr_4(Al,B)_{14}O_{25}:Eu^{2+},Tm^{3+}$ with Er^{3+} the long lasting spontaneous luminescence (LLSL) as well as the persistent photostimulated luminescence afterglow (PPSLA) increased by 100%. However, it has to be mentioned that the intensity of the PSL does decrease with increasing afterglow time. They concluded that the addition of Er^{3+} as a third dopant would change the ratio of deep traps and shallow traps. With Er^{3+} doping, the amount of shallow traps increases while the amount of deep traps is reduced. This results in a weaker PSL intensity but a longer afterglow since the process is supposed to involve de-trapping of charge carriers and re-trapping in more shallow traps. [3] The $SrAl_2O_4$ system doped with Eu^{2+} and Dy^{3+} is the most investigated aluminate owing to the excellent PP.

In 2016 Liu et al. also reported photostimulated luminescence by stimulating the phosphor with near infrared (NIR) light at 760 nm. From thermoluminescence measurements and also from previous reports from other research teams they concluded that there must be deep traps that are stable at room temperature which leads to PSL. The phosphor´s storage capacity is high and due to retrapping between a distribution of traps it could be stimulated by NIR light multiple times with the same PSL intensity, after only one charging process.[4] It can be seen that strontium aluminates are very promising for potential application as marker materials. However, the previously mentioned advances on strontium aluminates were all made on the micrometer scale. The task at hand is to find a reliable way to synthesise nanosized strontium aluminate with excellent performance.

In this work $SrAl_2O_4$ doped with Eu was chosen because it is known for its superb luminsecent properties, the chemical stability and low toxicity[5]. Co –doping with Sm should introduce deep traps into the material that are perfectly suited for the storage of energy.

2 EXPERIMENTAL SECTION

2.1 Synthesis procedure for nanosized $SrAl_2O_4:Eu^{2+},Sm^{3+}$

The precursor powders used were $Sr(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $SmCl_3$. Apart from that sodium oleate was synthesised by solving oleic acid and NaOH in 70 vol% Ethanol in a molar ratio of 1:1.
The nanoparticle synthesis was carried out as follows:

(1) The nitrates were solved in Di-water according to the stoichiometric ratio
(2) The sodiumoleate was solved in DI-water
(3) Dropwise adding the oleate-solution to the nitrate-solution
(4) The resulting suspension was centrifuged to get rid of the residual water
(5) The dried gel was ground in a mortar to achieve a homogeneous distribution of the particles in the matrix
(6) Firing in a muffle furnace
(7) The resulting particles were annealed in a reducing atmosphere of $5\%H_2/95\%N_2$ at 1100°C-1450°C for 1 – 4h.

2.2 Measurement of luminescent properties of the $SrAl_2O_4:Eu^{2+},Sm^{3+}$ nanoparticles

All measurements were executed with a JASCO spectrofluorometer FP8500 operating with a 150W xenon lamp and a photomuliplier detector. The samples were finely ground and put in a sample holder of 5 mm diameter. For the conventional emission and excitaition spectra measurments suitable long pass filters were put in front of the detection window. For PSL measurements an interference filter was used.

3 RESULTS AND DISCUSSION

3.1 XRD - measurements

At first a reliable procedure to obtain $SrAl_2O_4$ of a high purity grade had to be found. When Sr and Al precursors were taken in the right ratio to obtain the desired $SrAl_2O_4$ phase, another $SrAl_4O_7$ secondary phase was always there. Therefore a series was prepared in which the amount of $Al(NO_3)_3$ was reduced, since apparently there was too much Al precursor that promotes the second phase formation.

The peaks of the sample prepared with 90% $Al(NO_3)_3$ can not be ascribed to a specific phase but rather indicate the presence of an amorphous phase. The samples that were prepared with 30% $Al(NO_3)_3$ and 50% $Al(NO_3)_3$ show peaks that can be attributed to SrO and $Al_6O_{18}Sr_9$.

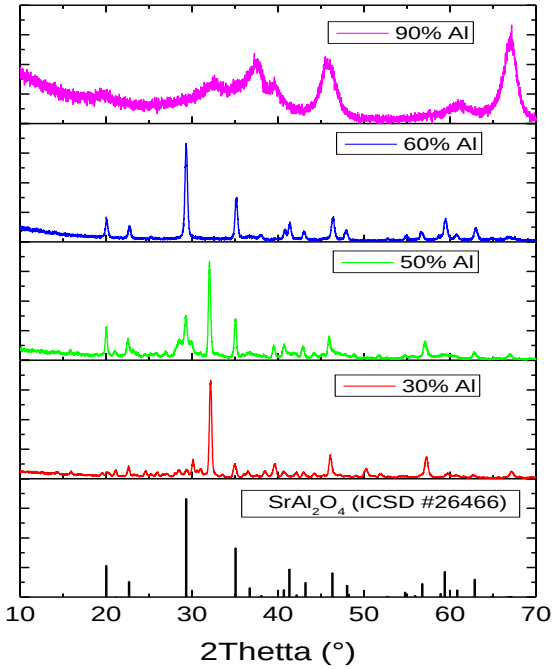


Figure 1: XRD - patterns of the $SrAl_2O_4$ samples prepared with 30%, 50%, 60% and 90% $Al(NO_3)_3$. All samples are prepared with 2,5 $_{mol}$% Eu. The sample prepared with 60% $Al(NO_3)_3$ shows the best fit to the desired $SrAl_2O_4$ phase.

Hovewer, the sample prepared with 60% $Al(NO_3)_3$ shows a perfect fit to the desired Eu-doped $SrAl_2O_4$ phase (Figure 1).The reason for the lower amount of Al needed might be the size of the particles. Since nanoparticles have a higher surface to volume ratio than particles of the micrometer scale, it can be assumed that more strontium or europium ions are situated on the surface which leads to a smaller amount of Al required to form the $SrAl_2O_4$ nanoparticles.

3.2 Particle size control

Following, the samples were prepared with 60% $Al(NO_3)_3$. The particle size can be tuned by annealing temperature and time (Figure 2).
It is obvious that annealing temperatures of 1250°C and 1350°C are too high, since these temperatures lead to particles which are not usable as nanomarkers due to their size. Unlike the annealing temperature, which has a tremendous influence on the particle size, the time of annealing does not affect the particle size. On the contrary, the sample that was annealed at 1100°C for 3h shows smaller particles than the samples annealed for 1h or 2h at the same temperature. Further samples are annealed at 1100°C for 3h.

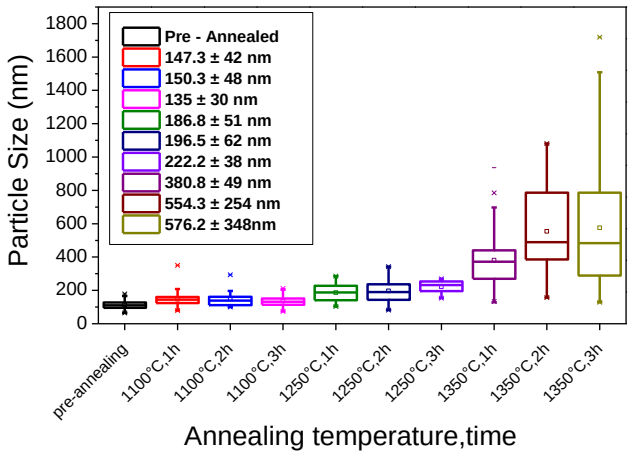


Figure 2: box chart displaying the particle size distribution of the $SrAl_2O_4$ sample doped with 2,5 mol% Eu. Displayed are the particle sizes of the not annealed sample, and nine samples annealed at 1100°C, 1250°C and 1350°C for 1h. 2h and 3h. The inset shows the average particle size and standart deviation.

3.3 PL and PSL properties

Five samples were prepared with 1 mol% Eu, 2,5 mol% Eu, 5 mol% Eu, 7,5 mol% Eu and 10 mol% Eu (Figure 3). The sample doped with 7,5 mol% Eu shows by far the highest PL intensity. Against expectation, the samples with 2,5 and 5 mol% Eu exhibit lower luminescence than the sample prepared with 1 mol% Eu. This might be due to Eu^{3+} ions that were not reduced to Eu^{2+} in some samples or contributed to poorer phase purity of the 2,5 and 5 mol% samples. Nevertheless 7,5 mol% seems to introduce the optimum amount of luminescence centres. On the basis of those findings the next series of samples was prepared with 7,5 mol% Eu and co-doped with 0,5 mol%, 1 mol%, 2,5 mol%, 5 mol% and 7,5 mol% of Sm respectively. The samples were measured as follows:

(1) Write-in: Irradiating the samples for 2 min
(2) Closing excitation and emission shutter for 5 min
(3) Read-out: Stimulating the sample with 650 nm light and measurement of emission

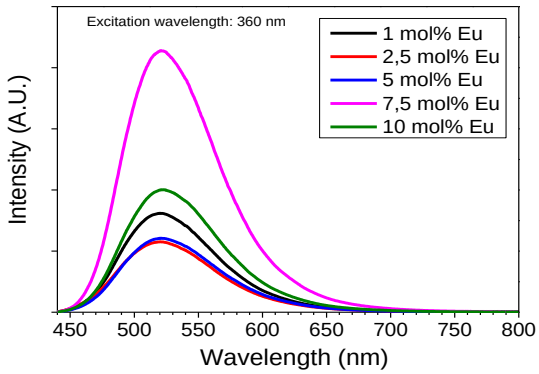


Figure 3: Emission spectrum of $SrAl_2O_4$ doped with different Eu amounts when excited with light of 360 nm wavelength

The sample of $SrAl_2O_4$ nanoparticles doped with 7,5 mol% Eu and 5 mol% Sm leads to the highest PSL intensity. Since the Sm-ions introduce deep traps into the crystal where the charge carriers are trapped until released by stimulation, it makes sense that a higher Sm amount would lead to more traps and hence a higher PSL intensity. The reason for the decrease in PSL intensity when co-doping with 7,5 mol% Sm is that the non equivalent substitution of divalent Sr-atoms with trivalent Sm-atoms leads to a deformation of the crystal. This quenching leads to the effect that the charge carriers cant be stored at trap-sites but rather recombine non-radiatively.

To further optimize the efficiency of the nanomarkers two measurment series were performed to investigate the effect of the write-in wavelength and read-out wavelength on the PSL intensity. For both write-in (Figure 4) and read-out (Figure 5) it can be seen that higher energetic light leads to an increase in PSL intensity. When looking closer at the write-in wavelengths, two observations can be made: (1) There is a peak in PSL intensity at 240 nm write-in wavelength. This peak is also found in conventional excitation spectra of $SrAl_2O_4$:Eu. (2) In the range of 280 nm to 480 nm the PSL intensity is roughly constant.

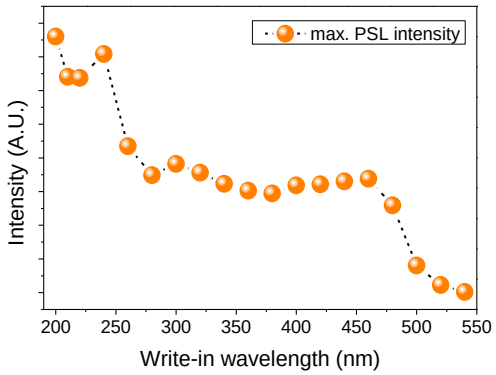
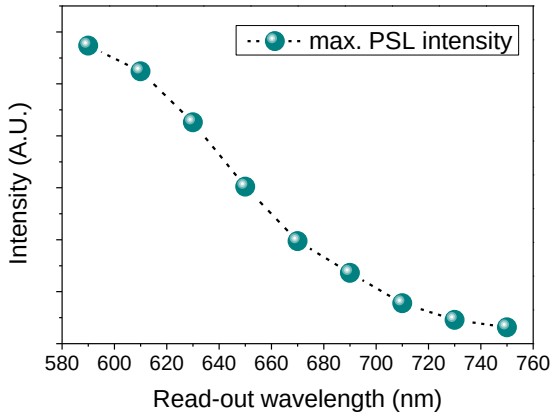


Figure 4: PSL intensity as a function of the write-in wavelength



Figur 5: PSL intensities as a function of the read-out wavelength

When the sample is irradiated with higher energetic light, more electrons can be transported to traps that are not in close proximity of the Eu^{2+} ion from where the electron originates.

The steady increase in PSL when stimulating with higher energetic light (Figure 5) can be attributed to the fact that photons of a short wavelength can reach deeper traps in the material and thus free more stored electrons at once and this leads to a higher PSL intensity.

3.4 Comparison of nano and micro-sized $SrAl_2O_4$

Because of the different synthesis methods the microparticles, synthesised by solid state reaction, and the nanosized $SrAl_2O_4$ particles obtained by co-precipitation, show different morphology. While the microparticles look sharp and edgy, the nanoparticles are more homogeneous in shape and size distribution.

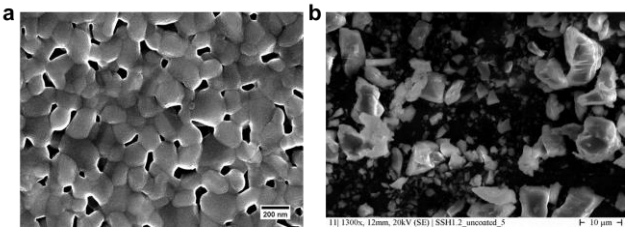


Figure 6: SEM-images of the nanoparticles (a) synthesised by co-precipitation and the microsized particles (b) synthesised by solid state reaction.

The nanoparticles that look to be in a cluster can easily be separated by sonication in liquid medium. It was impossible to create the same defect and the same high crystal quality in nano- and microparticles. As a result of that the nanoparticles have a much lower storage capacity than microparticles. Compared to microsized particles, the nanoparticles synthesised in this work show a maximum PSL intensity of ~7%.

The efficiency of the nanoparticles might still be increased by coating the $SrAl_2O_4$ particles.

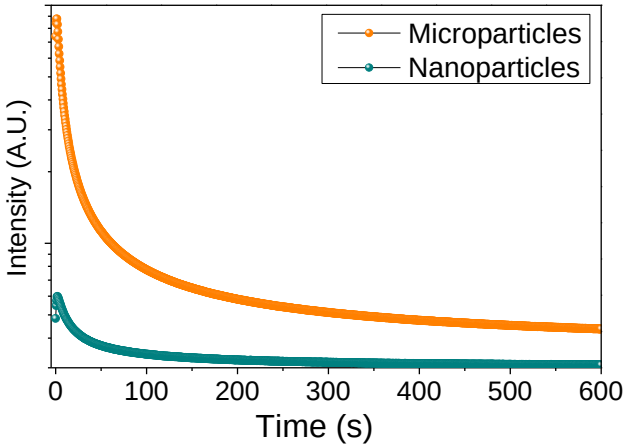


Figure 7: Photo-stimulated luminescence curves of micro- and nanoscale $SrAl_2O_4$ doped with Eu^{2+} and Sm^{3+}.

4 CONCLUSION AND OUTLOOK

$SrAl_2O_4:Eu^{2+},Sm^{3+}$ particles with the size of ~130nm and possessing photostimulated luminescence properties were synthesised by a novel precipitation method. The highest PSL intensity was achieved by doping with 7,5 mol% Eu and 5 mol% Sm.

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