

The luminescent properties of persistent strontium aluminate phosphor prepared by solar induced solid state synthesis

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 IOP Conf. Ser.: Mater. Sci. Eng. 38 012045

(<http://iopscience.iop.org/1757-899X/38/1/012045>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 87.110.245.89

The article was downloaded on 29/08/2012 at 20:44

Please note that [terms and conditions apply](#).

# The luminescent properties of persistent strontium aluminate phosphor prepared by solar induced solid state synthesis

V Liepina<sup>1,3</sup>, K Smits<sup>1</sup>, D Millers<sup>1</sup>, L Grigorjeva<sup>1</sup>, C Monty<sup>2</sup>

<sup>1</sup>Institute of Solid State Physics, 8 Ķengaraga street, Riga, Latvia

<sup>2</sup>PROMES CNRS, Material and Solar Energy Laboratory, BP5 Odeillo, France

E-mail: virginija.liepina@gmail.com

**Abstract.** A novel method – solar induced solid state synthesis – for the synthesis of aluminate phosphor doped with Eu and Dy and the study of its luminescent properties are presented in this article. Two kinds of samples of persistent strontium aluminate phosphor have been prepared – ones via this new method and ones via conventional high temperature solid state reaction. Both kinds of samples were made using the same raw materials. The samples were tested for their chemical composition using X-Ray diffraction method. The luminescence properties and phase composition of the obtained samples have been compared. The behaviour of afterglow, thermally stimulated luminescence, excitation and emission spectra are presented.

## 1. Introduction

Phosphorescence materials have been widely studied by many researchers due to their great potential for device applications. The possible applications such as luminous paints, emergency signs, and more, demand phosphors with qualities like long lasting afterglow, high luminescence intensity and chemical stability [1,2]. Therefore long lasting phosphors such as Eu and Dy doped silicates and aluminates have attracted researchers' attention due to their good luminescent properties: long lasting afterglow, high quantum efficiency and good chemical stability. The luminescence decay time varies depending on the type of the aluminate, for example,  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu, Dy}$  is a phosphor with over 20 hour afterglow and the luminescence peak is at 490 nm [2,3].

The properties of strontium aluminates phosphors strongly depend on material preparation. Many articles describe the different possible synthesis methods of these phosphors, i.e. combustion method, co-precipitation method, sol-gel method etc [4]. The typical solid-state reaction process has been used intensively for phosphor synthesis, but this process has some major disadvantages. It often results in poor homogeneity due to unreacted components and requires high reaction temperature to get high diffusion rates as well as small particle sizes in the starting materials to decrease diffusion length. Furthermore, for some applications very small grain powders are necessary, but alas, the grain size of phosphor powders prepared through solid-state reaction method is in several tens of micrometres. Phosphors of small particles must be obtained by grinding the larger phosphor particles [5]. Those processes easily introduce additional defects and greatly reduce luminescence efficiency. Also, heating in air can lead to the development of unnecessary oxygen compounds, which leads to the need for reducing or neutral atmosphere for the reaction (usually about 1400° in  $\text{H}_2 + \text{N}_2$  or  $\text{N}_2$  atmospheres), which creates the need for specified expensive furnaces. However, it is the most

---

<sup>3</sup> To whom any correspondence should be addressed

common method for the synthesis of this phosphor due to the simplicity of the process. Another common method for synthesis is the sol - gel method, which excludes the need for very high temperatures, but it also has some major disadvantages such as large shrinkage during processing, long processing time and the outcome can be still amorphous. In this paper particularly we have tried a new method for the synthesis of strontium aluminate phosphors – solar induced solid state synthesis (SISSS) method. We compare the luminescent properties of RE doped strontium aluminate long afterglow phosphor with sample synthesized by the conventional high temperature solid state (SS) method to one synthesized by the SISSS method. It has some advantages compared to others, for example, it gives the possibility of high temperature SS reaction in very clean environment and the gas atmosphere and pressure can be controlled. The optical properties of the obtained samples have been studied and compared with those for similar composition phosphor synthesized by conventional SS reaction using the same raw material.

## 2. Experimental

### 2.1. Samples

In this paper we have tried a new method for SS reaction exploiting solar energy. Solar furnaces (Figure 1) (PROMES CNRS, France) are constituted by mobile plane mirrors (“heliostats”) tracking the sun and reflecting the sunlight on a parabolic concentrator, thus it focuses to cooled sample holder. The sample are placed on holder and covered with glass balloons, thus allow prepare samples in vacuum or in different atmospheres. Peak power of such furnaces exceeds 2 kW and can heat the sample up to 3000°C. The main difference to convectional furnaces, is that the heat energy is transmitted in form of radiation, thus allow very fast heating of target, whereas other details of equipment were not heated. Two different samples were prepared - using conventional SS synthesis (Sample A) and SISSS (Sample B). For both methods the precursors were SrCO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Eu(NO<sub>3</sub>)<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>.7%; H<sub>2</sub>BO<sub>3</sub> was used as a flux agent. RE ions usually substitute Sr, that is why we chose 1 atomic % Dy and 1 atomic % Eu in order to obtain Sr<sub>4-x</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sub>x</sub>, Dy<sub>x</sub>. For the SS synthesis the precursors were mixed, pressed and heated in N<sub>2</sub> atmosphere for 4 hours at 1300° C. The synthesis was done according to the N. Suriyamurthy et.al. article „Effects of non-stoichiometry and substitution on photoluminescence and afterglow luminescence of Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor”[6]. For the SISSS method the synthesis time was about 15 minutes approximately in 2000° C.

### 2.2. Measurements

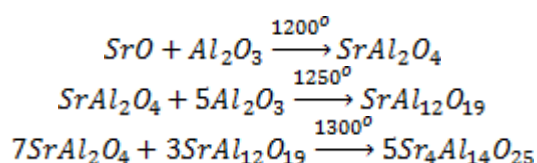
The phase identification of the synthesized samples was carried out by an X-ray Diffractometer Bruker AXS GmbH DS Advance. The measurements of luminescence emission spectra were carried out using three different excitation sources – YAG laser FQSS266 (CryLas GmbH) 4th harmonic, 266 nm (4.66 eV), 2 ns pulses and X-ray excitation by X-ray lamp (W anode, 45 kV, up to 10 mA) at room temperature, and for excitation spectra measurements optical parametric oscillator (OPO) of type NT342/3UV (EXPLA). The same area of the samples was used for measurements and thus the comparison of luminescence intensities between the samples was possible. The luminescence spectra were recorded by Andor Shamrock B303-I spectrograph (spectral resolution ≈0.1nm) equipped with a CCD camera (Andor DU- 401A-BV) at exit port. Thermally stimulated luminescence (TSL) measurements were carried out using X-ray irradiation at liquid nitrogen temperature and heating the samples in 85-600K range.

## 3. Results and discussion

The XRD patterns of the samples are shown Figure 2. The XRD pattern analysis shows that both obtained samples consist of different complex aluminate oxides - mostly of SrAl<sub>2</sub>O<sub>4</sub> and therefore the luminescent properties of the samples are comparable. SrAl<sub>2</sub>O<sub>4</sub>, is also a recognized and highly

effective long lasting phosphor. In sample A besides the  $\text{SrAl}_2\text{O}_4$ , also the preferred strontium aluminate  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  was formed, whereas the sample B consists of  $\text{SrAl}_2\text{O}_4$  and  $\text{SrAl}_2\text{O}_3$ .

Phases of the strontium aluminates change due to differences in heating speed, maximum temperature etc. The reason for the origination of resulting aluminates can then be explained by the fact, that the optimal heating speed and temperature was not considered. According to C. Chong, the  $\text{SrAl}_2\text{O}_4$  conversion to  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  occurs at  $1300^\circ$ [7].



For sample prepared by SS method the reaction temperature was not high enough. As for the SISS method, the temperature was so high, that  $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$  was again reduced to  $\text{SrAl}_2\text{O}_4$  and because of low atmospheric pressure in solar reactor, efficient oxygen reduction occurs and the  $\text{SrAl}_2\text{O}_3$  are formed.

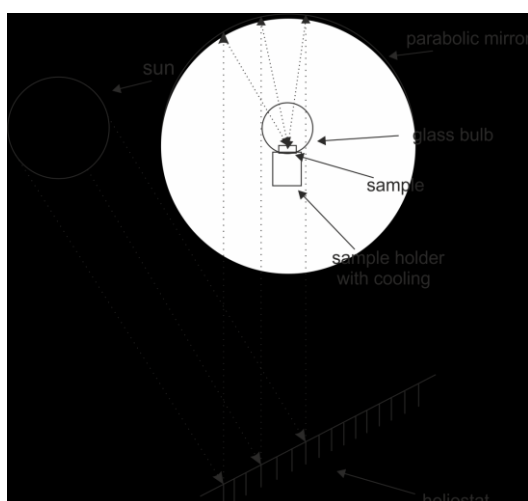


Figure 1. Solar furnace scheme

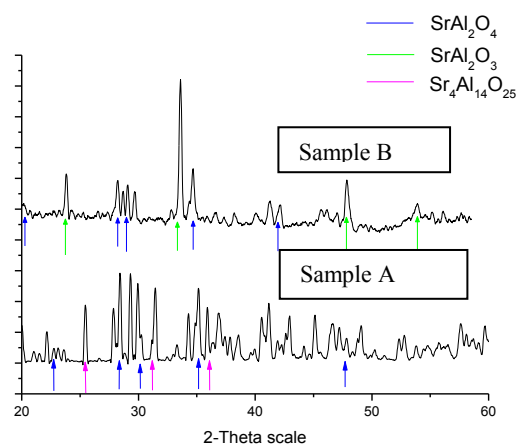


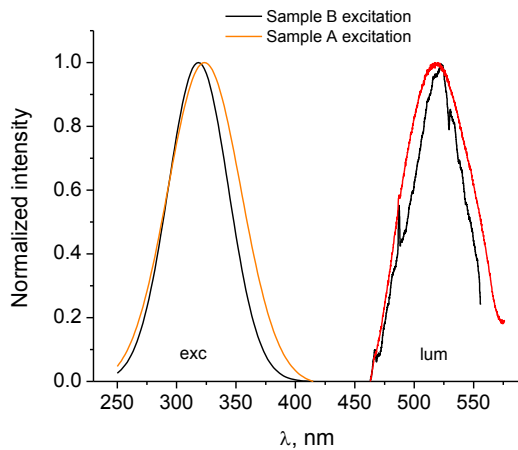
Figure 2. XRD Spectra

The excitation and laser (266 nm) excited luminescence spectra are shown in Figure 3. Similar excitation and emission spectra are observed for samples prepared via both processes. The excitation spectra (for emission at 520 nm) show a broad band from 260 nm to 400 nm. The emission for both phosphors is a symmetrical luminescence band at 520 nm due to the  $\text{Eu}^{2+}$  transition  $4f^65d^1-4f^7$ . As the peak position is strongly influenced by the surroundings of  $\text{Eu}^{2+}$ , a small displacement of the maxima of the emission and excitation spectra occurs and we can observe broadening in the excitation and emission spectra of Sample A. It could be explained by the changes in the crystal field around  $\text{Eu}^{2+}$  in different aluminates contents and thus the depth of the trapping centres.

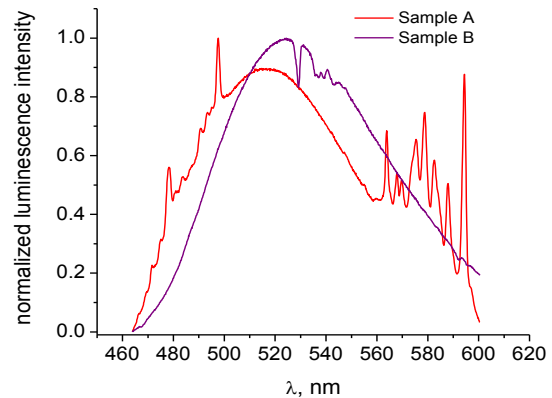
Slightly different luminescence spectra could be obtained by X-Ray excitation. In case of Sample A we can observe that not all RE ions have been incorporated during the reaction, and in X-ray excitation they emit typical RE emission lines –  $\text{Eu}^{3+}$  ion emission lines 570 – 750 nm and  $\text{Dy}^{3+}$  ion emission lines 470 – 500 nm. In sample B the RE ions have been fully incorporated, however some reabsorbtion lines appears.

For sample B, we can assume, that rare earth ion migration to the surface in the very high temperature reaction occurs, because in case of photoluminescence the light penetration depth is

relatively low and the luminescence is more from surface whereas X-rays penetrate deeply in the material and that is why reabsorption is possible by the surface RE ions. X-ray radiation creates electrons and holes which are migrating to luminescence centers, but in the case of photoluminescence the energy is lower than the band gap (~5eV) and the selective excitation of defects and RE ions occurs. We can note that the luminescence intensity of sample A is 3 times higher than that of sample B.



**Figure 3.** The excitation and emission spectra of Sample A and Sample B under UV irradiation



**Figure 4.** The emission of Sample A and Sample B under X-Ray irradiation

Figure 5 shows the luminescence intensity dependence of time after the termination of excitation light for Samples A and B. We can observe that the decay kinetics of Sample B is faster, which relates to the trap depth of the material – probably the traps are located deeper in the forbidden zone for Sample A. We can observe a long tail 5% the intensity of the initial luminescence 15 minutes after the termination of irradiation which descends very slowly.

The thermally stimulated luminescence (TSL) curve was recorded for both samples in order to obtain information about the trap depth in the material (Figure 6).

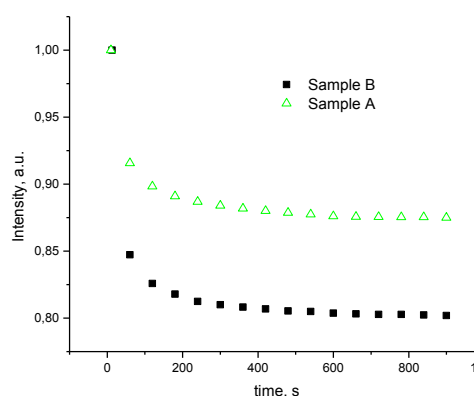
We can qualitatively tell from the spectrum that Sample B has only one major maximum in TSL curve at wavelength 536 nm ( $\text{Eu}^{2+}$  emission), which is a sign of an effective phosphor, but glow peak is below RT, which means that its trapping centres are located close enough to the conduction band for the electrons them to be easily taken up by thermal energy and the recombination could occur. That is a reason for faster luminescence decay kinetic.

For the first order process the TSL spectra were taken with 2 different heating rates – 6°/min and 12°/min to determine the depth of the trapping centres by using the formula:

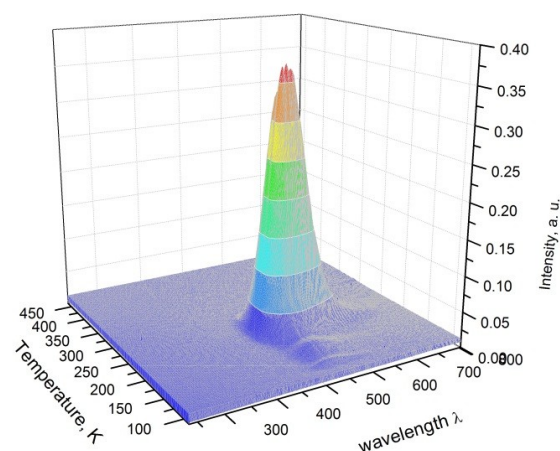
$$\frac{E_z}{kT_{maks}} = \frac{\omega_0}{\nu} * \exp\left(-\frac{E_z}{kT_{maks}}\right) \quad (1)$$

where  $E_z$  – trap depth,  $k$  – Boltzmann constant,  $T$  – temperature,  $\omega_0$  – frequency factor,  $\nu$  – heating speed.

The evaluated trap depth for Sample A is 0.26 eV and for Sample B is 0.19 eV.



**Figure 5.** The fading of luminescence in time for Sample A and Sample B



**Figure 6.** TSL Spectrum for Sample B at 12°/min.

To conclude, SISSS method proves itself to be a perspective method for phosphor synthesis. The synthesis temperature in case of SISSS sample was too high, but for SS to low. In perspective by changing the synthesis parameters it is expected to obtain one phase. Also for SISSS sample, all the RE ions had been incorporated. This method also reduces the possibility of unnecessary impurity incorporation due to the clean environment of the reaction. However, it also has some disadvantages, such as the unaccessibility of the solar reactor and the problematic control of heating rate, and temperature, thus lead decomposition of aluminates. Small depth of the trapping centres in the obtained material, leading to a faster kinetic. Never less this is a promising method for phosphor synthesis and should be explored more.

### Acknowledgements

The sample synthesis was supported by SFERA Access Programm SYNMAT (P10021900000067). Virgīnija Liepiņa is supported by Nr2010/0253/ 2DP/2.1.1.0/10/ APIA/VIAA/079 10032 LZP grant. Krišjānis Šmits is supported by EU SFP project 2009/0202/ 1D/1.1.1.2.0/09/APIA/VIAA/141

### References

- [1] Murayama Y, Takeuchi N, Aoki Y and Matsuzawa T 1995 *Phosphorescent phosphor, US Patent* 5,424,006
- [2] Koen Van den Eeckhout, Philippe F. Smet and Poelman D 2010 *Materials* **3** 2536
- [3] Gao F, Xiong Z, Xue H, Liu Y 2009 *Conference Series* **152** 012082
- [4] Eeckhout K, Smet P, Poelman D 2010 *Materials* **3** 2536
- [5] Dorenbos, P. *J. Electrochem. Soc.* 2005, **152**, H107–H110
- [6] Suriyamurthy N, Panigrahi B S 2008 *Journal of Luminiscence* **128** 1809
- [7] Chang C, Yuan Z and Mao D 2006 *Journal of Alloys and Compounds* **415** 220