Synthesis of Eu^{2+} and Dy^{3+} Doped Strontium Aluminates and Their Properties

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Abstract. Strontium aluminate phosphors were synthesized by the solution combustion method using citric acid, urea or glycine as reducing agent and europium and dysprosium as dopants. The content of both dopants was in the range of 1 – 2 mol%. Dependence of phase composition, crystallite size and specific surface area on calcinations temperature, used reducing agents and dopants were determined. Luminescent properties of the calcinated at 1300 °C powders contained $SrAl_2O_4$ (90 %) and $Sr_4Al_{24}O_{25}$ (10%) phases with crystallite size of 80 nm were determined.

Introduction

Last years the luminescent properties of SrO-Al_2O_3-Eu-Dy system have attracted much attention [1]. Strontium aluminates doped with rare earth ions were observed to be efficient light emitter and found many applications as long afterglow phosphors [2]. They are used in safety and emergency signs, in plasma screens, fluorescent lamps and light diodes. Strontium aluminates occur in several stoichiometries, for example $SrAl_{12}O_{19}$, $SrAl_4O_7$, $Sr_4Al_{14}O_{25}$, $SrAl_2O_4$ and $Sr_3Al_2O_6$, arranged according to an increasing molar ratio of SrO to Al_2O_3 [3]. The most researches in strontium aluminate phases are related with the strong green emision (~530nm) of Eu^{2+} in stoichiometric $SrAl_2O_4$ with monoclinic trydimite structure [4].

The long persistent luminescence mechanism of the rare earth doped ions have been explained by many researchers in their own views [5-8]. However, there is no comprehensive understanding of the luminescence mechanisms and the development of new materials is very often based on trial and error methods [9].

Luminescent properties of strontium aluminate depend on their phase composition, particle size, used dopants, and therefore on the preparation method. Several preparation methods of strontium aluminates such as solid state, liquid and gas phase processes have been elaborated. Among these methods combustion synthesis are very promising [10]. However a little is known about influence of reducing agents on phase composition, particle size of strontium aluminates.

In this study the influence of reducing agents (citric acid, glycine, urea) on the parameters and luminescent properties of the prepared by combustion synthesis was investigated.

Experimental

Strontium aluminate phosphors doped with Eu^{2+} and Dy^{3+} were prepared by the reaction between strontium nitrate ($Sr(NO_3)_2$), aluminium nitrate hexahydrate ($Al(NO_3)_3{\cdot}6H_2O$), europium nitrate hexahydrate ($Eu(NO_3)_3{\cdot}6H_2O$), dysprosium(III) oxide (Dy_2O_3) and organic combustion agents – urea ($CO(NH_2)_2$), glycine ($C_2H_5NO_2$), citric acid ($C_6H_8O_7{\cdot}H_2O$). Small amount of boric acid (H_3BO_3) was used as flux. The stoichiometric compositions were calculated using total oxidizing and reducing valences. The doping concentrations of the Eu^{2+} and Dy^{3+} ions were 1 and 1, 1 and 2, 2 and 1, 2 and 2 mol%, respectively.

The starting materials were dissolved in deionised water (Dy_2O_3 in diluted nitric acid) and stirred on the hotplate until the transparent solution boiled and underwent dehydratation.

After stirring the solution was taken into a furnace maintained at a temperature of 600°C. Spontaneous ignition occurred and underwent smouldering combustion, producing foamy and voluminous ash.

The prepared powders were homogenised in pestle, splitted in 3 parts and calcinated at 900°C, 1000 °C and 1300 °C temperature for 2 h. After the calcination, powders were homogenized again and treated in a protective N_2 atmosphere at 900 °C temperature for 1 h.

Phase identification, crystallite size and phase content calculation were carried out using a Bruker D8 Advance X-ray diffractometer equipped with Topas 4.1 software. The specific surface of powders was determined by argon adsorbtion-desorbtion method. SEM (scanning electron microscopy) pictures were obtained by the Tescan Lyra microscope. Photoluminiscence was excited by using 266 nm laser. The luminescence spectra was detected by using CCD camera Andor DU401_BV connected to Andor SR303i monochromator.

Results and discussion

Strontium aluminates were synthesized by the combustion method using urea, glycine and citric acid as reducing agents. Combustion processes went differently depending on the organic matter. Using urea the reaction mixture rapidly foamed and burned with orange flame and popping sound. Obtained precursor powder was white and fluffy. Combustion reaction with citric acid gave medium flame and black powder was obtained. Using glycine the reaction was less intense than in the case of urea or citric acid. Obtained powder was light brown. Colour of the as-prepared samples was connected with presence of decomposition products of organic compounds depending on reaction intensity and temperature. Further calcination was needed to get rid of black and brown powder colour as well as trying to get the single phase strontium aluminate.

Phase analysis. Calcination at 900 °C temperature is insufficient to get a single phase of strontium aluminate or at least one predominating phase. Mixed $SrAl_2O_4$, $SrAl_4O_7$, $Sr_3Al_2O_6$ phases were observed. Increased background line means that powder is partially amorphous.

Calcination at 1000 °C leads to increasing of $SrAl_2O_4$ phase and it can be considered as predominating.

Samples calcinated at 1300 °C contain $SrAl_2O_4$ (90 %) and $Sr_4Al_{14}O_{25}$ (10 %).

Regardless of used organic combustion agents, in all cases X-ray diffraction patterns of samples calcinated in high temperatures do not change significantly (Fig. 1).

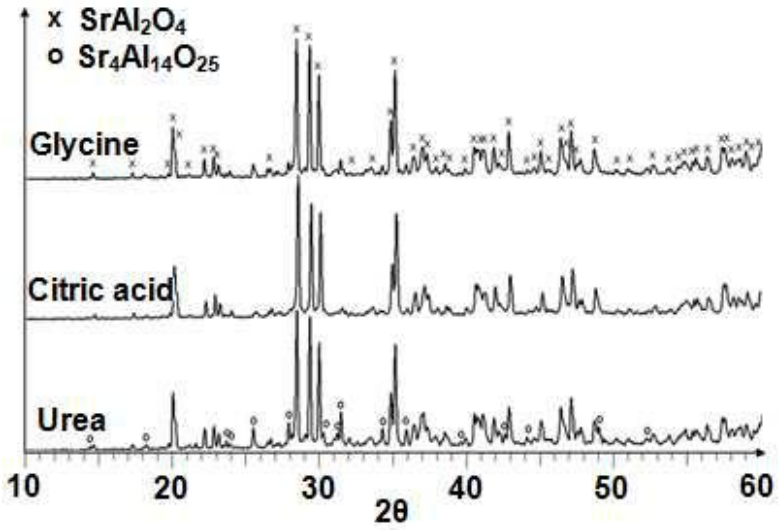

Fig. 1. XRD patterns of strontium aluminate synthesized using different combustion agents and calcinated at 1300 °C.

Surface morphology, specific surface area and crystallite size. Figure 2 shows SEM micrographs. The strontium aluminate powders consisted from irregular agglomerated particles, partially sintered due high calcinations temperature. Particle micrographs obtained at higher magnification showed that agglomerates involved smaller particles with various shapes.

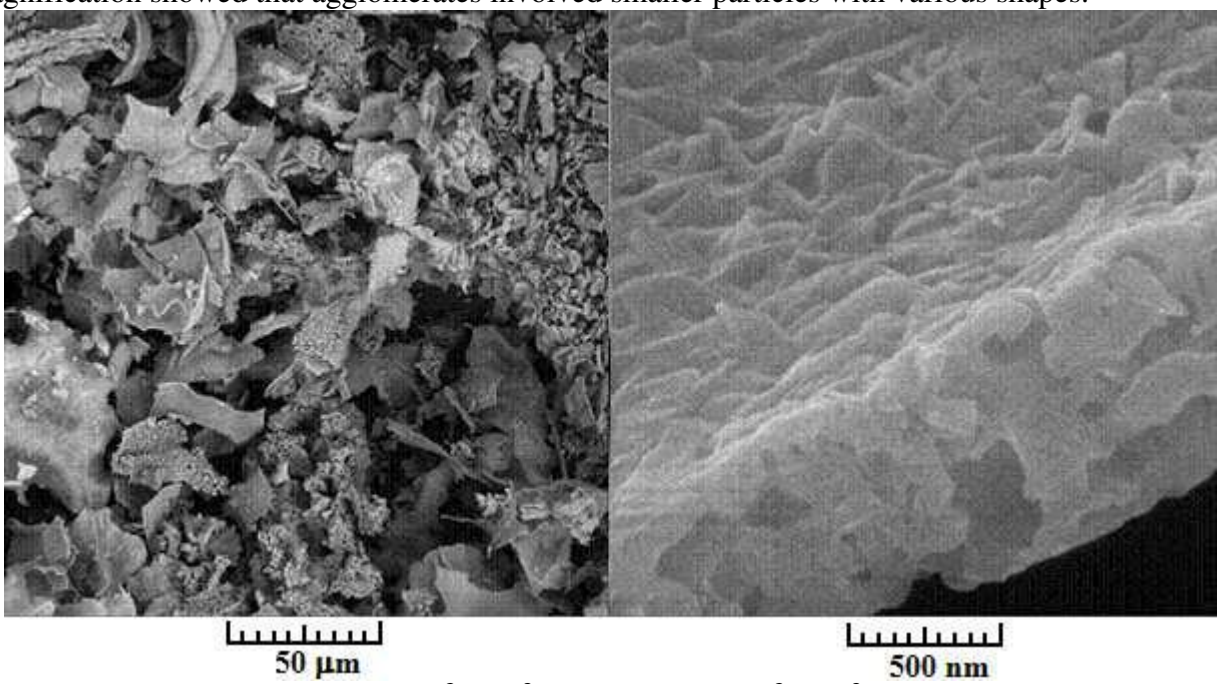

Fig. 2. SEM images of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$, prepared by using urea, 1 mol% Eu, 1 mol% Dy and calcinated at 1300 °C.

The results of measured specific surface area are summarized in Table 1. Samples treated at 900 ºC have a specific surface area in the range from 12 to 39 m^2/g. Increasing calcination temperature the specific surface area decreases. At 1300 ºC the surface is 6 – 9 m^2/g. The higher specific surface have strontium aluminate samples synthesized using citric acid, because lower reaction rate and presence of decomposition products.

Crystallite size varies from 20 to 30 nm for samples calcinated at 900 ºC, 50 – 60 nm at 1000 ºC and approximately 80 nm at 1300 ºC. Increasing of heating temperature promotes increasing the particle size of strontium aluminate due to particle growth and partial sintering of agglomerates.

Table 1. Specific surface area of strontium aluminate samples synthesized using different combustion agents and calcinating temperatures.

Combustion agent	Temperature of calcination, ºC	Specific surface area, m^2/g			
		1% Eu, 1% Dy	1% Eu, 2% Dy	2% Eu, 1% Dy	2% Eu, 2% Dy
Urea	900	11,9	17,4	19,5	17,3
	1000	8,1	12,4	16,2	15,7
	1300	5,7	9,4	6,9	7,7
Citric acid	900	38,9	18,3	37,7	37,1
	1000	24,4	10,3	27,2	26,6
	1300	6,0	9,9	7,4	7,2
Glycine	900	21,9	24,5	25,1	23,9
	1000	20,7	23,2	18,5	24,1
	1300	6,3	6,5	7,6	6,7

Luminescent properties. For photoluminiscence measurements samples calcinated at 1300 ºC with definite phase composition $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (90 %) and $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (10 %) were chosen. Emission spectra at room temperature showed broad centred on 525 nm and several peaks at 575 – 675 nm and 690 – 715 nm were observed. The broad maxima in the range of 400 – 650 nm corresponds emission spectra of $SrAl_2O_4:Eu^{2+}$ and $Sr_4Al_{14}O_{25}:Eu^{2+}$ [9]. Sharp peaks in the range of 575 – 675 nm will be connected with Eu2+, Eu3+ and Dy3+ luminescence, for example Eu3+ luminescence was observed in the Range of 570 – 600 nm ($5D_0 \rightarrow {}^7F_1$) and in the range of 600 – 640 nm ($5D_0 \rightarrow {}^7F_2$). However, the identification of the mentioned peaks demands more detailed studies.

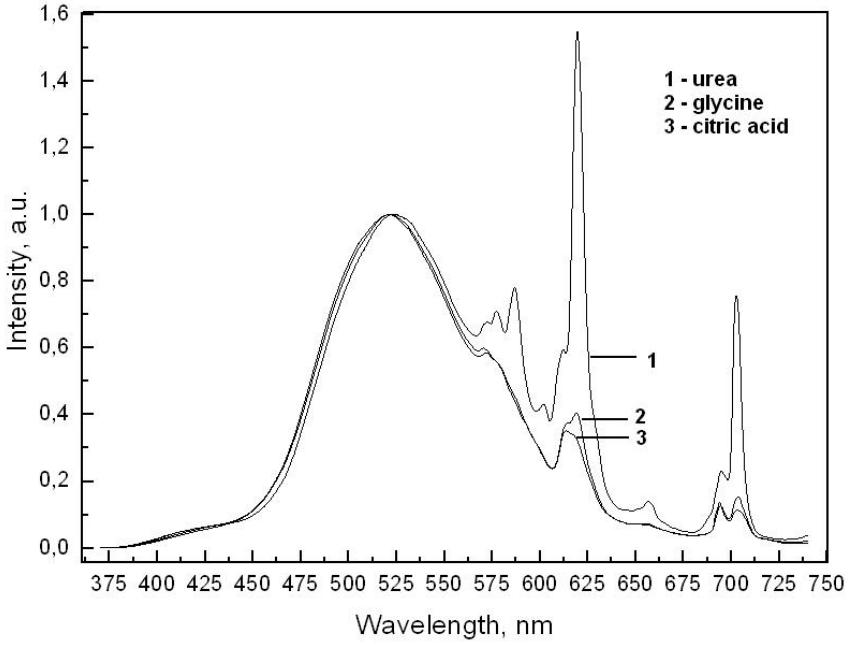

Fig. 3. Emission spectra of $SrAl_2O_4:Eu^{2+},Dy^{3+}$,$Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ radiation source 266 nm laser.

The luminescence afterglow decay curves of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor doped with various amounts of Eu^{2+} and Dy^{3+} ions are presented in Fig. 4. When doped Eu^{2+} concentration was 1 mol% and co-doped Dy^{3+} was 1 mol%, the phosphor exhibited the highest luminescence intesity. However, rapid luminescence decay was observed.

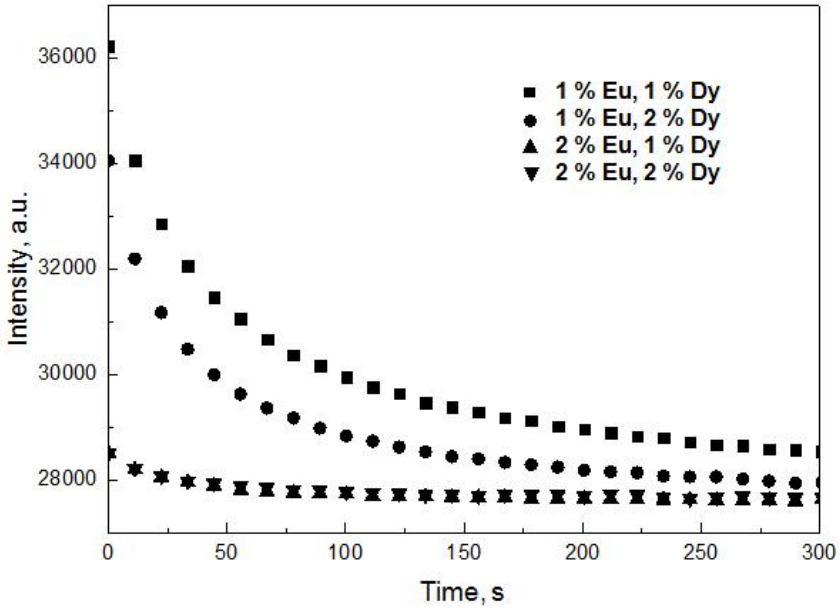

Fig. 4. Luminescence decay curves of $SrAl_2O_4:Eu^{2+},Dy^{3+}$, $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ with different dopant concentrations

Summary

1. Combining combustion synthesis and thermal treatment the nanoparticles of rare earth ions doped strontium aluminate were performed having a specific surface area in the range from 5,7 to 38,9 m^2/g and crystallite size from 20 to 80 nm depending on the calcinations temperature. Calcinated at 1300 °C powder contained $SrAl_2O_4:Eu^{2+},Dy^{3+}$ (90 %) and $Sr_4Al_{14}O_{25}:Eu^{2+},Dy^{3+}$ (10 %) phases.
2. The specific surface area and crystallite size of as-prepared powders depend on used organic reducing agent, determined reaction intensity and amount of decomposition products.
3. The luminiscence intensity were highest for samples containing smaller dopant concentrations (1 mol% Eu and 1 mol% Dy).

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