

# Microwave Synthesis of Eu-doped Silicate Phosphors

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A series of Eu-doped silicate phosphors was prepared in a microwave furnace using different charge mixture preparation methods. Synthesis parameters (time and power) were optimized to increase the yield and brightness of phosphors featuring with a “warm” white luminescence. The charge mixture prepared using sol-gel process provided phosphor with enhanced brightness compared with a solid phase preparation technique supposedly due to more uniform distribution and better introduction of the activator into the phosphor. White LED prototype was fabricated using synthesized phosphor.

## 1. Introduction

The effect of short-wavelength light (some 460 nm) onto human’s organism is known to effectively suppress melatonin secretion [1]. Melatonin, being produced during the sleeping phase, plays an important role in controlling the circadian system [2], so lighting designers should choose specific spectral distributions depending on the application: short wavelengths are bound to keep people awake, while low correlated color temperature (CCT) of “warm” white light of 2300 K does not suppress melatonin production [1] and would be ideal for evening indoor lighting. Thus, synthesis of phosphors for warm white light emitting diodes is an actual task nowadays.

Recently new methods were applied to improve phosphor synthesis technology: utilization of plasma, shockwave treatment and microwave radiation [3-6]. Particularly in paper [6] it was demonstrated that synthesis of silicate phosphors in a microwave furnace provides a number of advantages compared with the conventional procedures (synthesis in muffle furnace in hydrogen atmosphere [7-9] and under the layer of coal [10,11]) including increased brightness as well as significantly reduced processing time and cost.

Silicate and chlorine-silicate phosphors doped with Eu ions are of interest for white LED applications because of high chemical and thermal stability, durability and ability to form wide range of solid solutions. Moreover, they have high quantum yield and intensity of emission [12].

In this paper we report effect of synthesis conditions on properties of Eu doped silicate phosphors fabricated in microwave furnace.

## 2. Experiment

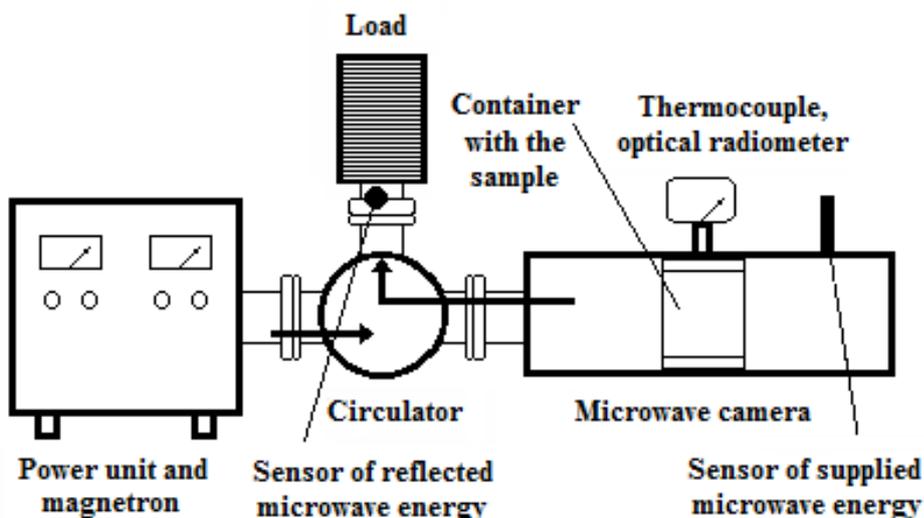
The charge mixtures for synthesis were prepared using two methods: (1) mechanical mixing of starting powders; (2) sol-gel process. Reagents of analytical purity grade were used for synthesis of the samples. In the case of mechanical mixing SiO<sub>2</sub>, SrCl<sub>2</sub>·6H<sub>2</sub>O, Ca(OH)<sub>2</sub>, Eu<sub>2</sub>O<sub>3</sub> powders were preliminary ground in a mortar, sieved and homogenized in a drum mixer for 3 hours.

To perform sol-gel synthesis Ca(OH)<sub>2</sub> and Eu<sub>2</sub>O<sub>3</sub> were dissolved in concentrated nitric acid, SrCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in the water. Then salt solutions and TEOS (tetraethoxysilane (C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Si) were sequentially added to water-alcohol mixture containing nitric acid as a catalyst. The gelation was carried out at 25 °C for 24 hours. Thus obtained gels were dried in an oven at 150 °C during 5 hours. Then dried gels were ground in the agate mortar and used for the synthesis of phosphors.

The phosphor synthesis was performed in the custom made microwave furnace (Fig. 1) with the frequency of 2.45 GHz using different experiment setups (Fig. 2).

In the case of setup shown in the Fig. 2 A), syntheses was carried out without preliminary annealing of the charge mixture containing crystallization water, which intensively interact with microwave radiation.

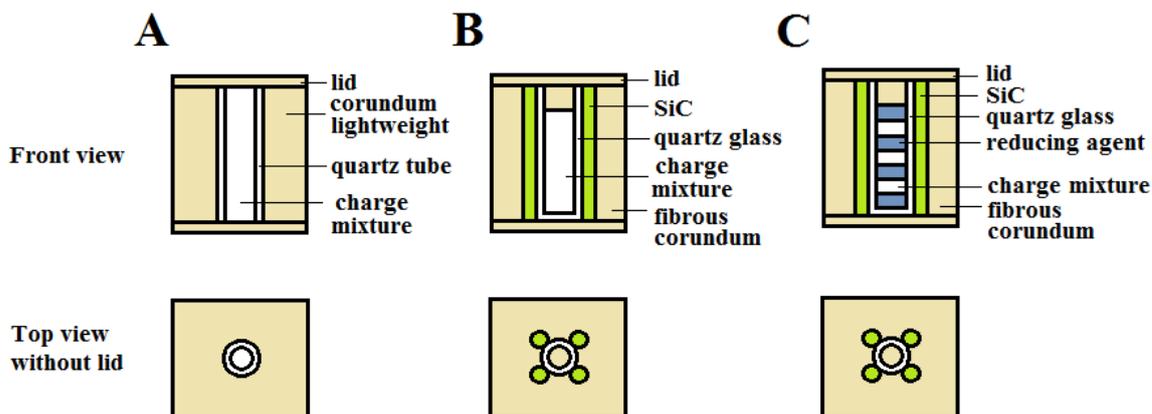
Powder was introduced into the system without a susceptor and heated by separate microwave pulses (each pulse is 1 min heating time, 1 min interval between pulses) to avoid intense outgassing from the reactor.



**Fig. 1** Schematics of microwave furnace

In the case of setups B and C in the Fig. 2 charge mixture was preliminary heated for 10 min in microwave furnace using setup A, that allowed to perform further synthesis in the continuous mode. However in this case susceptor was introduced to increase the process temperature. SiC featuring with a very strong intensity of interaction with 2.45 GHz microwaves was used as a susceptor [13].

In order to transform  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$  reducing conditions were provided in the system by the introduction carbon powder via either mixing with the initial charge mixture (Fig. 2, A, B) or as separate layers between the charge mixture layers (Fig. 2, C).

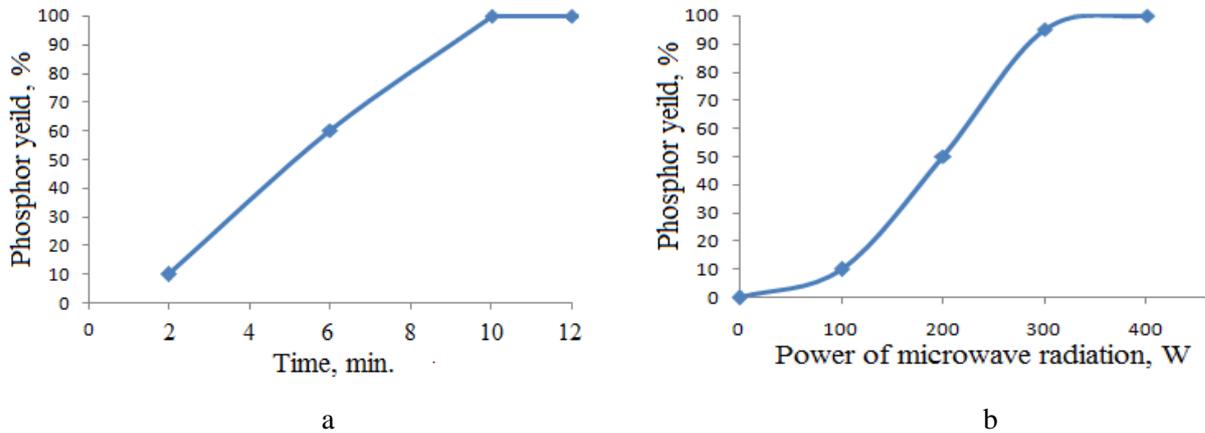


**Fig. 2** Experiment setups for the synthesis in microwave furnace without (A) and with (B, C) susceptor (SiC)

All the prepared phosphors were studied by measuring their photoluminescence (PL) emission spectra using AvaSpec-3648 spectrofluorimeter at 405 nm excitation wavelength. The luminescence brightness was measured using IL-1700 radiometer. Color coordinates were calculated from PL spectra using ColorLum software. X-ray diffraction analysis was performed using DRON-3 apparatus.

### 3. Results and discussion

Firstly optimization of synthesis parameters for “B” setup shown in the Fig. 2 was performed. If time or power of microwave radiation during synthesis were insufficient resulted material was only partly luminescent. Thus phosphor yield in each synthesis was determined as the ratio of luminescent material volume to the total volume of the resulted powder. Optimal synthesis time (10 min) and power of microwave radiation (300 W) were determined by the saturation of corresponding dependencies of phosphor yield (Fig. 3).



**Fig. 3** Phosphor yield as a function of synthesis time at the power 300 W (a) and as a function of microwave radiation power for the synthesis time 10 min (b)

Next phosphor synthesis with optimal parameters was performed using “A”, “B” and “C” setups (Fig. 2). Properties of resulted phosphors are shown in the Table I.

**Table I.** Synthesis conditions and performances of the prepared phosphors

Sample ID	Experiment setup	Method of charge mixture preparation	Brightness, a.u.	FWHM of PL spectrum, nm	Correlated color temperature, K
<b>A</b>	A (without susceptor)	mechanical mixing	38	122	4500
<b>B</b>	B (with susceptor)	mechanical mixing	50	111	3800
<b>C</b>	C (with susceptor, top layer)	mechanical mixing	52	138	5000
<b>D</b>	C (with susceptor, middle layer)	mechanical mixing	57	96	4100
<b>E</b>	C (with susceptor, bottom layer)	mechanical mixing	68	94	3400
<b>F</b>	B (with susceptor)	sol-gel	67	111	4200
<b>Reference [6]</b>	Muffle oven, 950 °C and 2,5 hours	mechanical mixing	38	114	~10000

It should be noted that time of microwave synthesis (10 min) was much lower comparing to 150 min needed to prepare efficient phosphor using muffle oven. Energy consumed by microwave furnace is also much lower (muffle consumes 1000 W). Finally temperature during microwave synthesis (700°C) was also lower comparing to conventional synthesis (900-1200°C). Nevertheless, phosphor synthesis using microwave furnace provided much higher brightness comparing to conventional method. This result may be explained by the effect of pondermotive forces (microwave vibration) produced by currents emerged from electromagnetic wave and electrodiffusive mass transfer. In complex system, like charge mixture, consisting of components with different dielectric permittivity and tangent of dielectric losses, non-uniform polarization field develops as a result of interaction with microwave energy. This process intensifies mass transfer proportionally to squared electric field intensity [14].

Photoluminescence spectra of the fabricated phosphors are presented in the Fig. 4. Deconvolution of spectra shows presence of the following bands:

- band of  $\text{Ca}_{0.47}\text{Sr}_{0.48}\text{Eu}^{2+}_{0.05}\text{SiO}_3\text{Cl}_{2/6}$  with the luminescence peak at about 580 nm - band 2 [7];

- two bands of  $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$  peaked at  $\sim 490$  nm and  $\sim 560$  nm - bands 3 and 4, which are attributed to  $5d-4f$  transitions of  $\text{Eu}^{2+}$  in 10 coordinated (M(I)) and 9 coordinated (M(II)) positions of  $\text{Sr}^{2+}$ , correspondingly. The M(I) site forms a chain along c-axis with one side of  $\text{Si}^{4+}$  ion and the other side of M(I). The M(II) sites are surrounded by nine oxygens and form chains of M(II) ions along the b-axis [15].

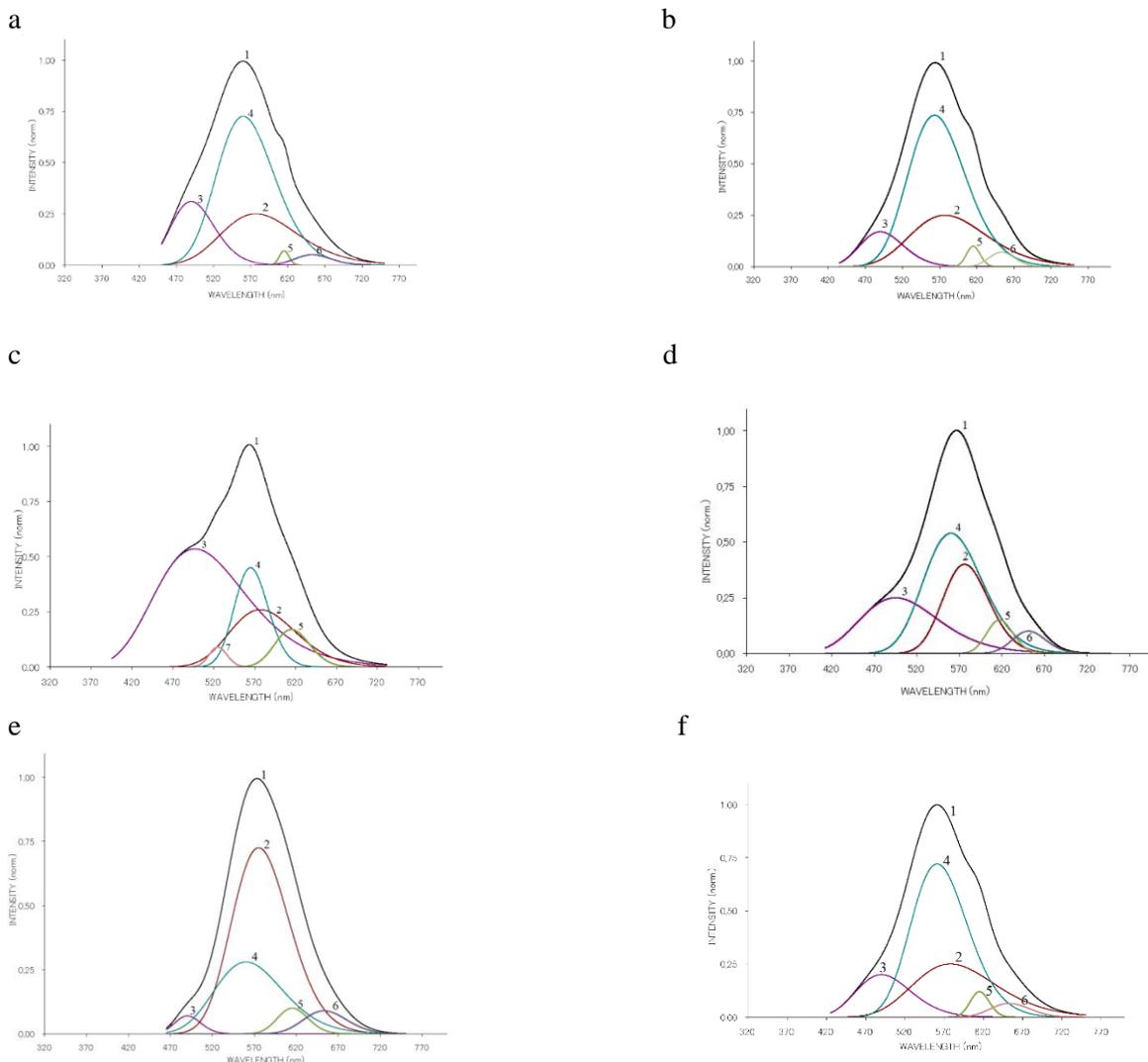
- two bands of  $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$  peaked at  $\sim 615$  and  $653$  nm - bands 5 and 6 which are attributed to  ${}^5\text{D}_0-{}^7\text{F}_2$  and  ${}^5\text{D}_0-{}^7\text{F}_3$  transitions of  $\text{Eu}^{3+}$  correspondingly [16].

XRD analysis confirmed the presence of abovementioned phases in the phosphor samples. The band 7 (Fig. 4c) peaked at 525 nm most probably corresponds to  $\text{Eu}^{2+}$  transition mediated by defect levels in band gap similar to what was observed for  $\text{ZnO}:\text{Eu}^{2+}$  phosphors [17].

Thus all samples were mixed phases and change of synthesis conditions allowed to control their phase composition and to adjust color properties of phosphors to achieve “warmer” or “colder” luminescence. All fabricated phosphors featured with high brightness and “warm” color of luminescence, which is another merit of the microwave synthesis in comparison with the conventional procedure [6].

Using synthesis setup “C” three layers of the phosphor were derived: top, middle and bottom. During the synthesis temperature gradually increases from the top to bottom level of reaction volume. The bottom layer has the highest brightness in combination with the “warmest” luminescence (correlated color temperature  $\sim 3400$  K), however FWHM of its emission spectrum has the lowest value among the prepared samples due to predominant formation of the chlorine-silicate phase.

On the contrary, the top layer features lower brightness and “colder” luminescence (correlated color temperature  $\sim 5000$  K) and larger value of FWHM of emission spectrum due to the formation of a relatively high amount of  $\text{Sr}_2\text{SiO}_4:\text{Eu}^{2+}$  phase.



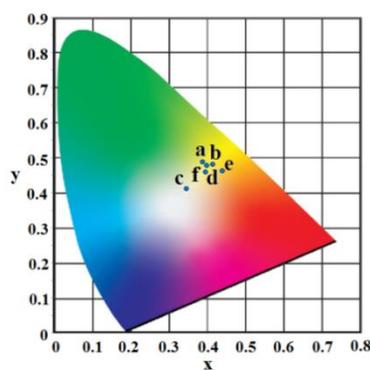
**Fig. 4** PL spectra (1) and their deconvolution into bands (2-7) for the synthesized phosphors ( $\lambda_{\text{ex}} = 405$  nm). Indexes a-f correspond to samples A-F in the table I

It should be noted that introduction of susceptor during synthesis provides increased yield of chlorine-silicate phase and correspondingly improved brightness of the obtained phosphors synthesized in all the reaction setups. Nevertheless, PL spectra of the phosphors prepared without susceptor features with relatively high FWHM (122 nm) which is promising in respect of obtaining white LEDs with high color rendering index.

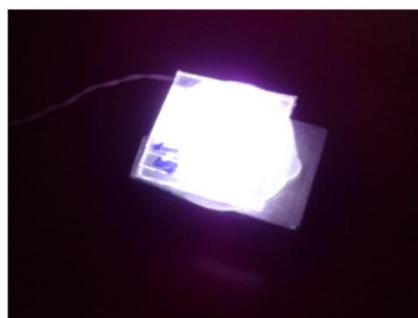
Next effect of sol-gel method of charge mixture preparation on phosphor properties was investigated. Comparison of samples B and F in the Table I shows that application of a sol-gel method provided ~35% increase in the synthesized phosphor brightness compared with mechanical mixing technique, while emission spectra of phosphors are nearly the same. This effect is supposedly caused by the improved incorporation of the activator into the phosphor and its more uniform distribution.

The CIE color coordinates  $x$  and  $y$  were calculated for the synthesized phosphors using luminescence spectra measured with  $\lambda_{\text{ex}} = 405$  nm, and are shown in the Fig. 5. The samples exhibit “warm” white (c, d, e) and yellowish (a, b and f) luminescence.

Generally, the phosphors synthesized using optimized in the paper conditions (e, f) are promising for the manufacturing of “warm” white LEDs. A pilot LED sample was fabricated using synthesized phosphor sample c having the widest emission spectrum, it is shown in the Fig. 6.



**Fig. 5** Color coordinates of phosphors obtained in syntheses summarized in table 1



**Fig. 6** White LED based on the synthesized phosphor

## 4. Conclusions

The adjustment of microwave synthesis conditions is found to provide a control over the phase composition, luminescence spectra, and color coordinates of Eu-doped silicate phosphors. Sol-gel preparation of the charge mixture instead of mechanical mixing resulted in ~35% increase of luminescence brightness. The phosphor prepared under optimal conditions exhibit “warm” white luminescence color in combination with high brightness. Generally, the considered synthesis procedure is promising for the manufacture of efficient phosphors.

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