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Polymer-assisted sol–gel synthesis and characterization of Zn_2SiO_4: Eu^{3+} powders

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ABSTRACT

The synthesis of nanophosphors for various applications and the improvement of their working parameters constitute one of the most topical problems of nowadays technology. Zinc-silicate has been extensively used as host material for phosphors in cathode ray tubes, and nowadays for phosphors in electroluminescent devices. In this work we present novel synthesis procedure for obtaining Zn_2SiO_4:Eu^{3+} powder, based on the combination of standard sol–gel and modified combustion method. Influence of preparation conditions on the structure and morphology are analyzed using X-ray diffraction and scanning electron microscopy. Luminescence properties of Eu^{3+} are investigated with fluorescence emission and lifetime measurements.

1. Introduction

Among inorganic phosphors zinc-silicate presents very suitable host for both rare earths (RE) and transition metals activators. When doped with transition metal ions of cobalt this material is used as blue pigments in ceramic industry [1] while doping with manganese ions provides long persistent green phosphor with main applications in lamps and CRTs [2–4]. However, the utility of this phosphor as green component for plasma display panels is limited due to long decay time of Mn^{2+} emission [5–7]. In our previous work we investigated, in more details, optical properties of Zn_2SiO_4 powders doped with transition metal ions of Ni, Co and Mn [8]. More recently rare earth doped Zn_2SiO_4 phosphors, in powder and thin film forms, have been attracted great attention for their luminescence properties and possible applications in flat panel display devices [9,10]. Therefore we performed a research in this area with an idea to create a simple and low-cost synthesis method which could be easily scaled up for industrial needs.

Many synthesis approaches for nanocrystalline phosphors have been developed such as sol–gel, precipitation, co-precipitation, spray and flame pyrolysis, combustion, etc. Among them the sol–gel technology offers several processing advantages as the starting materials are mixed at the nanoscale level. That ensures a complete and controlled mixing of components in the preliminary stage, increasing the reaction rate and decreasing the reaction temperature. For variety of materials good results were also gained with combustion synthesis using polymeric precursors. The utility of this polymeric approach comes from the chemical bonding of the cations onto the polymer chains during the gelation process resulting in very low cation mobility. The polymer precursor works both as chelating agent and as an organic fuel to provide combustion heat for the calcination process [11]. Up to now, the combustion process is not used at a large scale because of security problems. However, with a better process control this processing technique has a great perspective in the future.

We present here the results of a novel synthesis route based on the standard sol–gel method and non-conventional combustion method. This synthesis route enables fast and energetically efficient production of nanocrystalline Zn_2SiO_4 powder activated with europium ions, at much lower temperature than needed for the classical, solid state methods. The synthesis started from TEOS as an alkoxide precursor while polyethylene glycol (PEG) with different average molecular weights (200, 4000, 20,000) was used as a fuel. The resulting powders were fired in two ways: in a conventional furnace and in a microwave oven. We investigated the structure, morphology and luminescence emission and decay characteristics of obtained powders and how different ignition conditions, in a microwave oven and conventional furnace, affect these characteristics.

2. Materials and methods

Zn_2SiO_4 powder samples doped with 1 at.% of Eu^{3+} were prepared using polymer modified salted sol–gel method. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%), zinc(II)-oxide (Alfa Aesar, 99%) and europium(III)-oxide (Alfa Aesar, 99.9%) were used

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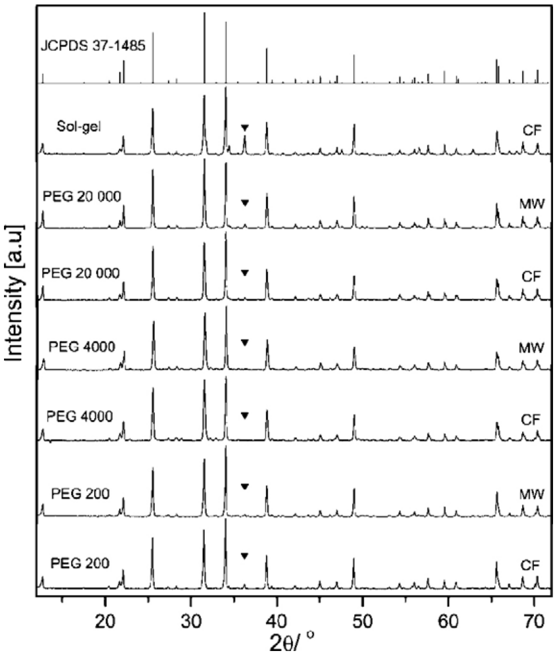

Fig. 1. From top to bottom are shown X-ray diffraction patterns of: crystallographic data according to JCPDS No. 37-1485 card, sol–gel obtained Zn_2SiO_4:Eu^{3+} powder (without PEG) and all PEG-obtained Zn_2SiO_4:Eu^{3+} powders combusted in microwave oven and in conventional furnace. With ▼ is denoted the strongest, 1 0 1 reflection of ZnO (JCPDS No. 36-1451).

as starting materials, while as solvent ethanol was used. Polyethylene glycols with average molecular weight 200, 4000 and 20,000 (Alfa Aesar; latter be denoted as PEG 200, PEG 4000 and PEG 20000) were used as fuel to provide the combustion reaction. Solutions containing appropriate concentrations of zinc and europium nitrates were prepared by dissolving zinc-oxide and adequate quantity of europium-oxide in 6 M nitric acid. Ethanol solution of equimolar TEOS was added to mixture. In the resulting sol we added PEG in 1:1 mass ratio to the expected mass of the final product, and stirred obtained mixture for 60 min at room temperature. The acidity was adjusted by slowly adding ammonia solution and stirring until gel was obtained. Drying is performed at 100 °C for 5 days. One half of resulted dry gel is fired in a conventional furnace, in air, at 1180 °C and left at the same temperature for 1 h. Other half of the sample is first combusted in a microwave oven, within 5 min, and after this thermally treated at 1180 °C for 1 h in a conventional furnace, in air.

Samples were characterized with X-ray diffraction technique for phase identification and line broadening analysis. XRD measurements are obtained on the Philips PW 1050 instrument, using Ni filtered Cu $K\alpha_{1,2}$ radiation. Diffraction data were recorded in a 2θ range from 10° to 80°, counting for 10 s in 0.05° steps.

The microstructure of the calcinated samples was observed in a scanning electron microscope (JEOL JSM 6460 LV). The composition of the sample was determined by energy dispersive X-ray spectrometry (EDX) using an Oxford Instruments X-ray microanalysis unit, acquiring a spectrum for 120 s (live time) at an accelerating voltage of 25 kV. The homogeneous distribution of the dopant throughout the material was verified with the EDX mapping technique, acquiring maps for 600 s (live time). For EDX analyses powders were cold pressed into pellets of 13 mm diameter under a load of about 3 tonnes and then coated with carbon.

Optical properties of synthesized powders were investigated using fluorescence emission and lifetime measurements. Luminescence emission measurements are performed at room temperature on the Fluorolog-3 Model FL3-221 spectroflurometer system (Horiba Jobin-Yvon), utilizing 450-W Xenon lamp as excitation source and R928P photomultiplier tube as detector. Lifetime measurements are done with TBX-04-D PMT detector, compact and integrated picosecond photon detection module. Samples were prepared as pellets under a load of 5 tonnes/cm^2.

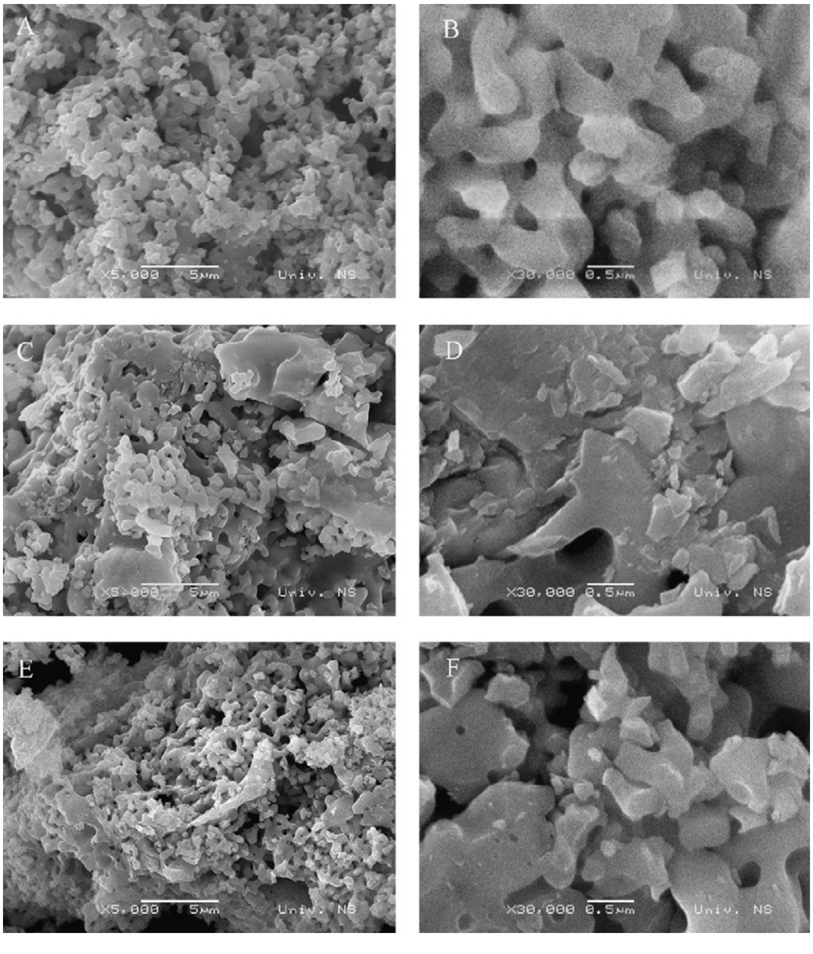

Fig. 2. SEM images of Zn_2SiO_4:Eu^{3+} powder combusted in the conventional furnace: (A and B) PEG 200, (C and D) PEG 4,000× and (E and F) PEG 20,000×. Images (A, C and E) are taken at low magnification (5,000×) and (B, D and F) at higher magnification (30,000×) of the corresponding samples.

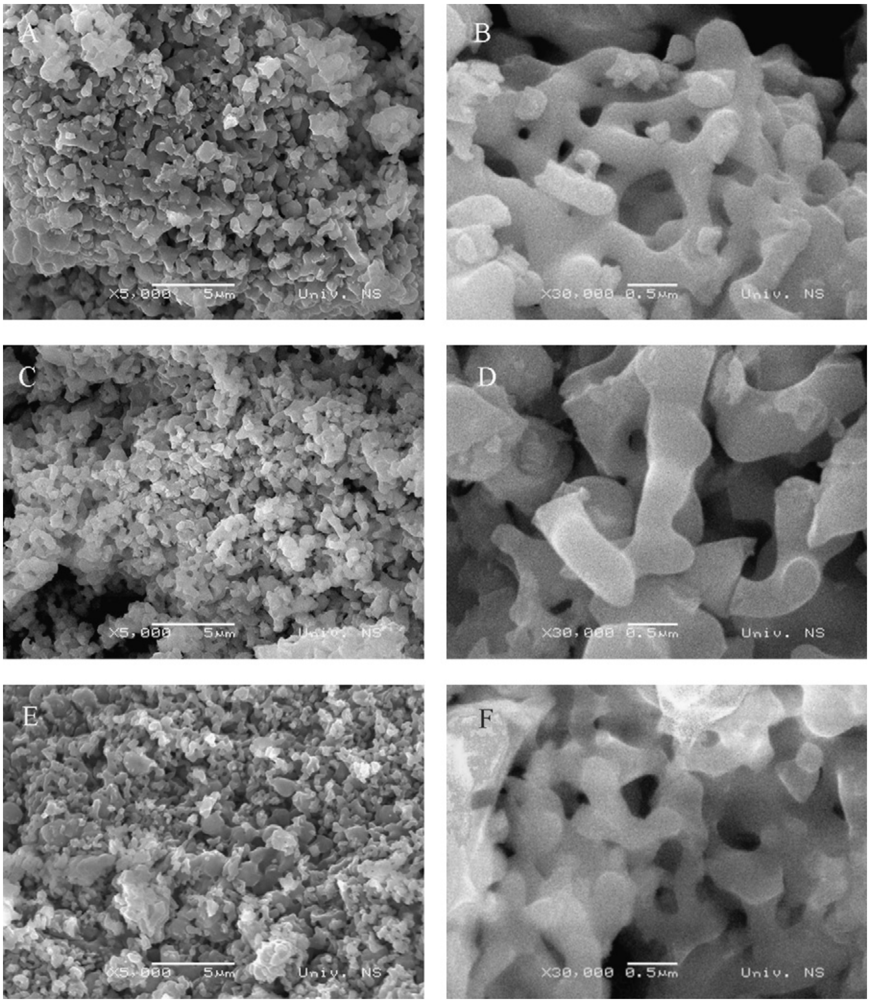

Fig. 3. SEM images of Zn_2SiO_4:Eu^{3+} powder combusted in the microwave oven: (A and B) PEG 200, (C and D) PEG 4,000× and (E and F) PEG 20,000×. Images (A, C and E) are taken at low magnification (5,000×) and (B, D and F) at higher magnification (30,000×) of the corresponding samples.

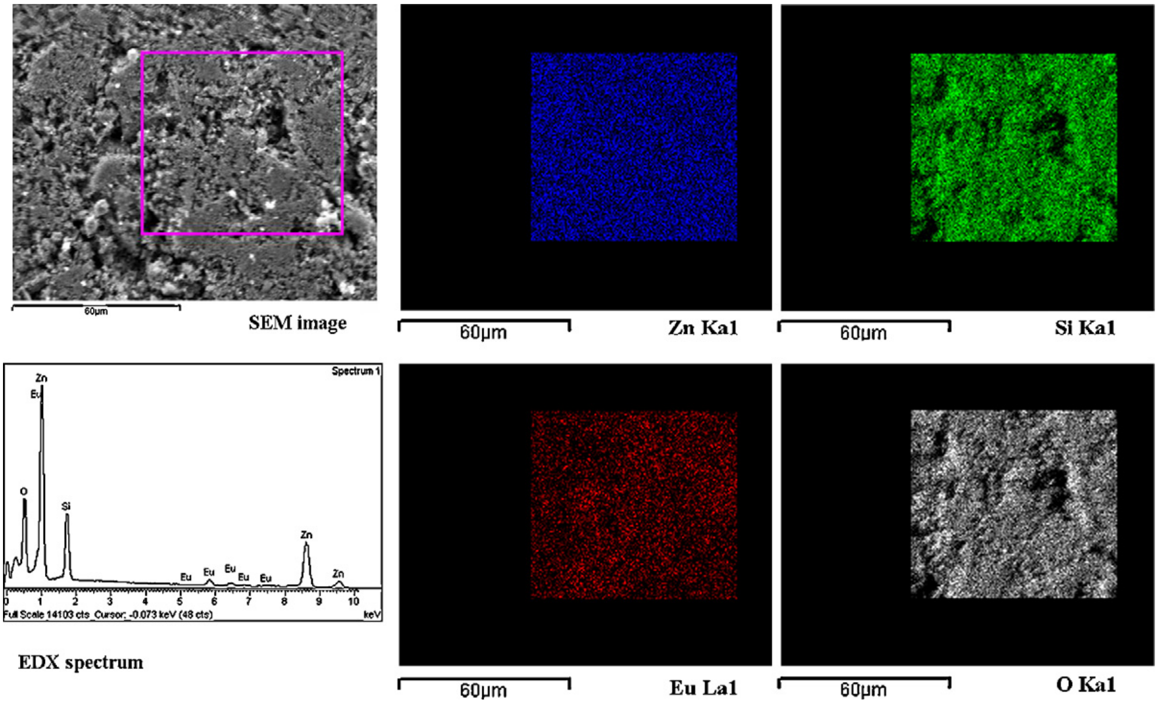

Fig. 4. EDX maps of a representative region of PEG 200 sample fired in a conventional oven.

3. Results and discussion

Under ordinary conditions Zn_2SiO_4 crystallizes in phenacite structure and belongs to the rhombohedral structure, space group *R*3, with both Zn^{2+} and Si^{4+} ions coordinated tetrahedrally to four oxygen atoms. It is very hard to obtain pure Zn_2SiO_4 phase using traditional, solid state procedure. Even under high temperatures and long thermal treatments Zn_2SiO_4 crystalline phase is accompanied by residual zinc-oxide and quartz phases [12,13]. Before this experiment we study classical sol–gel preparation as a synthesis approach. With this method we did not succeed in eliminating ZnO phase even though we tried several high temperature treatments (950 °C for 8 h, 1000 °C for 1 h, 1050 °C for 2 h, 1050 °C for 4 h and 1180 °C for 1 h for which XRD spectrum is shown in Fig. 1 under sol–gel label). Knowing that PEG is a strong organic fuel, able to provide high temperature for fast combustion reaction we decided to use it in our experiment in order to achieve direct forming of a pure zinc-silicate phase.

X-ray diffraction patterns of Zn_2SiO_4 powders obtained with PEG-assisted sol–gel method are presented in Fig. 1. One can notice complete matching of diffraction peaks and their agreement with the JCPDS No. 37-1485 data of Zn_2SiO_4. However, small quantity of ZnO (its strongest peak is marked with ▼, on the basis of JCPDS No. 36-1451) is observed in the samples obtained with PEG 200 and PEG 20000. For PEG 200 samples ZnO fraction is smaller in the microwave-treated sample then in the conventionally combusted one, while opposite happened for PEG 20000 samples. For PEG 4000 samples we obtained pure zinc-silicate phase for both cases, without any trace of ZnO. The average crystallite size of powders, according to the Scherrer's equation, is calculated using the strongest peak of (1 1 3) reflection, to be around 40–45 nm for PEG 4000 samples, and 60–65 nm for other four samples.

A final microstructure characterization of fired samples was carried out by SEM. The micrographs of samples treated in the conventional furnace are presented in Fig. 2, and those treated in the microwave oven in Fig. 3. SEM observations show that morphology of Zn_2SiO_4 powders slightly differ with the combustion treatment. At low magnification agglomerates of several tens of microns in size are visible in both kind of samples (see A, C and E in Figs. 2 and 3), which is common feature for the materials produced with combustion synthesis. The presence of pores and voids is a result of large quantity of escaping gases during combustion reaction. Observations at higher magnifications show a network of fused-like particles in microwave-treated samples, while in combusted samples the agglomerates are made up of a small, around half micron big, chunks. This difference is most clearly visible for PEG 4000 samples. The appearance of network and strong necking between particles in the microwaves-treated samples suggested that the higher temperature is achieved in the microwave oven during the combustion than in the conventional furnace [14].

The spectra obtained from the EDX analysis (see Fig. 4) qualitatively confirmed the purity of the material. Quantitative EDX analysis verified successful doping: an elemental ratio Zn/Eu ≈ 5.1 is obtained which is close to value expected for a solid solution (5.37) of the theoretical composition $Zn_{1.93}Eu_{0.07}SiO_4$. The chemical homogeneity of the samples is checked using an EDX mapping technique. The elemental maps of Zn, Si, Eu and O show a uniform density distribution, confirming that the distribution of europium is homogeneous throughout the material. As an example EDX maps obtained for PEG 200 sample are presented in Fig. 4.

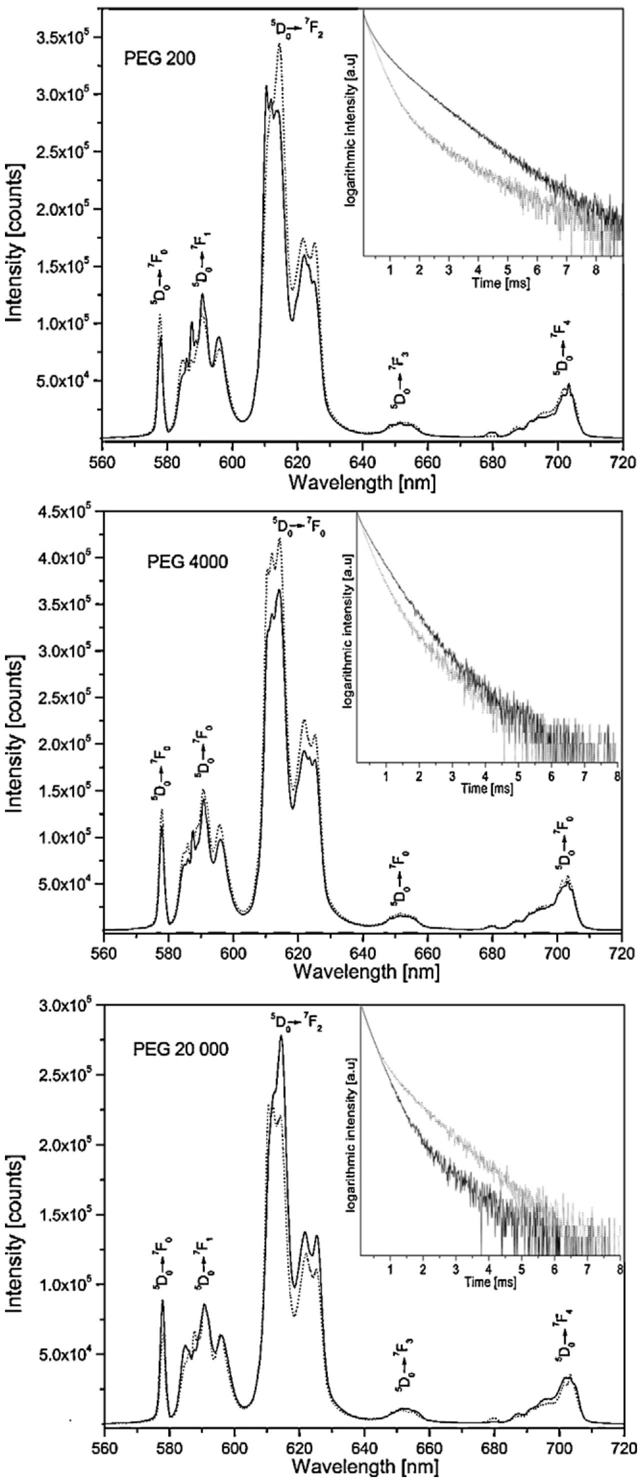

Fig. 5. Luminescence emission of Zn_2SiO_4:Eu^{3+} powders (as insert are given decay curves for $^5D_0$ level); data obtained with microwave fired samples are presented with full line, while data obtained with samples fired in conventional oven are presented with dotted line.

Emission spectra of Eu^{3+} doped samples (λ_{ex} = 393 nm) are presented in Fig. 5. In this picture, can be observed five bands centred at around 578, 590, 613–625, 653 and 702 nm, associated to $^5D_0 \to {}^7F_i$ (i = 0, 1, 2, 3 and 4) spin forbidden f–f transitions, respectively. For the $^5D_0 \to {}^7F_0$ transition we observe just one peak. At room temperature emission from different emission sites is practically indistinguishable, knowing that the coordination difference between two Zn^{2+} non-equivalent crystallographic sites is essentially negligible resulting in almost identical crystal field acting on europium ions [7]. For further investigation of europium emission from different crystallographic sites low-temperature experiments need to be performed. The $^5D_0 \to {}^7F_1$ transition is the parity-allowed magnetic dipole transition ($\Delta J = 1$) and its intensity does

Table 1
Emission lifetime values for the $^5D_0$ level for all samples. MW – microwave oven; CF – conventional furnace.

$^5D_0$ level Zn_2SiO_4:Eu^{3+}	MW samples (τ_{avg})	CF samples (τ_{avg})
PEG 200	0.8 ms	0.5 ms
PEG 4000	0.6 ms	0.5 ms
PEG 20000	0.5 ms	0.7 ms

not vary with the host. On the contrary, the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition ($\Delta J = 2$), which is in this case most dominant, is very sensitive to the local environment around Eu^{3+}, and its intensity depends on the symmetry of the crystal field around the europium ion. Lower energy transitions, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ are also clearly visible.

The fluorescence decay curves for all samples are presented as inserts in the emission spectra. As can be seen from the decay curves in Fig. 5 all can be fitted with at least two exponential functions. For this reason we found more appropriate to calculate an average lifetime values for all samples using following equation [3]:

$$\tau_{avg} = \frac{\int_0^\infty tI(t)\mathrm{d}t}{\int_0^\infty I(t)\mathrm{d}t} \quad (1)$$

where $I(t)$ represents the luminescence intensity at time t corrected for the background and the integrals are evaluated on a range $0 < t < t_m$ where $t_m \gg \tau_{avg}$. Calculated values are given in Table 1.

4. Conclusion

In this work we demonstrated a successful synthesis procedure for the fabrication of Zn_2SiO_4:Eu^{3+}, created on the combination of the sol–gel and combustion methods. XRD results clearly show that using PEG as a firing agent significantly reduces presence of unreacted ZnO phase in comparison with a classical sol–gel route. Moreover, these measurements indicate improved material characteristics when it is treated in microwave oven. So, we can conclude that microwave combustion leads to the material with better phase purity than conventionally combusted one. For all samples EDX spectral analysis and mapping technique confirmed that europium is fully and evenly integrated in the willemite solid solution, in agreement with the XRD results where no unreacted material is found. Luminescence emission measurements showed characteristic f–f electronic transitions of the trivalent europium ions with same positions of emission peaks. The $^5D_0$ emission decays have complex profiles and cannot be explained with single exponential functions. Average lifetimes values ranging from 0.5 ms to 0.8 ms are found for investigated samples.

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