

INFLUENCE OF SYNTHESIS PARAMETERS ON LUMINESCENCE EMISSION PROPERTIES OF SOME SOL-GEL DERIVED Eu^{3+} DOPED WILLEMITE PHOSPHORS

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ABSTRACT

Europium doped zinc silicate phosphor sample, corresponding to general formula, $\text{Zn}_{2-(x+y)}\text{Eu}_x\text{Li}_y\text{SiO}_4$, (where $x = 0.01$ or 0.02 and $y = 0, 0.01, \text{ or } 0.02$), have been synthesized by acid, or two steps (acid-base) catalyzed sol-gel processing, in the presence, or absence of Li^+ ions, as charge compensator. The obtained xerogel samples were successively annealed, at different steps, up to 1000°C , for 180 minutes time soaking for each temperature. Starting from 700°C temperature, the formation of Si-O-Zn linkage was put in evidence by FT-IR spectra. The appearance of IR signals corresponding to willemite vibration modes has been observed for 900°C calcined samples. At UV excitation beam, the luminescence spectra of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ synthesized phosphor samples show some emission peaks in the red region of spectra, assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$ and 5) spin forbidden f-f transitions of Eu^{3+} ions, respectively. Specifically they were situated around 575 nm, 590 nm, 615 nm, 624 nm, 650 nm and 700 nm. The most intense emission was observed for the 1000°C calcined sample, with 0.02 moles Eu^{3+} activator content, prepared with charge compensator.

INTRODUCTION

Among inorganic phosphors, willemite ($\alpha\text{-Zn}_2\text{SiO}_4$), with phenacite structure, is a very suitable host for both rare earths (RE) and transition metal activators [1]. Mn-activated willemite ($\text{Zn}_2\text{SiO}_4:\text{Mn}$) is an efficient green phosphor which has been widely used as a green component in cathode ray tubes, in fluorescent lamps and electroluminescent devices [2-3]. More recently, rare earth doped Zn_2SiO_4 phosphors have attracted great attention for their luminescence properties and possible applications in flat panel display devices [3-5]. The sol-gel technology offers several processing advantages over the conventional method, including lower temperature process, better homogeneity, and higher emission efficiency of the powder phosphors [1, 2]. In this paper are presented the synthesis studies by thermal analysis, FT-IR and luminescence spectroscopy of some europium doped willemite phosphors, obtained by sol-gel processing.

MATERIALS and METHODS

The powdered europium doped zinc silicate phosphor samples, corresponding to general formula, $\text{Zn}_{2-(x+y)}\text{Eu}_x\text{Li}_y\text{SiO}_4$, (where $x = 0.01$ or 0.02 and $y = 0, 0.01$ or 0.02 moles), have been synthesized by one step (acid) or two steps (acid-base) catalyzed alkoxy sol-gel method. For some samples, Li^+ ions were used as charge compensator. Tetraethyl orthosilicate (TEOS, 99%, Fluka), absolute ethanol (EtOH, Chimopar) zinc nitrate hexahydrate (Merck, extra pure), europium (III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9% Fluka, p.a.), lithium nitrate trihydrate 99%, Merck, p.a), distilled water, catalyst-hydrochloric acid (37%, Silal Trading,

p.a.) and ammonia solution (25%, Silal Trading) were used as starting materials. The EtOH/TEOS and HCl/TEOS mole ratios of 15/1 and 0.02/1 it was employed, respectively. The synthesis conditions are presented in table 1.

Table 1. The synthesis parameters of samples and gelation time

Sample	Europium content (x) [mole]	Lithium content (y) [mole]	NH ₃ [mole]	Gelation time
1	0.01	-	-	74 days 20 hours
2	0.01	-	0.00938	Instant
3	0.02	-	-	22 days 18 hours
4	0.02	-	0.010275	Instant
5	0.01	0.01	-	24 days 22 hours
6	0.01	0.01	0.07501	Instant
7	0.02	0.02	-	65 days
8	0.02	0.02	0.08308	Instant

The samples were prepared as follows: a mixture of calculated amounts of Zn(NO₃)₂·6H₂O, EuCl₃·6H₂O, LiNO₃·3H₂O, EtOH, HCl, and H₂O was added by slow dropping under vigorous stirring to a calculated amount of solution of TEOS, precursor dissolved into absolute EtOH. For two steps catalyzed samples, after the acid step, a 2.5% NH₃ solution was slowly dropped, until achieving the gelation point. After gelation, samples were successively dried at 45°C, 60°C and 105°C, for 10 hours, at each temperature. Further successively thermal treatments were performed at 300°C, 500°C, 700°C, 900°C and 1000°C, for 3 hours soaking time.

Thermal analysis was performed with a Mettler-Toledo unit, in air atmosphere from 25°C to 1000°C with a heating rate of 10°C min⁻¹. FT-IR (JASCO 430 FT-IR, KBr pellets) spectra were carried out, in the 4000-400 cm⁻¹ range. The photoemission and photoexcitation spectra were recorded with a Perkin Elmer LS55 luminescence spectrometer, by using a special holder for powdered solid samples. The luminescence spectra were recorded with constant slit widths, for excitation (5 nm) and for emission (4.5 nm). Excitation spectra were recorded by monitoring the red emission wavelength of 615 nm. Emission spectra were obtained using an excitation wavelength corresponding to maximum emission intensity for each sample. In order to eliminate harmonic or scattering peaks a 515 nm cut-off filter was used.

RESULTS and DISCUSSION

In Figure 1 are presented the thermal analysis results of xerogel sample labeled as 8. In the range 60-500°C, the DTA curve, shows some endothermic effects, which was ascribed to water evaporation, zinc nitrate dissolution in crystallization water, and residual solvent removal, respectively. Basic zinc nitrates formation, pyrolysis, and organic groups combustion, superimposed effects, can also occur in this temperature range. The exothermic effect, which appears between 680-830°C, was attributed to willemite crystalline network development [2, 6, 7]. The observed global weight – loss amount, from the TG curve, in the temperature range of 25-1000°C, was: 41.47%. No significant weight loss occurred above 800°C. However, DTA curves did not present a well-defined exothermic peak, indicating that crystallization occurred slowly in the samples [2].

In figure 2 are presented the overlapped FT-IR spectra of sample labeled as 8, calcined at different temperatures. In the range 350-750 cm⁻¹, FT-IR spectrum of xerogel sample 8, (curve (1)) presents a broad band corresponding to Zn-O vibrations and Si-O-Si bending modes [6, 7]; ~800 cm⁻¹ feature is due to symmetric Si–O–Si stretching vibration modes [6] ~830 cm⁻¹, 1385 cm⁻¹ and 1355 cm⁻¹ peaks correspond to NO₃⁻ ions [8]; 1090 cm⁻¹ band is

assigned to TO mode of Si-O-Si asymmetric stretching vibration; 960 cm⁻¹ signal was attributed to Si-OH and Si-O-H stretching of silanol terminal groups; ~1090 cm⁻¹ peak with a shoulder centred around 1200 cm⁻¹ is attributed to the LO mode of the Si-O-Si asymmetric stretching vibration [6].

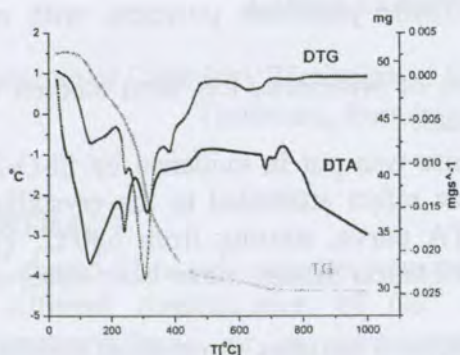


Figure 1. Thermal curves of xerogel sample labeled as 8, dried at 105°C

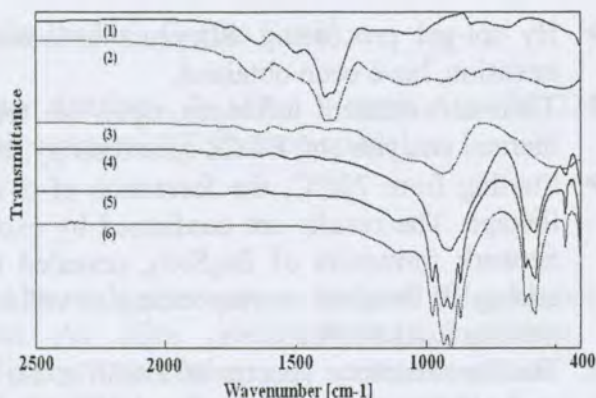


Figure 2. FT-IR spectra of 8 numbered sample, calcined at (1)-105°C, (2)-300°C, (3)-500°C, (4)-700°C, (5)-900°C and (6)-1000°C

At increased firing temperatures of the samples, the specific IR features of NO₃⁻, OH⁻, H₂O and silanol, and other organics groups, are gradually diminishing to disappearance. The peak width ranging in the 1000-1100 cm⁻¹ decreases, and the peak position shifts towards lower wave numbers, reflecting general trends to the depolymerization of silicate network [9]. The Si-O-Zn linkage can be observed by the shift of the Si-O stretching from 1096 cm⁻¹ to 940 cm⁻¹, and the shift of the Zn-O stretching vibration modes from 505 cm⁻¹ and 455 cm⁻¹ to 548 cm⁻¹. Consequently, from the spectra of samples fired at 900°C and 1000°C it can be observed the IR bonds signals corresponding to willemite: 872 cm⁻¹ (ν₁, SiO₄), 978, 934 and 905 cm⁻¹ (ν₃, SiO₄), 462, 396 and 380 cm⁻¹ (ν₄, SiO₄), 580 cm⁻¹ (ν₁, ZnO₄) and 617 and 600 cm⁻¹ (ν₃, ZnO₄) [10].

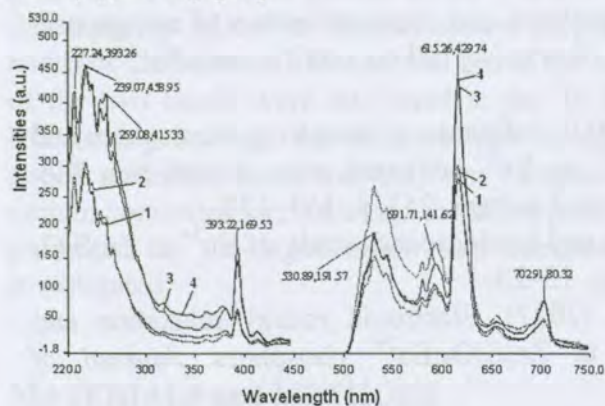


Figure 3. Excitation and emission spectra of samples 1-4, calcined at 1000°C

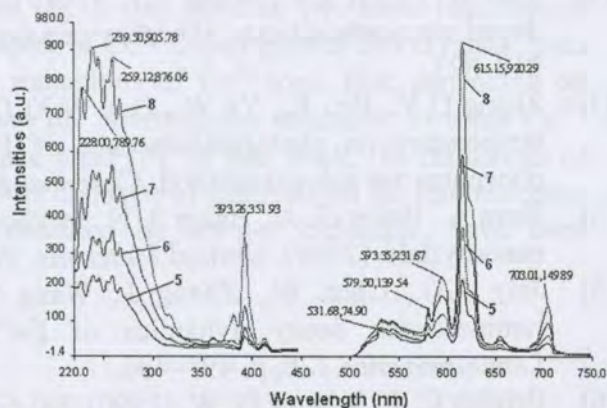


Figure 4. Excitation and emission spectra of samples 5-8, calcined at 1000°C

In the Figures 3 and 4 are presented the emission and excitation spectra of obtained samples, thermally treated at 1000°C. By UV excitation, the luminescence spectra of Zn₂SiO₄:Eu³⁺ synthesized phosphors samples show some emission peaks in the red region of spectra. The emission maxima were situated around 575, 590, 615, 624, 650 and 700 nm, this being assigned to ⁵D₀→⁷F_j (j= 0, 1, 2, 3, 4 and 5) spin forbidden f-f transitions of Eu³⁺ ions, respectively [1, 4, 5]. Comparing the activator content, better results were obtained for the samples with 0.02 moles Eu³⁺. The emission maxima were higher in the case of samples

prepared with charge compensator. The most intense emission was observed for the 1000°C calcined sample, with 0.02 moles Eu^{3+} activator content, prepared with charge compensator.

CONCLUSIONS

- By sol-gel processing europium activated willemite phosphor powders, with red emission, have been obtained.
- Thermal treatment influence, upon the formation of willemite, has been studied by thermal analysis and FT-IR spectroscopy techniques.
- Starting from 700°C, the formation of α -willemite was put in evidence by Si-O-Zn linkage. The results are confirmed by exothermic effect attributed to the crystalline network formation of Zn_2SiO_4 , revealed by DTA curve, starting from 680°C. The arising IR features corresponding to willemite vibration modes, have been observed starting from 900°C.
- The luminescence spectra of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphors samples show some emission peaks in the red region at around 575, 590, 615, 624, 650 and 700 nm. Comparing the emission intensities it can be seen that they are higher for all samples prepared with charge compensator. Taking into account the influence of activator content the better results were obtained in case of samples prepared with 0.02 moles Eu^{3+} .
- Overall, the best result, meaning the highest luminescence intensity it was obtained for 1000°C calcined sample, with 0.02 moles Eu^{3+} activator content, containing 0.02 moles K^+ , as charge compensator

ACKNOWLEDGEMENTS The authors thank to Romanian Academy.

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