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## Optical and Thermal Investigation of Sol-Gel Derived $\text{Eu}^{3+}:\text{Y}_2\text{SiO}_5$ Nanoparticles

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Investigation done on  $\text{Y}_2\text{SiO}_5$  nanoparticles doped with  $\text{Eu}^{3+}$  ions obtained with the alkoxy sol-gel route is presented in this paper. We investigate the optical and thermal properties of obtained material during the conversion of the gel into nanocrystalline form. Fourier transform infrared spectroscopy and fluorescence spectroscopy of  $\text{Eu}^{3+}$  ions are used for the optical characterizations, while thermal analysis is done with thermogravimetric-differential thermal analysis technique. Material exhibits characteristic luminescence emission of the trivalent europium ion.

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### 1. Introduction

Rare earth oxyorthosilicates ( $\text{RE}_2\text{SiO}_5$ ) doped with  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$ , and  $\text{Yb}^{3+}$  are well-known luminescent materials due to their cathodoluminescence, storage phosphor, scintillator and laser properties [1]. In particular,  $\text{Yb}:\text{Y}_2\text{SiO}_5$  (YSO) have demonstrated efficient laser action and the optical conversion exceeding 50% has been obtained [2]. On the other hand,  $\text{Y}_2\text{SiO}_5$  doped with  $\text{Eu}^{3+}$  is promising red phosphor in high resolution displays and candidate for coherent time-domain optical memory applications [3, 4].

In our previous work we studied  $\text{Gd}_2\text{SiO}_5$  sample, obtained via hydrothermal sol-gel synthesis, doped with  $\text{Eu}^{3+}$  in 1 at% concentration [5]. For this sample X-ray diffraction (XRD) analyses revealed the pure  $\text{Gd}_2\text{SiO}_5$  phase while strong red emission characteristic of  $\text{Eu}^{3+}$  ions has been observed from the emission spectra.

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In this work we present  $\text{Y}_2\text{SiO}_5$  nanopowder doped with 1 at%  $\text{Eu}^{3+}$ , obtained with alkoxy sol-gel route using tetraethylorthosilicate (TEOS) as silica source. The main objective was to observe the evolution of optical and thermal properties during conversion of YSO gel into nanocrystalline form. With this view, the prepared powder was characterized by differential thermal analysis (DTA), thermogravimetric (TG) analysis, Fourier transformed infrared (FTIR) spectroscopy, luminescence spectroscopy and scanning electron microscopy (SEM).

## 2. Experimental

The sample  $\text{Y}_2\text{SiO}_5$  with 1 at%  $\text{Eu}^{3+}$  was prepared with alkoxy sol-gel method. In brief, tetraethyl orthosilicate (TEOS, Alfa Aesar, 98%), yttrium oxide ( $\text{Y}_2\text{O}_3$ , Alfa Aesar, 99.9%) and europium oxide ( $\text{Eu}_2\text{O}_3$ , Alfa Aesar, 99.9%) were used as the starting materials, and ethanol (EtOH) as solvent. Aqueous solution containing appropriate concentrations of yttrium and europium nitrates was prepared by dissolving their oxides in 6M nitric acid. Ethanolic solution of equimolar tetraethoxysilane is added to the mixture. The resulting sol was stirred for 60 min at room temperature. Acidity of obtained sol was adjusted by slowly adding ammonia solution with stirring until transparent gel is obtained. The excess of ethanol in the gel was removed at approximately  $70^\circ\text{C}$  and then dried in oven at  $120^\circ\text{C}$  for 5 days. The final calcination, done at  $1025^\circ\text{C}$  for 2.5 hours, resulted in white color YSO powder.

TGA and DTA measurements have been performed on the SETARAM SETSYS Evolution-1750 instrument. Dried gel of  $\text{Y}_2\text{SiO}_5$  (about 20 mg) was heated from  $30^\circ\text{C}$  to  $1500^\circ\text{C}$  at the heating rate of  $10^\circ\text{C min}^{-1}$  in air atmosphere with the gas flow rate of  $16 \text{ ml min}^{-1}$ .

FTIR spectra of dried gel and calcinated YSO samples were recorded at room temperature in the wave number range of  $4000\text{--}400 \text{ cm}^{-1}$  on a Nicolet spectrophotometer (Model 380, Thermo Nicolet Corporation, Madison, USA), with  $4 \text{ cm}^{-1}$  resolution. The sample of the calcinated powder was prepared as standard KBr pellet (4% of the sample), while dried gel has been used as prepared for attenuated total reflection (ATR) measurement.

The emission spectra and lifetime measurements were done at room temperature, on the Fluorolog-3 Model FL3-221 spectrofluorometer system (HORIBA Jobin-Yvon). For emission spectra measurements a 450 W xenon lamp and R928P photomultiplier tube are used, while for the single photon timing lifetime measurements 150 W pulsed xenon lamp and TBX detector are used for time-correlated single-photon counting (TCSPC).

The microstructure of the calcinated sample was observed by SEM (JEOL JSM 6460 LV) equipped with an Oxford Instruments X-ray microanalysis unit. The purity of the sample was checked by X-ray energy-dispersion spectrometry (EDS) acquiring a spectrum for 120 s (live time) at the accelerating voltage of 25 kV.

### 3. Results and discussion

The thermal decomposition behaviour of the dried YSO gel is studied with TG-DTA technique and the obtained TG-DTA curves are presented in Fig. 1. DTA curve shows several endothermic peaks at approximately 140°C, 400°C, and 470°C. The first peak could be assigned to the removal of absorbed water and other volatiles present in the gel sample, and decomposition of nitrate ions, while latter peaks are due to the complete removal of nitrates at around 400–470°C. On the same curve extremely strong exothermic peak at approximately 300°C is present. Two smaller exothermic peaks are found at around 1025°C and other, very broad starting at 1200°C and finishing before 1500°C. This thermal behaviour can be explained knowing that  $Y_2SiO_5$  is a polymorphic silicate that crystallizes in two different types depending on the crystallization temperature. At low temperatures (below 1190°C) YSO crystallizes in the monoclinic  $X_1$ -type (crystallographic group  $P2_1/c$ ) and at higher temperatures (over 1190°C) in the monoclinic  $X_2$ -type (crystallographic group  $B2/b$ ) [6]. The transformation between the two phases takes place around 1190°C, and actually this is straightforward from our DTA analysis.

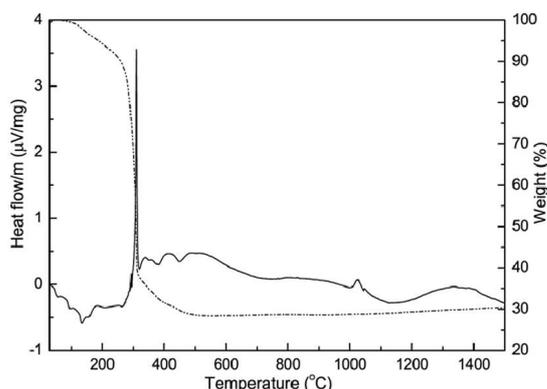


Fig. 1. TG-DTA curves of YSO:Eu<sup>3+</sup> gel: dotted line is TGA curve ( $y$  axis on the right-hand side) and solid line is DTA curve ( $y$  axis on the left-hand side).

Thermogravimetric analysis shows three distinct weight loss steps: (1) gradual weight loss of about 10% in the temperature region 30–250°C, (2) the biggest weight loss of 50% in the narrow temperature region 250–350°C accompanying the strongest exothermic peak in DTA curve and (3) practically no weight loss in the 500–1500°C region, probably due to oxidation of residual organic groups.

The crystallization process of YSO was studied by FTIR spectroscopy and spectra recorded for the dried gel and calcinated powder are shown in Fig. 2. To identify the changes taking place within the gel due to the calcination, two spectral ranges have to be considered: (1) 3000–35000  $cm^{-1}$  where the OH stretching

vibrations of water and OH groups appear and (2) 400–1100  $\text{cm}^{-1}$  where the Si–O and Y–O vibrations occur.

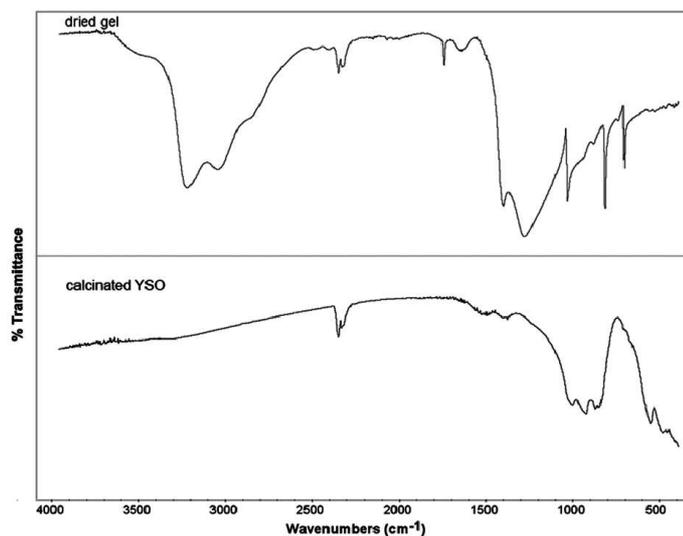


Fig. 2. FTIR spectra of dried gel and calcinated YSO:Eu<sup>3+</sup> sample.

FTIR spectrum of the gel obtained after heat treatment at 120°C for 5 days shows three main absorption regions: the first in the range 2600–3600  $\text{cm}^{-1}$ , with two broad maxima at 3230 and 3057  $\text{cm}^{-1}$  assigned to the stretching mode of OH groups; the second region in the range 1280–1760  $\text{cm}^{-1}$  originates from the absorption of H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> groups; in the third region a peak at 1040  $\text{cm}^{-1}$  originates from the absorption of Si–O–Si asymmetric stretching vibrations. The water in the silicate lattice gives rise to characteristic sharp bands in the third region of these spectra.

Second FTIR spectra belong to the YSO powder calcinated at 1025°C for 3 h. We can immediately notice that after heating the absorption peaks from –OH, H<sub>2</sub>O and NO<sub>3</sub><sup>-</sup> disappear completely and new absorption bands arise. Inorganic silicates have a characteristic, strong band centred around 1100  $\text{cm}^{-1}$  that in some cases appear as multiple bands. In our case, the band noticed at 1040  $\text{cm}^{-1}$  of dried gel sample transformed into four well differentiated absorption peaks of SiO<sub>4</sub> at 1012, 934, and 880  $\text{cm}^{-1}$  in calcinated sample, suggesting the formation of well-crystallized silicate. New absorption peak at 563  $\text{cm}^{-1}$  is due to bonding vibrations of Y–O bonds.

SEM observations of the sample show agglomerates ranging from few microns to a few tens of microns with highly porous morphology (see Fig. 3a). Observations at higher magnification show the presence of highly agglomerated particles, few hundred nanometers in size, with irregularly spherical morphology (Fig. 3b).

Energy-dispersion X-ray spectrometry (EDX) analysis qualitatively confirmed the purity of the material.

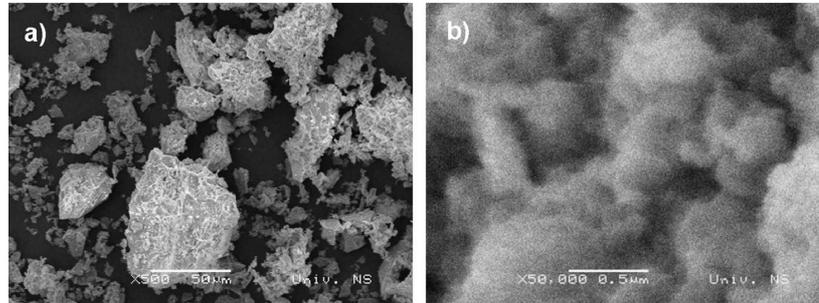


Fig. 3. SEM images taken at: (a) low (500 $\times$ ) and (b) high magnification (50000 $\times$ ).

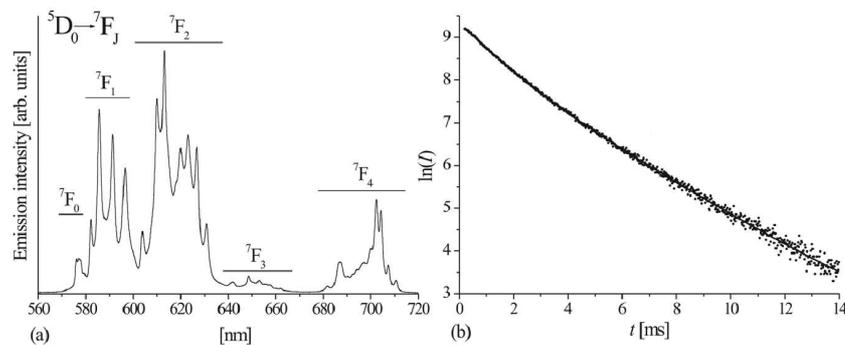


Fig. 4. (a) Luminescence emission spectra of YSO:Eu<sup>3+</sup> sample excited at 393 nm. (b) <sup>5</sup>D<sub>0</sub> decay profile at room temperature (the decay times  $\tau_1 = 1.451$  ms and  $\tau_2 = 2.893$  ms).

The room temperature luminescence spectrum for the 1% Eu<sup>3+</sup> doped YSO nanopowder is obtained under direct excitation in the <sup>5</sup>L<sub>6</sub> energy level of Eu<sup>3+</sup> ion with 393 nm radiation (Fig. 4a). In the emission spectra there are five groups of lines, corresponding to the transitions <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> ( $J = 0, 1, 2, 3, 4$ ), as indicated in Fig. 4a. Similar results are reported in number of papers [7, 8]. The most dominant are emission bands located around 610 nm which correspond to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> electric dipole transition, with the strongest emission line at 613 nm. This transition is very sensitive to the local environment around the Eu<sup>3+</sup> ion, i.e. to the crystal field and its symmetry. A weaker emission bands observed at about 590 nm are assigned to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition. Very weak features due to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub>, <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>3</sub> and <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>4</sub> transitions are observed around 577, 645, and 700 nm, respectively. As expected, two site occupancy corresponding to two different coordination numbers (7 for Y<sub>I</sub> and 6 for Y<sub>II</sub> site) is observed

from the  ${}^5D_0 \rightarrow {}^7F_0$  transition. As  $\text{Eu}^{3+}$  and  $\text{Y}^{3+}$  have very similar ionic radii, the site occupancy should be very close and the bands observed at about 577 and 578 nm are in agreement with the value reported in the literature for those two sites [9]. The fluorescence decay curve for the  ${}^5D_0$  level at emitting 613 nm under excitation at 393 nm in the  ${}^5L_6$  energy level is shown in Fig. 4b. The best fit of the experimental curve is obtained with double exponential decay lifetime (see inset in Fig. 4b) yielding the decay times  $\tau_1 = 1.45$  ms and  $\tau_2 = 2.89$  ms. This result correlates well with the previous findings [7, 8] and justifies our assumption of two sites occupancy.

#### 4. Conclusion

$\text{Y}_2\text{SiO}_5:\text{Eu}^{3+}$  powder is successfully obtained with the alkoxy sol-gel method. The thermal analysis present the typical behaviour of materials produced by sol-gel, with removal of residual water and solvents at lower, and organic compounds at higher temperatures. FTIR technique served well to identify the transformations in the sol precursors during their evolution to the final product. Comparing the FTIR spectra of the gel and calcinated sample we got the evidence for the dehydration and dehydroxylation of the YSO sample exposed to the heat treatment at 1025°C for 3 h, and for its crystallization. Using excitation wavelength at 393 nm,  $\text{Eu}^{3+}$  ions show its characteristic strong red emission from two nonequivalent sites in the structure.

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