SYNTHESIS AND LUMINESCENCE PROPERTIES OF SOME Ce^{3+} DOPED SILICA SOLS

Corina Enache[1], Zoltán Dudás[1], Cecilia Savii[1]

Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazul Ave., 300223, Timisoara, Romania, e-mail:corinaen2003@yahoo.co.uk

ABSTRACT

Ce^{3+}-doped silica sols samples were prepared by acid, or two steps catalyzed sol-gel process, at different concentration of Ce^{3+} dopant. As silica precursors, tetraetoxysilane, or tetrametoxysilane, or a precursors mixture consisting of tetraetoxysilane and isobuthyltrietoxysilane, were used. By UV excitation, all synthesized samples presented strong luminescence emission with maxima situated at ~ 386 nm. Regarding the emission efficiency, better results were achieved at lower Ce^{3+} concentrations. Depending on precursors nature, a favorable influence had the use of precursors mixture.

INTRODUCTION

Research into lanthanide-doped organic–inorganic hybrid materials resulted in the development of high efficiency and stable materials for optics [1]. The incorporation of cerium, as dopant in silicate glasses, has been widely studied for applications as phosphors, scintillators, detectors, UV absorbers, emitters and activators due to its luminescence properties [2]. While the usual method of preparation of such glasses is conventional melting, the sol-gel processing technique has also been used to prepare them [2, 3]. In Ce doped glasses, cerium can be present as Ce^{4+}, or Ce^{3+} ions, depending on preparation conditions, and this aspect is related to distinct optical properties [4]. It was reported two main luminescent bands of Ce^{3+} ions at 357 and 450 nm in the samples of Ce^{3+}-doped glasses and crystals. Both of the two bands were attributed to the 4f–5d transitions of Ce^{3+} ions. But, depending on relationship between the luminescence bands and the environment structure, in some Ce^{3+}-doped materials, there was only one luminescence band [5]. In this work, the influences of cerium concentration, nature of the silica precursors and type of catalysis on the luminescence properties of Ce-doped silica sols samples, obtained by sol-gel technique, have been investigated.

MATERIALS and METHODS

The Ce^{3+} ions doped silica sols were synthesized by sol-gel process, starting from: tetraetoxysilane (TEOS ≥ 99%, Merck), tetrametoxysilane (TMOS ≥ 99%, Acros Organics) isobuthyltrietoxysilane (iBT, ≥98, Fluka), absolute ethanol (EtOH, p.a., Chimopar), cerium (III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$, ≥ 98%, Fluka), distilled water, catalyst – hydrochloric acid (HCl, 37%, p.a., Silal Trading) and sodium fluoride (NaF, 99%, Scharlau). The H_2O/silica precursors, EtOH/silica precursors, HCl/silica precursors, NaF/silica precursors used mole ratio were in all cases, 6/1, 8/1, 0.01/1, and 0.02/1 respectively. Synthesis scheme are presented in Figure 1. In the Table 1 the synthesis parameters of samples are presented.

Table 1. Synthesis parameters of samples

Sample	Silica precursor	Catalyst	Ce/silica precursor mole ratio	Observation
0	TEOS	HCl	0	
0-b	TEOS	HCl, NaF	0	Instant gelation
1	TEOS	HCl	0.01	
1-b	TEOS	HCl, NaF	0.01	
2	TEOS	HCl	0.02	
2-b	TEOS	HCl, NaF	0.02	
3	TEOS	HCl	0.04	
3-b	TEOS	HCl, NaF	0.04	
4	TEOS	HCl	0.08	
4-b	TEOS	HCl, NaF	0.08	
5	TEOS	HCl	0.1	
5-b	TEOS	HCl, NaF	0.1	
6	TEOS	HCl	0.14	
6-b	TEOS	HCl, NaF	0.14	
7	TEOS	HCl	0.18	
7-b	TEOS	HCl, NaF	0.18	
8	TEOS	HCl	0.2	
8-b	TEOS	HCl, NaF	0.2	
9	TMOS	HCl	0	
9-b	TMOS	HCl, NaF	0	Instant gelation
10	TMOS	HCl	0.01	
10-b	TMOS	HCl, NaF	0.01	
11	TMOS	HCl	0.02	
11-b	TMOS	HCl, NaF	0.02	
12	TMOS	HCl	0.04	
12-b	TMOS	HCl, NaF	0.04	
13	TEOS/iBT (1/1 mole ratio)	HCl	0.01	
13-b	TEOS/iBT (1/1 mole ratio)	HCl, NaF	0.01	

The photoemission and photoexcitation spectra were recorded with the help of a Perkin Elmer LS55 luminescence spectrometer. The luminescence spectra were recorded at a 100 nm/min, with constant slit widths, for excitation (15 nm) and for emission (2.5 nm). Excitation spectra were recorded by monitoring the blue emission wavelength at 386 nm, corresponding to maxima intensities. Emission spectra were obtained by using an UV excitation wavelength corresponding to maximum emission intensity for each sample. A 390 nm cut-off filter to eliminate harmonic or scattering peaks was used.

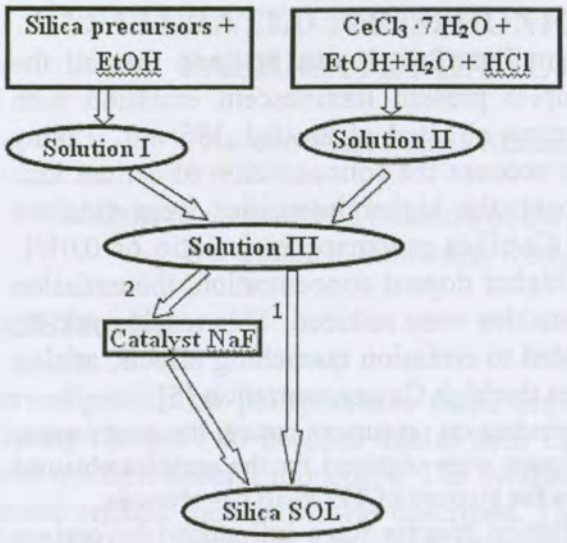

Figure 1. Synthesis flow chart for obtaining Ce^{3+} doped silica sols

RESULTS

The luminescence spectra of obtained Ce doped silica sol samples are presented in Figures 2-6

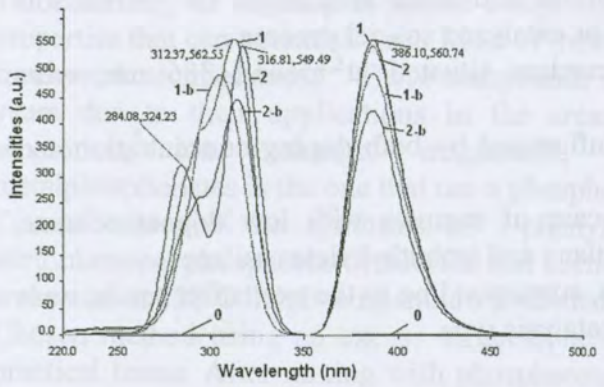

Figure 2. Excitation and emission spectra of samples 0, 1, 1-b, 2 and 2-b

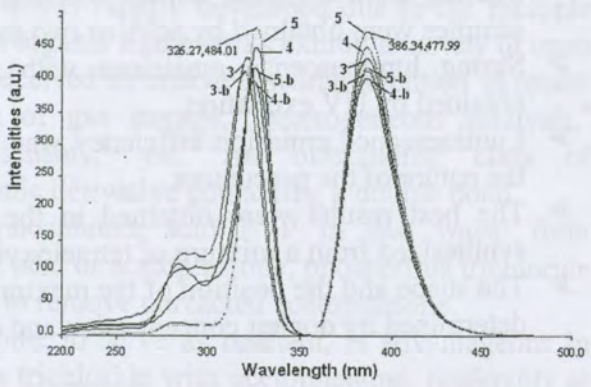

Figure 3. Excitation and emission spectra of samples 3, 3-b,4, 4-b, 5 and 5-b

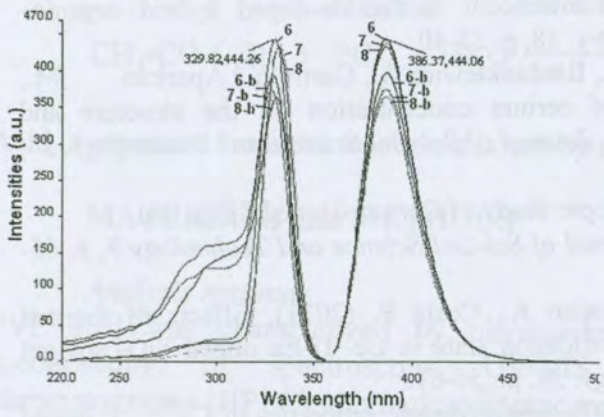

Figure 4. Excitation and emission spectra of samples 6, 6-b,7, 7-b, 8 and 8-b

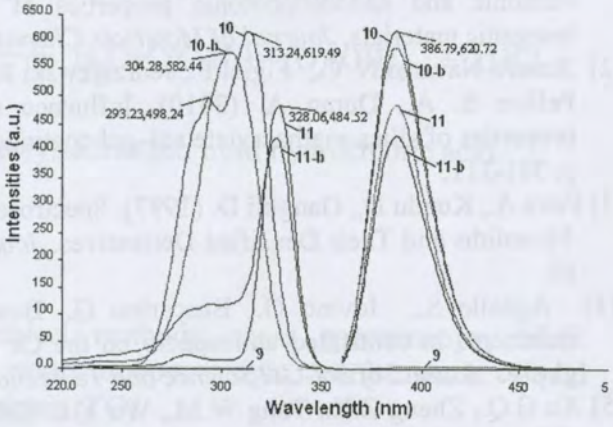

Figure 5. Excitation and emission spectra of samples 9, 10, 10-b,11 and11-b

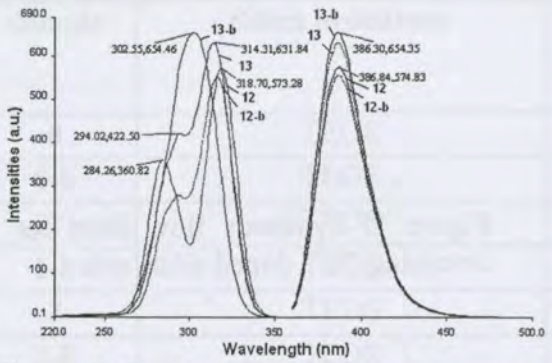

Figure 6. Excitation and emission spectra of samples 12, 12-b,13 and13-b

From Figs. 2-6, it can be seen that all the samples present luminescent emission with maxima situated at around 386 nm. Taking into account the concentration of cerium ions dopant, the higher intensities were obtained for Ce/silica precursor mole ratio of 0.01/1. At higher dopant concentration, the emission intensities were reduced. This result could be related to emission quenching effects, arising from the high Ce concentration [5]

Depending on precursors nature, the most intense emission were obtained for the samples obtained from the mixture of TEOS-iBT precursors.

The width, shape and maxima position of the excitation spectra were influenced by cerium concentration and catalysis type. The dopant content increasing has led to a bathochromic shift of excitation maxima.

CONCLUSIONS

- Starting from different dopant concentrations and silica precursors, Ce^{3+} silica sols samples were obtained by acid, or two steps catalyzed sol-gel process.
- Strong luminescence emissions with maxima situated at around 386 nm, were obtained by UV excitation.
- Luminescence emission efficiency was influenced by both doping concentration and the nature of the precursors
- The best results were obtained in the case of samples with low dopant content, synthesized from a mixture of tetraetoxysilane and isobuthyltrietoxysilane .
- The shape and the position of the maxima, corresponding to the excitation bands, were determined by dopant concentration and catalysis type.

LIST OF REFERENCES

[1] Escribano P., Julian-Lopez B. Planelles-Arago J., Cordoncillo E., Viana B., Sanchez C. (2008). Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic–inorganic materials, *Journal of Materials Chemistry*. 18, p. 23-40.

[2] Rosero-Navarro N. C., Figiel P., Jedrzejewski R., Biedunkiewicz A., Castro Y., Aparicio M., Pellice S. A., Duran A. (2010). Influence of cerium concentration on the structure and properties of silica-methacrylate sol–gel coatings. *Journal of Sol-Gel Science and Technology*. 54, p. 301-311.

[3] Patra A., Kundu D., Ganguli D. (1997). Spectroscopic Study of Cerium-Doped Silica Gel Monoliths and Their Densified Derivatives. *Journal of Sol-Gel Science and Technology* 9, p. 65-69.

[4] Agnello S., Iovino G., Buscarino G., Boscaino R., Costa F. (2011). Effects of thermal treatments in controlled atmosphere on the Ce oxidation state in Ce–Ti-Eu doped SiO_2 sol–gel glasses. *Journal of Sol-Gel Science and Technology*. 58, p. 56-61.

[5] Xu G.Q., Zheng Z.X., Tang W.M., Wu Y.C. (2007). Spectroscopic properties of Ce^{3+} doped silica annealed at different temperatures. *Journal of Luminescence*. 124, p. 151-156.

ACKNOWLEDGEMENTS: The authors thank to Romanian Academy.