

# Luminescent Light Filters Based on Ce-, Sm- and Ce-Sm-Doped Silica Gel-Glasses for Laser Heads

G.E. Malashkevich<sup>1</sup>, E.N. Poddenezhny<sup>2</sup>, I.M. Melnichenko<sup>2</sup>, A.A. Boiko<sup>2</sup>, V.I. Gaishun<sup>2</sup>, A.V. Semchenko<sup>2</sup>, *Strek*  
and K. Maruszewski<sup>3</sup>

<sup>1</sup> Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus, Minsk, Belarus.

<sup>2</sup> Gomel State University, Gomel, Belarus.

<sup>3</sup> Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

## ABSTRACT

The high concentrated silica glasses doped with Ce and Sm ions were prepared by the sol-gel technique. The preparation of the Ce-doped glasses with a low absorption coefficient ( $< 90 \text{ cm}^{-1}$ ) in the optical range above 350 nm and luminescence quantum yield  $\geq 90\%$  is reported. Such glasses seem to be promising as filters for laser heads. The high light scattering for Sm-doped glasses has been also observed.

**Keywords:** sol-gel silica, Ce and Sm ions

## 1. INTRODUCTION

One of the methods of enhancement of the efficiency of the lamp pumped lasers and removal of light degradation using of luminescent light filters in laser heads<sup>1-3</sup>. Such filters must be stable to photo-chemical active radiation, absorb this radiation and transform it to the operative absorption bands of active elements. For lasers working in pulse regime it is important to use the selective light filters which are transparent in the absorption of the active element, absorptive in the range of its superluminescence. The aim of present paper is to present a new class of such filters - Ce- and Sm-doped silica gel-glasses which possess the appropriate physico-chemical characteristics.

## 2. MATERIALS AND EXPERIMENTAL PROCEDURE

We have prepared for our studies the silica gel-glasses with high volume concentration<sup>4</sup> of Ce and Sm ions. Starting materials were tetraethylorthosilicate, hydrochloric acid (as a catalyst), aerosil (finely dispersed powder  $\text{SiO}_2$ ) and samarium chlorides and distilled water. The process of synthesis included a tetraethylortho-silicate hydrolysis, solution of the acid to obtain a sol, preparation of the colloid by adding aerosil into the sol, the addition into the system of cerium chloride, the neutralization of the activated sol-colloid system up to  $\text{pH} \approx 6.5$  by introducing an ammonia solution, liquid slip casting, gel-formation, drying and vitrification at  $1250^\circ\text{C}$ , and finally inertial cooling. Sm- and Ce-doped glasses were prepared by impregnation of xerogels. The redox conditions of glass preparation were varied by oxidation in oxygen or annealing in hydrogen.

The absorption spectra were measured on a spectrophotometer (Beckman-UV5270). The spectra of luminescence and excitation spectra were detected on a spectrofluorometer (SDL-2) and corrected with regard to the spectral sensitivity of the recording system and the spectral density distribution of exciting radiation. The luminescence kinetics were measured using a spectrofluorometer (PRA-3000). The quantum yield of luminescence was determined<sup>5</sup> by comparing the corrected luminescence spectra of the glasses and the standard with regard to the refractive indices and the amount of the exciting light absorbed by the samples.

### 3. RESULTS

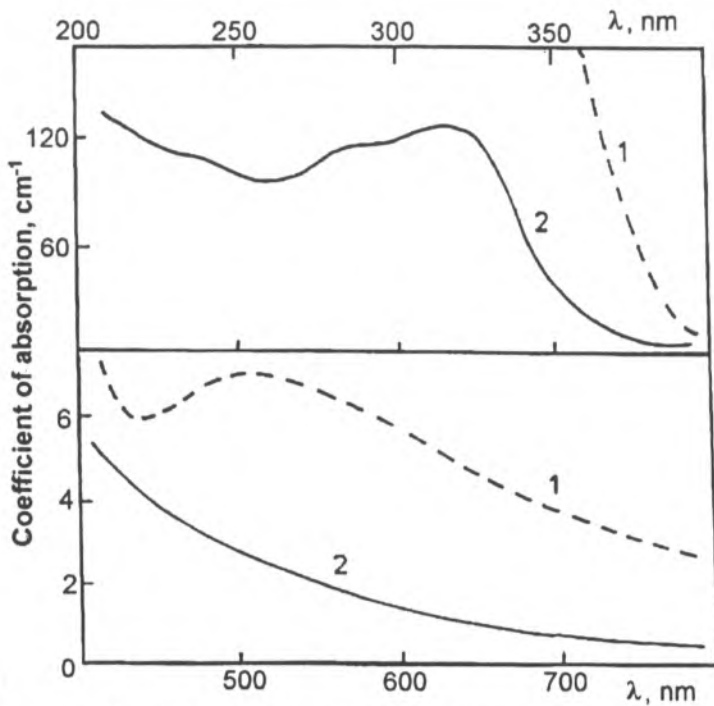


Fig. 1. Absorption spectra of Ce-containing glasses obtained in oxidizing (trace 1) and reducing (trace 2) conditions;  $N_{Ce} = 1.4 \times 10^{20}$  ions/cm<sup>3</sup>.

$\lambda_{exc}$ . At the excitation at the region above 280 nm the value of  $\eta$  is  $\geq 90\%$ .

Figure 3 shows the luminescence excitation spectra of Ce-doped glasses with  $N_{Ce} = 1.4 \times 10^{20}$  ions/cm<sup>3</sup> obtained at different redox conditions. It is seen that for the glass obtained in the oxidizing conditions the spectrum contains the band with  $\lambda_{max} \approx 315$  nm and shows some increase of the intensity in the region below 250 nm (Fig. 3 trace 1). For the glass obtained in the reducing conditions there is observed a significant change of spectrum, which consists of the overlapped bands with the maxima at 245, 280 and 325 nm (Fig. 3 curve 2). At the change of  $\lambda_{exc}$ , the positions and relative intensities of these bands also change (Fig. 3 trace 3).

Figure 4 shows the light attenuation spectra of Sm- and Ce-Sm-doped glasses obtained at the oxidizing conditions. The concentration of SmCl<sub>3</sub> in the impregnating solutions was about 4 mass %, the concentration of CeCl<sub>3</sub> was 0.5 mass %. As it is seen, the spectrum of the single doped glass is characterized by a series of narrow bands in the range 900-1700 nm and a monotonous intensification of light attenuation at  $\lambda$  decrease (Fig. 4 trace 1). The value of  $k$  is 1.3 cm<sup>-1</sup> at  $\lambda = 1.06 \mu\text{m}$ . For the co-doped glass there takes place the decrease of narrow band relative intensities, which correlates with  $N_{Ce}$ , and the increase of light attenuation many times in the region shorter than 400 nm (Fig. 4 trace 2). The reducing conditions are reflected mainly by a decrease of  $k$  in UV region and an intensification of broad band luminescence at 450 nm.

Figure 1 shows the absorption spectra of Ce-doped silica gel glasses with  $N_{Ce} = 1.4 \times 10^{20}$  ions/cm<sup>3</sup> obtained at different redox conditions. It is seen that the glass obtained at the oxidizing conditions is characterized by the structureless broad band in the visible region at  $\lambda_{max} \approx 500$  nm and the intensive absorption in the region below 400 nm (Fig. 1 trace 1). For the glass obtained at the reducing conditions can be observed a significant weakening of the visible absorption intensity and the change of the spectrum in UV region, which is manifested in the appearance of the complex band with maximum at 315 nm (Fig. 1 trace 2). The minimal value of natural absorption coefficient,  $k$ , at the short-wavelength side of this maximum is about 90 cm<sup>-1</sup>.

Figure 2 shows the luminescence spectra of Ce-doped glasses with  $N_{Ce} = 1.4 \times 10^{20}$  ions/cm<sup>3</sup> obtained at different redox conditions. As it is seen, the luminescence of glass obtained at oxidation conditions presents the weak intensity broad band with  $\lambda_{max} \approx 450$  nm (Fig. 2 trace 1). The value of  $\eta$  for the glass is  $< 1\%$ . For the glass obtained in the reducing conditions there are observed the luminescence enhancement (Fig. 2 trace 2) and the small displacement of its position at the excitation wavelength

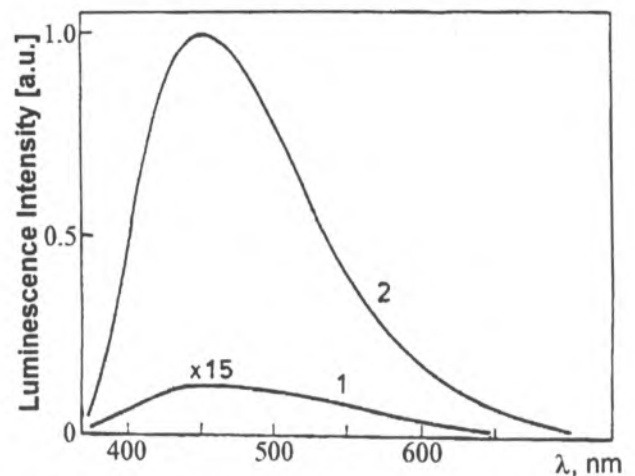


Fig. 2. Luminescence spectra of Ce-containing glasses obtained in oxidizing (trace 1) and reducing (trace 2) conditions;  $N_{Ce} = 1.4 \times 10^{20}$  ions/cm<sup>3</sup>,  $\lambda_{exc} = 340$  nm.

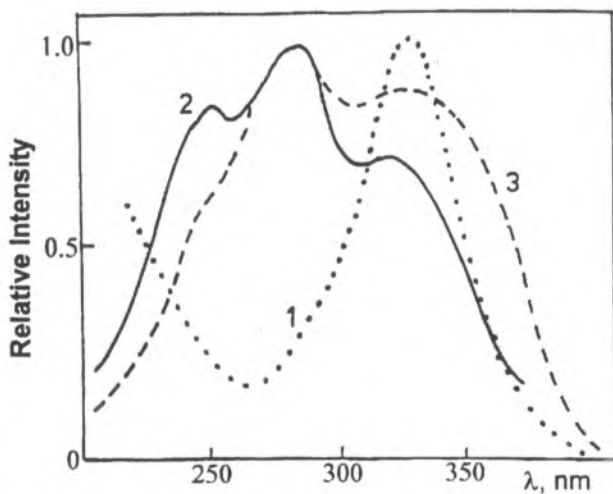


Fig. 3. Excitation spectra of Ce-containing glasses obtained in oxidizing (trace 1) and reducing (traces 2, 3) conditions;  $N_{Ce}=1.4 \times 10^{20}$  ions/cm<sup>3</sup>,  $\lambda_{mon} = 390$  nm (curve 2) and 430 nm (curves 1, 3).

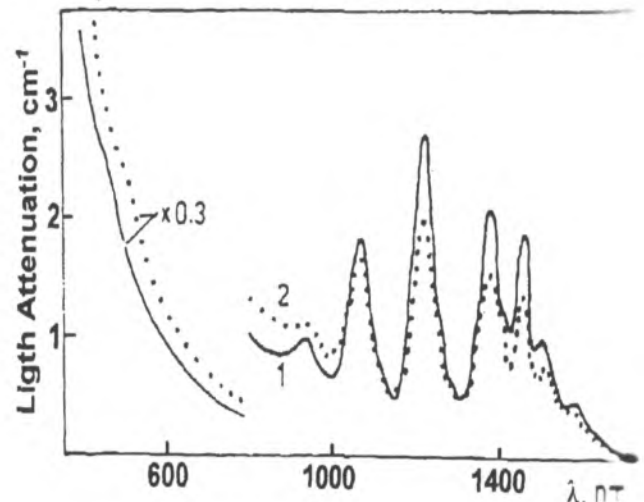


Fig. 4. Light attenuation spectra of Sm-containing (trace 1) and Ce-Sm-containing (trace 2) glasses obtained in oxidizing conditions. The concentration of SmCl<sub>3</sub> and CeCl<sub>3</sub> in the impregnating solutions were 4 and 0.5 mass%, respectively.

It should be noted that for a low doped Sm-doped glass the light attenuation intensity in the visible region decreases many times and becomes apparent in the narrow absorption bands at 400 and 470 nm. The intensity of these bands is approximately one order of magnitude than intensity of the IR bands. The luminescence of the Sm-doped glasses is characterized by a number of narrow bands located in the visible and near IR regions, among which the band at 652 nm is the most intensive. The luminescence decay average duration for these glasses is  $\sim 1.5$  ms. For the Ce-Sm-doped glass there takes place the dramatic change of spectrum which is manifested mainly in weakening of the band at 652 nm and intensification of bands at 570 and 615 nm. The luminescence average decay of the co-doped glass rises to 0.5 ms.

#### 4. DISCUSSION

It is known that the UV absorption bands of Ce-doped glasses are due to the electron transfer from the ligand to the quadruple charged Ce ions ( $\lambda_{max} \approx 265$  nm) and the interconfiguration transitions of the triply charged Ce ions ( $\lambda_{max} \approx 320$  nm). The section of absorption for the transitions with electron transfer is approximately 5 times stronger than for interconfiguration transitions<sup>6</sup>. For the highly concentrated glass the significant contribution to the UV absorption centers are Ce-doped associates also, which are characterized by the absorption band at 290 nm<sup>6</sup>.

It is not difficult to calculate that the share of pumping radiation at  $\lambda < 350$  nm, passing through such glass with 1 mm thickness, is about  $2 \times 10^{-6}$ . The relatively intense absorption of the glass in visible region is connected to the Ce-clusters.

The decrease of the UV absorption intensity and the strong intensification of luminescence for the glass obtained in reducing conditions (Fig. 2) are explained by a significant increase of the Ce(III) oxygen complexes fraction. The parallel decrease of absorption intensity in the visible region permits us to conclude that the Ce clusters, causing this absorption include the ions of quadruple charged cerium. Judging from the differences in excitation luminescence spectra of glasses obtained in the oxidizing and reducing conditions (Fig. 3), there takes place an essential reorganization of optical center structure. The non-exponentiality of their luminescence decays and the change of its average duration at variation of conditions can be connected with a non-equivalence of the local surrounding of the activator ions.

The narrow bands in the range 900-1700 nm of Sm- and Ce-Sm-doped glasses (Fig. 4) are due to the f-f-transitions of triply charged samarium ions<sup>7</sup>. The increase of the light attenuation with  $\lambda$  decrease is stipulated by the light scattering because of phase separation, which is connected to the difficulty of incorporation of the highly-coordination Sm<sup>3+</sup> ions in SiO<sub>2</sub> matrix. The weakening of the IR narrow bands with a simultaneous dramatic change of the luminescence spectrum of these ions in co-doped glass can be connected to the forming of the complex Ce-Sm-centers, which are characterized by more high covalence degree of the Sm-O-bond and the higher symmetry of local surroundings of the Sm<sup>3+</sup> ions. The decrease of the luminescence averaged decay time in co-doped glass is associated with the quenching by the Ce clusters.

necessary to note that the obtained results suggest that the luminescence decay of glass obtained at the reducing conditions should be non-exponential with regard to  $\lambda_{exc}$ . With an increase of  $\lambda_{exc}$  the non-exponentiality decreases and the decay duration raises.

The average duration of the latter in the co-doped glass is obviously connected to its quenching by the Ce clusters. The absence of appreciable rise of the light attenuation in the red and more shorter wavelength regions (the absorption in these regions of spectrum is characteristic for the Sm(II) oxygen complexes) for glass obtained in the reducing conditions suggests the significantly more difficult reduction of Sm(III) to Sm(II) than Ce(IV) to Ce(III).

## 5. CONCLUSIONS

The light filters based on the high concentration Ce-doped silica gel-glass obtained at oxidation conditions can provide a good protection of active elements from photo-chemical active radiation of pumping lamps. However, the presence of absorption of such glasses in the visible region prevents their effective using in laser heads.

The annealing in hydrogen atmosphere permits to obtain the high concentrated Ce-doped silica gel-glasses with minimum of absorption in UV region  $> 90 \text{ cm}^{-1}$  and also much lower intensity of visible absorption, and the effective luminescence at 450 nm after a UV excitation. The light filters from such glasses are promising for using in laser heads for avoiding the photo-chemical active radiation of pumping lamps and its transformation into the blue-green region of spectrum.

The light filters based on the Sm-doped silica gel-glasses provide absorption intensity in the IR region sufficient for suppression of the superluminescence of the neodymium active elements. The significant light scattering of such glasses can play both negative and positive role. On the one hand it weakens the pumping intensity but on the other hand it increases the uniformity of its distribution on section of the active element. The use of  $\text{Sm}^{3+}$  luminescence for pumping is not effective because of the small overlap integral of the absorption bands of  $\text{Nd}^{3+}$  ions and a large decay time which significantly exceeds the luminescence decay time of these ions.

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