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COMPARISON OF OPTICAL PROPERTIES OF Eu^{3+} IONS IN THE SILICA GEL GLASSES OBTAINED BY DIFFERENT PREPARATION TECHNIQUES

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Silica sol-gel glasses doped with Eu^{3+} ions were obtained by different preparation techniques. The absorption, emission and excitation spectra of the obtained glasses were measured in the range of 77–300 K. The energy level diagrams of Eu^{3+} ions were derived. An intensity analysis of $f-f$ transitions was performed. In particular, polymeric structure behaviour of europium compounds entrapped in silica gels glasses was temperature controlled during the preparation of glasses. Their optical properties were investigated.

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1. Introduction

Recently a great interest concerns looking for new materials doped with lanthanide ions (Pr, Ce, Nd, and others) in silica glasses obtained by means of sol-gel technique. Some of them could be applied as lasers, others as scintillator materials [1–6]. Most of the optical properties of these glasses depend often on the structure of active ions, their oxidation state, and the type of polymeric forms created in the materials [1, 2, 5, 7, 8]. The purpose of the present paper is to analyse changes of optical properties of few types of compounds (simple and polymeric ones) in the glasses obtained by different methods, before and after heating to high temperatures. Another question that we try to find an answer is how the concentration of active ions affects the probabilities of electronic transitions in glasses, and further how it influences emission properties of the systems under investigation.

Since those properties can be most easily analysed in europium systems, Eu nitrate and chloroacetate were used.

2. Experimental

The chemicals used for preparations were tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$, nitric or trichloroacetic acid, water and mixed H_2O +ethanol solutions. Europium salts were $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{CCl}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$.

The process of synthesis involved hydrolysis of tetraethoxysilane in aqueous solution of acid to obtain sol, neutralization of the sol-colloid system by introducing ammonium solution, gel formation, drying, vitrification under varying time-temperature conditions. Finally, the state of transparent glass was obtained. The same experimental synthesis conditions were kept in whole concentration range, in both the synthesis procedures.

Absorption spectra were measured by a Cary-Varian 5 spectrophotometer. Integrated intensities were calculated using ICII 10 program and transformed to the oscillator strength values. The excitation and emission spectra were recorded at 77 and 293 K using a SLM AMINCO SPF 500 spectrofluorometer. The EPR measurements were made by a Bruker ESP 300E spectrometer at 77 K.

3. Results and discussion

The room temperature absorption spectra in the region 800–300 nm of the silica sol-gel obtained with $\text{Eu}(\text{NO}_3)_3$, before heating, where concentration of europium ions is 5%, are shown in Fig. 1. The relative intensities of ${}^7F_0 \rightarrow {}^5D_J$ transitions indicate rather low symmetry of the system formed. It was also quite well recorded forbidden ${}^7F_0 \rightarrow {}^5D_0$ transition. In the presented spectral region, a very weak broad band at ≈ 650 nm was recorded, which can be attributed to a charge-transfer (CT) transition from Eu^{2+} to ligand. However, EPR measurements at 77 K exclude existence of Eu^{2+} ions in the glasses.

Fig. 1. The absorption spectrum of $\text{Eu}(\text{NO}_3)_3$ (5%) doped silica sol-gel at RT.

In the systems under consideration the most declared is the ${}^7F_0 \rightarrow {}^5D_2$ transition, which obeys the selection rule $\Delta J = 2$, and is most sensitive to the changes of europium ion environment. Let us consider further the splitting of these levels and the changes of electron transition probabilities with concentration, different preparation methods, as well as degradation of polymeric structure of

initial systems encapsulated in gel. Note also that gel glasses are of excellent optical quality, their transparency reaches 350 nm, at higher energies the CT transition of Eu^{3+} ion overlap the $f-f$ transitions.

Confrontation of the ${}^7F_0 \rightarrow {}^5D_2$ bands for the two systems (1% $\text{Eu}(\text{NO}_3)_3$, obtained by aqueous and alcoholic techniques) leads to conclusion about strong difference in europium ion structure in these silica sol-gel glasses before heating (Fig. 2a). The structure differences can be also found in glasses obtained by aqueous procedure with europium nitrate and chloroacetate. After heating of the both above systems up to 1100 K (the ${}^7F_0 \rightarrow {}^5D_2$ band becomes broad), destruction of the initial Eu^{3+} ion structure is observed (Fig. 2b).

Fig. 2. The absorption spectra of $\text{Eu}(1\%)$ doped silica sol-gel at RT. (a) $\text{Eu}(\text{NO}_3)_3$ from water solution (I) and from alcohol solution (II); (b) $\text{Eu}(\text{CCl}_3\text{COO})_3$ from water solution; (b') the ${}^7F_0 \rightarrow {}^5D_2$ transition for $\text{Eu}(\text{CCl}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$ single crystal [11].

Besides, temperature controlled drying of gel up to 440 K shows that the structure of Eu^{3+} ion is partially preserved in the glasses obtained with $\text{Eu}(\text{CCl}_3\text{COO})_3$ salt (Fig. 2b). In this range of temperatures according to the thermogravimetric analysis a decomposition of carboxylates occurs. How do these effects manifest in the $f-f$ transition probabilities, especially in the region of hypersensitive ones? Table collects oscillator strength values for glasses with different concentration of active ions. Linear dependence of intensity vs. concentration is broken at 5% amount of Eu^{3+} ion in the system under study. In the glasses after heating, the intensities increase markedly. Drastic differences in the intensities were found for glasses obtained by different synthesis procedures. Note that intensities of ${}^7F_0 \rightarrow {}^5D_2$ transitions remain almost unchanged up to 540°C in the polymeric europium chloroacetate, indicating significantly conservation of the polymeric structure of the initial system. Significant differences were registered after heating up to 1100 K.

Now, let us confront these results with emission properties of the systems under consideration. Luminescence spectra of the obtained glasses are shown in Fig. 3.

TABLE

Intensities of $f-f$ transitions of silica sol-gel glasses doped with $\text{Eu}(\text{CCl}_3\text{COO})_3$ and $\text{Eu}(\text{NO}_3)_3$.

		$P' \ ^7F_0 \rightarrow \ ^5D_2$	
$\text{Eu}(\text{CCl}_3\text{COO})_3$ sol-gel obtained from aqueous solution	1%	2.03	
		2.16	dried at 440 K
		2.50	dried at 540 K
		5.47	heated at 1100 K
$\text{Eu}(\text{NO}_3)_3$ sol-gel obtained from aqueous solution	0.1%	0.16	
	1%	1.89	
		6.71	heated at 1100 K
	2%	3.95	
		11.48	heated at 1100 K
	5%	12.02	
$\text{Eu}(\text{NO}_3)_3$ sol-gel obtained from alcoholic solution	1%	3.08	

$P' = P \times 10^{-8}/d$ (d — thickness of the sample [cm]).

The relative intensities of $^5D_0 \rightarrow ^7F_J$ transitions at 77 K indicate a lower symmetry of active centre in glasses obtained by alcohol procedure. Thus, the electric-dipole $^5D_0 \rightarrow ^7F_2$ transition probability is the greatest (Fig. 3). Optical spectra of glasses obtained from $\text{Eu}(\text{NO}_3)_3$ and $\text{Eu}(\text{CCl}_3\text{COO})_3$ salts differ both in their structure and intensities. A careful analysis of the $^5D_0 \rightarrow ^7F_0$ transition indicates that this band is composed of more than one component. Its half-width is $\approx 30 \text{ cm}^{-1}$. The strong vibronic components in the range 582–586 nm indicate a relatively great vibronic coupling. An inspection of the IR data of the glasses in far IR region shows comparatively the strong $\delta(\text{OSiO})$ or τSiOC , δOMO bending or torsion vibration modes [9] which are responsible for vibronic transitions.

The excitation spectra shown in Fig. 4(I) and (II) confirmed the emission and absorption results concerning the structure of active centres. However, the differences in the intensities of $^7F_0 \rightarrow ^5L_6$ transition and higher lying levels indicate the role of CT transition (located at lower energies for the alcoholic systems) in luminescence quenching. The above meets good confirmation in temperature dependences of relative intensities of $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$ transitions, whose relative intensities show less quenching at low temperatures (Fig. 4(I) and (II)). Moreover, in this system the population of 7F_1 multiplet at 293 K is relatively high, due to smaller splitting between 7F_0 and 7F_1 levels (Fig. 4(I)).

Fig. 3. The emission spectra of $\text{Eu}(1\%)$ doped silica sol-gel at 77 K. (a) $\text{Eu}(\text{NO}_3)_3$ from alcohol solution; (b) $\text{Eu}(\text{NO}_3)_3$ from water solution; (c) $\text{Eu}(\text{CCl}_3\text{COO})_3$ from water solution.

Fig. 4. The excitation spectra of $\text{Eu}(1\%)$ doped silica sol-gel. (I) at RT, (II) at 77 K. (a) $\text{Eu}(\text{NO}_3)_3$ from alcohol solution; (b) $\text{Eu}(\text{NO}_3)_3$ from water solution; (c) $\text{Eu}(\text{CCl}_3\text{COO})_3$ from water solution.

Emission spectra of silica glasses heated at 1100 K are presented in Fig. 5. Neither differences in relative intensities nor those in splittings were detected at room temperature for the two types of glasses tested. No remarkable differences of emission line intensities with concentration were detected for the silica glasses doped with 2% Eu^{3+} .

The broadening of all the bands and relative decreasing of $^5D_0 \rightarrow ^7F_1$ transition, which is of magnetic dipole origin, seem also worth noting; compare Fig. 5 with Fig. 3.

Let us discuss now the effect of concentration on the emission properties of glasses, especially at higher concentrations. A reverse relation of intensities of respective $^5D_0 \rightarrow ^7F_J$ transitions in 2% glasses was observed, compared to the

Fig. 5. The emission spectra of Eu(1%) doped silica sol-gel glasses (heated at 1100 K) at 77 K. (a) $\text{Eu}(\text{NO}_3)_3$ from alcohol solution; (b) $\text{Eu}(\text{CCl}_3\text{COO})_3$ from water solution.

Fig. 6. The excitation spectra of Eu(1%) doped silica sol-gel glasses (heated at 1100 K). (I) at RT, (II) at 77 K. (a) $\text{Eu}(\text{NO}_3)_3$ from alcohol solution; (b) $\text{Eu}(\text{CCl}_3\text{COO})_3$ from water solution.

Fig. 7. The excitation spectra of Eu(2%) doped silica sol-gel. (I) at RT, (II) at 77 K. (a) $\text{Eu}(\text{NO}_3)_3$ from alcohol solution; (b) $\text{Eu}(\text{NO}_3)_3$ from water solution.

1% glasses obtained by two different techniques. Strong differences were found in high energy range (UV region) in both excitation spectra (aqueous and alcoholic) at 77 K, compared to those of 1% concentration (compare Fig. 6(I) and (II) with Fig. 7(I) and (II)). The intensities of $^5\text{L}_6$ lines are enhanced significantly in higher concentrated glasses. It seems to indicate an influence of concentration of active Eu centre on the energy and slope of the parabola of CT transition, as well as the changes of their role in emission quenching. Kinetic of this process needs further investigation [10].

Finally, we will compare the results for gel glasses synthesised with $\text{Eu}(\text{CCl}_3\text{COO})_3$ with the optical spectra of single crystals of this salt. A question arises, how far the single crystal spectra remind those of sol-gel. The above confrontation allows to establish a very similar structure of europium surrounding in both the systems. It seems to be an important result of these investigations [11].

4. Conclusions

1. The silica sol-gel obtained by different techniques did not exhibit differences after heating up to 1100 K.
2. Significant differences were recorded between emission and excitation spectra of silica glasses obtained by sol-gel method in the region of ${}^7F_0 \rightarrow {}^5D_J$ and ${}^5D_0 \rightarrow {}^7F_J$ transitions respectively.
3. Not strictly linear dependences of intensities vs. concentration of active ions were found.
4. Essential changes of relative intensities were recorded for the silica sol-gel containing different lanthanide salts in the excitation spectra at 77 K.
5. A comparison of the absorption and excitation spectra allows us to conclude that the CT transition plays an important role in the emission properties of Eu ion.
6. Emission properties of europium silica sol-gel containing different salts were detected, and relative intensities indicate drastic differences in the symmetries of active ions.
7. Confrontation of optical data for monocrystals of europium chloroacetates with those in glass indicates similar structures of europium ions in both these materials.

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