

Luminescent properties of rhodamine 6G dye in silica sol-gel matrices

O.N.Bezkrovnaya, I.M.Pritula, V.V.Maslov^{}, V.M.Puzikov, M.I.Kolybayeva, A.V.Kosinova, Yu.A.Gurkalenko^{**}, A.V.Lopin*

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

^{*}O.Usikov Institute of Radiophysics and Electronics, National Academy of Sciences of Ukraine, 12 Proskura Str., 61085 Kharkiv, Ukraine

^{**}Institute for Scintillation Materials, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received July 15, 2010

Matrices based on silica gel with incorporated rhodamine 6G (Rh6G) molecules were synthesized by the sol-gel method. SiO₂-based sols were prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS) in ethanol with HNO₃ acid used as a catalyst. Visually transparent silica gels and xerogels based on SiO₂ were obtained at the ratio $n(\text{HNO}_3)/(1 \text{ mole TEOS})$ varying from 0.66 to 0.02. The gelation time was found to decrease with an increase of the acid content, due to high rates of hydrolysis and condensation. Luminescence spectra were studied of the silica gel samples containing Rh6G synthesized by the sol-gel method at the ratio $n(\text{Rh6G})/(1 \text{ mole of TEOS})$ varying from $1.90 \cdot 10^{-7}$ mole to $3.18 \cdot 10^{-5}$ mole. A red shift of the luminescence maximum was observed with increasing dye concentration, which is caused by formation of its associates. Incorporation the dye molecules into the xerogel network decreases their association.

Золь-гель методом синтезированы матрицы на основе силикагеля с инкорпорированными молекулами родамина 6G (Rh6G). Золи на основе SiO₂ приготовлены гидролизом и поликонденсацией тетраэтоксисилана (TEOS) в этаноле в присутствии кислоты HNO₃ в качестве катализатора. Визуально прозрачные силикагели и ксерогели на основе SiO₂ получены при соотношении $n(\text{HNO}_3)/(1 \text{ моль TEOS})$ от 0,66 до 0,02. Обнаружено, что с увеличением содержания кислоты сокращается время гелеобразования благодаря высоким скоростям гидролиза и конденсации. Исследованы спектры люминесценции синтезированных золь-гель методом образцов с Rh6G при соотношении $n(\text{Rh6G})/(1 \text{ моль TEOS})$ от $1,90 \cdot 10^{-7}$ моль до $3,18 \cdot 10^{-5}$ моль. Наблюдается bathochromный сдвиг максимума люминесценции при увеличении концентрации красителя, что обусловлено образованием его ассоциатов. Инкорпорирование молекул красителя в сетку силикагеля сопровождается снижением ассоциации Rh6G.

1. Introduction

Numerous investigations performed during recent few years have been aimed at obtaining active laser media on the base of polymers, composite sol-gel glasses and silica gels with incorporated luminophores [1–12]. These studies are topical due to simplicity of the use of such kind of matrices,

as well as to the possibility of development of hybrid structures for optics and spectroscopy. The solid-state matrices with dye have been used to create tunable lasers, light guides and active elements for nonlinear optics and photonics [1, 2, 6, 8]. Thus, special attention has been paid to the obtaining of composite materials by the sol-gel method

and to studies of such materials [1–4]. The sol-gel method makes it possible to obtain one- or many-component glasses at temperatures lower than the melting point, as well as to create hybrid materials on the base of organic and inorganic components. The matrices based on silica are promising for the use as of optical media, since in inorganic matrices the photostability of incorporated dyes is much higher in comparison with that in polymeric environment [13]. The dye rhodamin 6G (Rh6G) in SiO_2 -matrix annealed at 750°C [11] possesses high photostability in comparison with Rh6G ethylene glycole solution used as an additive for dye lasers.

The classical process of preparing SiO_2 matrices includes hydrolysis and polycondensation of tetramethoxy- or tetraethoxysilanes [1, 2, 4, 5]. This process leads to the formation of gel which, after drying, forms xerogel with nanometric pores [1]. Organic dyes can be incorporated both into the matrix at the stage of gel formation [1, 14], or into the solid glasses obtained after xerogel annealing [1, 10]. An advantage of introduction of luminescent dyes into sols is their uniform distribution in inorganic sol-gel matrices.

In the present work, the influence of HNO_3 acid concentration on the obtaining of transparent silica matrices on the base of tetraethoxysilane (TEOS) by the sol-gel method was studied. Special attention was paid to the decrease of the association of Rh6G dye molecules in the process of their incorporation into the silica gel network.

2. Experimental

As initial reagents for silica gel synthesis, we used tetraethoxysilane (TEOS, Aldrich), additionally purified ethanol, formamide (FA, Aldrich) and twice distilled water. At the stage of sol preparation, the ethanol solution of Rh6G (Aldrich) was introduced into the samples as a luminescent additive.

The sol-gel matrices were prepared by acid-catalyzed hydrolysis and condensation of TEOS, which was dissolved in a mixture of ethanol, water and HNO_3 acid. HNO_3 acid was added to all the samples as a reaction catalyst, with FA introduced into some samples as a drying control chemical additive.

The mixture TEOS/ethanol (Rh6G)/ $\text{HNO}_3/\text{H}_2\text{O}/\text{FA}$ (or the one without FA) was agitated during two hours in a magnetic mixer. Then the obtained sol was poured into plastic cuvettes or tubes, which were

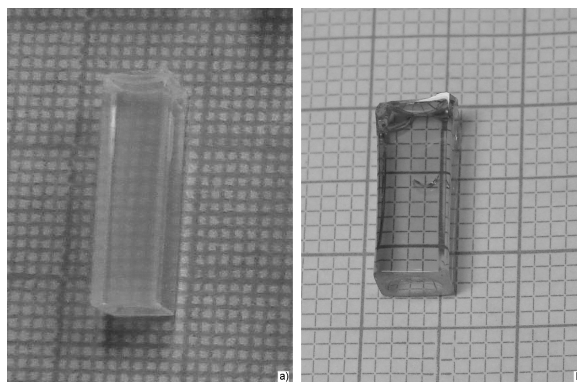


Fig.1. SiO_2 matrices with Rh6G dye prepared by sol-gel method: with FA, $3.18 \cdot 10^{-5}$ mole Rh6G/(1mole TEOS) (a), without FA, $4.8 \cdot 10^{-5}$ mole Rh6G/(1mole TEOS) (b).

hermetically sealed and kept till the formation of the gel. Afterwards the samples were withdrawn and dried during 3–4 weeks at 30°C and then at 60°C for 7 days. After drying, the samples decreased in volume by 10–14 times with the corresponding rise of the dye concentration. Thus, the sol-gel matrices on the base of SiO_2 with incorporated molecules of Rh6G dye were obtained using FA and without the latter (Fig. 1).

The absorption spectra of all the samples were recorded using a Lambda 35 (Perkin-Elmer, USA) spectrophotometer in the spectral range 200–1100 nm, the luminescence spectra were measured by a FluoroMax-4 (Horiba Jobin Yuon, USA) spectrophotometer. The size of SiO_2 nanoparticles forming the xerogel structure was checked on a transmission electron microscope (TEM-125). It was shown that the skeleton of the xerogels (obtained without FA and dried at 150°C) was formed by ~ 3 –7 nm particles touching each other (Fig. 2).

3. Results and discussion

The process of sample gelation directly depends on the molar ratio of the mixture of TEOS, water, acid, ethanol, and on the addition of drying control chemical additive such as FA. The sol-gel process included TEOS hydrolysis and polycondensation in the presence of HNO_3 acid used as a catalyst [1, 2, 5]. Visually transparent gels based on SiO_2 were obtained for $n(\text{HNO}_3)/(1 \text{ mole TEOS})$ ratio ranging between 0.66 and 0.02. Thus, with the increase of the acid content the gelation time decreases (Fig. 3) due to high rates of hydrolysis and condensation [14]. When the ratio $n(\text{HNO}_3)/(1 \text{ mole$

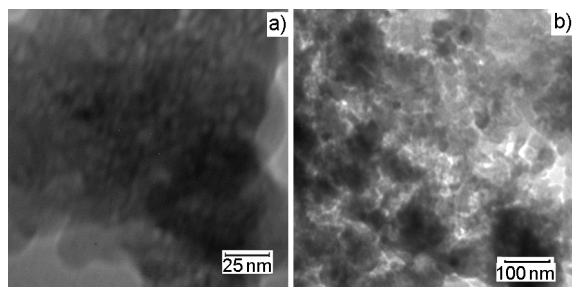


Fig.2. TEM images of SiO_2 xerogels (obtained without FA and dried at 150°C) at different magnifications.

$\text{TEOS}) = 0.002$, the gelation time was the longest, since at low acid content the rate of condensation and polymerization was very low. In the case when the content of HNO_3 was less than 0.02 mole per 1 mole of TEOS, the obtained silica gels were less transparent. At low molar ratio $n(\text{HNO}_3)/(\text{1 mole TEOS})$ the catalyst quantity was insufficient, therefore the hydrolysis and condensation proceeded incompletely [14]. At the rise of HNO_3 content up to 0.66 mole per 1 mole of TEOS and higher, the cracking resistance of the xerogels in the process of drying (at 60°C and 100°C) decreased. This is related to the fact that the processes of hydrolysis, polycondensation and polymerization lead to the formation of highly cross-linked structures prone to compression cracking [14].

It was found that with the rise of the temperature up to 40°C the gelation time decreased, but the transparency of the samples worsened due to probable aggregation of the silica gel particles. An essential decrease of the gelation time also occurred through the addition of FA. The mechanism of the action of FA is based on simple removal of water from the surface of SiO_2 silica gel particles. Such a process of elimination of water adsorbed by a large number of $\equiv\text{Si}-\text{OH}$ bonds on the gel surface is caused by the formation of hydrogen bonds in the system $\text{SiO}-\text{H}-\text{OH}_2$ [4, 5].

Moreover, the duration of SiO_2 sol gelation can be shortened by the addition of the dye Rh6G at the stage of gel formation. Thus, the introduction of more concentrated dye solutions favors the formation of the gel network and separation of moisture from the samples in the process of gel formation. The samples become uniformly colored.

When the concentration of Rh6G in silica sol changes from $2.4 \cdot 10^{-7} \text{ M}$ to $7.09 \cdot 10^{-6} \text{ M}$, the value of absorption increases linearly

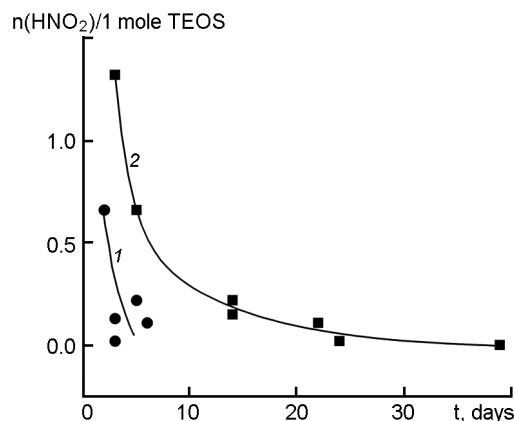


Fig.3. Dependence of the gelation time of the SiO_2 sols on the HNO_3/TEOS molar ratios at: 20°C (1), 40°C (2).

with the dye concentration. The maximum of the monomer band of Rh6G ($S_0 \rightarrow S_1$ transition) is 532 nm (Fig. 4). Such a maximum is also characteristic of Rh6G in ethanol and in newly solidified gel. There is observed the blue shift of 4 nm for the absorption maximum of Rh6G in SiO_2 matrix dried at 60°C .

At a low content of the luminophor ($1.9 \cdot 10^{-7} \text{ M}$ of Rh6G/1 mole of TEOS) in FA-containing SiO_2 matrix the luminescence band has a maximum at 550 nm. The increase of the molar ratio Rh6G/TEOS leads to the red shift of the luminescence peak followed by concentration quenching of the luminescence (Fig. 5) [15]. Characteristically, the rise of the Rh6G concentration is accompanied with the formation of luminescent dimers [16]. However, with further increase of this concentration non-luminescent fluorescent H-dimers may also be formed.

The maximum of Rh6G luminescence in ethanol solution ($6.3 \cdot 10^{-5} \text{ M}$ Rh6G) is 562 nm (Fig. 6). This is related to high concentration of the dye and, consequently, to association of its molecules [14–16]. The widening of the luminescence band in the long-wavelength region and the shift of the maximum to 574 nm (Spectrum 2) in silica gel ($6.3 \cdot 10^{-5} \text{ M}$ Rh6G in sol) is caused by the formation of dye associates in the residual moisture in the SiO_2 network. At further drying of the sample (4 weeks) the dye association decreases. The luminescence maximum is shifted to 570 nm (Spectrum 3). Drying of the sample at 60°C leads to the shift of the luminescence maximum to 555 nm (Spectrum 4).

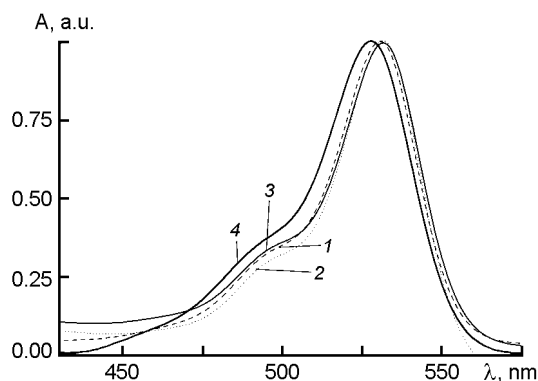


Fig. 4. Normalized visible spectra of Rh6G in: $1.26 \cdot 10^{-5}$ M Rh6G ethanol solution (1), $1.26 \cdot 10^{-5}$ M Rh6G in SiO_2 gel (2), $1.18 \cdot 10^{-6}$ M Rh6G in SiO_2 gel (3), $1.26 \cdot 10^{-5}$ mole/ dm^3 Rh6G in SiO_2 xerogel (4).

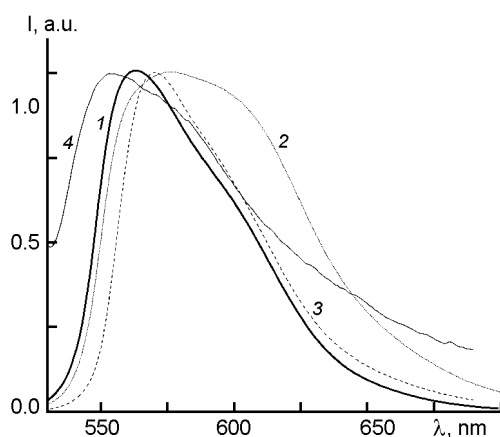


Fig. 6. Luminescence spectra of 6.310^{-5} M Rh6G in ethanol solution (1) and SiO_2 matrix with $4.8 \cdot 10^{-5}$ mole Rh6G/(1mole TEOS): silica gel without of FA after 2 weeks drying at 20°C (2), after 4 weeks drying at 20°C (3), and SiO_2 xerogel was dried at 60°C (4).

With the increase of the concentration of incorporated Rh6G molecules in SiO_2 matrix the formation of dye associates becomes more intense. The dye molecules may be built into the structures formed by silanole (Si-OH) and siloxane (Si-O-Si) groups. The decrease of the concentration of the associates in the sample due to drying at 60°C is caused by the removal of residual water molecules from the matrix, since in aqueous medium Rh6G dye forms dimers and complex associates [14, 15, 17]. Thus, the luminescence maximum is characterized by the blue shift (Spectrum 4, Fig. 6). The introduction of Rh6G into silica matrix (Fig. 1b) may lead to the appearance of both the monomer form of the dye and its associates.

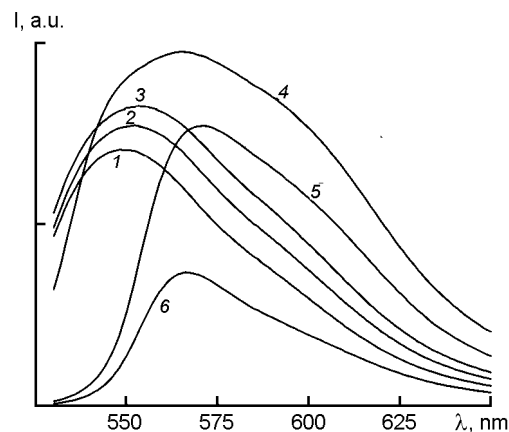


Fig. 5. Luminescence spectra of Rh6G in SiO_2 matrix with FA at $n(\text{Rh6G})/(\text{1mole TEOS})$ ratio: 1.9010^{-7} mole (1), $5.72 \cdot 10^{-7}$ mole (2), $9.5 \cdot 10^{-7}$ mole (3), $5.72 \cdot 10^{-6}$ mole (4), $3.18 \cdot 10^{-5}$ mole (5), $5.82 \cdot 10^{-5}$ mole (6). The samples were dried at 30°C .

4. Conclusion

The performed investigations show the possibility to create a luminescent material on the base of silica gels and Rh6G dye. The absorption and luminescence spectra of silica gel matrix with incorporated dye molecules have been studied. The widening of the luminescence spectrum of the dye-containing sample in the long-wavelength region is related to the formation of the dye associates in the residual aqueous medium in the silica gel network. It is shown that when the silica gel is dried at 60°C , the dye association decreases due to trapping of its molecules into the sol-gel matrix network. This leads to the blue shift of the luminescence maximum.

Acknowledgement. The authors are grateful to Dr.O.M.Vovk for measurement of TEM.

References

1. F.Salin, G.Le Saux, P.Georges et al., *Opt. Lett.*, **14**, 785 (1989).
2. M.Sharma, D.Mohan, R.D.Singh et al., *Opt. Mater.*, **30**, 1273 (2008).
3. R.Reisfeld, T.Saraidarov, *Optical Materials*, **28**, 64 (2006).
4. N.N.Khimich, *Glass Phys. Chem.*, **30**, 107 (2004).
5. N.N.Khimich, *Glass Phys. Chem.*, **30**, 430 (2004).
6. Q.Y.Zhang, W.X.Que, S.Buddhudu et al., *J. Phys. Chem. Solid*, **63**, 1723 (2002).
7. R.Gvishi, U.Narang, G.Ruland et al., *Appl. Oganometal. Chem.*, **11**, 107 (1997).
8. E.Yariv, S.Schultheiss, T.Saraidarov et al., *Optical Materials*, **16**, 29 (2001).

9. T.Saraidarov, R.Reisfeld, *Opt. Lett.*, **31**, 356 (2006).
10. R.Reisfeld, *J. Fluorescence*, **12**, 317 (2002).
11. I.I.Ganina, Yu.N.Velikhov, V.K.Klochkov et al., *Nanostrukturnoe Materialovedenye*, **1**, 19 (2009).
12. T.A.Blank, I.I.Ganina, Yu.V.Malukin et al., *Functional Materials*, **16**, 517 (2009).
13. J.B.Benedict, P.M.Wallace, P.J.Reid, *Advan. Mater.*, **15**, 1068 (2003).
14. A.P.Rao, A.V.Rao, *Scien. Techn. Advan. Mater.*, **4**, 121 (2003).
15. A.Anedda, C.M.Carbonaro, R.Corpino et al., *J. of Non-Crystalline Solids*, **353**, 481 (2007).
16. R.Vogel, M.Harvey, G.Edwards et al., *Macromolecules*, **35**, 2063 (2002).
17. G.E.Malashkevich, E.N.Poddenezhnyi, I.M.Mel-nichenko et al., *Fizika Tverdogo Tela*, **40**, 466 (1998).

Люмінесцентні властивості барвника родаміну у силікатних золь-гель матрицях

**О.М. Безкровна, І.М. Притула, В.В. Маслов, В.В. Пузіков,
М.І. Колибаєва, А.В. Косінова, Ю.А. Гуркаленко, О.В. Лопін**

Зол-гель методом синтезовано матриці на основі силікагелю з інкорпорованими молекулами родаміну 6G (Rh6G). Золі на основі SiO_2 приготовано гідролізом і поліконденсацією тетраетоксисилану (TEOS) в етанолі у присутності кислоти HNO_3 у якості каталізатора. Візуально прозорі силікагелі і ксерогелі на основі SiO_2 отримано при співвідношенні $n(\text{HNO}_3)/(1 \text{ моль TEOS})$ від 0,66 до 0,02. Виявлено, що із збільшенням вмісту кислоти скорочується час утворення гелів завдяки високим швидкостям гідролізу і конденсації. Досліджено спектри люмінесценції синтезованих зол-гель методом матриць з Rh6G при співвідношенні $n(\text{Rh6G})/(1 \text{ моль TEOS})$ від $1,90 \cdot 10^{-7}$ моль до $3,18 \cdot 10^{-5}$ моль. Спостерігається батохромний зсув максимуму люмінесценції при збільшенні концентрації барвника, що обумовлено утворенням його асоціатів. Інкorpорування молекул барвника в сітку силікагелю супроводжується зниженням асоціації Rh6G.