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Spectroscopic study of Eu^{3+}-doped and Eu^{3+},Y^{3+}-codoped SiO_2 sol–gel glasses

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Abstract

Eu^{3+}-doped and Eu^{3+},Y^{3+}-codoped SiO_2 glasses were prepared through sol–gel technology. Effects of annealing on the spectroscopic properties, including photoluminescence, decay processes and spectral hole burning, were investigated. It was found that clusterization of Eu and Eu–Y may take place during the annealing process, and the environment of Eu ions was changed from a site of near inversion symmetry to one with more non-inversion character, resulting in an increase of the $^5D_0 \rightarrow {}^5F_2$ transitions relative to that of the transitions to $^5F_0$ and $^5F_1$. The affects of clusterization on the spectroscopic properties are discussed.

Keywords: Photoluminescence; Hole burning; Nanoclusters; Eu^{3+}–SiO_2

1. Introduction

Eu^{3+}-doped SiO_2 sol–gel glasses are very interesting materials for luminescence applications, and have been extensively studied in recent years [1–3]. The red emission of $^5D_0$ to $^5F_2$ near 615 nm and the convenience of thin film preparation through sol–gel technology offer potential advantages for emissive displays [4]. On the other hand, the material is also of interest because in the last two years persistent high temperature spectral hole burning was observed [5,6]. Hole burning has been suggested as the physical basis for high density frequency-domain optical data storage. Eu–SiO_2 glasses have shown favorable spectroscopic features for this application: wide inhomogeneous linewidths, high transparency, and high hole persistent temperature (78 K).

The mechanism of the persistence of the spectral hole observed in the Eu-doped silica glass is unclear. It was generally ascribed to certain photophysical processes. Nogami and Hayakawa correlated it with water molecules entrapped in the sol–gel silica glasses [5]. In order to understand the physical processes which govern the spectral hole burning, a thorough spectroscopic study is necessary.

In this work, the influence of the annealing process on photoluminescence, decay dynamics and spectral hole burning was investigated. Large changes in spectroscopic properties with annealing temperatures were observed, which are ascribed to clusterization during the annealing process. Heavy codoping with Y^{3+} may inhibit the clustering and disperse the distribution of Eu^{3+}, thereby reducing the concentration quenching and enhancing the luminescence and spectral hole burning. Actually, Eu^{3+}:Y_2O_3 itself is one of the most important materials for display applications [7].

2. Experimental

The samples of Eu^{3+}-doped and Eu^{3+},Y^{3+}-codoped SiO_2 glasses were prepared by the sol–gel method, with three doping concentrations: 1at% Eu; 0.7at% Eu+2.5at% Y; and 1at% Eu+10at% Y. The precursors used were tetraethoxysilane [TEOS=Si(OEt)$_4$], yttrium isopropoxide, $Y(OC_3H_7i)_3$, in toluene–isopropanol, mixed with ethanol and water. The mixture was stirred using an ultrasonic stirring machine. The aqueous solution of $EuCl_3$ was added dropwise to achieve the required doping level. The

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dry gels were annealed in air at temperatures from 130 to 1000°C for 2 h. The details of the sample preparation are given in Ref. [3].

The emission line at 457.9 nm of a Coherent Ar laser was used to pump the $^7F_0 \rightarrow ^5D_2$ transition of Eu. Photoluminescence was measured with a SPEX double spectrometer equipped using photon counting techniques. Low temperatures were obtained with a helium closed cycle cryostat TS-20. For lifetime measurements, the harmonic outputs, 532 nm or 355 nm, of a Nd–YAG laser were used to pump the samples. The decay process of luminescence was recorded with a Stanford Research SR 430 transient scaler. Spectral holes were burnt through excitation of the $^7F_0 \rightarrow ^5D_0$ transition using Rodamine 6G in Coherent 599 or 899 dye lasers, pumped by a Coherent INNOVA 300 Ar laser. The Coherent 599 dye laser had a line width of 0.15 cm^{-1}, used to burn a wider spectral holes. Narrow holes were burnt by the Coherent 899 dye laser with the line width 2 MHz (2×10^{-4} cm^{-1}) at temperatures from 1.5 to 30 K.

3. Experimental results

Luminescence spectra of 1at% Eu^{3+}-doped SiO_2 glass samples, annealed at different temperatures, are shown in Fig. 1. All the emission lines are the transitions from the metastable orbital singlet state $^5D_0$ to the spin–orbit states of ^7F_J ($J=0$–6). The emission line at 578 nm is assigned to the transition to $^7F_0$, the peaks at 592 nm to $^7F_1$, the peaks near 616 nm to $^7F_2$. It can be seen from the figure that the effects of annealing are very striking. With increasing annealing temperatures, the luminescent intensity is greatly increased. The single emission line at 578 nm is very weak in the unannealed samples, and almost buried in the emission background from certain organic residuals. It becomes stronger and well resolved in the samples annealed above 400°C. The ratio of the integrated intensity of $^5D_0$ emission to $^7F_0$ and $^7F_1$ to that of $^7F_2$ decreases with an increase of annealing temperature (Fig. 2a). The red emission peaks near 616 nm become dominant after annealing above 600°C. For the samples of Eu^{3+} and Y^{3+}-codoped silica glasses, similar results were obtained. It was found that the luminescence intensity of the codoped samples was at least three times stronger than that of single doped samples if both were annealed at the same temperature.

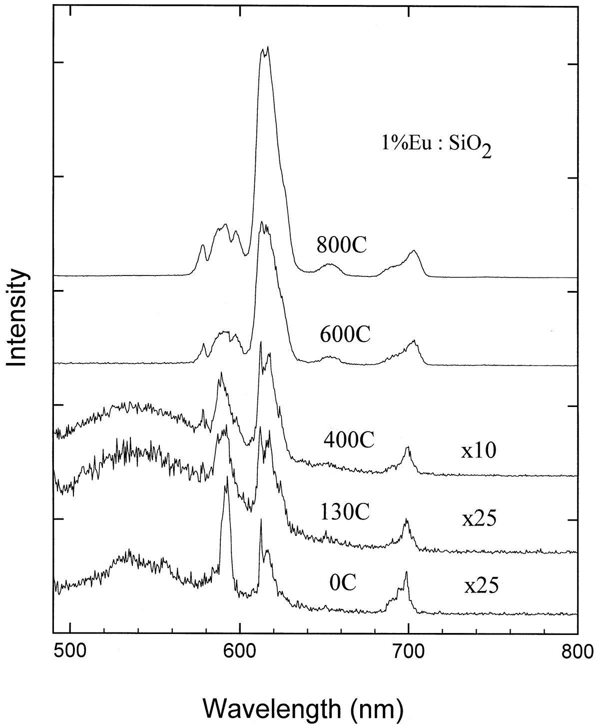

Fig. 1. Luminescence spectra of 1% Eu^{3+}–SiO_2 glass samples annealed at different temperatures in air. The broad band background at 530 nm is from some organic groups entrapped in the glass.

The annealing process also significantly affected the luminescent decays. With increasing annealing temperatures, the lifetimes of the luminescence of the samples were increased as shown in Fig. 2b. For the samples

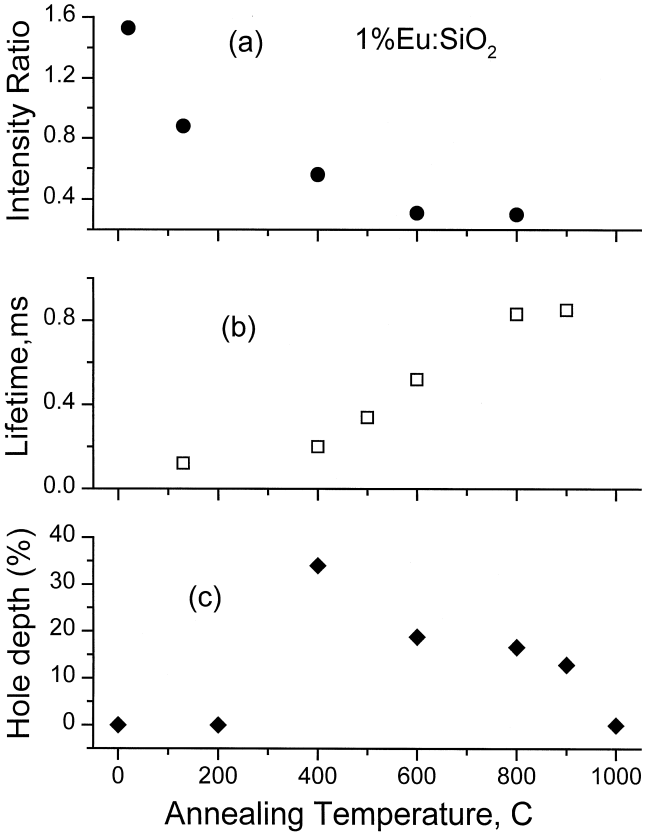

Fig. 2. (a) The ratio of the integrated intensity of $^5D_0$ emissions to $^7F_0$ and $^7F_1$ over that of the emission to $^7F_2$; (b) Lifetimes of the $^5D_0$ emission; (c) Spectral hole depths in 1% Eu–SiO_2 samples annealed at different temperatures. Holes were burnt at 8 K for 20 min by a Coherent dye laser 599 with spectral width of 0.15 cm^{-1} and power of 40 mW.

annealed above 900°C, the lifetimes reached a stable value of about 0.9 ms for the single doped samples and 1.8 ms for the double doped (10% Y) samples. The temperature dependence of the lifetimes of samples with 1% Eu, 0.7% Eu–2.5% Y and 1% Eu–10% Y, annealed at 900°C, were measured in the temperature range from 8 to 300 K, and it was found that the lifetimes did not obviously depend on the temperature. With heavy codoping of Y_2O_3, the lifetimes of Eu emission increased, and the decay curves became more exponential than the single doped Eu samples.

In measurements of spectral hole burning, it was found that the critical temperature, at which spectral holes could be burnt, depended on the linewidths of the pump laser beams. With a narrow bandwidth laser, holes could be burnt only up to 35 K. The observed hole widths are unusually wide for the glasses, about 1 GHz (0.03 cm^{-1}), more than 30 times broader than that observed in regular Eu-doped melt glasses. With increasing temperature, the hole width exhibits a temperature dependence of T^{α} with $1<\alpha<1.3$ (Fig. 3), as has been observed in a number of melt glasses. A similar temperature dependence of the homogeneous line width was obtained with fluorescence line narrowing (FLN). However, the hole width is three times wider than the FLN linewidth, suggesting that there exists a fast spectral diffusion process. Much narrower holes in the Eu–Y-codoped glasses (0.03 cm^{-1}, compared with 0.1 cm^{-1} in 1% Eu–SiO_2 at 5 K) is observed.

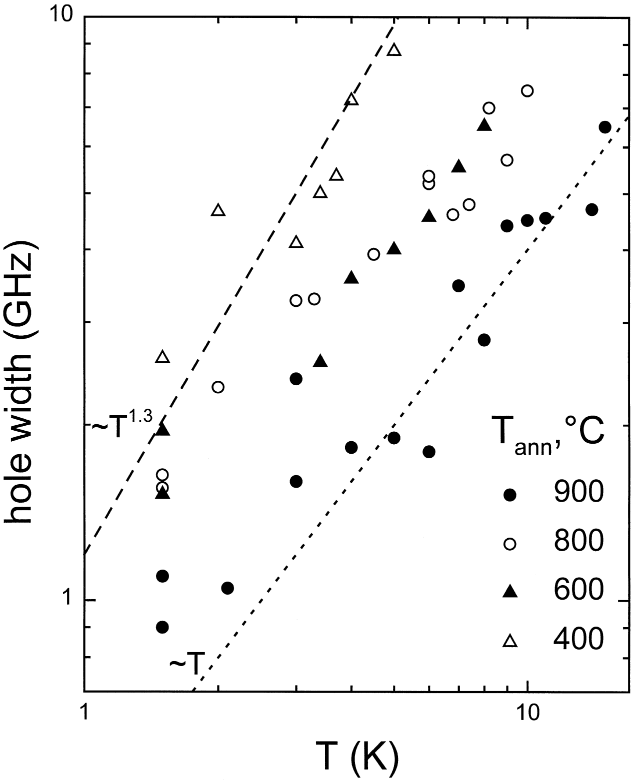

Fig. 3. Temperature dependence of hole widths in the series of 1% Eu, 2.5% Y–SiO_2 samples, annealed at 400, 600, 800 and 900°C. The holes were burnt at 1.5 K by a Coherent dye laser CR899 with line width 2 MHz.

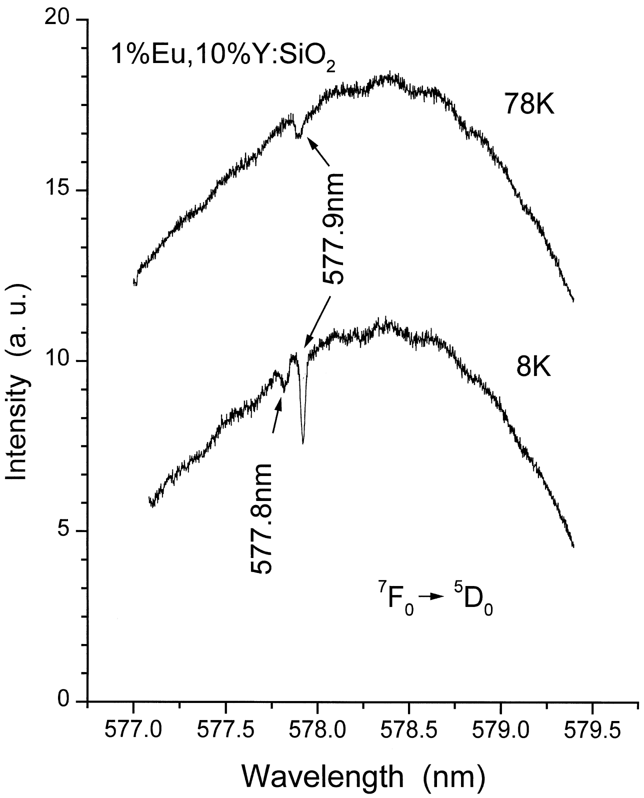

Fig. 4. Spectral holes burnt at 8 and 78 K by a Coherent laser CR599 with line width of 0.15 cm^{-1} and power of 40 mW. The hole at 578 nm was burnt 1.5 h before the hole at 578.5 nm.

Using a laser with a wider linewidth (0.15 cm^{-1}), a hole with a width of 0.3 cm^{-1} could be burnt at 78 K. Fig. 4 shows spectral holes burnt at 10 and 78 K, respectively, in the sample of 1% Eu, 10% Y–SiO_2 annealed at 800°C. The hole at 577.8 nm on curve 8 K was burnt and read out after 1.5 h at the same time as a new hole was burnt at 577.9 nm. From the depths of the two holes, one can estimate the decay rate of the holes. The hole at 577.9 nm on the curve 78 K. Annealing temperatures significantly affected the spectral hole burning (Fig. 3). No persistent holes were observed in the samples unannealed or annealed below 200°C or above 1000°C. The maximum hole depth, 35%, was observed in the sample annealed at 400°C.

4. Discussion

In the gellation process, dry gels formed through hydrolysis always entrap some water, alcohol, and other organic groups. The density of the gels are very low, and can be less than 30% of the theoretical density of SiO_2. Annealing has been widely used to reduce or eliminate residual hydroxyl in sol–gel glasses and to densify the samples [1,3]. It is a routine procedure for the improvement of sol–gel optical materials. The density of sol–gel SiO_2 glasses can be close to 100% of the theoretical value if annealed above 1200°C. In general, the organic residuals have high vibration frequencies and can efficiently quench luminescence of optically active ions. For example, the OH vibration frequency can be as high as 3340 cm^{-1}, so that only five phonons are needed to bridge the excited state $^5D_0$ and the ground state ^7F_J levels of Eu^{3+}, providing a non-radiative relaxation pathway. It is believed that the luminescence intensity and lifetime increase with increasing annealing temperature due to the reduction of the quenching centers, as shown in Figs. 1 and 2a and b.

The second important effect of annealing is to activate the lattice relaxation of the glass network and ion migration in the glass host. The size of rare earth ions is in the range of 0.99–1.13 Å, much larger than that of Si^{4+} (0.4 Å). The solubility of rare earths in SiO_2 glass is very limited. During the annealing process, the rare earth ions may migrate and form clusters [8–10]. The clustering process makes the local concentration of Eu very high and causes serious fluorescence quenching in single doped systems. Consequently, the luminescent intensity is relatively low and the lifetime is shorter. After annealing above 800°C, the lifetimes of the luminescence of Eu doped samples are still far below the normal value (1.5–2.0 ms) of the lifetime of Eu in most crystals. This is ascribed to the concentration quenching. Although the nominal concentration (1at%) in the silica samples prepared in this work is not very high, the real local concentration of Eu can be much higher owing to clustering in the single doped samples. The shortened lifetime is ascribed to clusterization.

In addition, the clusterization may also change the symmetry of the lattice environment of the Eu^{3+} ions. The transition $^5D_0$ to $^7F_0$ is both spin and electric dipole forbidden and gives rise to a weak peak at 578 nm. The transitions of $^5D_0$ to $^7F_1$ at 587, 592 and 598 nm are magnetic dipole allowed and less sensitive to the lattice environment [11]. It is a dominant transition for Eu ions in an environment with inversion symmetry. On the other hand, the $^5D_0$ to $^7F_2$ transitions at 613, 616 and 626 nm are parity (electric dipole) forbidden. It becomes allowed when the lattice environment is distorted and contains non-inversion symmetry. It is a forced electric-dipole transition and is hypersensitive to the environment [11]. The relative intensities of transitions to $^7F_1$ and $^7F_2$ seen from Fig. 1 indicates that Eu ions in the dry gels are present in an environment with near inversion symmetry. With increasing annealing temperature, Eu ions may migrate and form clusters of Eu. Eu_2O_3 is monoclinic without inversion symmetry, and the transition $^5D_0$ to $^7F_2$ is dominant. The spectral result in Fig. 1 indicates that clusterization of Eu is initiated in the annealing process.

To disperse the Eu ions and reduce concentration quenching, Costa et al. suggested using modifying cations, such as La, Sr, Gd, Lu, Y, Sc and Ga [1]. It is expected that, with heavy doping of Y_2O_3, Eu may prefer to enter into Y_2O_3 nanoclusters which are expected to form in silica matrix. The concentration quenching of luminescence can therefore be greatly reduced. Consequently, the luminescent intensity should be much stronger and the lifetime should be longer as observed in the experiments.

The influence of annealing on spectral hole burning can be also seen from Fig. 2c. The influence might be associated with the physical mechanism producing the spectral holes. Nogami and Hayakawa proposed that the formation of the spectral holes were due to reorientation of water molecules bound with Eu ions [5], since the hole depth and the water content were both reduced in the samples with annealing temperature and annealing period. However, such correlation between these two events may be just a coincidence. All organic groups were decomposed and released with annealing. Due to the OH vibration quenching, the content of water may not be an important factor for producing a spectral hole. The excitation photo energy stored in the excited ions could be quickly released through non-radiative multiple phonon processes, i.e. vibration quenching. Then the excited Eu ions could immediately return to the initial state and participate in absorption again. In other words, no hole could be observed as seen in the case of unannealed samples.

The existence of clusterization is an indication that the Eu ions in the sol–gel SiO_2 are not strongly bound with the porous glass network, and relatively mobile. Laser excitation may serve as a driving force to move the excited ions (or their ligands) to a quasi-stable state (potential minimum), and leave a spectral hole there. After clusterization and densification, Eu ions are more strongly bound within the clusters and the contribution to the persistent hole becomes smaller.

Although all the spectroscopic results support the model of clusterization, the microstructure of the clusters is not clear. Y_2O_3 crystals have a cubic structure, while nanoparticles of Y_2O_3 were found to be monoclinic [12,13]. Bihari et al. [13] showed that there were three nonequivalent sites of Eu in the monoclinic nanoparticles. Three groups of emission lines were resolved. The fluorescence lifetimes of the three site Eu ions are different. In homogeneous broadening of the luminescence, our samples do not allow us to resolve the fine spectral structure. However, it is very interesting to note that the decay of luminescence of Eu, Y–SiO_2 is almost exponential, in contrast to that of the single doped sample Eu–SiO_2, which is non-exponential. This indicates that the clusters related with Y^{3+} may not have the same microstructure as the nanoparticles studied by Bihari et al. It may not be pure clusters of rare earth oxides, it is likely that there exist some kinds of rare earth rich regions, in which the sites of Eu ions are almost equivalent and have a similar decay time.

Investigation of the size and morphology of the clusters is an important issue to understand the nature and process of clustering. Raman scattering from undoped, Eu single doped and Eu–Y-codoped SiO_2 were measured. A broad band between 400 and 550 cm^{-1} is obviously related with Y–O or Eu–O vibrations. The results indicate that the clusters, if any, must be very small and in an amorphous state. TEM micrographs have been taken on the 1% Eu,10% Y-doped SiO_2 samples, annealed at 600 and 900°C. Due to the similar contrast of Si and Y, it is difficult to make a clear identification of Y clusters. Some darker dots with a size of subnanometer scale might be related with such clusters.

5. Conclusion

Eu-doped and Eu,Y-codoped silica glasses were prepared by the sol–gel method. Annealing can be used to exclude the entrapped hydroxyl and organic groups in the samples, reduce OH vibration quenching, and consequently increase the luminescence intensity. Due to the lattice rearrangement during annealing, which eventually leads to clusterization of Eu ions, the local Eu environment changed from one of near inversion to one with relatively more non-inversion symmetry. As a result, the $^5D_0$ red emission to $^7F_2$ becomes more allowed and dominates over the emission lines to $^7F_0$ and $^7F_1$. However, the clusterization caused concentration quenching, shortened the lifetime and limited the improvement of luminescence.

On the other hand, annealing at higher temperatures resulted in denser samples, where the lattice bonding becomes harder and Eu ions tend to form clusters. This might be the reason for the reduction of the spectral hole depth and eventually inhibition of the persistent hole burning for the samples annealed at the highest temperatures.

Codoping with Y^{3+} could inhibit the clusterization of Eu ion since Eu ions may prefer to enter into Y clusters and therefore be diluted. Evidence for this includes the fact that codoping further increased the luminescence intensity and the lifetime of Eu, along with the reduction in the spectral hole width.

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References

[1] V.C. Costa, M.J. Lochhead, K.L. Bray, Chem. Mater. 8 (1996) 783.
[2] M. Nogami, T. Yamazaki, Y. Abe, J. Lumin. 78 (1998) 63.
[3] W. Jia, Y. Wang, M. Santiago, L. Castro, H. Liu, Mat. Res. Soc. Symp. Proc. 519 (1998) 271.
[4] H. Yamamoto, J. SID 3–4 (1996) 165.
[5] M. Nogami, T. Hayakawa, Phys. Rev. B56 (1997) 14 235.
[6] M. Nogami, Y. Abe, Appl. Phys. Lett. 71 (1997) 3456.
[7] T. Kano, K. Kinameri, S. Seki, J. Electrochem. Soc. 129 (1982) 2296.
[8] I.M. Thomas, S.A. Payne, G.D. Wilke, J. Non-Cryst. Solids 151 (1992) 183.
[9] W.V. Moreshead, J.R. Nogues, R.H. Krabill, J. Non-Cryst. Solids 121 (1990) 267.
[10] L. Lee, D. Tsai, J. Mater. Sci. Lett. 13 (1994) 616.
[11] W.T. Carnall, P.R. Fields, K. Ranjnak, J. Chem. Phys. 49 (1968) 4412.
[12] D.K. Williams, B. Bihari, B.M. Tissue, M. McHale, J. Phys. Chem. B 102 (1998) 916.
[13] B. Bihari, H. Eilers, B.M. Tissue, J. Lumin. 75 (1997) 1.