

STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF SILICA GELS DOPED WITH OPTICALLY ACTIVATED Er³⁺ IONS BY SOL-GEL PROCESS

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SUMMARY

This paper is devoted to the study of the relationship between structure and optical properties of silica glasses doped with optically active Er³⁺ ions and reported the influence of the suitably selected heat treatment on the optical properties of silica glasses. The physico-chemical properties of Er³⁺-doped silica are presented, which has been related with the effects of hydroxyl groups on the luminescence property of Er³⁺ in the host matrix of silica.

I - INTRODUCTION

The development of new photonic materials has been studied for the purpose to generate, guide, switch, multiplex, and amplify light, which has become very necessary in many areas in photonic technology such as high power fiber, solid state lasers. To date, Er³⁺-doped silica is one of the most attractive and potential photonic materials for Er³⁺-doped fiber amplifiers (EDFA). Moreover, sol-gel technology has been used to incorporate erbium ions into silica gel. Specially, trivalent erbium is characterized by an optical transition at 1.54 μm , an important standard wavelength in optical telecommunication, which is utilized for optical amplification to compensate the loss of information signal occurring in the long-distance transmission networks [1]. The main problems that influence the optical performance of sol-gel method-based devices are the non-radiative relaxation channels (due to rare earth

concentration quenching) and vibrations of the OH groups [2 - 3]. However, the relationships between the structure and physico-chemical properties of Er³⁺ doped silica glasses have not been expressed clearly in the most of works, especially the effects of hydroxyl groups on the optical quality of Er³⁺ doped glasses [1-4]. The main object of this paper is to focus on the two issues concerning the above silica materials.

II - EXPERIMENTAL PROCEDURE

1. Sol-gel Process

The starting materials in the experiments are tetraethylorthosilicate (TEOS), ethanol or isopropanol, deionized water and acid catalyst. TEOS, ethanol and deionized water were used in the molar ratios 1: 4: 4, respectively. Erbium was introduced by ErCl₃ or Er(NO₃)₃·9H₂O. The basic chemical reactions of sol-gel process on undergoing hydrolysis and condensation under HCl catalyst are:

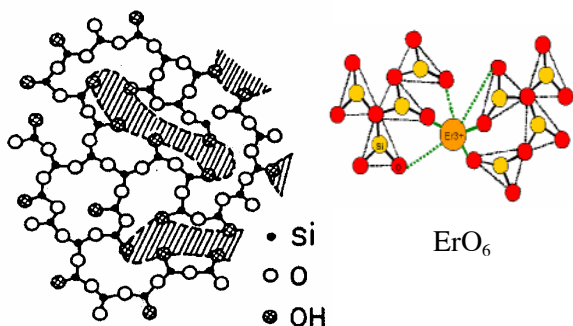
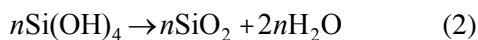
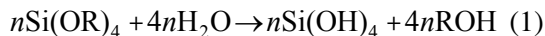


Fig. 1: Disordered covalent polymeric networks (shaded areas represent pores) with Si-O-Si bonds [5] and a ErO_6 configuration with covalent bonds ([6])

The solutions were maintained at 40°C until gelled. After gelation, the samples were dried slowly at 90°C to form monolithic silica gel doped with erbium. Gelation occurs and an extensive amorphous three-dimensional network of Si-O-Si bonds is formed with a diversity of pores, where erbium ions can be incorporated and the covalent bonds between Er and Si or O are formed. The schematic representation of structures on the silica surface, as discovered from infrared spectra by Wood *et al.* [5], is shown in figure 1 and 2. The figures show the formation of clusters of $\text{Si}(\text{OH})_m \cdot (\text{H}_2\text{O})_n$. However, there are still many difficulties in sol-gel process, mainly concerning with the presence of a large number of hydroxyl groups in gel bulk and on surface of silica gel, which decreases the emission of the rare earth ions at $1.5 \mu\text{m}$.

So far, a great number of researches dealing with the hydroxyl problems has been carried out. It is evidently seen that a lot of papers concerning with different methods removing hydroxyl groups.

2. Heat treatment process for obtaining Er^{3+} doped silica glass with high optical quality

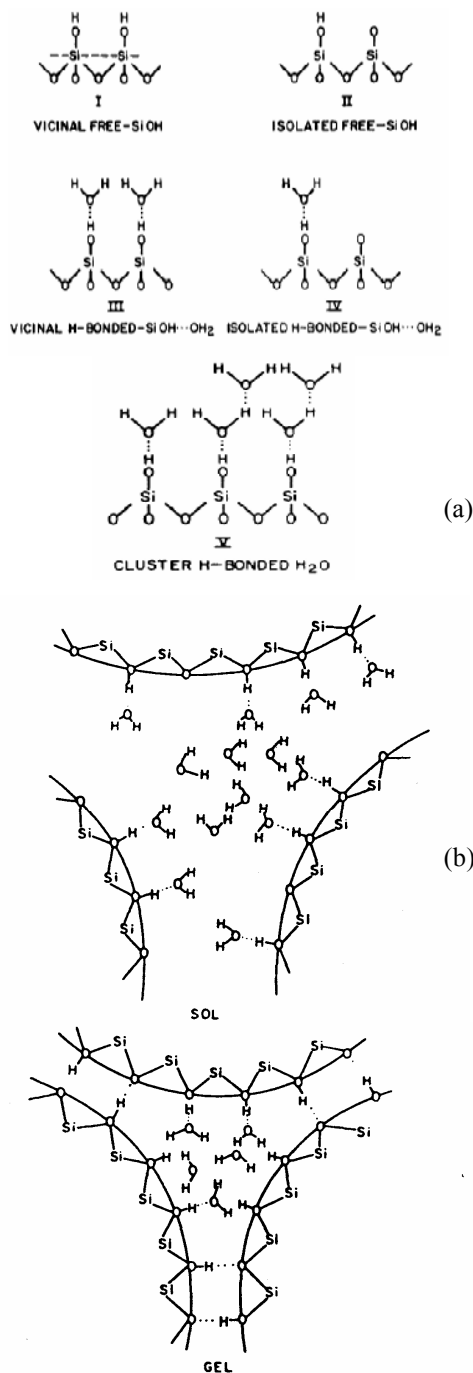


Fig. 2a: Schematic representations of structures on the silica surface present in gel as revealed from IR spectra. Hydrogen bonds are represented by dotted lines. Fig. 2b. Diagram of changes during the gelation of particulate sols. Dots represent hydrogen bonds; curved lines represent micelle surfaces [5]

The main objective of this paper is to present a suitable heat treatment aim to remove hydroxyl groups which are formed in silica gel doped with certain concentration of erbium for purpose to increase the emission performance of Er^{3+} ions. For the purpose of reducing hydroxyl groups, isothermal treatment was carried out for interval periods of time. Samples were isothermally annealed at 200°C for 24 h, and then temperature was increased slowly with a heating rate of $0.5^\circ\text{C}/\text{min}$, to 400°C and isothermally annealed at 400°C for 24 h and so on to the next heating stage at 600°C , 800°C , 950°C , 1100°C This selected heat treatment process allows getting the final silica glasses doped with erbium with a minimised content of hydroxyl groups. However, an amount of -OH groups is existent, which of course exhibits the natural property of sol-gel derived glasses. The samples of silica gel contained 2 - 7 wt.% Er_2O_3 . After heat treatment, the color of the samples looks slightly pink (this color is typical for Er^{3+} doped silica glasses). Er^{3+} -doped monolithic silica glasses have been prepared with high optical quality by stepwise heat treatment process. The detail of experimental measurement of silica glasses could be seen in Long, et. al [7, 8].

III - RESULTS AND DISCUSSION

1. Effects of hydroxyl groups on optical property of Er^{3+} doped silica glass

It has been known that one impurity strongly quenching emission of Er is OH groups, as the second overtone of the OH stretch vibration is resonant with the first excited state of Er. In highly Er^{3+} doped glass, in which energy migration can take place over a significant distance, a small concentration of OH will cause significant quenching. In fact, the quenchers come from water in the solvents used to prepare these glasses and these unwanted channels decrease the fluorescence intensity of Er^{3+} ion. It is composed of a superposition of SiO-H stretching vibrations: (i) vicinal free SiO-H stretching, (ii) isolated free SiO-H stretching vibrations, (iii) vicinal H-bonded-SiOH---OH₂ stretching vibrations, and (iv) isolated H-bonded-SiOH---OH₂ stretching vibrations; (v)

cluster H-bonded H₂O [5]. In addition to the envelope of vibrations corresponding to O-H stretching, and also the band at 1643 cm^{-1} was formed due to a deformation mode of adsorbed molecular water. It has been known that there are three possible quenching mechanisms: (i) temperature quenching for the measurements depending on temperature (small and not dominant), (ii) quenching by the nearest C-H neighbours (very small and not dominant), (iii) quenching by different hydroxyl groups (dominant). OH groups are present in the liquids (mainly alcohols) used in the preparation of the Er^{3+} -doped glasses, and they can be present also in the solvent used in the experimental measurements. It is therefore likely that OH groups are coordinated to the Er^{3+} . It has been found that one OH molecule can penetrate the first coordination shell of the ion Er^{3+} . In particular, water may preferentially solvate the Er^{3+} ; therefore, OH groups decrease the fluorescence of Er^{3+} ions. It is the most potent quencher of the rare-earth luminescence, and has a stronger interaction to the rare earth. Because its second vibrational overtone ($E_0 = 3400\text{ cm}^{-1}$) is strongly resonant with the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} ion [6] ($E = 6500\text{ cm}^{-1}$ corresponding to $\lambda = 1540\text{ nm}$), an OH group only near Er^{3+} ions will result in efficient quenching of the luminescence. This is an undesirable effect leading to limit optical gains.

2. Investigation of Fourier Transform Infrared (FTIR) spectra

The experimental FTIR spectra were recorded in the frequency range $400 - 4000\text{ cm}^{-1}$. All of infrared investigations of the fundamental network vibrations often make dilution in infrared transparent media with KBr. In FTIR spectra, the most intense peaks around 1080 cm^{-1} and 1220 cm^{-1} were found. Variations in the peak positions and the number of peaks can be seen in FTIR spectra with different structural morphologies of silica from amorphous structure to crystal structure and then structure of quartz, which pointed out that possibly crystallization occurs for samples annealed at $1000, 1200^\circ\text{C}$. Most of the peaks in the FTIR spectra are consistent with the peaks in

the Raman spectra except the bands at 1220 cm^{-1} and 460 cm^{-1} . It has been obvious that the major features of FTIR spectra associated with vibrational network of Er^{3+} -doped silica glasses are located at 460, 800, 1080, and 1220 cm^{-1} [7 - 9]. The most intense 1080 and 1220 cm^{-1} bands in the FTIR spectra are assigned to the TO and LO modes of the asymmetric Si-O stretching vibration of microstructure of silica glasses, respectively. An O-H stretching broadband between about 3000 and 3800 cm^{-1} centered at near 3440 cm^{-1} corresponding to the fundamental stretching combined vibrations of different hydroxyl groups comes from the vibration of surface isolated silanol groups or silanol groups on the surface, which is hydrogen bonded to molecular water. The vibrational intensity of this band decreased significantly (not shown here) during the heating treatment and the fluorescence of Er^{3+} ions increased (the OH groups are the most potent quenchers of the Er^{3+} luminescence).

Transverse optical rocking vibration (TO_1), symmetric stretching vibration (TO_2) and asymmetric stretching vibration (TO_3) are vibrations of 460 cm^{-1} , 800 cm^{-1} and 1080 cm^{-1} are assigned to the Si-O-Si vibrational modes, respectively. A strong shoulder at about 1220 cm^{-1} is assigned to longitudinal optical component (LO_3) of the high-frequency vibration of SiO_2 . All of spectra exhibit a band centered at near 940 - 960 cm^{-1} , which is due to stretching vibrations of Si-OH. This band did not appear in the samples annealed at 800, 950, 1100, and 1200°C. Moreover, there is an evidence in the FTIR spectra with the samples annealed at 1100, 1200°C for symmetric ring breathing modes due to the D2 vibrations in the Raman spectra [8]. Finally, we suggested that optical transparent glasses and specific vibrational rings best describe the structure and optical properties of silica glasses. In other words, FTIR spectra are useful in distinguishing between physically adsorbed water and various hydrogen-bonded silanol species. The main effects of hydroxyl impurities (in figure not shown here) is seen that the spectral region centered at 3440 cm^{-1} consists of combination bands associated with various silanol species,

adsorbed water, and residual organics and the band at 1643 cm^{-1} was formed due to a deformation mode of adsorbed molecular water. It has been also shown that hydroxyl groups can be present even at high annealing temperature and functionalize the sol-gel-derived glasses. In fact, to understand the behavior of the structural and dynamic changes during gel-to-glass transitions is to improve the optical quality of Er^{3+} doped silica glass. It has been suggested that the SiO_4 units (in which a silicon (Si^{4+}) atom (ion) in the tetrahedron is covalently ionically bonded to four oxygen atoms (ions) which may be a fundamental tetrahedral microstructure unit of silica glasses and exhibit the nature of Si-O-Si vibrational modes. Further studies have shown that Er^{3+} ions incorporated into glassy matrix in form of ErO_6 bonded cluster configuration. See more in the works of A. Polman in [6]. Moreover, controlling a gel-to-glass process can be accomplished with a great ease by using suitably selected heat treatment for obtaining the optimal amorphous structure, which is necessary to get the highest fluorescence of Er^{3+} . However, there was an important thing to determine the temperature range, which pores were collapsed for more Er^{3+} ions incorporating into matrix network of SiO_2 . But it is also seen that at the beginning of gelation most of Er^{3+} ion has been incorporated into polymer matrix. It means that selected heat treatment process has only reduced the content of OH hydroxyl population. In my point of view, it has been seen that this temperature range for reducing most of remaining OH groups of samples to being in the range of 800 - 1100°C.

3. X ray diffraction

Sharp diffraction peaks show the presence of two phase crystalline quartz of SiO_2 , hexagonal and tetragonal respectively, which leads to decrease the fluorescence of Er^{3+} ion in the matrix of silica host. The above effects due to the structural changes are very important in order to prepare silica materials with the desirable structure and properties as well as optically improved quality. According to the above results about X-ray and FTIR, some remarks on the heat treatment procedure to the

evolution of structure silica glass are described as below: (i) It is obviously shown that the vibrations are present mainly for OH vibrational groups and matrix vibrations of with specific bonds existing in silica gel in the temperature range of 25 - 150°C; (ii) It is clearly shown that in the heat treatment range of 100 - 400°C, the intensity of OH vibrational groups was reduced significantly. In the intermediate heat treatment range of 400 - 800°C, a continuous decrease of OH groups as shown in FTIR spectra, which leads to being nearly a minimum of OH groups. Many authors have determined that the densification of silica gel is achieved at about 800°C, see more in the works in [7, 8]; (iii) It is clearly shown that most of remaining OH groups are reduced in the heat treatment range of 900 - 1100°C to be completely minimised; however, it is also emphasized that the crystallization process of SiO₂ occurs simultaneously. At 1200°C, the crystallization process had occurred; (iv) It is shown that the amorphous structural phase of silica gel by synthesizing sol-gel method was gradually converted into the different crystal phases at higher temperature heat treatment and the structure of SiO₂ exists both amorphous. Crystal phases of SiO₂ are formed in the higher temperature range of 1000 - 1200°C.

4. Photoluminescence spectra (PL)

The ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ fluorescence of Er³⁺ at 1.5 μm from silica samples was shown in figure 3. The structure of this transition is of particular interest for application in wavelength division multiplexed signal amplifiers (WDM) in telecommunication. We used the samples with ~4 wt.% Er₂O₃ because of the optically active Er concentration to get the highest luminescence as presented in our previous report. This is a suitable concentration in application for Er³⁺-doped amplifiers (EDFA).

Erbium-doped silica glasses have been successfully fabricated by sol-gel process. The structure of glassy network has been investigated by FTIR and X-ray diffraction spectroscopy. It has been shown that characterization of sol-gel derived glasses is the fact that a OH content is left in the final silica

glass samples. It has seen that the O-H stretching vibration affects the fluorescence decay at 1.5 μm because two O-H vibrations are enough to bridge the gap of about 6500 cm⁻¹ between the ground state ${}^4I_{15/2}$ and the first excited state ${}^4I_{13/2}$ of the Er³⁺ ion. This problem was dealt with by suitably isothermal annealed processes at higher temperature to minimise the residual OH content and make good optical silica glasses. It have been also found that the intensity of Er³⁺ fluorescence in sol-gel silica glasses increases with increasing heat treatment temperature due to the removal of adsorbed water or residual hydroxyl groups. An important advantage of isothermally selected heat treatment at 950°C for 24 h lies on the fact that the structure of SiO₂ was still amorphous, and that an amount of residual OH groups was significantly minimised leading to the highest increase of fluorescence.

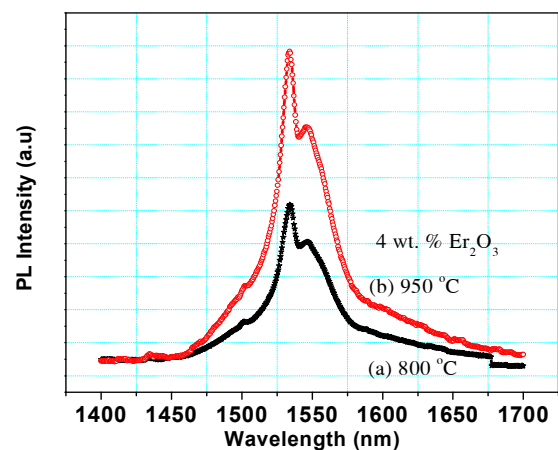


Fig. 3: Room temperature ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er³⁺ ions of 4 wt.% Er₂O₃ silica samples

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