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Low Hydroxyl Erbium-Doped and Undoped Gels

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A non-hydrolytic sol-gel process was developed to fabricate low-hydroxyl hard gels. The reaction of tert-butyl alcohol with silicon halides provided transparent low-hydroxyl hard gels. Some properties such as transparency, density, and refractive index were investigated in the aspects of the usefulness of the hard gels as matrices for optical applications. Erbium iodide was successfully doped into the hard gel matrices. The absorption spectrum of an erbium-doped methylsilsesquioxane was investigated to decide the pumping wavelength of an argon laser. The luminescence of the erbium-doped gel at 664 nm seems to be due to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition.

Key words : Sol-gel process, Low-hydroxyl gels, Erbium-dopedgel, Luminescence, Matrices for optical applications

I. Introduction

Trivalent rare-earth ions (RE^{3+}) have been attracting interest since they have characteristic emission properties for the application of lasers.[1-4] The RE^{3+}-doped inorganic matrices such as silica glasses have been fabricated by the conventional glass melting method which requires heat treatment at high temperatures or by the conventional sol-gel method. The conventional sol-gel method typically involves the hydrolysis reaction of metal alkoxides such as tetraethylorthosilicate (TEOS) with water followed by the condensation reaction of the hydrolyzed alkoxides to release water, and form three dimensional network gel matrices.[5-9] The voids in the gel matrices act as trap sites for the RE^{3+}.

In the case of silica gel matrix, the condensation reaction is very slow, and it is unavoidable that there exists a significant amount of unreacted hydroxyl groups which will quench the emission spectra of the RE^{3+}. Thus, different approaches to avoid the formation of the hydroxyl groups should be explored. One of the most promising approaches will be modifying the silica gel matrix through the inclusion of unreactive hydrophobic organic component such as methyl group under controlled atmosphere.[10,11]

In the present work, a non-hydrolytic sol-gel process was developed. The fabrication of the low-hydroxyl gel matrices will be described. Some properties such as transparency, density, and refractive index of the undoped matrices will be discussed. Finally, the absorption and emission spectrum of an erbium-doped low-hydroxyl hard matrix will be discussed.

II. Experimental Details

1. Preparation

Tert-butyl alcohol ($(CH_3)_3COH$) from Aldrich Chemicals was dropped into silicon halide solutions from Aldrich Chemicals with stirring in a Schlenk line under nitrogen or argon atmosphere. The used silicon halide solutions were silicontetrachloride ($SiCl_4$), methyltrichlorosilane (CH_3SiCl_3), dimethyldichlorosilane ($(CH_3)_2SiCl_2$), and methyldichlorosilane (CH_3SiHCl_2). The reacted solution was poured into glass vials and kept in a nitrogen or argon-filled glove box at room temperature during gelation and drying. Erbium-doped gel samples were fabricated by the addition of anhydrous erbiumiodide (ErI_3) from Aldrich Chemicals into the reacted solution prior to gelation.

2. Measurements

The densities of the undoped gel matrices were measured via pycnometry. For the measurements of the refractive indices and the amount of hydroxyl groups, silicon wafers were dip-coated with the reacted solutions before gelation. The refractive indices of the undoped matrices were measured using an ellipsometer (Autoeller-II, Rudolph Research).

The relative amount of hydroxyl groups in the undoped matrices was evaluated using Fourier transform infrared (FTIR). The triethoxyvinylsilane (TEVS)-derived gel, which was made by conventional sol-gel process, was used as a reference sample. The thermal properties of the undoped matrices were investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The optical absorption of the erbium-doped methysilsesquioxane ($CH_3SiO_{1.5}$) hard gel in the wavelength range 340-820 nm was measured using a Diode Array Spectrophotometer (HP8452A, Hewlett-Packard). The luminescence of the erbium-doped gel was measured using an argon laser at room temperature.

III. Results and Discussions

1. Undoped gels

Table 1 shows some characteristic properties of the prepared undoped gel matrices. As expected, the gel matrices made from trifunctional or tetrafunctional precursors were hard, whereas the gel matrices made from bifunctional precursors or the mixture of bifunctional and tetrafunctional precursors were robbery. The gelation time of $SiCl_4$ was relatively short, whereas the one of CH_3SiHCl_2 or CH_3SiCl_3 took much longer time to gel.

Figure 1 shows the FTIR spectra of the undoped gel matrix made from CH_3SiCl_3 and the TEVS-based gel which was chosen as a reference sample. In the figure, the strong absorption peak of the TEVS-doped gel sample at the wavenumber of 3500 cm^{-1} is corresponding to the vibration of hydroxyl groups in the gel sample. It is obvious that the undoped hard matrix has much smaller amount of hydroxyl groups than the TEVS-derived gel sample, which was made by the conventional sol-gel process. This result confirms that the developed non-hydrolytic sol-gel process can be one of the best method to prepare non-hydroxyl matrices for optical applications.

Figure 2 shows the DTA and TGA result of the CH_3SiCl_4-derived gel matrix. As we can see, there was continuous weight loss up to 900°C and a little sharp weight loss and exothermic reaction around 500°C. This seemed to be due to the decomposition of unreacted halide groups and carbonization.

In the aspect of optical applications, the refractive index values of transparent hard matrices are very important. The densities and refractive indices of the prepared hard gel matrices are listed in Table 2. The measured density and refractive index values ranged from 1.129 to 1.136 and from 1.434 to 1.459 respectively. However, the matrix with larger density had larger refractive index and smaller surface area. Among the matrices, the matrix made from $SiCl_4$ seemed to one of the most appropriate candidates for optical applications.

Table 1. Characteristics of the Undoped Gel Matrices Made from Several Precursors.

Precursor	Gelation time (Hour)	Transparency	Hard/ Rubbery
$SiCl_4$ (A)	3	Yes	Hard
CH_3SiHCl_2 (B)	20	Yes	Hard
CH_3SiCl_3 (C)	27	Yes	Rubbery
$(CH_3)_2SiCl_2$ (D)	No Gel	Yes	N/A
50% A + 50% B	7	Yes	Hard
80% A + 20% C	11	Yes	Hard

Table 2. Densities and Refractive Indices of Hard Gel Matrices.

Precursor	Density (g/cm^3)	Refractive index
$SiCl_4$	1.136	1.459
CH_3SiHCl_2	1.129	1.434
0.5 $SiCl_4$+0.5 CH_3SiCl_3	1.133	1.448
0.8 $SiCl_4$+0.2 CH_3SiHCl_2	1.130	1.443

2. Erbium-doped gels

Most commercially available erbium compounds, such as oxide, nitride, chloride, fluoride, pentanedionate, and alkoxides, were insoluble in the reacted silicon halide solutions, but erbium iodide was soluble in the solutions. Upon dissolution of the iodide, the color of the solution turned to pink. Fig. 3 shows the absorption spectrum of an erbium-doped methylsilsesquioxane ($CH_3SiO_{1.5}$) gel sample. The absorption lines were labeled from the ground state. Since the absorption peaks below the wavelength of 488 nm were weak, 488 nm was chosen as the pumping, that is, excitation wavelength of an argon laser.

Figure 4 shows the emission spectrum of the erbium-doped gel sample under excitation at 488 nm with the argon laser. The emission at 664 nm corresponds to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The observation of the luminescence

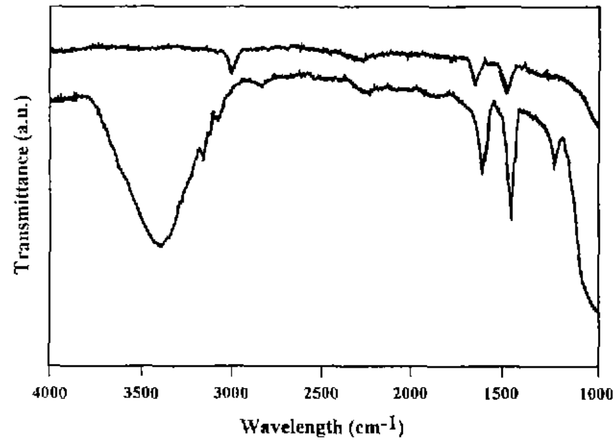

Fig. 1. The FTIR spectra of low-hydroxyl (top) and conventional (bottom) gel matrix.

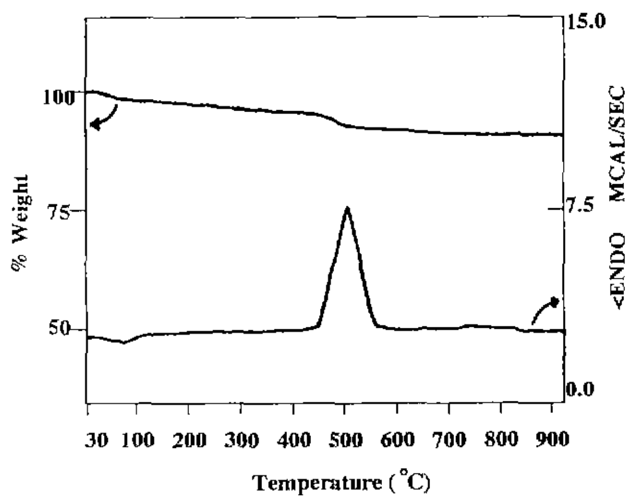

Fig. 2. DTA/TGA of low-hydroxyl gel matrix.

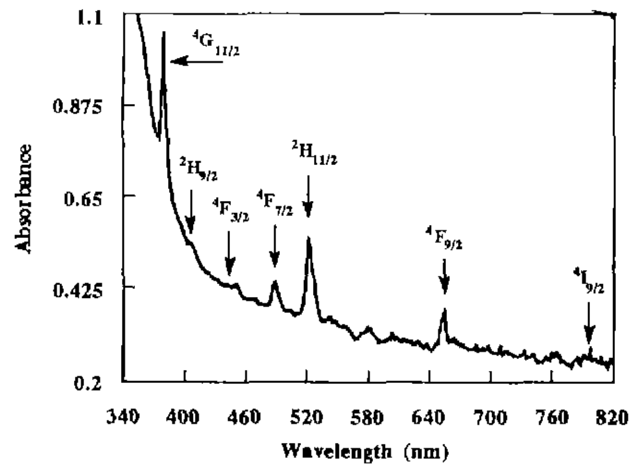

Fig. 3. Absorption spectrum of Er^{3+} in CH_3SiCl_3-derived gel matrix.

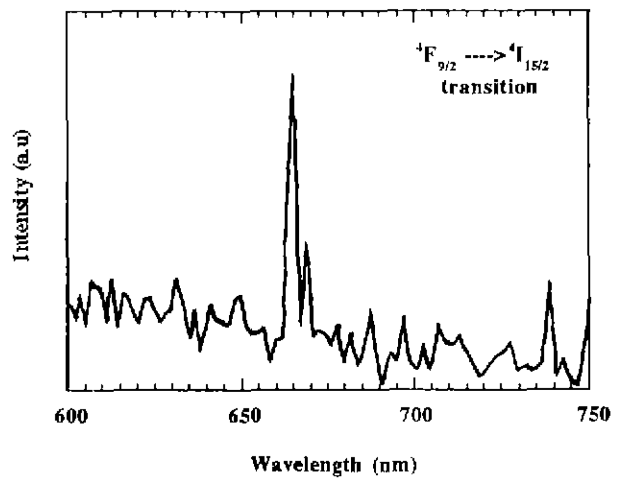

Fig. 4. Luminescence of Er^{3+} in $SiCl_4$-derived gel matrix.

seemed to be contributed to low-hydroxyl matrix. We are currently exploring infrared luminescence, which are more sensitive to hydroxyl quenching. The structures and microstructures of the hard gel matrices are also currently examined.

IV. Conclusion

Non-hydroxyl hard gels were fabricated using a non-hydrolytic sol-gel process. The hydrolysis and polycondensation reaction, which could result in the formation of hydroxyl groups, were not involved in the process to form the gel matrices. It was confirmed that the undoped-gel matrices contained little or no amounts of hydroxyl groups. Under excitation at 488 nm, the luminescence of the erbium-doped gel was detected at 664 nm. The luminescence corresponds to the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition. The luminescence seems to be attributed to the low-hydroxyl gel matrix.

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