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Optical properties of holmium-doped in sol-gel silica glass

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In this work holmium (Ho^{3+})-doped in silica glass was prepared by sol-gel technique which relies on the chemical reaction of liquid precursors to form the glass. TEOS: H_2O:C_2H_5OH:HNO_3 in the molar ratio 1:5.5:3.5:0.1 was used in the preparation with $HoCl_3.6H_2O$ as the Ho^{3+} source. Porous silica gel was obtained after stirring the mixture and ageing for few weeks. Annealing of the gel was done up to 1000°C to obtain densified glass samples with density 2.2 g/cm^3 and refractive index 1.46. Absorption spectrum was recorded in the visible region which shows several peaks resulting from the transition from ground state $^5I_8$ to various excited states. The hypersensitive transition $^5I_8 \rightarrow {}^5G_6$ at 454 nm was observed to be particularly strong. This strong absorption in the blue-violet region gives the glass sample a pale-yellow appearance. Judd-Ofelt parameters were obtained from the absorption spectrum and used to study the optical properties of the prepared glass sample. Large value of the parameter Ω_2 shows that the bonding of the dopant to the host network is more covalent than ionic. Photoluminescence spectrum was recorded in the visible region using 450 nm excitation which excites the Ho^{3+} ions to the $^5G_6$ state. Luminescence peaks were observed at 490, 550, 662 and 756 nm resulting from the radiative relaxations from the $^5F_3$ and $^5S_2$ states to the lower energy states. Photoluminescence of considerable intensity was not observed in samples pre-annealing which is due to hydroxyl quenching caused by the residual hydroxyls from the starting materials for the preparation. Annealing was shown to significantly improve the luminescence which is attributed to the removal of residual hydroxyls.

Keywords: Holmium (Ho^{3+}), sol-gel, annealing, Judd-Ofelt, photoluminescence.

INTRODUCTION

Sol-gel silica glass has acceptable properties as a host for trivalent rare earth (RE) ions (Ramteke *et al*., 2017; Vega *et al*., 2017). Semiconductor has the main focus of tremendous research activities due to their promising prospective in optoelectronic device applications in lasers and for optical communication systems (Qiao *et al.*, 2018; Snitzer, 1961; Furuse and Yasuhara, 2017; Secu *et al.*, 2011; Seshadri *et al.*, 2015). Silica glass is an acceptable material for the rare earth host along with ii-vi semiconductors (Rai and Bokatial, 2011; Rai and Fanai, 2016). The optical properties of RE ions arise from the transitions between the different $4f^n$ energy states (Peacock, 1975). In the ground state the RE ion may be excited to a higher energy state with absorbing radiation and may relax back to the lower energy levels with emitting radiation with energy equivalent to the energy difference between the ground state and that particular excited state.

Sol-gel technique (Rai and Fanai, 2016) allows the synthesis of glass at lower temperatures so that it does not require melting. Silica gel is used for coating because of wide band gap. Sol-gel method is used for preparing the sample in which the mixing of two or more phases can be controlled by the nano-scale or even molecular levels. The specific uses of these sol-gel produced glasses are derived from the various material shapes generated in the gel state. Ho^{3+} is one of the most attractive candidate among the RE ions, it shows strong luminescence at various wavelengths including visible region (Wang *et al*., 2007).

In the present work, we describe the Absorption, Judd-Ofelt intensity parameters, Photoluminescence properties and effect of annealing temperature on the

optical properties. The optical properties are studied from the absorption spectra using Judd-Ofelt analysis in the visible region. The glass samples are prepared by sol-gel process by controlling with the concentration of the dopant.

MATERIALS AND METHODS

Sample preparation

For the preparation of glass sample by sol-gel method, tetraethyl orthosilicate (TEOS) is used as a precursor, in the presence of H_2O to form SiO_2 network. For a sample with particular Ho^{3+} concentration, $HoCl_3.6H_2O$ is dissolved in deionised water, and then added with C_2H_5OH and then TEOS is added drop wise. Small amount of HNO_3 is also used to lower the pH and increase rate of hydrolysis. TEOS: H_2O: C_2H_5OH: HNO_3 in the molar ratio 1:5.5:3.5:0.1 was used in the preparation and the mixture is stirred for two hours to form sol by using a magnetic stirrer. After that the sol is placed in a small sealed plastic container to prevent evaporation and left for few days to form stiff gel. Some pin holes are made in the cover of the container for allowing slow evaporation and left for three weeks. After that the gels are dried slowly up to 90°C, and then annealed by electric furnace up to 1000°C at the heating rate 1°C per minute to obtain densified glass samples with density 2.2 g/cm^3 and refractive index 1.46.

Experimental set-up

Optical absorption and PL spectra of the prepared samples were recorded by using iHR320 imaging spectrometer using Syner JY^{TM} software from Horiba.

RESULTS

Absorption spectra

The absorption spectrum of the prepared sample is shown in Figure 1. Here absorption peaks are observed at 418, 454, 468, 487, 539 and 643 nm resulting transition from the ground state $^5I_8$ to the excited states $^5G_5$, $^5G_6$, $^5F_2$+$^3K_8$, $^5F_3$, $^5S_2$+$^5F_4$, and $^5F_5$ respectively. Absorption spectrum was recorded in the visible region which shows several peaks resulting from the transition from ground state $^5I_8$ to various excited states. The hypersensitive transition $^5I_8 \rightarrow {}^5G_6$ at 454nm was observed to be particularly strong. This strong absorption in the blue-violet region gives the glass sample a pale yellow appearance. Judd-Ofelt parameters were obtained from the absorption spectrum and used to study the optical properties of the prepared glass sample.

Photoluminescence spectra

The PL spectra the Ho^{3+} doped sample is shown in Figure 2. Photoluminescence spectrum was recorded in the visible region using 450nm excitation which excites the Ho^{3+} ions to the $^5G_6$ state. Luminescence peaks were observed at 490, 550, 662 and 756 nm resulting from the radiative relaxations from the $^5F_3$ and $^5S_2$ states to the lower energy states as $^5F_3 \rightarrow {}^5I_8$, $^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2 \rightarrow {}^5I_7$ respectively as shown in Figure 3. Photoluminescence of considerable intensity was not observed in samples pre-annealing which is due to hydroxyl quenching caused by the residual hydroxyls from the starting materials for the preparation. Annealing was shown to significantly improve the luminescence which is attributed to the removal of residual hydroxyls.

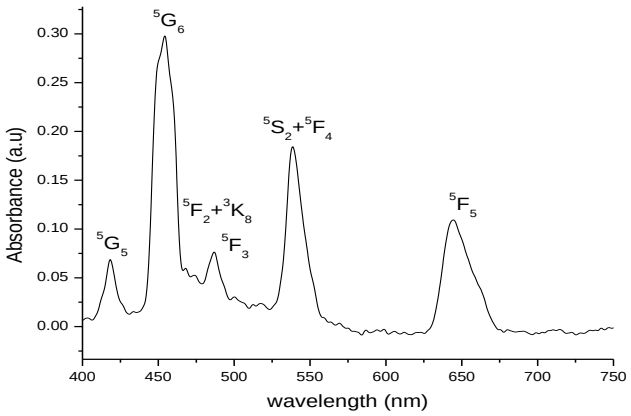

Figure 1: Absorption spectrum of Ho^{3+} sol-gel silica glass.

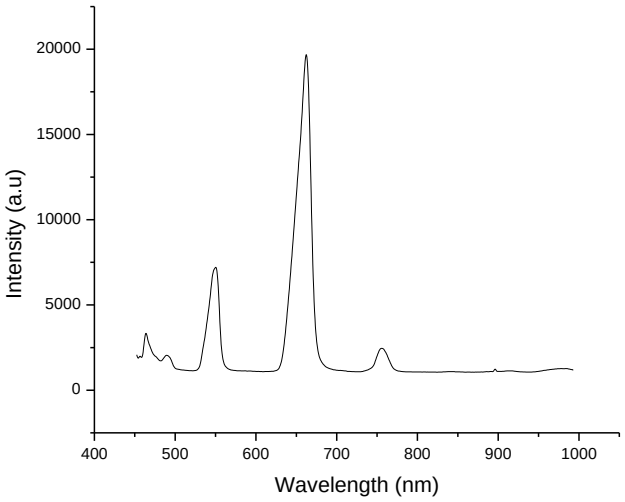

Figure 2: PL spectra of Ho^{3+} sol-gel silica glass.

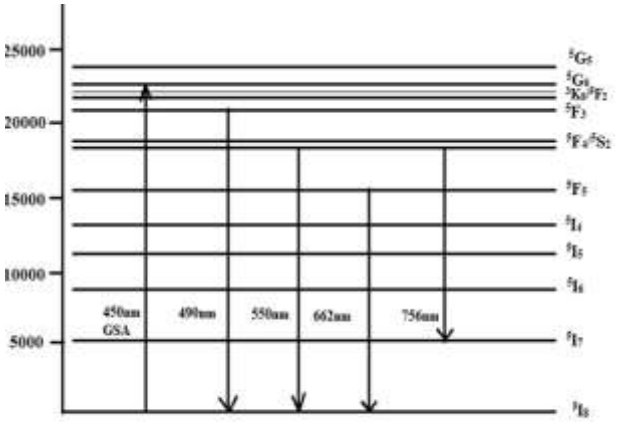

Figure 3: PL mechanism of Ho^{3+} ion in the visible range.

Table 1: Oscillator strengths and J-O intensity parameters for holmium-doped sample. $\Omega_2=2.05 \times 10^{-20}cm^2$, $\Omega_4=1.55 \times 10^{-20}$ cm^2, $\Omega_6=1.68 \times 10^{-20}$ cm^2 and $\Omega_4/\ \Omega_6= 0.92$

Transition $^5I_8\rightarrow$	Energy (Cm^{-1})	$f_{exp}(\times10^{-6})$	$f_{cal}(\times10^{-6})$
$^5G_5$	23920	1.34	1.62
$^5G_6$	21960	8.30	8.29
$^5F_2+^3K_8$	21360	0.59	1.23
$^5F_3$	20550	0.75	0.99
$^5F_4+^5S_2$	18540	3.1	2.96
$^5F_5$	15550	2.56	2.08

DISCUSSION

Absorption spectra and Judd-Ofelt analysis

By Judd-Ofelt (J-O) theory (Judd, 1962; Ofelt, 1962), the analysis of the radiative transition in the 4f states of Ho^{3+} is performed. According to J-O theory, the calculated oscillator strength (f_{cal}) of the electric dipole transition between two states $|\ I^NSLJ > \rightarrow |\ I^NS'L'J' >$ can be expressed as,

$$f_{cal}^{ed} = \frac{8\pi^2 mc\bar{\nu}(n^2+2)^2}{3h(2J+1)9n}\sum_{\lambda=2,4,6}\Omega_\lambda\left|\langle I^NSLJ\|U^{(\lambda)}\|I^NS'L'J'\rangle\right|^2 \quad (1)$$

where m is the mass of electron, c is the velocity of light, h is Planck's constant, J is the total angular momentum of the initial state, n is the refractive index, Ω_λ are the J-O intensity parameters and $||U^{(\lambda)}||$ are the reduced matrix elements evaluated in the intermediate coupling approximation for transition $|I^NSLJ > \rightarrow |I^NS'L'J' >$ at energy $\bar{\nu}$ expressed in cm^{-1}. The reduced matrix elements $||\ U^\lambda||$ are known to be relatively host independent, so the values obtained by Carnall *et al*. (1968), are used in the calculations.

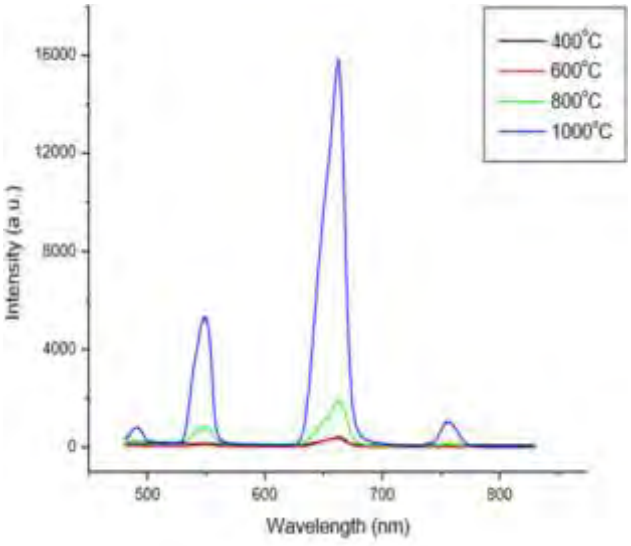

Figure 4: PL spectra of Ho^{3+}-doped sol-gel silica glass at different annealing temperatures.

The experimental oscillator strengths for transitions from the ground state to the excited states are determined from the absorption spectrum, using the following relation:

$$f_{exp} = 4.319 \times 10^{-9}\int \varepsilon(\bar{\nu})\,d\nu \quad (2)$$

Where, $\varepsilon(\bar{\nu})$ is the molar absorptivity at energy $(\bar{\nu})$ cm^{-1}. The Judd-Ofelt intensity parameters are evaluated using least square fitting and the oscillator strengths obtained from equation (2) which is experimentally determined values and co-related with the theoretical expression given in Equation (1). The J-O intensity parameters along with the experimental and calculated oscillator strengths of holmium-doped sample heated to 1000°C and the refractive index of glass sample as n=1.46 is given in Table 1.

The J-O intensity parameters are found by comparing experimentally and theoretically calculated oscillator strengths, but in our present studies have found some trend that relates the parameters to the local environment of the Ho^{3+}ions. From Table 1 it is found that J-O parameters have the following trends $\Omega_2 > \Omega_6 > \Omega_4$. The large value of Ω_2 indicates the presence of covalent bonding between the rare earth ions and glass host. The J-O parameter Ω_2 is very sensitive to the structure and it is associated with the symmetry and covalency of lanthanide sides. On the other hand, Ω_4 and Ω_6 values show the viscosity and dielectric of the media and also affected by the vibronic transition of the rare earth ions bond to the

ligand atoms. J-O intensity parameters can be used to calculate the spectroscopic quality factor (SQF = $\frac{\Omega_4}{\Omega_6}$) = 0.92 which determines the stimulated emission for the laser active medium.

Effect of annealing

There is a significant effect of annealing on the RE dopants as is reflected by the PL spectra shown in Figure 4. Comparing the spectra of the samples at different stages of annealing, it is observed that the intensities of the emission peaks increase dramatically with annealing. In the initial stages before annealing, the samples are highly porous and these pores are filled with residual liquids such as ethanol, water etc. during the ageing process. Slow annealing gradually removes these residual fluids but due to the high porosity, atmospheric water vapour tends to get re-absorbed by the porous samples. After annealing to high temperatures at 1000°C the pores gradually close and shrinking the size of the sample and sealing from atmospheric moisture. The low PL emission in the lower temperature treated samples may be due to the presence of residual hydroxyl contents. Moreover, the porous samples tend to reabsorb atmospheric water vapour which could lead to the RE ions experiencing a hydroxyl rich environment. The increase in luminescence with annealing is mainly attributed to the removal of residual hydroxyls.

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