

Synthesis of Er^{3+} and $\text{Er}^{3+} : \text{Yb}^{3+}$ doped sol–gel derived silica glass and studies on their optical properties

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Abstract. Er^{3+} and $\text{Er}^{3+} : \text{Yb}^{3+}$ doped optical quality, crack and bubble free glasses for possible use in making laser material have been prepared successfully through sol–gel route. The thermal and optical, including UV-visible absorption, FTIR etc characterizations were undertaken on the samples. The absorption characteristics of Er^{3+} doped samples clearly revealed the absorption due to Er^{3+} ions. On the other hand $\text{Yb}^{3+} : \text{Er}^{3+}$ doped samples showed enhanced absorption due to ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. The absorption and emission cross-section for ${}^2F_{7/2} \leftrightarrow {}^2F_{5/2}$ of Yb^{3+} were estimated. FTIR absorption spectra have clearly shown the reduction of the absorption peak intensity with heat treatment in the range 3700–2900 cm^{-1} . The 960 cm^{-1} band also showed progressive decrease in the absorption band peak intensity with heat treatment. The result of the investigations with essential discussions and conclusions have been reported in this paper.

Keywords. Sol–gel silica glass; laser material; absorption and emission cross-section.

1. Introduction

Sol–gel glasses doped with rare-earth (RE) ions are of interest for various applications including solid state lasers, optical waveguides and fibre amplifiers. The main characteristics of spectroscopic transition involving RE ions are long lifetime of metastable states (ranging from tens of microsec to a few millisecc) and narrow absorption and emission lines in the near infrared regions. The most widely used wavelength for amplification and transition of optical signal are around 1.3 and 1.5 μm . It is observed that as compared to other RE ions, erbium (Er^{3+}) is the most suitable for amplification at 1.5 μm . Besides, Er^{3+} silica glasses co-doped with ytterbium (Yb^{3+}) are chosen for getting better lasing property that can act as a eye-safe laser sources near 1540 nm, which is the range of wavelengths focused on the retina of the human eye (Winburn 1985).

Er^{3+} emission transition occurs within this wavelength range corresponding to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. However, Er^{3+} absorbance itself is too weak to allow direct pumping and so, energy transfers are required. The most efficient ones are given by Yb^{3+} ions under absorption from the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition, followed by energy transfer to the ${}^4I_{11/2}$ Er^{3+} level and fast nonradiative transition to the ${}^4I_{13/2}$ level which emits the expected fluorescence. As a matter of fact, Yb^{3+} concentration has to be optimized to get the highest absorption coefficient.

It is to be mentioned that it is very difficult to prepare REs doped silica glass by the conventional technique in-

volving the quenching of an oxide melt due to the high melting temperature of SiO_2 . But silica based glasses show excellent durability and optical quality. The sol–gel process offers an attractive method for preparing these materials at relatively lower temperature without melting, and it produces an opportunity of having a control over the microstructure and composition of host matrix (Brickner and Scherer 1990). However, high concentration of hydroxyl groups that remain in sol–gel glasses is a disadvantage of the sol–gel method as it decreases the fluorescence efficiencies and shorten luminescent level lifetimes of dopant ions in glasses, adversely affecting optical device performance (Phalippou *et al* 1984; Berry and King 1989). Techniques leading to the low hydroxyl sol–gel glasses include high temperature treatment in the presence of carbon tetrachloride (Phalippou *et al* 1984), inclusion of hydrofluoric acid in the initial solution (Pope and Mckenzie 1993) and heat treatment in different atmospheres (oxygen, vacuum, carbon tetrachloride and helium) (Ainslie *et al* 1988). The other problem associated with sol–gel process is RE ions clustering (Fujiyama *et al* 1990), leading to concentration quenching of luminescence through cross-relaxation or energy transfer process.

In view of the above, a comprehensive work on the synthesis of Er^{3+} and $\text{Er}^{3+} : \text{Yb}^{3+}$ doped silica glasses by sol–gel technique and their optical characterization have been undertaken in our laboratory having the following objectives in mind.

- (I) Synthesis and perfection of techniques of synthesis of these class of rare-earth doped glasses by sol–gel technique.
- (II) Understanding the actual absorption, energy transfer

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and emission mechanism involved in these materials so as to examine the suitability of these prepared glass for use in making laser material.

Transparent, crack and bubble free glasses were thus prepared reproducibly.

2. Experimental

Silica sols containing 1.0 mol% Er_2O_3 and different mol% (0.5, 1.0, 1.5) Yb_2O_3 were prepared using tetraethyl orthosilicate, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, deionized water, HCl and NH_4OH . The chemicals used were all AR (analytical reagent) grade. Calculated amount of dopant salts were poured in TEOS under stirring condition at room temperature. The molar ratio of TEOS : H_2O : HCl was 1 : 14 : 0.01. The pH of the sols were adjusted to 3.5 by addition of NH_4OH solution in it. The sols were cast into petri dishes and kept for 10 days for aging at room temperature. They were then dried for three weeks at 55°C and finally heat treated at 900°C in air.

Transparent, crack and bubble free glasses were thus prepared reproducibly. The absorption spectra of the samples were taken in the wavelength range 300–1100 nm using UV-vis spectrophotometer (Perkin Elmer Instruments, Lambda 25). TGA/DTA analyses were carried out using a Perkin-Elmer Instrument (Pyris Diamond TG/DTA, thermogravimetric/differential thermal analyser). XRD studies were conducted in (15 – 50°) 2θ range using a PW 1710 diffractometer with CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$). The infrared (IR) spectra were measured with the help of infrared spectrophotometer (Thermo Nicolet, NEXUS 870). All measurements were carried out at room temperature (25°C).

3. Results and discussion

3.1 Visual characteristic

All the gel samples were transparent (figure 1). The colour of the gels was found to depend on the dopant ions (bright



Figure 1. Photograph of a gel sample sintered at 900°C .

pink for Er and comparatively less bright pink for Er–Yb) and was found to deepen with dopant concentrations.

3.2 Thermal characteristics

The dried gels when heated above 50°C , underwent weight loss and consequently shrinkage. Figures 2 and 3 show DTA and TGA curves of 1.0 mol% Er_2O_3 doped dried gel up to 1200°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air. An endothermic peak is observed in DTA curve from 50°C and 200°C . The TGA curve shows a 10% weight loss around this temperature range. The peak associated with the weight loss may be attributed to the escape of absorbed water. The second stage of weight loss as shown in TGA curve occurred due to decomposition and oxidation of organic matters as supported by the appearance of a broad exothermic band at 500°C in DTA curve. Beyond 700°C , the weight loss is small and gradual with further heat treatment (indicated in TGA curve). The weight loss at elevated temperatures is probably due to removal of water during con-

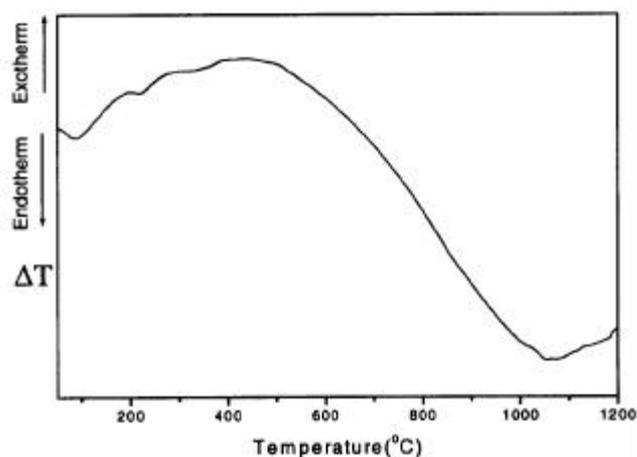


Figure 2. DTA curve for 1.0 mol% of Er_2O_3 doped silica gel.

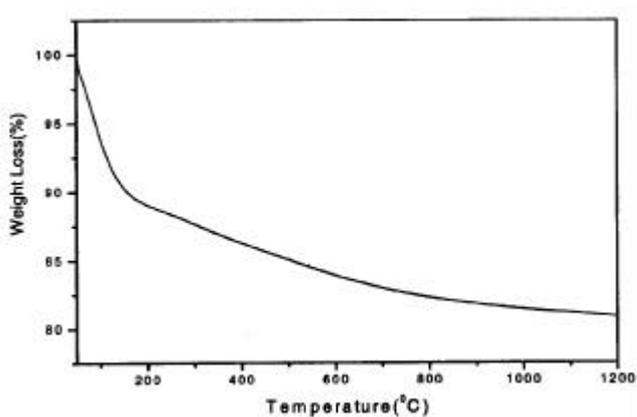


Figure 3. TGA curve for 1.0 mol% of Er_2O_3 doped silica gel.

densation. A total weight loss of about 18% and 19% are observed for heating up to 1000°C and 1200°C, respectively.

3.3 Structural analysis

Figures 4 and 5 show XRD patterns of 1.0 mol% Er_2O_3 and 1.0 mol% Er_2O_3 with 1.0 mol% Yb_2O_3 doped silica gels sintered at 900°C, respectively. In both the cases, only broad diffraction peaks were observed. The broadness of these peaks indicate amorphous nature of glassy phase. Therefore, it can be concluded that there is no chance of forming crystalline phase up to 900°C sintering.

3.4 Absorption spectra

Figure 6 shows the absorption spectra (300–1100 nm range) of 1.0 mol% Er_2O_3 doped silica gels (B) and 1.0 mol% Er_2O_3 and 0.5 mol% Yb_2O_3 doped silica gels (A) densified at 900°C. All the absorption peaks correspond to the atomic transitions of Er^{3+} ions. In contrast to many excited-state multiplets of Er^{3+} , the Yb^{3+} ion has only one excited-state multiplet ($^2F_{5/2}$), and the respective absorptions from the $^2F_{7/2}$ ground state multiplet are observed around 976 nm. The spectra is similar to the one reported earlier (Ainslie *et al* 1988) for Er^{3+} doped sample. The absorption cross-section of $^2F_{7/2} \rightarrow ^2F_{5/2}$ is more than an order of magnitude greater than for the Er^{3+} , $^4I_{15/2} \rightarrow ^4I_{11/2}$ absorption in this wavelength range. The different transitions of Er^{3+} from the $^4I_{15/2}$ ground state to excited states are shown in table 1.

3.5 Absorption ($s_{ab}(I)$) and emission ($s_{emi}(I)$) cross-sections

From the Lambert-Beer dependency, the absorption cross-section of the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb^{3+} ions have

been determined from the absorption spectra using the formula

$$s_{ab}(I) = 2.303 \log(I_0/I)/(NI), \quad (1)$$

where $\log(I_0/I)$ is absorbance, l the sample thickness, and N the Yb^{3+} ion (ions/cm³) concentration.

There are a number of ways (MaCumber 1964; Koehnner 1986; Martin and Milam 1982) by which emission cross-sections can be determined. Here the emission cross-

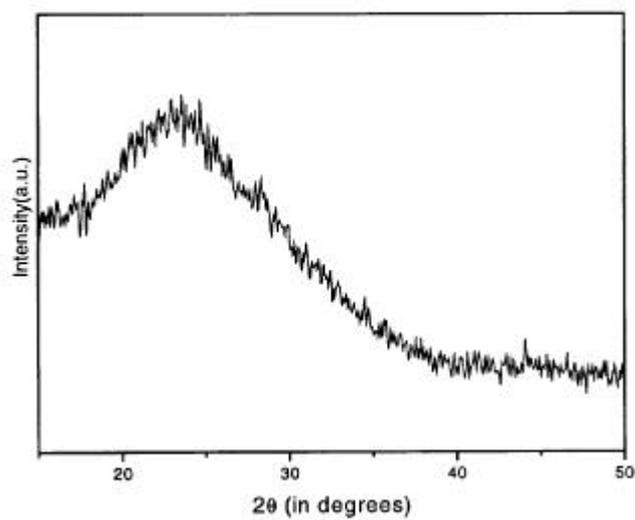


Figure 5. XRD pattern for 1.0 mol% of Yb_2O_3 and 1.0 mol% of Er_2O_3 doped silica gel sintered at 900°C.

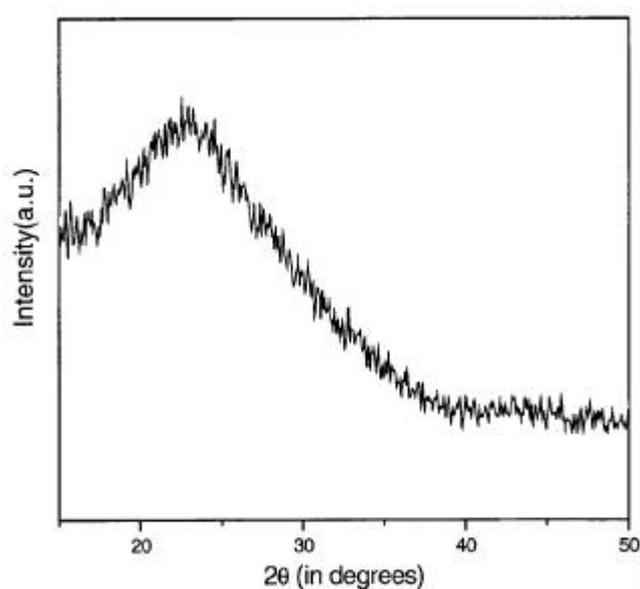


Figure 4. XRD pattern for 1.0 mol% of Er_2O_3 doped gel sintered at 900°C.

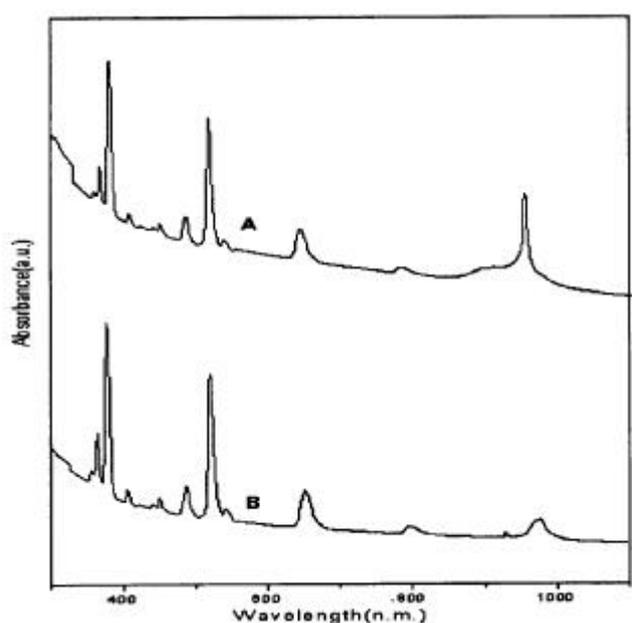


Figure 6. The UV-vis absorption spectra of (A) 0.5 mol% Yb_2O_3 and 1.0 mol% Er_2O_3 doped silica gels sintered at 900°C, and (B) 1.0 mol% Er_2O_3 doped silica gel heated at 900°C.

section is calculated using MaCumber (1964) theory. The absorption and emission cross-section are related as

$$s_{\text{emi}}(\mathbf{I}) = s_{\text{ab}}(\mathbf{I}) \exp[(E - h\nu)/kT], \quad (2)$$

where \mathbf{n} is the phonon frequency, E the net free energy required to excite one Yb^{3+} from ${}^2F_{7/2}$ to ${}^2F_{5/2}$ state at temperature T , h the Planck's constant, and k the Boltzmann constant. Figures 7–9 illustrate the calculated absorption and emission cross-sections for the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb^{3+} ions in silicate glasses. The calculated absorption and emission cross-section values of $s_{\text{ab}}(\mathbf{I})$ and $s_{\text{emi}}(\mathbf{I})$ are shown in table 2 (also seen in figures 7–9). The values of cross-sections are larger than the previously reported fluoride glasses (Weber *et al* 1983) and silicate glass (Allain *et al* 1993).

The most important laser parameter, b_{min} , is defined as the minimum fraction of Yb^{3+} ions that must be excited to balance the gain exactly with the ground state absorption at laser wavelength, \mathbf{I}_0 . The parameter, b_{min} , is of crucial importance for quasi four-level systems such as in Yb^{3+} doped glasses. The value of b_{min} is simply given by (Deloach *et al* 1994)

$$b_{\text{min}} = \frac{s_{\text{ab}}(\mathbf{I}_0)}{s_{\text{emi}}(\mathbf{I}_0) + s_{\text{ab}}(\mathbf{I}_0)}, \quad (3)$$

when b_{min} fraction of Yb^{3+} population is excited, the upward and downward transition rates are equal, and the

Table 1. Absorption band positions of Er^{3+} ions in the wavelength range 300–1100 nm.

| Level transition from the ground state, ${}^4I_{15/2}$ to | Wavelength (nm) |
|---|-----------------|
| ${}^2K_{15/2}$ | 363 |
| ${}^4G_{11/2}$ | 377 |
| ${}^2H_{9/2}$ | 405 |
| ${}^4F_{3/2}$ | 451 |
| ${}^4F_{7/2}$ | 489 |
| ${}^2H_{11/2}$ | 519 |
| ${}^4S_{3/2}$ | 543 |
| ${}^4F_{9/2}$ | 653 |
| ${}^4I_{9/2}$ | 800 |
| ${}^4I_{11/2}$ | 976* |

*Here level transition from the ground state ${}^2F_{7/2}$ to excited ${}^2F_{5/2}$ also exists by the influence of Yb^{3+} ions.

Table 2. Absorption and emission cross-sections and laser performance parameters for Er : Yb doped silica glasses with different compositions.

| Sample composition (mol%) | $s_{\text{ab}}(\text{pm}^2)$ | $s_{\text{emi}}(\text{pm}^2)$ | b_{min} |
|--|------------------------------|-------------------------------|------------------|
| 1.0Er ₂ O ₃ ·0.5Yb ₂ O ₃ ·98.5SiO ₂ | 0.79 | 0.73 | 0.51 |
| 1.0Er ₂ O ₃ ·1.0Yb ₂ O ₃ ·98.0SiO ₂ | 0.83 | 0.92 | 0.47 |
| 1.0Er ₂ O ₃ ·1.5Yb ₂ O ₃ ·97.5SiO ₂ | 0.63 | 0.70 | 0.47 |

glass essentially becomes transparent at \mathbf{I}_0 , such that there is neither gain nor loss for a weak laser probe beam.

The laser performance parameter, b_{min} , for this study has been calculated and is shown in table 2. The b_{min} parameter addresses the effect of the resonant absorption loss of Yb^{3+} at \mathbf{I}_0 . Here favourable spectroscopic parameters include a large emission cross-section and absorption cross-sections for corresponding laser transition.

3.6 IR spectra

The infrared spectra (4000–400 cm^{-1}) of 1.0 mol% Er₂O₃ and 1.0 mol% Yb₂O₃ doped silica gels dried at 55°C and sintered at 900°C are shown in figures 10 and 11, respec-

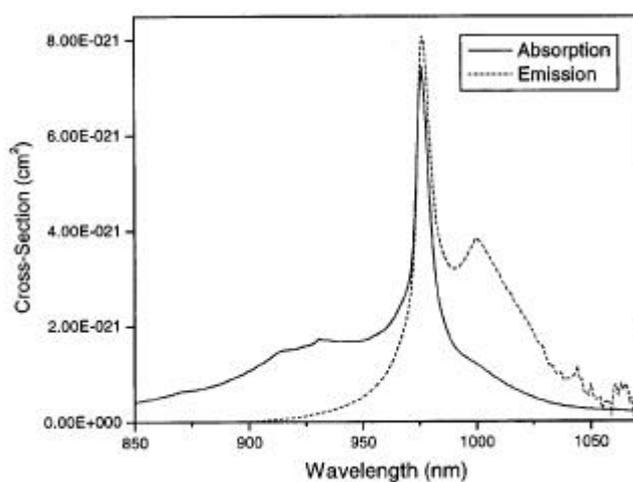


Figure 7. The absorption and emission cross-section spectra for 1.0 mol% of Er₂O₃ and 0.5 mol% of Yb₂O₃ doped silica gels sintered at 900°C.

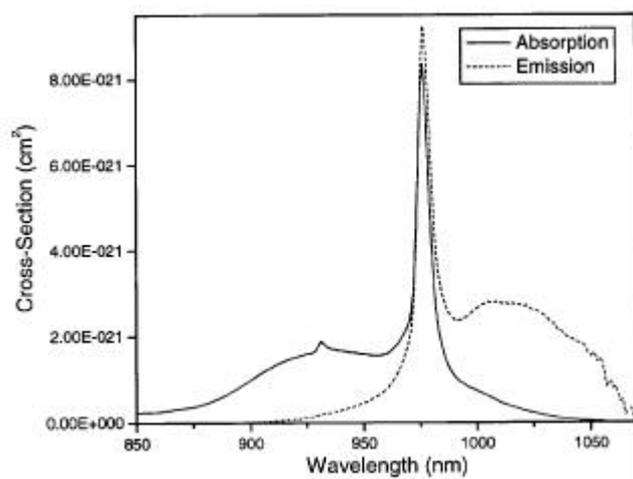


Figure 8. The absorption and emission cross-section spectra for 1.0 mol% of Er₂O₃ and 1.0 mol% of Yb₂O₃ doped silica gels sintered at 900°C.

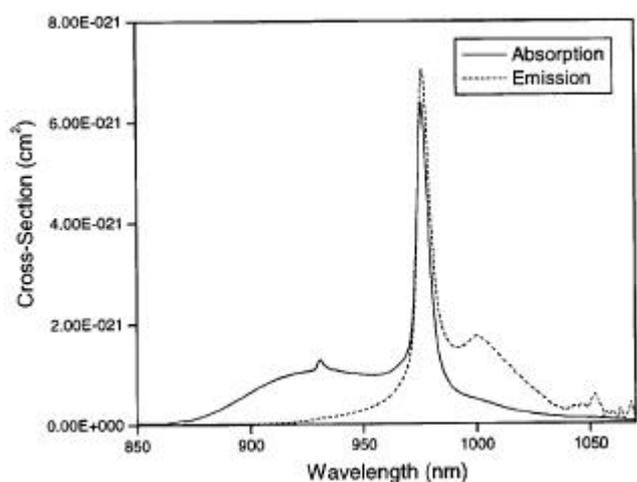


Figure 9. The absorption and emission cross-section spectra for 1.0 mol% of Er_2O_3 and 1.5 mol% of Yb_2O_3 doped silica gels sintered at $900^\circ C$.

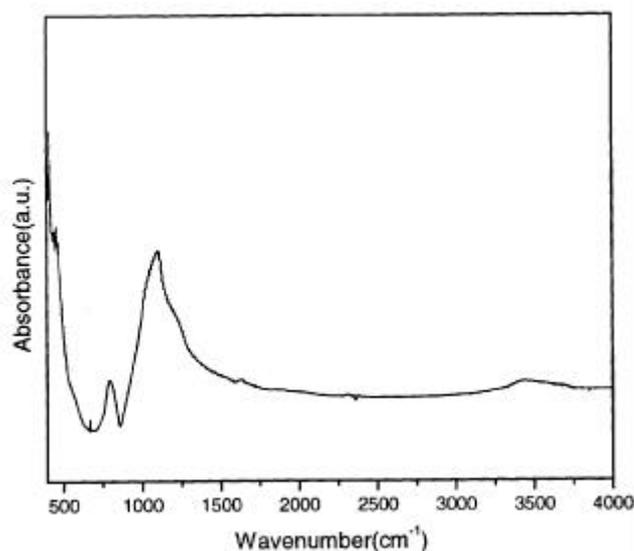


Figure 11. FTIR spectra of 1.0 mol% Yb_2O_3 and 1.0 mol% Er_2O_3 doped silica gels sintered at $900^\circ C$.

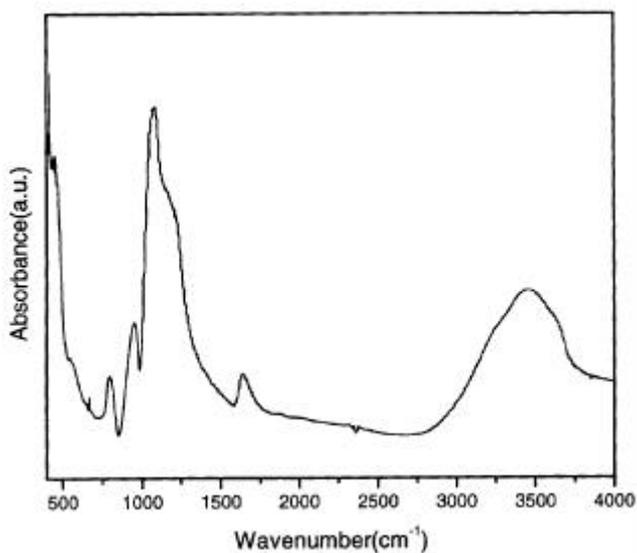


Figure 10. FTIR spectra of 1.0 mol% Yb_2O_3 and 1.0 mol% Er_2O_3 doped silica gels dried at $55^\circ C$.

tively. The figures show a broad absorbance ranging from $3700\text{--}2900\text{ cm}^{-1}$. This is attributed to the presence of Si–OH stretching vibration and absorbed water. The area under the curve and intensity, which are highest for gel, dried at $55^\circ C$, progressively diminishes with the heat treatment. This indicates the decrease in absorbed water in the gel structure. The peak at 1630 cm^{-1} caused by the –OH bending vibration (Herzberg 1985) also behaves similarly showing escape of water from the structure of the gels. The 960 cm^{-1} band induced by the Si–O asymmetric stretching vibration progressively gets weakened with rise of temperature (during heat treatment) suggesting gradual increase in strength of the silica network. At high temperature ($\sim 800^\circ C$), the spectra resemble that of fused silica

glass (Ocana *et al* 1989). The absorption peaks are assigned to the Si–O asymmetric stretching vibration (1200 cm^{-1}) and the vibration of siloxane chains (1080 cm^{-1}). The peak at 810 cm^{-1} is due to Si–O–Si bending mode while that at 465 cm^{-1} is due to O–Si–O bending mode (Bechstedt and Hubner 1987).

It is seen from figure 11 that, with the rise in sintering temperature, the band $3700\text{--}2900\text{ cm}^{-1}$ shifts towards higher frequency region and the area under the band decreases. This is likely to be due to the removal of ethyl groups during heating. The absorbance due to C–O stretching vibration at 1050 cm^{-1} too is obscured by the strong bands due to Si–O vibration. Thus, complete removal of carbon from the gel-derived glass, on pyrolysis, could not be conclusively proved.

4. Conclusions

The possibility of synthesizing optical quality crack and bubble free silica glasses doped with rare-earth ions (Er^{3+} , $Er^{3+} : Yb^{3+}$) have been demonstrated. The thermal and optical characterization on some typical samples have been undertaken. The transitions responsible for absorption and emission have been identified. The increased absorption and emission cross-section at 975 nm indicates better luminescence emission in near infrared region for its possible use as a laser material.

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