

Characteristic studies of Erbium: Nickel doped Silicate Glasses

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Abstract - Transparent crack free monoliths containing Nickel and Erbium were prepared by solgel technique. The optical properties of luminescent rare earth ions depend on the local bonding environment and the distribution of the dopant ions. The base matrix was doped with different concentrations of Erbium & Nickel. Doped samples of $\text{Er}^{3+}:\text{Ni}^{2+}$:silica xero gels and silica glasses were prepared from hydrolysis and condensation of Tetra Ethyl Ortho Silicate (TEOS) by sol-gel method. The xero gels were characterized by XRD, FTIR and UV/VIS absorption spectra. The amorphous nature of gel glasses have been confirmed by XRD spectra. The FTIR & UV/VIS absorption spectra lead to the study of the structure of the samples. The Sol gel derived silica glasses are pure and have superior optical properties and hence they are widely used in both electronics and in optical communications.

Key words: Sol-Gel, XRD, FTIR, UV/VIS Absorption Spectra.

I. INTRODUCTION

The sol gel technique is a low temperature method of preparing glass that allows the incorporation of impurity ions during the aging of the gel to glass process. Sol gel derived SiO_2 glasses and Xerogels are amorphous materials of very low dimensions and are designed to have desired optical and electrical properties by doping transition metal ions and /or luminescence species in glasses. The sol gel technique is an excellent method to prepare hybrid materials and the low temperature enables organic and inorganic species to be incorporated into rigid silicon oxide matrices without degradation

The low temperature sol gel glasses have a mesoporous structure in which small metal ion particles substitute the Si site or the porous centers. Silicate glasses doped with different inorganic compounds are widely used in laser technologies and opto electronics. Rare-Earth doped materials are widely investigated in optical integrated devices, such as laser active materials and optical communication [1-4]. Sol gel glasses are porous networks that have been densified through chemical processing and heat treatments. The composition of the host materials tend to change the local structure and covalency and there by related optical properties of rare earth ions could be enhanced [5]. Glass formation is possible for a system of any composition provided that it contains sufficient of the component called 'network former'. Thus, a wide variety of multi - component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. The lack of regularity of the atomic arrangement over a long range, i.e. the randomness of the structure, is essential to the understanding of the physical and chemical features relevant to those glasses which have the special properties is reviewed. In recent years, preparation of active glasses using the sol-gel method has attracted a considerable interest [6, 7]. The Sol – Gel glasses could be prepared from a water ethanol mixed solution of silicon alkoxide and dopants at room temperature, kept for 3-4 weeks, forms as wet solid referred as xerogel [8]. Inorganic amorphous materials have shown to be very

useful as host media in which small metallic particles can be grown. Most of these studies concerned with silica gels and gel-derived silica glasses owing to their potential applications in frontier areas.

A lot of studies have been reported on the doping of solgel monoliths with erbium and other fluorescent rare earth ions. The fluorescence lifetime, a useful indicator of the molecular environment of the ions have been low compared to that of melt glasses. Since OH groups are well known to quench rare earth fluorescence, and hydrolysis is an inherent part of solgel processing, the presence of OH groups is a likely cause of reduction in lifetime. Erbium doped materials have been widely adopted in optical communication system because of their emission band in the infra red region [9]. The use of Er^{3+} as an optical dopant has had a long history of research and success [10]. The luminescence efficiency of the rare-earth ions in solgel host materials is comprised due to the tendency of the rare earth ions to form clusters. The presence of the hydroxyl ions and remnant organic solvent clustering results in concentration quenching due to non radiative energy transfer between the rare earth ions within the clusters. The hydroxyl quenching, on the other hand is caused by residual water, solvent and silanol groups present in the sol gel glass and lead to the enhancement of non radiative decay pathway of the rare-earth ions. The present study is to investigate the effects of doping with $\text{Er}^{3+}:\text{Ni}^{2+}$ on the structure of silica gels and gel-derived silica glasses.

II. EXPERIMENTAL DETAILS

The silica gels were synthesized from Tetra ethoxy – silane $(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}$ (TEOS), of density 93 Kg/L, water, ethanol and the nitrates of the dopants [11]. The molar ratio of ethanol to TEOS and water to TEOS were made 2:1 and 14:1 respectively. The dopants were added in the form of their nitrates. The preparation method is found elsewhere [12]. Samples co-doped with $\text{Er}^{3+}:\text{Ni}^{2+}$ were prepared in the different weight %. Samples list is shown in Table 1. The glass structure was characterized by XRD spectra and Fourier transform Infra Red (FTIR) spectroscopy. XRD was recorded by D8 Advance X-ray Diffractometer with x ray source Cu, Wavelength 1.5406 Å. The FTIR spectra were recorded over the frequency range 4000 – 500 cm^{-1} using Thermo Nicolet, avatar 370 FTIR Spectrometer with a resolution of 0.9 cm^{-1} . The absorption spectra were recorded in a Shimadzu spectrophotometer (UVPC 2450) in the wavelength range 200-900 nm. All measurements were done at room temperature and for the same instrument parameters.

Sample code	Erbium	Nickel
A	1%	0.5%
B	1%	1%
C	1%	1.5%
D	1%	2%
E	0	0

III. RESULTS AND DISCUSSIONS

(i). X-ray Diffraction Pattern (XRD)

The XRD pattern of the sol gel glass doped with Er & Ni shown in figure 1 exhibit irregular peaks which reveal that the planes in the sample are irregularly arranged. It indicates the absence of long-range order in the distribution of planes in these samples. The XRD spectrum clearly indicates the amorphous nature of the glassy materials. The use of X-ray diffraction in the determination of glass structure is limited due to the absence of long range order in the glass.

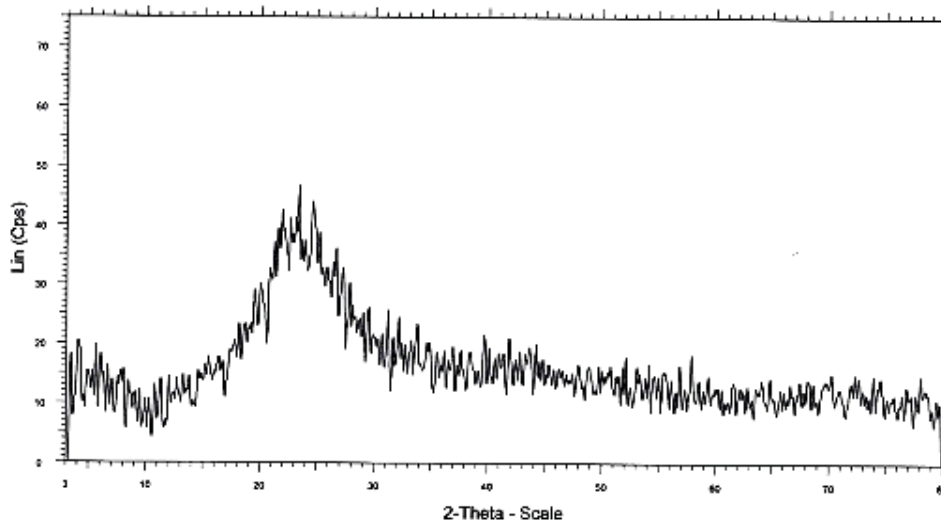


Fig. 1.XRD spectrum of sample (B)

(ii). FTIR Studies

The FTIR Spectra of the sample (B) is shown in figure 2. The broad band at 3477cm^{-1} agrees well with the previous FTIR investigations of Silica based materials. The most prominent region of these spectra lies in the range $1000 - 1300\text{cm}^{-1}$ also reported by others [13-16]. The characteristic peak shown at 1076 and shoulder at 1200cm^{-1} were assigned to asymmetric stretching vibration of the three dimensional Si-O-Si network [17]. According to Perry et al the peak at 1076cm^{-1} could be assigned to transverse optical mode of asymmetric vibration, while the shoulder at 1200 could be assigned to the longitudinal mode of the same vibration.

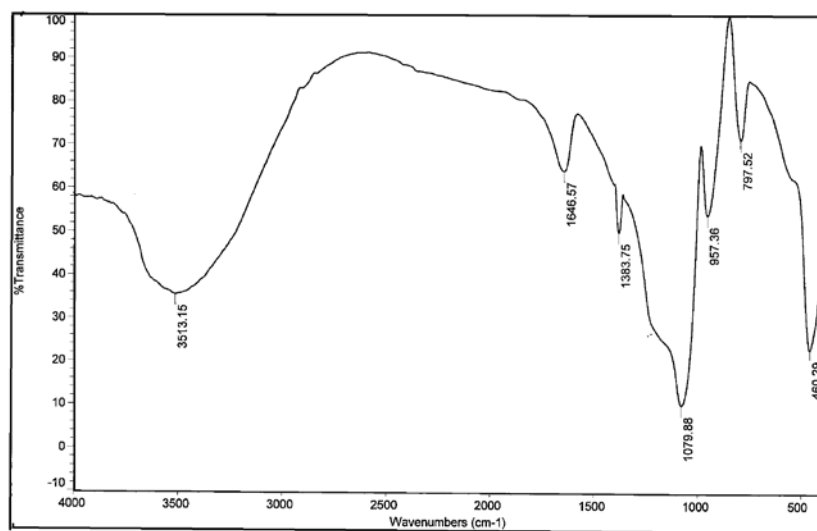


Fig 2. FTIR Spectra of the bare sample E

A weaker peak at approximately 796cm^{-1} corresponds to the symmetric stretching vibration of Si-O-Si net work [13, 18 - 20]. The peak at 459.44cm^{-1} assigned to the bending mode of the same bond. Peak at 954cm^{-1} assigned to surface S-O groups [19, 21]. Abroad peak observed in the O-H stretching region are approximately at 3500cm^{-1} . Finally the peaks at approximately 3450cm^{-1} and 1640cm^{-1} were attributed to molecular water absorbed on the surface

of the oxide [14]. A peak at 1373cm^{-1} was present in the spectra of mixed metal oxides. All samples showed identical spectra

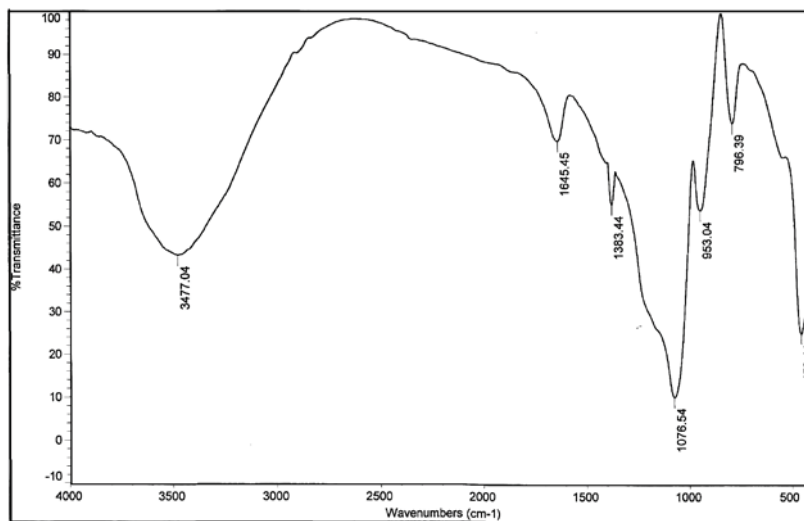


Fig. 2 (a). FTIR Spectra of the sample B

(iii) Absorption Spectra

The absorption spectra of the sample (C) heat treated at $100, 200, 300$ and 400°C are shown in figure 3. The spectra are recorded using UV-VIS-Spectrophotometer (shimadzu 2450). The spectra show a prominent shoulder at around 247 nm with an absorption tail in the wavelength range $200\text{-}225\text{ nm}$.

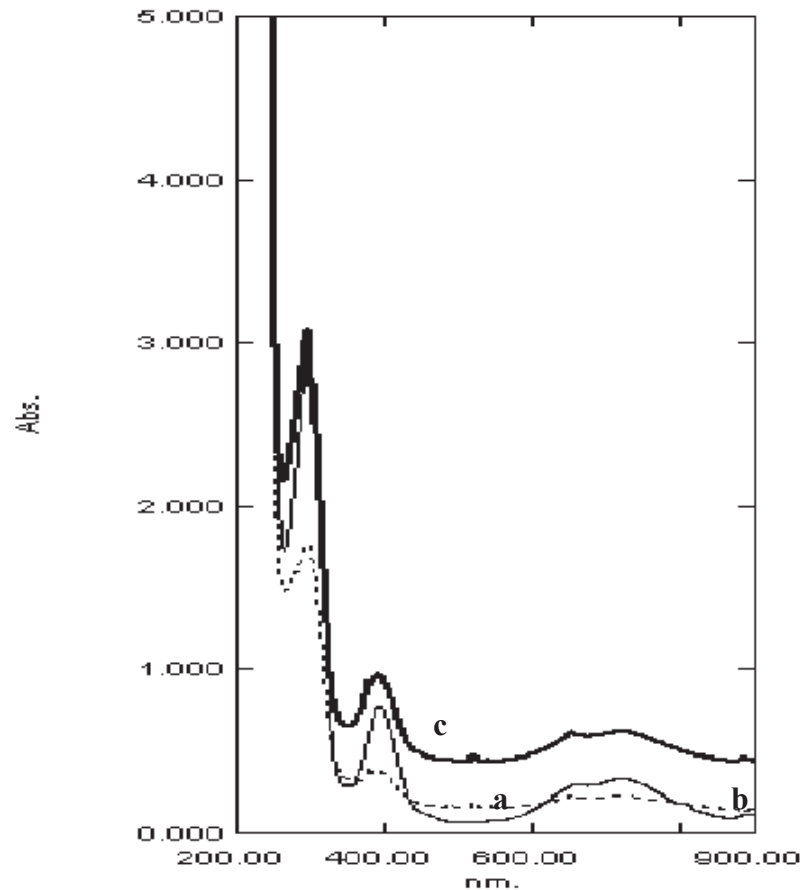


Fig 3. Absorption spectra of sample (B) heated at (a) 150^oC (b) 300^oC (c) 400^oC

All the samples showed two prominent peaks at 390nm and 680 nms. The peaks at 390nm is the characteristic of Nickel. The broad band at 680nm is that of Erbium. The peaks get sharpened on heating. when sample C is heated to various intervals of temperature, the prominent peaks are get shifted towards the lower wavelength region. ie a blue shift occurs in the absorption spectrum and also the absorption intensity of the peaks get increased.

IV. CONCLUSION

The Sol gel method is used effectively to incorporate Nickel and Erbium into a silica gel network. The characteristic silicon-oxygen-silicon IR peaks observed at 1080 and 798cm⁻¹ in the pure silica gel shifted to lower wave numbers in the spectra of the mixed metal oxide systems, suggesting that the incorporation of the second metal decreased the strength of silicon- oxygen bonds. The XRD spectrum indicates the amorphous nature of the samples. The absorption spectrum of the heat treated sample shows a blue shift.

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