

Structural and Optical Studies of Nano-structure Monolithic Silica-Gel Derived Glasses Containing Nd^{3+}

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The sol-gel process was applied for the preparation of neodymium (Nd^{3+}) doped silica gel derived glasses. Two different procedures have been studied using two different precursor materials, Tetramethoxy-silane (TMOS) and Tetraethoxy-silane (TEOS), giving silica gel and silica doped with Nd^{3+} of type I and type II, respectively. Both type materials were subjected to the same heat-treatment temperature. The normal transmission was measured using Fourier Transform Infrared Spectrometer FTIR, Raman analysis and X-ray diffraction (XRD), were carried out to determine the crystal structure of the prepared samples. The prepared samples change from amorphous to α -cristoballite phase at higher temperature regardless the two type materials. The crystallite size was found to be as small as 10.4 nm at 1400°C for pure sample type II. The thermally treated sample microstructures were investigated using scanning and transmission electron microscope. Also DTA and TGA Characteristic techniques were used. The photoluminescence PL measurements for pure sample (type I) heat-treated at 1400°C shows bands of maximum in the blue green spectral region at 535 and 546 nm accompanied with band of weak intensity at 590 nm. Doped sample (type I) heat-treated at 1400°C shows new bigger, sharper and intense bands at 875, 889 and 900 nm that were interpreted on the light of $4F_{3/2}$ to $4I_{9/2}$ transitions of Nd^{3+} ion. PL spectra are found to be sensitive to defects such as impurities and E' centers.

Introduction

Nanoparticle silica-gel derived glasses is an attractive amorphous material, that is applied, as a wave-guide [1], chemical gas sensor [2] and so on. It can be prepared by sol-gel method, which is being actively studied in leading laboratories all over the world [3]. The advantage of this process is to avoid generation of dangerous dust, as would be produced in conventional ceramics processing. The primary attention was paid to its low temperature nature [4-11].

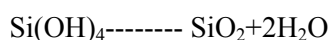
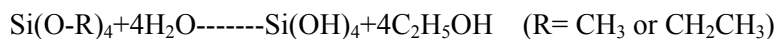
One of the major advantages of the sol-gel process is the possibility to prepare multi-component systems. The glasses in the system $\text{SiO}_2\text{-Nd}_2\text{O}_3$ possess many favorable properties as thermo-stable medium for optical performance. Previous coworkers [9] successfully obtained neodymium doped silica glass containing up to 20 wt % Nd_2O_3 using the sol-gel process. They suggested oxygen coordination number to be 6 around neodymium. Although the sol-gel process allows the preparation of glasses with much higher concentrations of neodymium the problem of microscopic clustering remains even if some other appropriated components are added. That is why further research is required to understand more fully the local environment of neodymium in silica glass.

Rare earth ions are used as dopants in glasses mainly for two reasons. The first one is their well defined and sharp energy levels, which may serve as structural probes for the environment of the dopants, and the other one is the modifications of the energy level structure of the rare earth ions caused by the glassy environment may lead to interesting applications, e.g., solid state lasers [12]. The glass compositions are more favorable for high-density memory devices, because the inhomogeneous widths of the transition between the energy levels are much broader than those of crystals. In addition, the high transparency and easy mass production are also particularly promising for practical application in optical device [13].

In the present work, nano-structure monolithic silica gel derived glasses pure and doped with Nd^{3+} ion using two different precursor materials TMOS and TEOS, were successfully prepared by a simple sol-gel method. The effect of increasing the heat-treatment temperature on the microstructure of the prepared samples was studied. The data are presented for the structure evolution of pure and doped samples by XRD, the transmission FTIR and Raman spectroscopy [14,15]. Scanning and transmission electron microscope studied the morphology and the microstructure of the prepared samples. DTA and TGA techniques were used with increasing the temperature up to 1000°C [16,9]. The PL spectra were found to be sensitive to the defects in the bulk materials, it had made possible the extensive characterization of radiation recombination processes through the intrinsic defects in this materials.

Experimental

Pure silica gels and silica gel doped with neodymium (Nd^{3+}) were prepared using two different procedures via the hydrolysis and condensation of two different precursor materials TMOS and TEOS. The first procedure is prepared from $(\text{CH}_3\text{O})_4\text{Si}$ (Tetramethoxy-silane) TMOS, methanol and distilled water, in the presence of nitric acid (type I). The second one is prepared from $(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}$ (Tetraethoxy-silane) TEOS, ethanol and distilled water, in the presence of hydrochloric acid (type II). The overall process can be written as:



The molar ratio in the starting solution was 0.44: 0.25: 0.074: 0.052: 0.001 for H_2O : CH_3OH : HNO_3 : TMOS: Nd_2O_3 , and 0.39: 0.152: 0.0823: 0.028: 0.001 for H_2O : $\text{C}_2\text{H}_5\text{OH}$: HCl : TEOS: Nd_2O_3 . Neodymium was introduced in the initial stage of the process, by dissolving 0.137 g. of neodymium oxide in nitric acid under heating, resulting in a clear violet solution then the precipitate is dissolved in the silica sol-gel solution prepared before. This solution is then filtered, followed by stirring for one hour at room temperature. The resultant homogeneous solutions were filled in a mould and placed in a drying oven type GFL 7105 at 60°C . The gelation act after approximately 2 days by using TMOS and after about 4 days by using TEOS. The final products were monolithic cubes $15 \times 15 \times 3$ mm. All samples were clear and transparent. The pure samples are colorless and the samples containing neodymium have violet color. After gelation the samples were still left inside the oven for 21 days for aging (which result in a further shrinkage and stiffening of the gel), until no shrinkage appear. Densification of the prepared glass samples was obtained by annealing in air for two hours at temperature ranging from 300 up to 1500°C in a muffle furnace type (Lento) with heating rate $1.5^\circ\text{C}/\text{min}$.

The X-ray diffraction (XRD) patterns of the prepared samples were recorded with X'Pert-Philips X-ray diffractometer with monochromatised CuK_α radiation of wavelength 1.5406\AA at 55 kV and 40 mA. The crystallite size was calculated applying fourrier analysis after correcting the diffraction data for the instrumental broadening using LaB_6 as a standard material (win fit program).

FTIR study of the two types I and II was performed with a Perkin Elmer 1600 (spectrophotometer) in the $4000\text{--}100\text{ cm}^{-1}$ region. Raman spectra were recorded using BRUKER IFS 6/S with Nd-Yag with wavelength $1.064\text{ }\mu\text{m}$ laser as light source. The surface morphology and microstructure of the prepared samples was evaluated using scanning electron microscope (SEM) (JEOL JSM-T330 A) and transmission electron microscope (TEM) [EM 10 Zeis] respectively. The weight loss Endothermic peaks were performed using thermal

gravitational analysis (Shimadzu TGA and DTA 50), from room temperature up to 1000°C under inert gas, N₂ with 10°C/minute. Optical transmission spectra for the prepared samples were measured using Jasco V-570 spectrophotometer, in wavelength range (400-1000) nm. The PL emission obtained using luminescence spectra JASCO FP-777 conventional spectrofluorimeter. The 488 nm line of a spectra-Physics 2017 Argon laser was used to excite room temperature luminescence spectra. A fiber optic probe coupled to a Dilar Superhead, equipped with a suitable notch filter, was employed. A 150 lines/mm grating was used for measuring laser excited luminescence spectra.

Results and discussion

The effect of heat treatment temperature on the structure of the prepared pure silica gel derived glasses and doped with Nd³⁺ ion (type I&II) is shown in Figure (1). No peaks are observed in samples fired below 1050°C (type II) except for the harrow-like pattern at 2 θ between 12 and 24° attributed to amorphous silica gel. However, a small and broad peak at 2 θ between 26 and 26.4° in the samples containing Nd³⁺ (type II) appears after firing the samples at 1050°C for 2 hours, which may be ascribed to preliminarily crystallization of samples. While at 1300°C two broad and small peaks at 2 θ = 21.9 and 31.4° appeared, can be indexed as (101) and (102) diffraction principle line of tetragonal alpha cristobalite respectively, indicating the beginning of crystallization. Which shifted at higher temperature up to 1500 °C in pure and doped samples (types I and II) to 2 θ = 22 and 31.5° indexed as (101) and (102), also new peaks appeared at 2 θ = 25.2, 28.4 and 36.4° indexed as (110), (111) and (112) diffraction principle line of tetragonal alpha cristobalite (JCPDS card num. 82-1403). A peak at 2 θ = 28° with no defined phase was appeared. A similar suggestion was done by Bouajaj [14], who found that, at 1300°C the silica xerogels partially crystallize in the α -cristoballite phase as detected by the Raman analysis. The XRD patterns of prepared samples type I showed the same peak positions as type II with different intensities, (accordingly we found it is unnecessary to go in small steps in pure samples, so we took the sample treated at 1500°C to compare it with that of the two doped types). It is observed that, by increasing the heat treatment temperature both the intensity of the peaks increases and the broadening decreases, indicating the enhancement of crystallinity. While both of them decreased by doping the sample with Nd³⁺ than the pure one regardless the two type materials. At 1500°C, the peak intensities of doped sample type II decrease than the peak intensities of doped sample type I. The calculated crystallite size from XRD data; for pure sample heat treated at 1400 °C was as small as 10.4 nm.

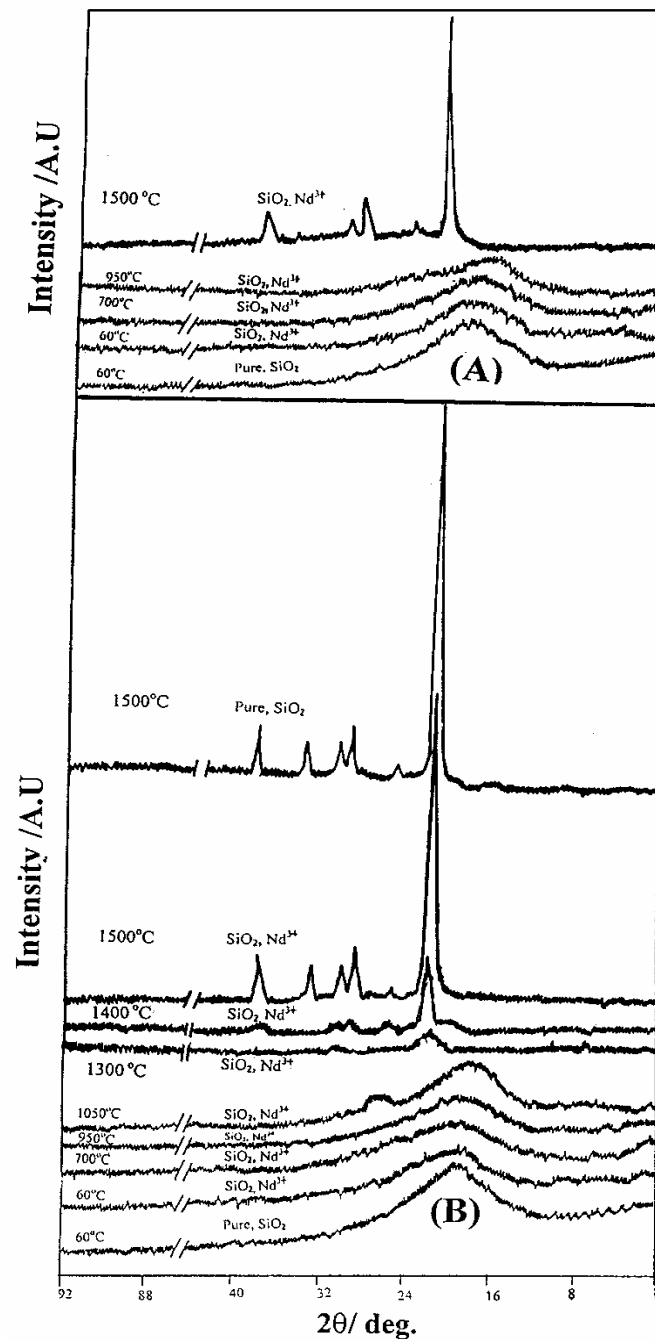


Fig. (1): XRD patterns of pure silica gel dried at 60°C & heat-treated at 1500°C and silica gel doped with neodymium, dried at 60°C & heat-treated from 700 upto 1500°C, (A) type I & (B) type II.

Transmission electron micrographs of fracture surfaces of pure silica gel derived glasses and doped with Nd^{3+} ion are shown in Fig. (2 a-e). A distinct difference in ordering and coalescence of crystallite between pure sample (type II), and doped samples (type I and II), heat-treated at different heating temperature appeared. Amorphous phase is observed at 700°C for doped sample (type II), as shown in Fig. (2 a), which shows particles with undefined shape and randomly distributed. The appearance of the aggregates might be as a result of the low solubility of the neodymium in silica [17]. While, by increasing the heat-treated temperature up to 1400°C for the same sample, smaller structural particles appeared and become nearer to each other as shown in Fig. (2 c and d). These observations might be due to that, at lower heat-treatment temperature it rests some residual water and hydroxyl groups which prevent the density to increase. The gel gradually loosed some of its weight by increasing the firing temperature causing increase in its density, giving rise to the change from amorphous to crystalline phase. This result is in good agreement with the DTA and TGA results in this work and those published before by Battisha [18].

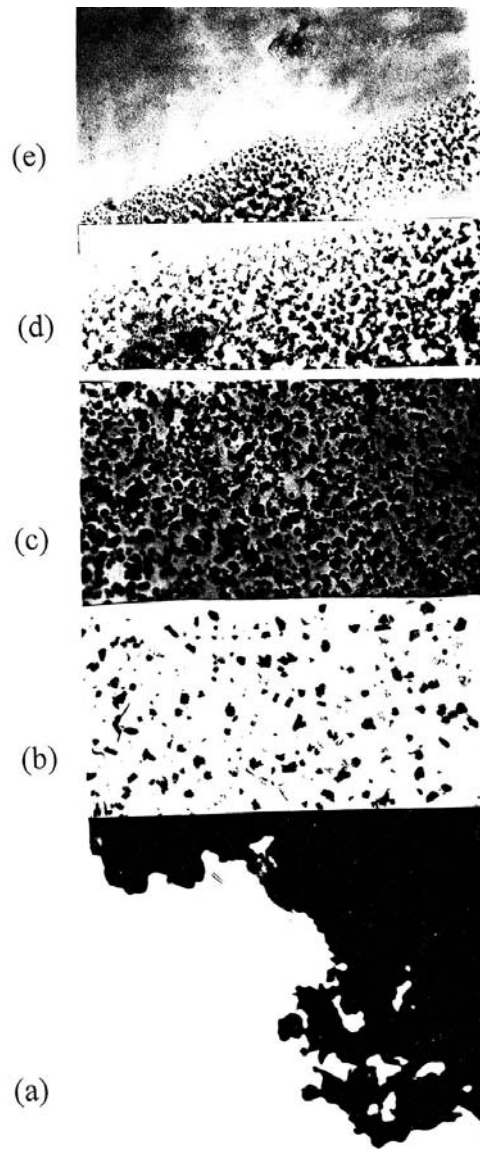


Fig. (2 a-e) TEM micrographs of silica gel doped with Nd^{3+} (type II) (a, c & d) heat treated at: a) 700°C (50000 X), c) 1400°C (80000X) & d) 1300°C (100000X), (b) pure sample (type II) heat treated at 1400°C (80000X) and (e) doped sample (type I) heat treated at 1300°C .

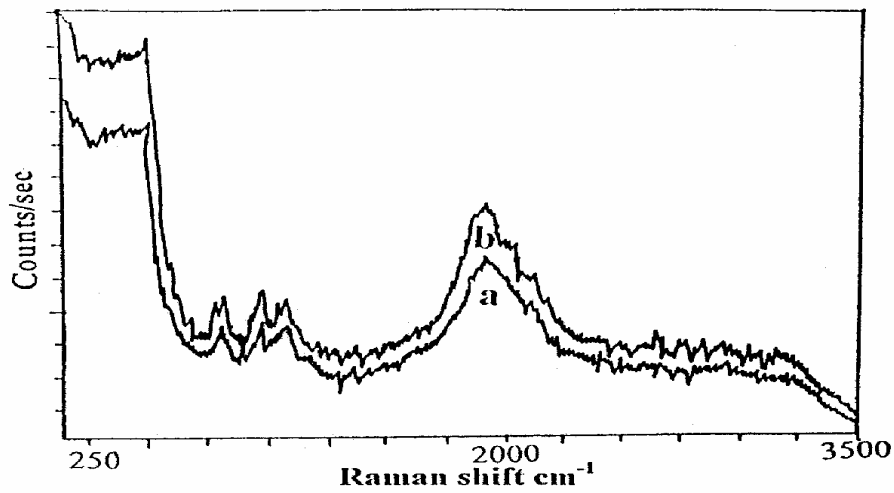


Fig. (3): Raman spectra of silica gel doped with Nd^{3+} and heat treated at 950°C : a) type I and b) type II.

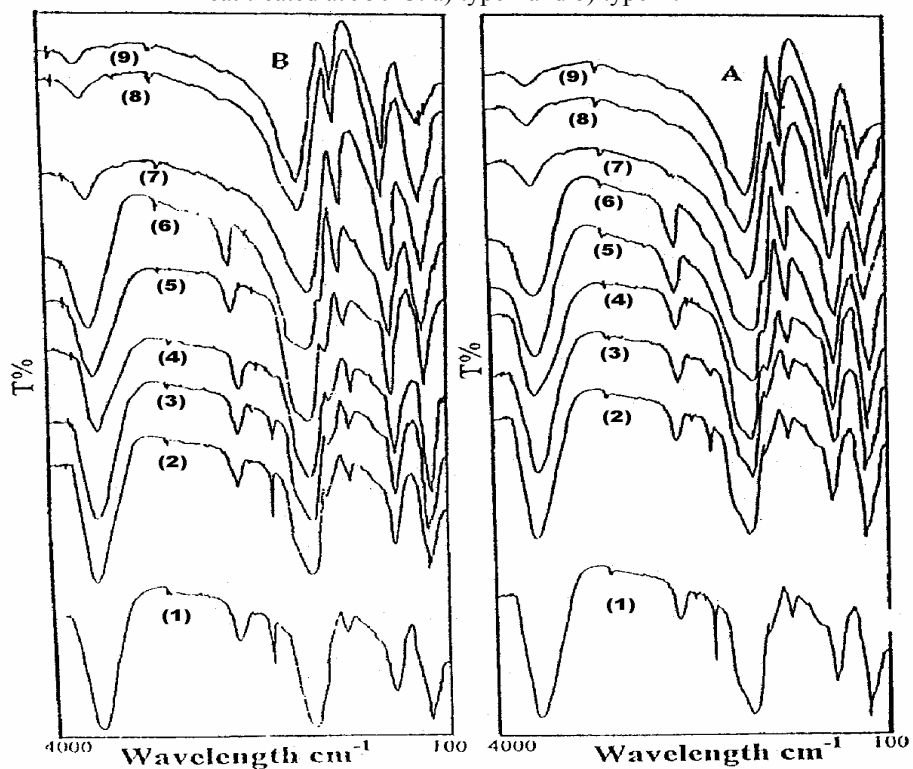


Fig. (4): Transmission FTIR spectrum of Silica gel doped with Nd^{3+} , heat treated at 60°C for: 1) 2 days, 2) 21 days, and heat treated at: 3) 300°C , 4) 500°C , 5) 700°C , 6) 850°C , 7) 950°C , 8) 1050°C and g) pure silica gel heat treated at 1050°C .

where, the structure collapses: The pore is expected to close and fuse together, a smooth material was obtained. These results confirmed the results obtained by XRD analysis. The electron diffraction patterns were analyzed, displaying faint rings. Particles smaller than 10 nm diameters were observed for samples doped with Nd^{3+} heat-treated at 1400°C (type I and II) shown in Fig. (2 f and g).

Both Raman and FTIR spectra of the two prepared types I and II using acid catalyzed process, at constant heat treatment temperature 950°C for Raman and heat treated from 60 up to 1050°C for FTIR are shown in Figs. (3 a & b) and (4 a & b), respectively. The major features of the Raman spectrum associated with network vibrational modes are the 520, 800, 1070, 1925 and 3425 cm^{-1} bands [19]. Corresponding FTIR bands of the two types material I and II are observed at about 470, 802, 985, 1097, 1384, 1636 and 3429 cm^{-1} .

Hydroxyl groups are evident in the Raman and FTIR spectra, we observed bands at 1925 cm^{-1} assigned to Si-OH stretching vibrations in the Raman spectrum, which disappeared in the FTIR spectrum. The band centered between 3400 and 3450 cm^{-1} , corresponding to the fundamental stretching vibrations of different hydroxyl groups, decreases by heat-treatment up to 1050°C in the FTIR spectrum. This reveals that the $\text{Si}(\text{OH})_4$ is not converted into SiO_2 in the initial state of preparing the material. This band seems broad and weak in the Raman spectrum, and then become stronger in the FTIR spectrum. This result is in agreement with previous coworkers [20], who found that for some group frequencies, the associated infrared bands are weak and the Raman bands strong, or vice versa. In addition, the presence of adsorbed water is indicated by the absorption band at 1636 cm^{-1} , which is assigned to the bending mode of water molecules. There is also a noticeable decrease in the intensity of the H_2O absorption in this band until it disappears at 950 and 1050°C for the two types. The peaks located at 1384 cm^{-1} in FTIR spectrum, which is assigned to vibrations of (TMOS, methoxy group and TEOS, ethoxy group) [21], were very unstable, it disappeared easily with temperature. Its absence from 500 up to 1050°C may be due to the completely hydrolyzed and no reesterification of the methoxy and ethoxy groups occurs during drying. The peaks at 1070 cm^{-1} (Raman) which changed to the strong and broad peaks at 1097 cm^{-1} (FTIR), are assigned to Si-O-Si asymmetric stretching mode, it shifted to a higher wave number with increasing temperature in the FTIR spectrum, superimposed on this broad bands a shoulder at 985 cm^{-1} . The 800 (Raman) and 802 (FTIR) cm^{-1} vibration is associated with symmetric Si-O-Si stretching or vibrational modes of ring structures. The 520 (Raman) and 470 (FTIR) cm^{-1} vibrations assign to Si-O-Si bending modes [22]. The 800 (Raman) and 802 (FTIR) cm^{-1} vibration is associated with symmetric Si-O-Si stretching or vibrational modes of ring structures. The increased intensity of the bands centered between 200 and 400 cm^{-1} may be due to a very strong modifying

effect of the Nd^{3+} ions, which seems active. The excess of water at the gel-point after 2 and 4 days for type I and II dried at 60°C shown in Figs (4 a & b) respectively, however, leads to the retention of methoxy and ethoxy groups in the samples. The excess of gelation time of type II than type I is probably due to more internal silanols in the near FTIR region and due presumably to their microporous nature, then type I may loses water easily than type II.

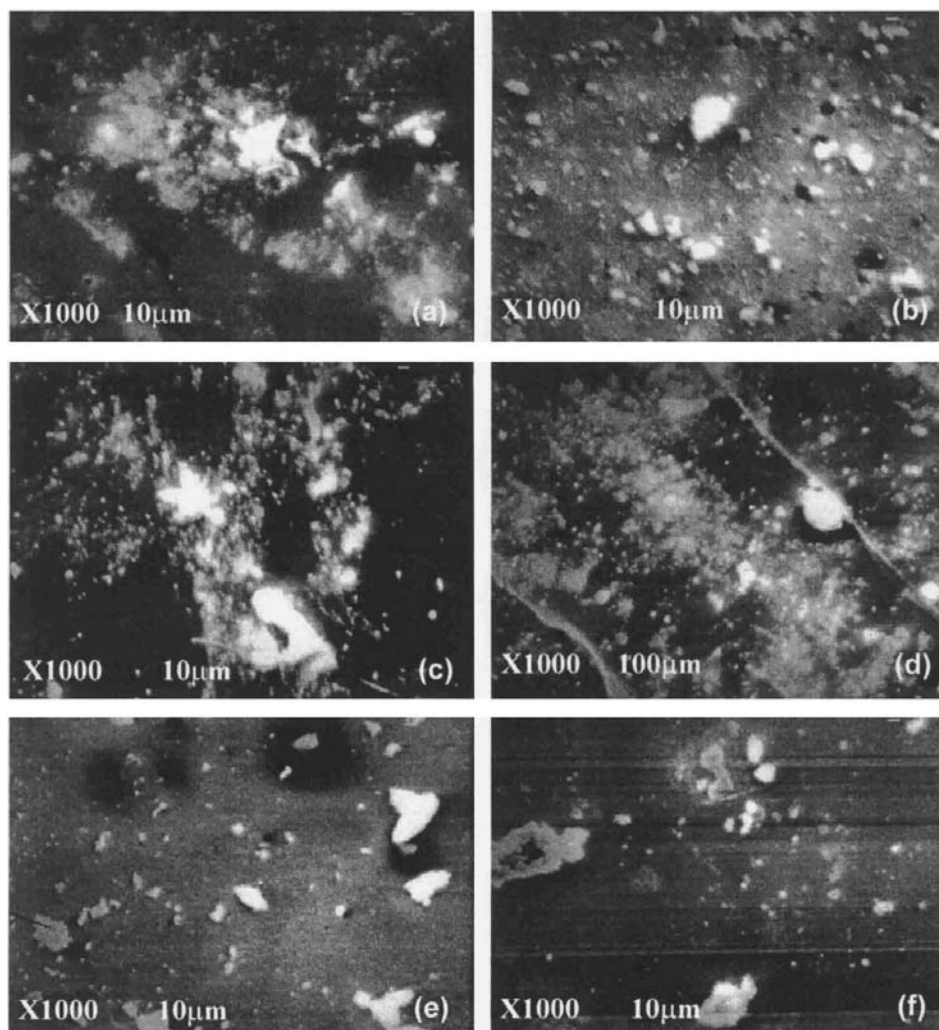


Fig. (5): SEM micrographs of silica gel doped with Nd^{3+} , a & b- dried at 60°C for 21 days (type I & II), c & d- heat treated at 500°C (type I & II) and e & f- heat treated at 700 & 950°C (type I), (X1000).

SEM of silica gel derived glasses doped with Nd^{3+} , dried at 60°C for 21 days, heat-treated at 500°C (type I&II) and heat-treated at 700 and 950°C (type I), are shown in Figs. (5 a, b, c, d, e & f), respectively. It is observe that,

by using TMOS (type I) material we obtain more dense gel that retains less organic material than (type II), while the samples of (type I) leads to gels with finer and dense structure, figures (5: a, b). The surface morphology of the dried samples at 60°C for 21 days is less dense than the samples heat-treated at 500°C for both types I and II. This might be due to the existence of solvent and water molecules imbedded in the silica gel derived glasses, figures (5: a, b, c & d). While a decrease in the cluster regardless the use of (type I or II) at 500°C appeared. The morphology changes from coarse scale to fine one by increasing the heat-treated temperature up to 950°C (type I), Figs. (5: a, c, e & d). These morphology might be due to condensation, strengthening and densification of the gel at higher temperature [7]. Where at higher temperature the water content as well as solvent molecules showed drastic decrease giving rise to a relatively fine and dense material.

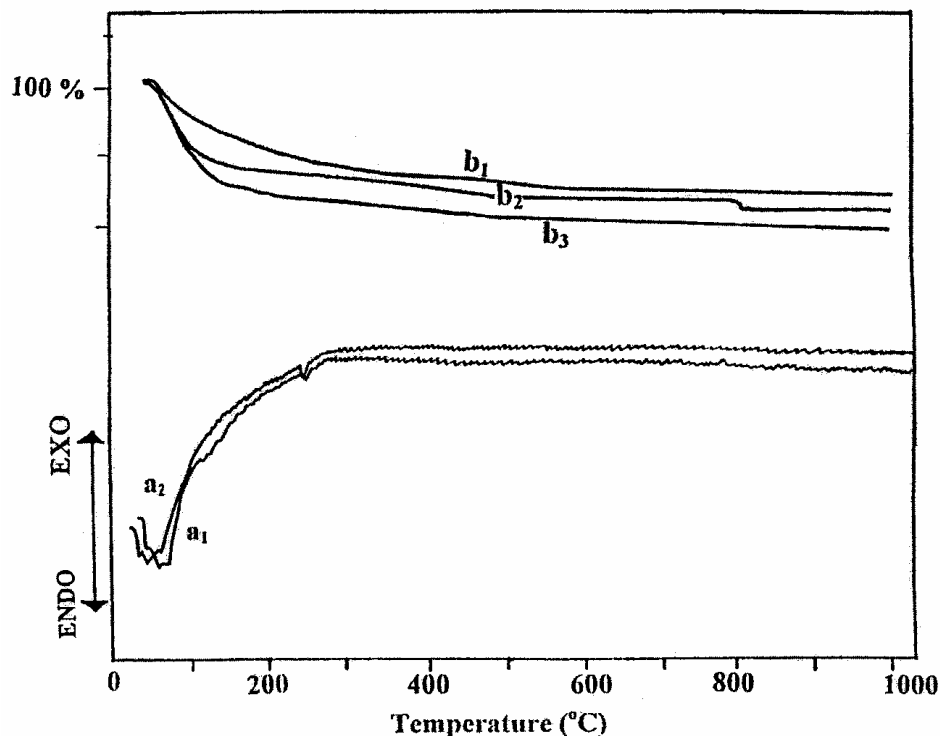


Fig. (6): TGA curves of (b_1 , b_2 & b_3) pure silica gel (type II) and silica gel doped with Nd^{3+} (type I & II) respectively, and DTA curves of (a_1 & a_2) pure silica gel and silica gel doped with Nd^{3+} (type II), all of them are dried at 60°C.

When the gels are heated, the alkoxy and hydroxyl groups are removed by condensation reactions that cause the large weight loss illustrated in Figs. (6 a_1 , a_2 , b_1 , b_2 & b_3) of the different thermal analysis (DTA) and the thermal gravitational analysis (TGA). Figs. (6 a_1 , a_2) shows the DTA traces of pure

silica gel and silica gel doped with Nd^{3+} (type II), both was dried at 60°C for 21 days. Two endothermic peaks system are observed, a big one around 700°C and a small one around 265°C . The first might be attributed to the desorption of residual traces of water as a result of hydrolysis and condensation, while the second one might be attributed to decomposition and evaporation of traces organic residues. This effect is as obvious in the FTIR spectra. DTA studies by previous workers [19] have confirmed that the 100°C endothermic results from the desorption of the physically adsorbed water. The combustion losses using TGA experiments confirms the previous hypothesis resulting from the DTA. The calculated total weight loss of pure silica gel (type II) and silica gel doped with Nd^{3+} (types I & II) shown in Figs. (6 b1, b2 & b3) was [(11.5), (19) & (21)] %, [(14.5), (25) & (28)]% and [(19), (26) & (29)]% in the temperature intervals ($25\text{--}150^\circ\text{C}$), ($150\text{--}600^\circ\text{C}$) and ($600\text{--}1000^\circ\text{C}$), respectively. The percentage weight loss attributed primarily to H_2O and OH in the temperature intervals ($25\text{--}150^\circ\text{C}$), whereas, it is attributed to the organic compound in the temperature interval ($150\text{--}600^\circ\text{C}$). We can conclude that, doping the samples with neodymium enhance the percentage weight loss, while using TMOS decreasing it. These results are computable with the FTIR results where the peaks at 1600 and 3400 cm^{-1} decreased by increasing the heat treatment up to 1050°C .

The prepared pure silica gel is colorless, while the silica gel containing Nd^{3+} has a violet color. Fig. (7) shows the transmission spectra of pure and doped silica gel prepared samples (type I & II) with constant thickness 3 mm. It is observed that, the pure prepared sample (a) at 60°C for 21 days (type I) has high transmission. No peak appeared in the Uv. Vis. While by doping the prepared samples at the same condition (b & c) (type I & II) with Nd^{3+} ion the transmission decreased, and many peaks appeared, their relative intensities have been related to the effect of neodymium ions in the silica gel glass. A notable feature of Nd^{3+} spectra is the asymmetry of the absorption lines, which may be attributed to systematic distortions of the octahedral sites of the Nd^{3+} ions [12]. It was observed from Figs. (7, b & d) that, by increasing the heat treatment temperature of doped sample (type I) from 60°C up to 950°C the scattering increased and the transmission decreased, this might be due to the condensation and densification produced by increasing the heat treatment temperature causing totally different structure in this case, which may give a much smaller pore size. This result is in agreement with XRD, SEM, DTA and TGA results obtained in the present work and with previous workers [24].

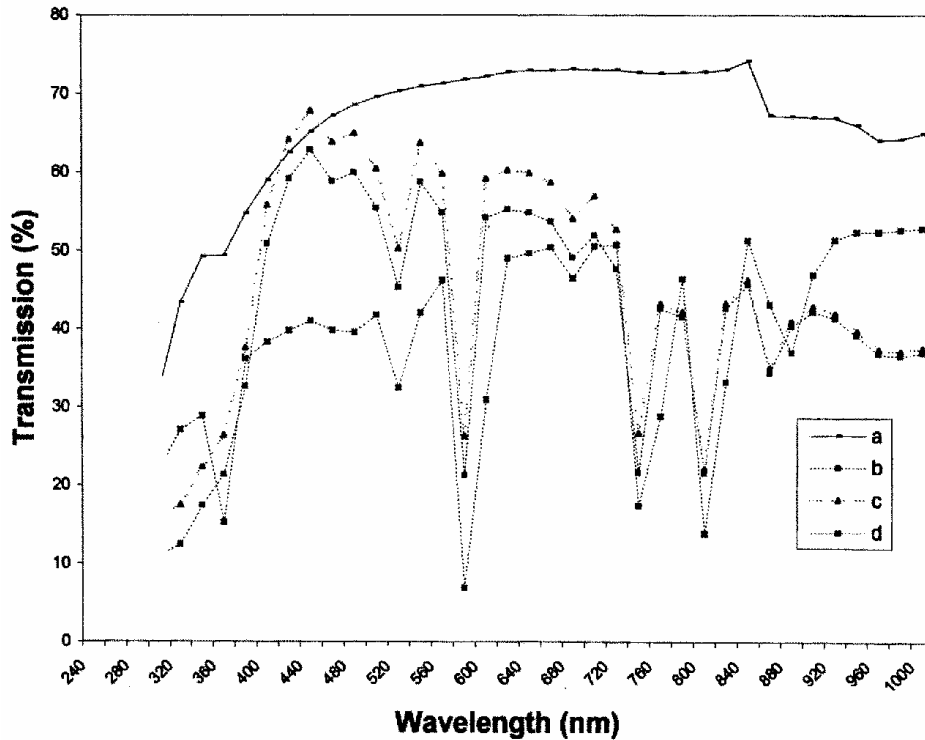


Fig. (7): The transmission spectra at 3 mm thick of: (a) pure silica gel dried at 60°C for 21 days, type I, b) & c) silica gel doped with Neodimim, dried at 60°C for 21 days, type I & II and d) doped sample type I, heat treated at 950°C.

Figure (8) shows the PL measurements of silica gel doped with Nd^{3+} heat-treated in air for two hours at 1400°C type (I). The inset in Fig. (8) shows the PL of pure silica gel heat-treated in air for two hours at 1400°C type (I). PL bands of maximum in the blue green spectral region at 535 and 546 nm and other band of weak intensity at 590 nm were appeared for pure and doped samples. It is expected that, these PL bands are of pure silica gel. They are originating from Si-O-Si assymmetric stretching appeared at 1070 cm^{-1} (Raman), which changed to the strong and broad peak at 1097 cm^{-1} (FTIR), and from defects such as impurities and E' centers [23]. While for the doped sample with Nd^{3+} bigger, sharper and intense bands at 875, 889 and 900 nm in addition were detected due to 4F3/2 to 4I9/2 transitions of Nd^{3+} ion.

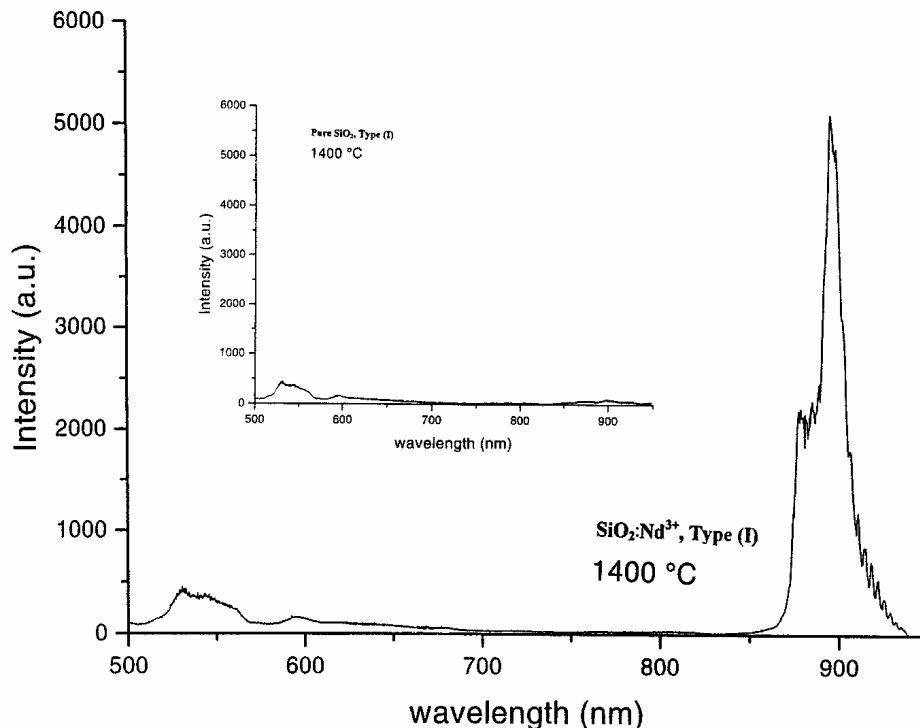


Fig. (8): Photoluminescence spectra of silica gel doped with Nd^{3+} heat-treated at 1400°C type II, the inset is for the photoluminescence of pure silica gel heat-treated at 1400°C .

Conclusions

A simple sol-gel method was successfully used for the preparation of both pure silica gel derived glasses and doped with Nd^{3+} ion, using two different type precursors. The prepared samples were subjected to heat-treatment temperature for 2 hours ranging from 200 up to 1500°C . The XRD studies showed that, by increasing the heat-treatment temperature the amorphous phase changed to α -cristobalite phase. It was found that, doping the sample with Nd^{3+} decreases the crystallite size. The crystallite size was found to be as small as 10.4 nm at 1400°C for pure sample type II. The SEM observations confirmed the advantages of the sol gel process for obtaining amorphous materials at lower temperature and that; dense and more homogeneous materials were obtained at higher temperature. DTA and the TGA studies indicated the effect of Nd^{3+} doping on the enhancement of the weight loss, confirmed by the FTIR results. The Raman and FTIR spectra elucidate the bonding system of the constituent atoms and groups such as Si, O and OH that throw light to the expected

structure intense. The optical studies revealed that, the present of Nd^{3+} ion in the net-work silica gel glasses decreased the transmission, and many peaks appeared, their relative intensities have been related to the effect of Nd^{3+} ion. PL bands for pure sample heat-treated at 1400°C (type I) appeared in the blue green spectral region at 535, 546 and 590 nm. While in doped sample heat-treated at 1400°C (type I), new PL bands at 900 nm and two other bands at 875 and 889 nm appeared due to $4\text{F}_{3/2}$ to $4\text{I}_{9/2}$ transitions of Nd^{3+} ion. The investigation showed that it is possible to incorporate neodymium cations into silica gel network in a condensation process by use of Nd_2O_3 .

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