



Structural and optical studies of nano-structure silica gel doped with different rare earth elements, prepared by two different sol - gel techniques

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Abstract

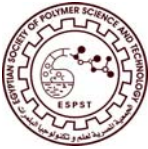
Structural and optical characteristics of pure silica gel (silica-xerogel, SiO₂) and silica gel doped with different concentrations ranging from 1 up to 6% of some rare earth (REEs) ions such as, praseodymium Pr⁺³, Europium Eu⁺³, Erbium Er⁺³ and Holmium Ho⁺³ ions, in the form of thin film and monolith materials were prepared by sol – gel technique, Using tetra-ethoxysilane as precursor materials, which are of particular interest for sol-gel integrated optics applications. Some structural and optical features of sol-gel derived monolith and thin films are analyzed and compared, namely the structure of nano-particle monolith and thin film silica-gel samples, based on X-ray diffraction (XRD). The types of structural information obtainable are compared in detail. We show that the XRD spectra of α -cristobalite are obtained for the two type materials and even by doping with the four REEs ions. Optical measurements of monolith and thin films were also studied and compared, the normal transmission and specular reflection were measured.

Introduction

Ultra fine microstructures having an average phase or grain size on the order of nanometer (10⁻⁹m) are classified as nano-structured materials (NSMs) [1, 2]. Currently, in a wider meaning of the term, any material that contains grains or clusters below 100 nm, can be considered to be nano-structured [3-5]. The interest in these materials has been stimulated by the fact that, owing to the small size of the building blocks (particle, grain, or phase) and the high surface-to-volume ratio, these materials are expected to demonstrate unique mechanical, optical, electronic, and magnetic properties [6].

The synthesis of inorganic materials using sol-gel techniques is an attractive field of research worldwide [7-17]. The sol-gel technique has been proven for several years

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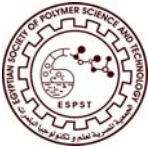
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now to be efficient for the processing of silica gel (SiO_2) as monolith and thin film materials, to be applied as a waveguide [18], chemical sensors[19] up-conversion [20, 21] and so on [22-27]. The primary attention was paid to the low temperature nature of the sol-gel process. This dictate that, one of the main advantages of the sol-gel Process is the low energy cost since silica gel can be obtained at quite low temperature [28-30]. The sol-gel researchers, however, soon became aware of the potential of the sol-gel method to provide new advanced functional materials based on the various microstructures [31-37]. Sol-gel derived monolith glasses may differ from conventional thin film glasses owing to the microstructures existing at the gel state, such that, even after gel densification, some differences may remain in their composition and molecular structure. The overlap between the drying stage and the aggregation/gelation and aging stages of sol-gel film formation establishes a brief time for further condensation reactions to occur. For this reason, the structures of films are often considerably more compact, generally denser and less cross-linked than those of the corresponding monolith gels or xerogels prepared from the same precursors, these factors enhance the densification rate of the film.

In the present work, a simple sol-gel procedure was successfully used for the preparation of silica gel as monolith and thin film forms prepared from the same precursor materials, using the tetra-ethoxysilane as alkoxide precursor. The effect of different heat treatment temperature ranging from 60 up to 1200°C on the structural and optical studies of pure samples is proposed, to obtain nano-crystallite materials. The effect of doping these two form of materials with four REEs ions on the structure and optical properties is discussed. XRD and optical analysis, were used to study the pure and doped properties of the prepared samples. Results of monolith materials and thin films were discussed and compared.

Experimental

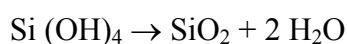
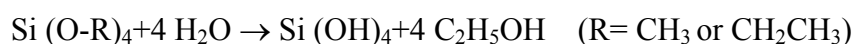
Pure silica gel and doped with different molar ratio of some rare earth as Erbium Er^{3+} , holmium Ho^{3+} , praseodymium Pr^{3+} and europium Eu^{3+} ions, used in this experiments was prepared in the form of monolith, using the acid catalyst procedure,



via the hydrolysis and condensation of tetra-ethoxysilane (CH₃CH₂OH)₄Si (TEOS), ethanol (CH₃CH₂OH) and distilled water (H₂O), in the presence of hydrochloric acid (HCl), with molar ratios; 0.028: 0.174: 0.28: 0.0823 for TEOS: CH₃CH₂OH: H₂O: HCl, respectively.

Er³⁺, Ho³⁺, Pr³⁺ and Eu³⁺ ions, were introduced in the initial stage of the process, by dissolving Er (NO₃)₃-H₂O, Ho (NO₃)₃-H₂O, Pr (NO₃)₃-H₂O and Eu (NO₃)₃-H₂O solutions in to the initial precursors with different molar ratios ranging from 1 up to 6 % of Er³⁺, Ho³⁺, Pr³⁺ and Eu³⁺ ions, respectively.

These solutions were then filtered, followed by stirring for one hour at room temperature. The resultant homogeneous solutions of monolith materials were filled in molds and aged in a drying oven type GFL 71.5, at about 60°C for about 21 days until no shrinkage appears. The final products were monolithic samples of cubic shape with dimension sizes 15x15x3 mm. Samples were clear, transparent and without cracks. Densification of gel was obtained, by annealing in air for two hours at temperature ranging from 100 up to 1200°C, in a muffle furnace with heating rate 1.5 °C/min. Preliminary crystallization was obtained by heating the samples at 1100°C for 2 hours. After the treatment at higher temperature beginning from 1050°C, the samples changed shape and looked externally like ceramics. After cutting, the inner part of the samples at (1200 °C) looked spongy. The overall process can be written as;



Silica substrates (optical treated on one side) were used as substrates for the deposition of pure silica gel and silica gel thin film doped with REEs, with different concentrations, using the same solution as for the preparation of monolith. This solution was dispersed on the silica glass substrate and then spun at 3500 rev./min for 30 seconds. At least 5 successive coatings were required to provide suitable effective film thickness. Then the thin film sample was annealed in air in a conventional oven at 1200°C for 2 hours.

Characterization

The X-ray diffraction (XRD) patterns of the prepared samples were recorded with Diano X-ray diffractometer using monochromatised CoK_{α1} radiation of



wavelength 1.79026\AA at 45 kV and 9 mA. The accurate crystallite sizes at the Full Width at Half Maximum FWHM were determined from the Scherrer's equation; ($G = \lambda / D \cos \theta$) where G is the grain size, λ is the wavelength of the X-rays (1.79026\AA), θ is the angle of incidence of X-ray beam and D is the corrected width (in radian) of the peak at half maximum which equal to $(D_s - D_q)^{1/2}$, where D_s is the FWHM of the investigated samples and D_q is the FWHM of the quartz sample, where, in order to obtain the values of the instrumental parameters, scan has been carried out for strain free quartz sample of crystallite size ranging between 5 and 10 micron with exactly the same conditions used for the investigated samples. To confirm the data obtained from Scherrer's equation, the micro-strain and crystallite size were calculated by win-fit programme for some prepared samples, using standard sample for calculation the instrument broadening. The crystallite sizes from Fourier analysis were obtained.

Nearly normal transmittance and reflectance spectra were done by Jasco V-570 spectrophotometer, in wavelength range (0.2 - 2.5 μm). The refractive index (n), absorption and extinction coefficients (α and K) for all investigated samples are calculated. The film thickness was calculated from the envelope of the transmittance spectra, which have maxima and minima extremes due to interference; also it was measured by using the tally-step instrument with an experimental error $\pm 3.5\%$, in the National Institute of Standard.

The recorded charts for transmittance measurements at normal incidence, while reflectance measurements were performed at incident angle of 8° .

Results and discussion

Figure (1.a,b) shows XRD patterns of monolith silica gel samples dried at 60°C for 3 weeks and sintering for 2 hours at heat treatment temperature ranging from 800 up to 1200°C Fig. (1.a). No peaks are observed in samples fired below 1100°C except the hump at 2θ between 12 and 24° attributed to amorphous silica gel. However, small and broad peaks at $2\theta = 25$ appeared after firing the samples at 1100°C for 2 hours, which may be ascribed to preliminary crystallization of samples and can be indexed as (110) diffraction principal line of tetragonal α -cristobalite, its intensity increases from 1100 to 1200°C . Also at higher temperature new peaks appeared at $2\theta = 32$ and 38.6 . indexed as (102) and (201) diffraction line of tetragonal α -cristobalite, respectively. These

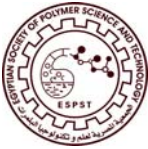


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results are an indication of the beginning of crystallization at 1100°C and that the increase in temperature enhances the crystallization. This is in agreement with Bouajaj et. Al., [38] who suggested that at 1050°C is the beginning of crystallization, where at 1100°C the crystallization occurs. While Fig. (1.b) shows XRD patterns of pure thin film silica gel sintering at 1200°C heat treatment temperature. It is evident that, at 1200°C the principle peak of α -cristobalite at $2\theta = 25^\circ$ indexed as (110) becomes dominant relative to the other peaks, and it's intensity decreases at 1200°C rather than in monolith samples. These results indicate that preparing silica gel in thin film form has the same crystalline phase as preparing the monolith form samples.

The magnitude of line broadening defined as the full-width at half-maximum (FWHM) intensity of the debye-Sherer line was obtained. The crystallite size was calculated from Sherer relation-ship to give the following values, 17.6, and 20 nm for bulk monolith samples heat-treated at 1100 and 1200°C respectively. It was found that, the crystallite size increases by increasing the heating temperature of the monolith samples. Comparison between crystallite size of monolith and thin film samples at 1200°C revealed that, the crystallite size of thin film sample is smaller, where the broadening of the peaks is higher than in the case of monolith, indicating a decrease in the crystallite sizes of thin film sample. These results might be due to the very different microstructures developed into a monolithic bulk and thin film silica gel samples. In fact, the heating rate depends on the density and pore size, where by increasing the temperature the pore size decreases and a uniform surface appeared. In the formation of the monolithic gel, the clusters grow until they fill the available volume: the impinging clusters then link together in a percolation process. The resulting three-dimensional network shrinks considerably, but it eventually becomes stiff enough to withstand the capillary forces, so that shrinkage stops and a porous solid is obtained. To make a film, it is necessary to start with a sol having low viscosity. As the film is deposited, the clusters are brought together by the rapid evaporation of the solvent, so there is little time for formation of cross-link.

By confirming these data using the Win-fit programme in the calculation of the crystallite size of the pure silica gel in the form of monolith, sintering at the heat treatment temperature 1200°C it was found to be 20.9 nm as detected from Fourier analysis Fig (2).

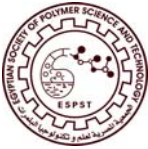


From the preceding results it can be concluded that the evaporation process during the gelation and sintering heat treatment temperature play an important role in the crystallization of the nano-particles γ -cristoballite. Then, by increasing the heat treatment temperature, the intensity of the peaks increases. The crystallite sizes of thin film and monolith samples at sintering temperature 1200°C revealed a decrease for the prepared sample in the thin film form.

Figs. (3 – 6.) show the XRD patterns of monolith silica gel doped with different concentrations of REEs, Eu^{3+} , Pr^{3+} , Ho^{3+} and Er^{3+} , ions ranging from 0.5 up to 6 %, for monolith samples. While Fig (7. a - d) shows the thin film silica gel samples doped with constant concentration 2 % of each REEs (as a representative curve for thin film) sintering at the heat treatment temperature 1200°C. Single-phase tetragonal α -cristoballite as in the pure samples were produced by doping the prepared samples in both forms.

By doping the monolith prepared samples with the different concentrations of the trivalent REEs. Generally, a lower concentrations of REEs imbedded in silica gel will result in better crystallinity than the higher doped concentration samples, while the XRD intensity is higher at lower REEs concentration for both kind of prepared samples, (figures of increasing the concentrations of the REEs embedded in the thin films are not shown here because their large number and their trend are the same as of the monolith samples). The relative decreases in these sample intensities with increasing the concentrations of dopant ions as detected from XRD pattern may be due to the increase of the dopant weight percent into the host silica gel, creating recrystallization in the host compound.

The crystallite sizes of the trivalent REEs dispersed in silica gel with constant concentration 2 %, at the constant optimum sintering temperature 1200°C were found to be lower than pure samples and in the range of nano-crystal size, where their full-width at half-maximum (FWHM) increases indicating the decrease of the crystallite sizes by doping with the trivalent REEs. The crystallite sizes of the four trivalent REEs are shown in Table (4.2.). By confirming these data by using the Win-fit programme the crystallite size were found to be 18.6, 17.4, 15 and 14 nm for 2 % of the four trivalent REEs Pr^{3+} , Eu^{3+} , Ho^{3+} and Er^{3+} , respectively embedded in the silica gel in the form of



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monolith, all sintering at the heat treatment temperature 1200°C. By decreasing the trivalent REES concentrations the crystallite size decreases as detected from Table (1).

These values reveal large crystallite size and lower microstrain by increasing the REEs concentrations. But there is a noticeable difference between the four investigated systems. The largest crystallite size belongs to Pr³⁺ -system, followed by Eu³⁺ -system and the smallest one belongs to Ho³⁺ and Er³⁺ – system. On other hand, there are noticeable variations among each system, may be attributed to the difference in the ionic radius of each REEs (the ionic radius of Eu³⁺, Pr³⁺, Ho³⁺, Er³⁺ cations, which are (1.12, 1.09, 0.97 and 0.96, respectively). The general behavior observed from the values of the crystallite size is its decrease trend with increasing the dopant concentration. But the rate of the crystallite growth differs from one system to another.

It is obvious, that the increase of the crystallite size is always accompanied by a decrease in the microstraine by increasing the REEs concentrations. This result was reported previously [39].

One can conclude that no change in the characteristic peaks positions was observed in samples by increasing both the concentrations of doped with the four REEs, Pr³⁺, Eu³⁺, Ho³⁺ and Er³⁺ ions and the sintering heat treatment temperature. This means that the doped silica gel samples retain the tetragonal α -cristobalite structure. It was observed that there is a change in the height and broadening of the appeared peaks. No characteristic peaks corresponding to each incorporated element or its oxides are detected in the XRD patterns. The degree of crystallinity for silica gel samples doped with different elements decreases gradually by increasing the concentration of the dopants as showing in Figs (3 - 6), respectively. The observed induced change in the peaks height as well as the broadening could be attributed to the change in the scattering factor corresponding to each incorporated element or the decrease in the crystallite size or both. In addition, for thin film samples could be interpreted by the adsorption of the incorporated atom on the surface of the growing silica gel microcrystal.

The normal transmission, specular reflection, the absorption coefficient and the refractive index are helpful to forecast the behavior of the material with the electromagnetic radiation such as light. Therefore their behavior for the investigated samples were studied in the wavelength range between 200 and 2500 nm. Pure silica



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gel glasses thin film and monolith forms are colorless and transparent, while the samples obtained by doping with the four REEs ions are still transparent but the color changed, while the silica gel containing Pr^{3+} , Eu^{3+} , Ho^{3+} and Er^{3+} , has a green and off white colour for the first two rare earth and faint rose color for both Ho^{3+} and Er^{3+} . The coloration was dependent on both the concentrations of the dopant and the sintering temperature, where a less intense color and higher transparency at lower concentrations of dopant material and at lower sintering temperature characterize the prepared samples. But at higher sintering temperature $\geq 700^\circ\text{C}$ the monolith samples became opaque and the transmission measurement failed.

The normal transmission and specular spectra of the investigated pure thin film shown in Fig (8), at different sintering heat treatment temperature ranging from 500 up to 1200°C . It is observed that, by increasing the heat treatment temperature of the prepared thin film sample from 500 up to 1200°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, results obtained in the present work. The salient features of the transmission curves for the investigated samples, are the fluctuations on the spectra due to interference fringes for the two samples sintering at 1100 and 1200°C , which may be attributed to the film crystallinity as revealed from the XRD. While these interference fringes are not present in sample sintering at 500°C .

The normal transmission spectra of monolith pure silica gel samples sintering at different heat treatment temperature ranging from 60 up to 500°C , is shown in Fig (9). The curves show the well known absorption bands due silanol groups (Si-OH) and molecular water [40 - 42]. With the stabilization temperature increasing, two phenomena occur in both form of prepared samples: (1) the absorption bands decrease in intensity corresponding to the release of water by the sample, and (2) the transmission cut off shifts to lower wavelengths. For the sample sintered at 1200°C the spectrum presents only the major absorption bands of Si – OH. These results are previously reported [43]

It is obvious that the transmission decreases in monolith sample than thin films Fig (8.) and Fig (9.). This may be rendered to the increase or the big difference between the thickness of thin film (280 nm) and the monolith sample (3 mm) at 60°C .



Also these results might be due to the very different microstructures developed into a monolithic bulk and thin film silica gel samples appeared in the XRD.

The effect of the four REEs ions embedded in the host thin film silica gel on the on the normal transmission spectra of the investigated samples prepared at the sintering heat treatment temperature 1200°C for pure silica gel and doped samples at 2 % of each REEs are shown in fig (10). By doping the prepared samples with the four REEs ions, the transmission decreased may be due to the coloration in them.

Conclusion

A simple sol-gel method was successfully used for the preparation of both pure silica gel derived glasses and doped with four REEs ions namely; praseodymium Pr^{+3} , Europium Eu^{+3} , Erbium Er^{+3} and Holmium Ho^{+3} , using two different techniques monolith and spin coating thin film. The prepared samples were subjected to different sintering heat-treatment temperature for 2 hours ranging from 800 up to 1200°C. The XRD studies showed that, by increasing the heat-treatment temperature the amorphous phase changed to α -cristobalite phase at 1100°C. The evaporation process during the gelation and sintering heat treatment temperature play an important role in the crystallization of the nano-particles γ -cristobalite. By increasing the heat treatment temperature, the intensity of the peaks increases in both form of samples. It was found that the optimum temperature, which give better crystallinity and higher XRD intensities is at 1200°C. The comparison between the crystallite sizes of thin film and monolith samples at 1200°C sintering temperature revealed a decrease for the thin film sample. One can conclude that no change in the characteristic peaks positions was observed in samples by increasing both the concentrations of doped with the four REEs, Pr^{3+} , Eu^{3+} , Ho^{3+} and Er^{3+} ions and the sintering heat treatment temperature. This means that the doped silica gel samples retain the tetragonal α -cristobalite structure. It was observed that there is a change in the height and broadening of the appeared peaks. No characteristic peaks corresponding to each incorporated element or its oxides are detected in the XRD patterns. The XRD intensities for silica gel samples doped with different elements decreases gradually by increasing the concentration of the dopants. The observed induced change in the peaks height as well as the broadening could be



attributed to the change in the scattering factor corresponding to each incorporated element or the decrease in the crystallite size or both.

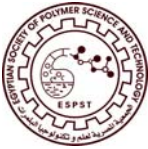
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Figure caption

Fig (1 a & b) XRD patterns of (a) pure silica gel in the form of monolith, dried at 60°C for three weeks & sintering at different heat treatment temperature ranging between 500 up to 1200°C for 2 hours and (b) pure thin film samples sintering at 1200°C.

Fig (2) The deconvolution curve for the calculation of the crystallite size from the fourrier transform using Win-fit programme for pure monolith heat treated at 1200°C.

Fig. (3) XRD patterns of monolith silica gel doped with different concentrations of Pr³⁺ ions (a) pure, (b) 0.5 %, (c) 1 %, (d) 2 %, (e) 3 % and (f) 6 %. All sintering at 1200 °C.

Fig. (4) XRD patterns of monolith silica gel doped with different concentrations of Eu³⁺ ions (a) pure, (b) 0.5 %, (c) 1 %, (d) 2 %, (e) 3 % and (f) 6 %. All sintering at 1200 °C.

Fig. (5) XRD patterns of monolith silica gel doped with different concentrations of Ho³⁺ ions (a) pure, (b) 0.5 %, (c) 1 %, (d) 2 %, (e) 3 % and (f) 6 %. All sintering at 1200 °C.

Fig. (6) XRD patterns of monolith silica gel doped with different concentrations of Er³⁺ ions (a) pure, (b) 0.5 %, (c) 1 %, (d) 2 %, (e) 3 % and (f) 6 %, all sintering at 1200 °C.

Fig. (7) XRD patterns of pure thin film and thin film silica gel doped with 2% of four REEs ions sintering at heat treatment temperature, 1200 °C.

Fig (8) The transmission and reflection spectra of silca gel in thin film form sintering at different heat treatment temperature, (a) 500 °C, (b) 1100 °C, and (c) 1200°C.

Fig (9) The transmission spectra of silca gel in monolith form sintering at different heat treatment temperature, (a) 500 °C, (b) 200 °C, and (e) 60°C.

Fig (10) The transmission spectra of silca gel in thin film form (a) pure, and doped with 2 % of (b) Pr³⁺ (c) Eu³⁺ (d) Ho³⁺ and (e) Er³⁺ ions, all sintering at 1200 °C.



**Table (1)
Crystallite sizes of monolith silica gel doped with the
four REEs**

REEs Concentration (%)	Monolith Crys. Size (nm)			
	Pr³⁺	Eu³⁺	Ho³⁺	Eu³⁺
0.5 %	19 nm	18 nm	16 nm	15 nm
2 %	18.6 nm	17.4 nm	15 nm	14 nm
6 %	16 nm	14 nm	12 nm	11 nm



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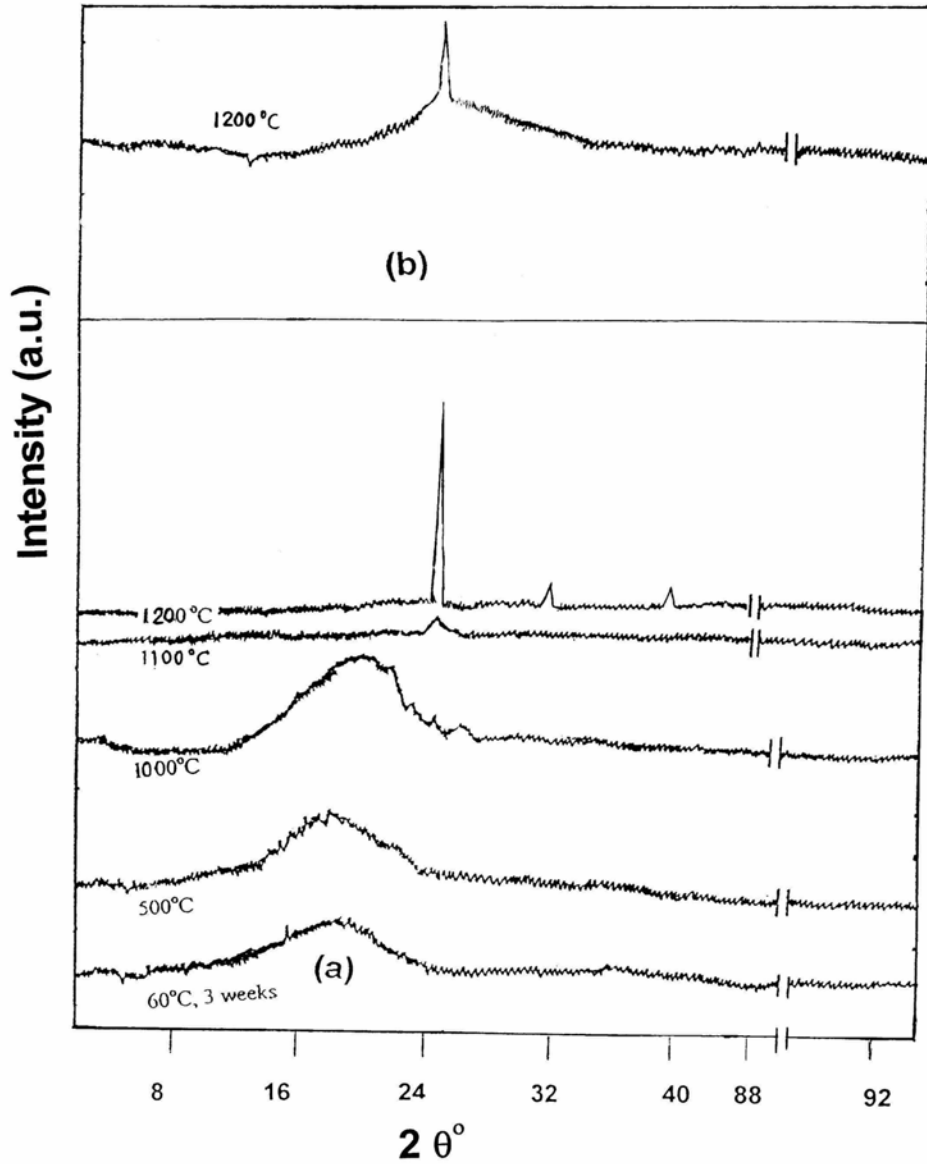


Fig (1 a & b) XRD patterns of (a) pure silica gel in the form of monolith, dried at 60°C for three weeks & sintering at different heat treatment temperature ranging between 500 & 1200°C for 2 hours and (b) pure thin film samples sintering at 1200°C for 2 hours.

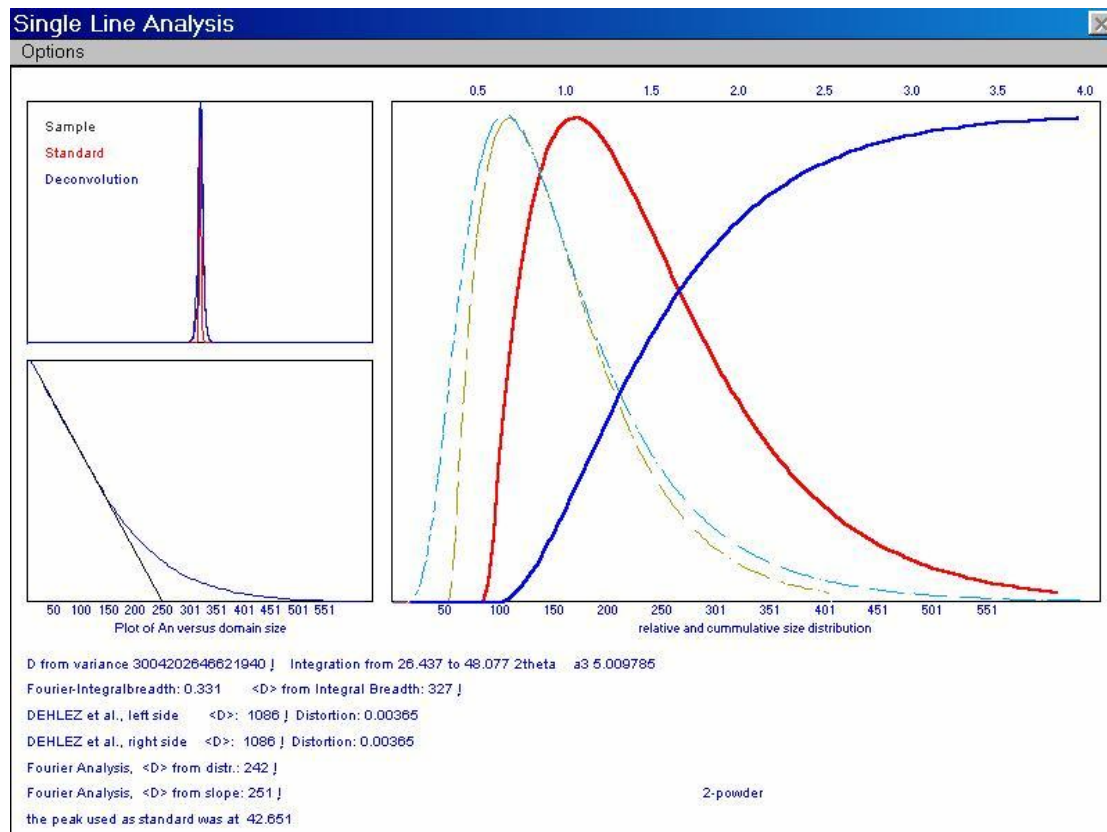
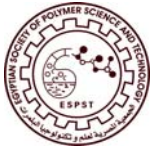
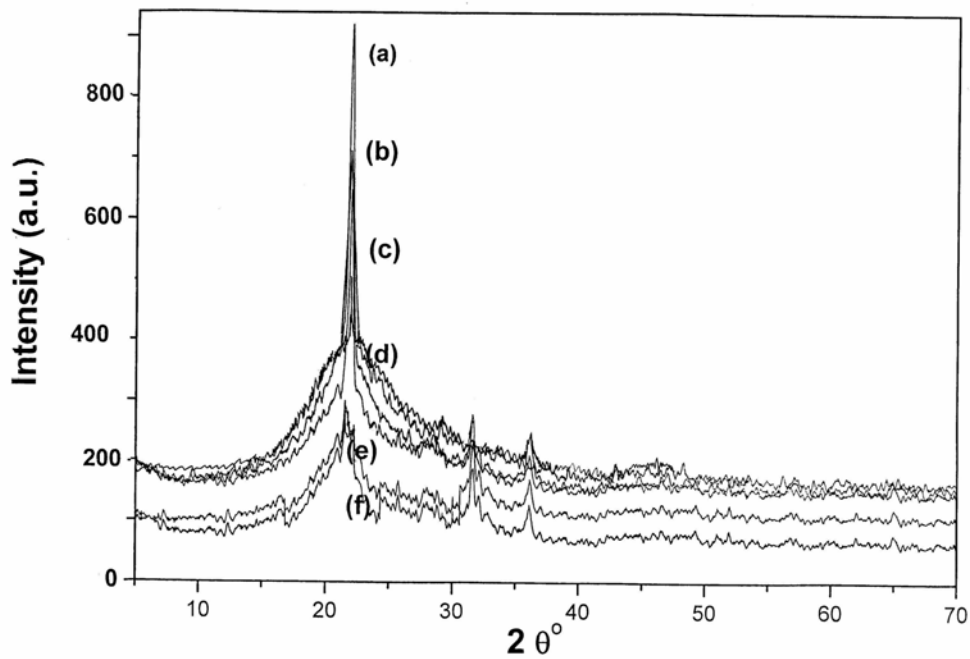
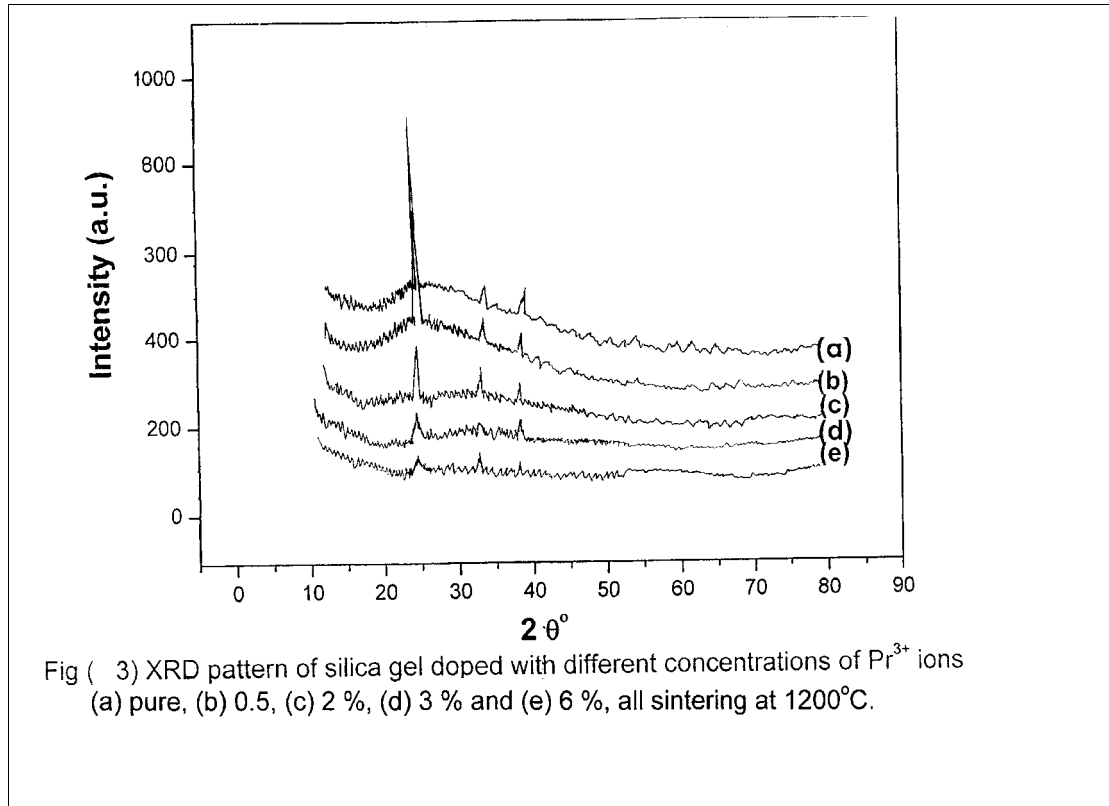


Fig (2) The deconvolution curve of the calculation of the crystallite size from the Fourier transform using Win-fit programme for pure silica gel heat treated at the optimum sintering heat treatment temperature 1200°C (as a representative curve) .



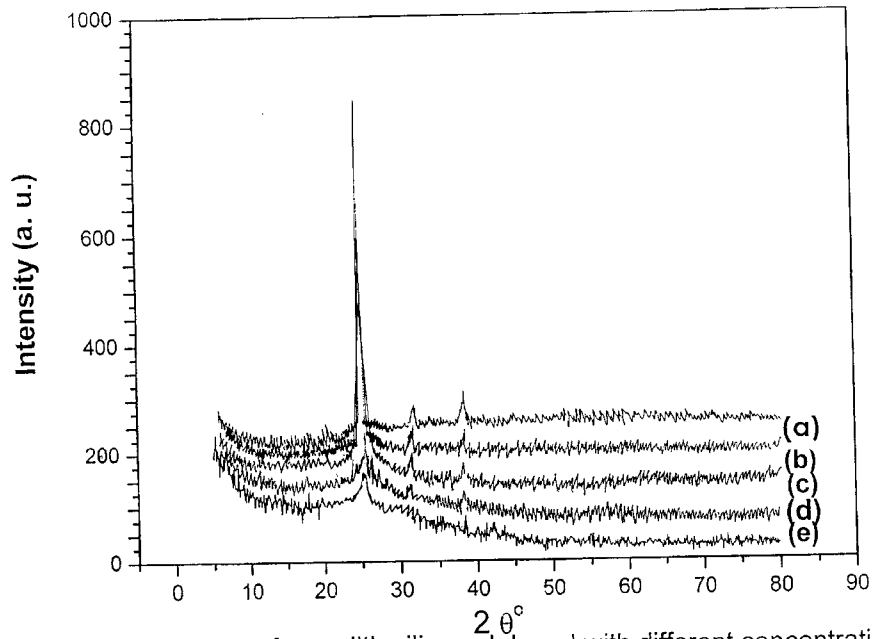


Fig (5.) XRD patterns of monolith silica gel doped with different concentrations of Ho^{3+} ions (a) pure, (b) 0.5 %, (c) 2 %, (d) 3 % and (e) 6 %, all sintering at 1200°C .

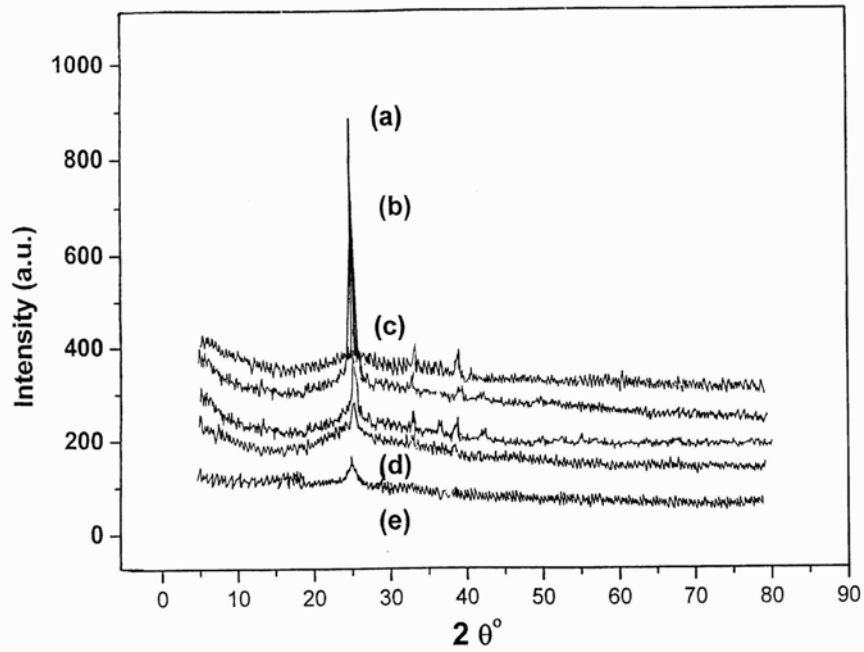


Fig (6) XRD pattern of pure silica gel doped with different concentrations of Er^{3+} ions (a) pure, (b) 0.5, (c) 2 %, (d) 3 % and (e) 6 %, all sintering at 1200°C.

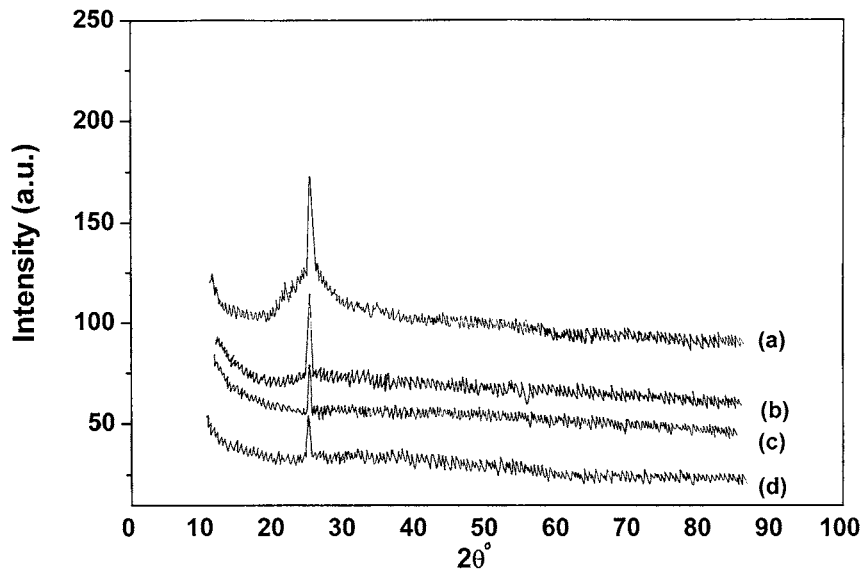


Fig (7.) XRD patterns of thin film silica gel doped with constant concentration 2 % of the four REEs elements (a) Pr^{3+} , (b) Eu^{3+} , (c) Ho^{3+} and (d) Er^{3+} all sintering at 1200°C heat treatment temperature.

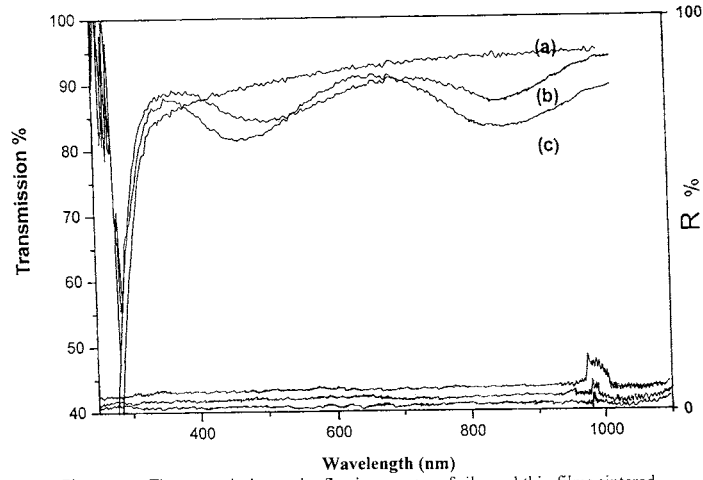


Fig (8) The transmission and reflection spectra of silica gel thin films sintered at different heat treatment temperature (a) 500, (b) 1100 and (c) 1200°C.

Fig (9)

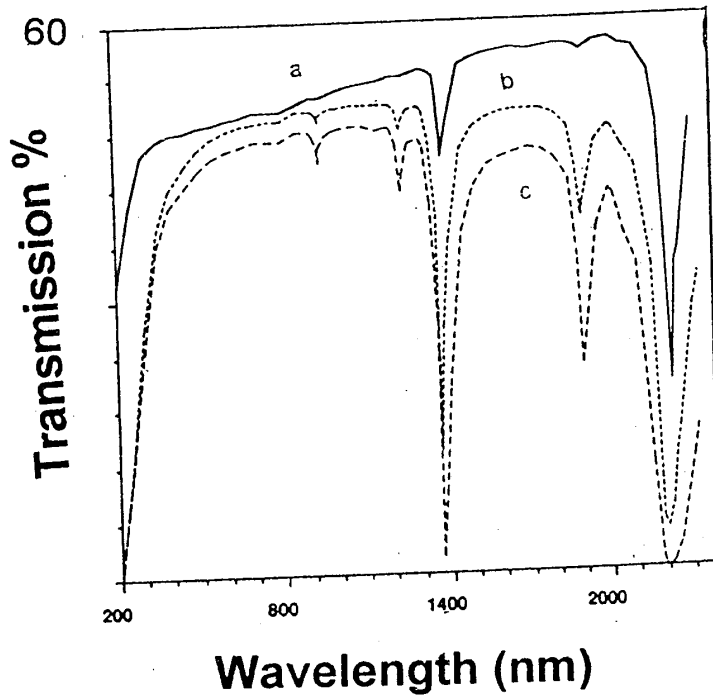


Fig () The transmission spectra of silica gel in monolith form sintering at different heat treatment temperature, (a) 500 °C, (b) 200 °C, and (e) 60°C.

Fig (10)

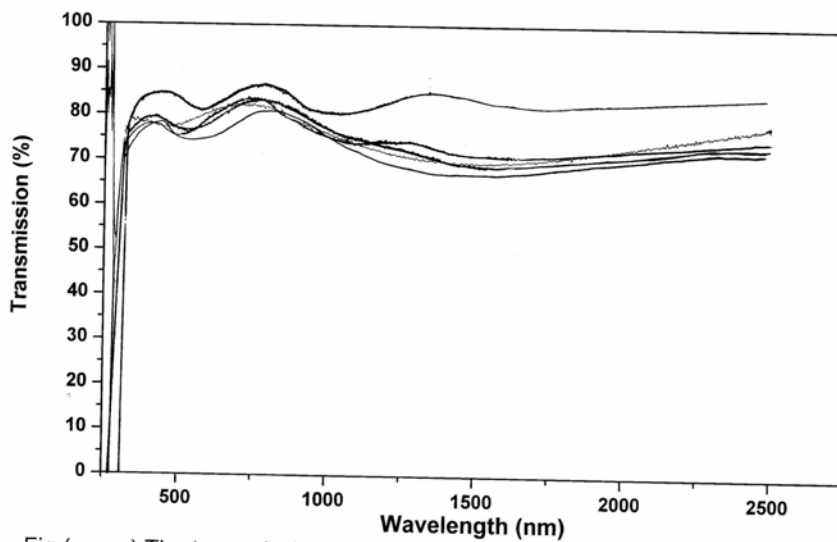


Fig (11) The transmission spectra of silca gel in thin film form (a) pure, and doped with 2 % of (b) Pr^{3+} , (c) Eu^{3+} , (d) Ho^{3+} and e) Er^{3+} , all sintering at 1200°C



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