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Study the spectroscopy of samarium encapsulated in silica Xerogel matrices

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Abstract

The sol-gel preparation technique of transparent silica monoliths containing up to 0.5 M of samarium have been described. The sol-gel processing parameters are: acid catalyzed hydrolysis and controlled drying. The prepared monoliths are analyzed by X-ray diffraction, pycnometer measurements, Fourier transformation infrared spectroscopy and optical spectroscopy. The oscillator strengths of the Sm^{3+} ions in the silica monoliths are calculated. The results show a linear concentration dependence of some Sm^{3+} transitions in UV/Vis absorption spectra and formation of Sm^{3+} clusters inside the pores structure of silica monoliths at high Sm^{3+} concentration.

Key words
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دراسة مطيافية السماريوم المغلف بمصفوفات السيليكا Xerogel

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الخلاصة

تم وصف تقانة ال Sol-Gel لتحضير كتل حجمية من السيليكا الشفافة المطعمة بتراكيز مختلفة لغاية 0.5 تركيز مولاري من ايونات السماريوم. ان المتغيرات الخاصة بعملية ال Sol-Gel كانت: العامل المساعد الحامضي لعملية الهدرجة والسيطرة على عملية التجفيف. تم تحليل نماذج الكتل الحجمية المحضرة باستخدام حيود الاشعة السينية، قياسات الكثافة، مطيافية الاشعة تحت الحمراء و المطيافية البصرية. تم حساب شدة التذبذب لانتقالات ايونات السماريوم في نماذج السيليكا الحجمية. لقد أظهرت النتائج وجود اعتماد خطي لقمة حزم بعض انتقالات ايون السماريوم مع التركيز ضمن المدى الطيفي الفوق بنفسجي/ مرئي، كذلك أظهرت النتائج تشكل مجاميع من ايونات السماريوم داخل المسامات التركيبية لنماذج السيليكا الحجمية عند التراكيز العالية للسماريوم.

Introduction

The sol-gel process is a convenient and versatile method of preparing transparent optical materials at low temperature [1]. Sol –gel derived inorganic network materials doped with Lanthanide compounds have demonstrated interesting optical prosperities like luminescence, coloration and energy transfer [2,3].

Several methods have been developed to fabricate Lanthanide (rare earth) ions - doped silica, including plasma- enhanced chemical – vapor- deposition, ion implantation, flame hydrolysis, and ion exchange [4]. An alternative technique to prepare rare earth doped silica films or monoliths are by using a wet chemical process. The preparation of transparent monoliths, containing Sm^{3+} - coumarin complexes $[Sm (K4)_2 (H_2O)_4]\times(NO_3)_3$ or $[Sm(K2)_2(H_2O)_2]\times(NO_3)_3$ was demonstrated. Here, K4 and K2 are different coumarine molecules, K2 is 3-(3-4-(dimethyl-amino) phenyl)-2H-chromen-2-one and K4 is ethyl 2-(7-

hydroxy-2-oxo-2H-chromen -4-yl) acetate. It was shown that sm^{3+}-doped ceramic powder or sol-gel glass is promising material for luminescent light filters [5].

In this paper, we investigated the spectroscopic prosperities of the highly doping levels of Sm^{3+} ions in silicate sol-gel materials in order to obtain more information about the nature of rare–earth optical centers in such materials.

Experimental:

Chemicals

The chemical materials used in the synthesis of silica Xerogel samples doped with samarium ions were: tetraethoxysilane (TEOS, purity > 98%), spectroscopic grade ethyl alcohol (C_2H_5OH), N,N dimethaylformamide (C_3H_7NO), analytical grade samarium chloride ($SmCl_3.6H_2O$), deionized water catalyzed by hydrochloric acid (HCl, 0.15 M).

Sample preparation

The preparation of the monoliths was based on the sol-gel scheme described in figure (1). TEOS and absolute EtOH were mixed together in a molar ratio of 1: 2. For the Sm^{3+}-doped monoliths, a 1 ml of 0.5 mol/l solution of samarium chloride with pH 3 was added to the mixture of TEOS and absolute EtOH, before the hydrolysis. After homogenization of the mixture, deionized H_2O (pH 1) and absolute EtOH mixture in a molar ratio of 2:1 was added for the hydrolysis. The final solution was left for 30 minutes under magnetic stirring, after this stage 0.5 ml of C_3H_7NO, as drying control chemical additive, was added. pH value of the final solution was 2, and this solution was left 2 hour at room temperature. The gelation of monoliths was achieved by pouring the sol into covered glass tube at room temperature. After aging for 24 hour, the covers were removed in order to permit solvent evaporation through the drying process. This process was achieved at 60 °C for two days.

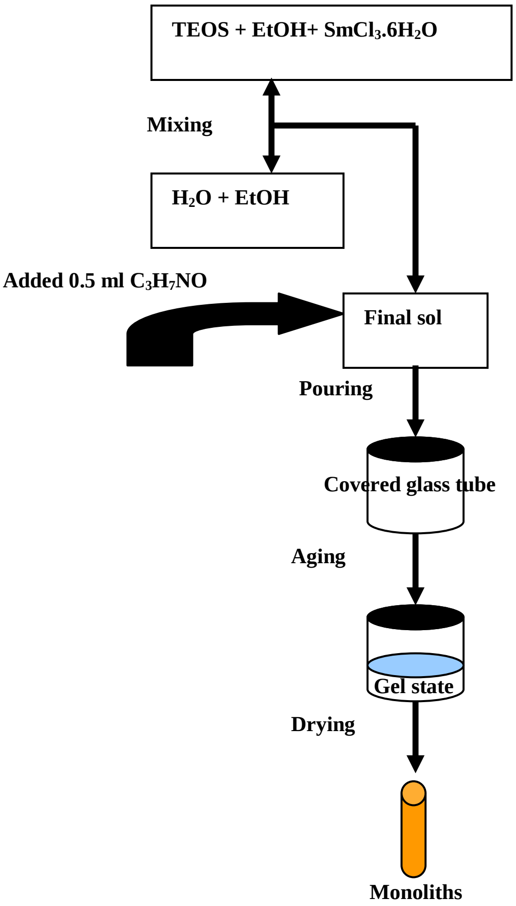

Fig. 1: Sol-gel preparation scheme for samarium doped monoliths.

The described procedure allowed to prepare transparent monoliths with diameter of 0.37 – 0.40 cm, length of 1.20-1.42 cm and weight of 0.2203-0.3942 gm.The density of the obtained monoliths were measured depending on gas displacement method, using pycnometer device. The results show that the density of prepared monoliths is 1.4 ± 0.1 g/cm^3. Transparent non-doped monoliths, as well as monoliths containing 0.01, 0.05, 0.1 and 0.5 molar concentration of Sm^{3+} were prepared. Photographs of some monoliths were presented in figure (2). At high concentrations of Sm, the color of the samples turned slightly yellow due to the 4f-4f Sm^{3+} transitions.

Fig. 2: Photographs of transparent monoliths with different Sm content, (a) non-doped, (b) 0.01M (c) 0.05M , (d) 0.1M and (e) 0.5 M

Results and discussion

Crystalline phases were not observed in the samarium doped samples in agreement with the X-ray diffraction measurements as shown in figure (3). The broad peaks presented in figure (3 b, c), of Sm doped monoliths at about $2\theta = 43.5°$, show that the activator ions (Sm^{3+}) can be randomly distributed in the SiO_2 network. This broad peak was disappeared for the sample of 0.5 M Sm^{3+} (maximum level of Sm concentration in the present work), which give an indication about the clustering of these ions in the pores structures of sol-gel materials. The question about the state of rare-earth clusters in silica networks is still open and requires additional investigations.

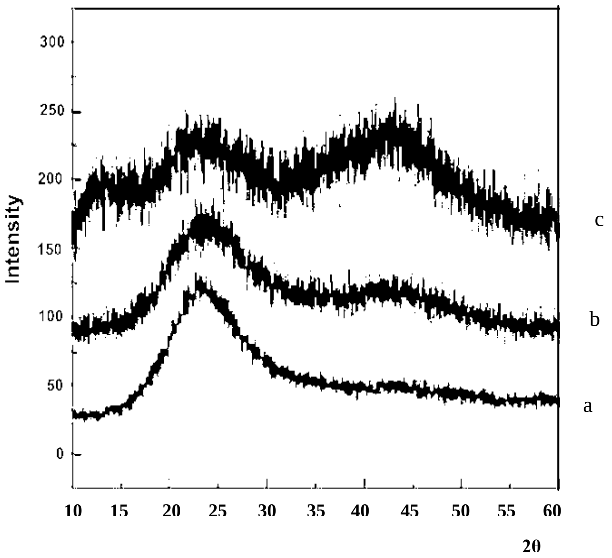

Fig. 3: X-ray diffraction patterns of some monoliths ;(a) non-doped monolith, (b) 0.01M Sm doped monolith and (c) 0.1M Sm doped monolith.

The FTIR spectrum of one monolith was illustrated in figure (4). The characteristics vibrational bands of silica were found in the FTIR spectra., where; the absorption bands at about 470 cm^{-1}, 800 cm^{-1} and 1100 cm^{-1} which were due to bending, symmetric stretching and asymmetric stretching vibrations of Si-O-Si groups respectively, while the weak band at about 960 cm^{-1} was due to stretching vibration of Si-OH groups[6,7]. Another two bands were appeared at about 1600 $cm^{-1}$and 3400 cm^{-1}. These two bands were the characteristics vibration of O-H bond in water molecules[8], and indicating that the drying process at 60 ºC dose not completely trap the water molecules from the pores of silica Xerogel network. Therefore, the monoliths produced from TEOS and samarium chloride solution needs heating at temperatures higher than 500 ºC to obtain sol-gel silica glass. Because of silica sol-gel glasses obey Zickeriazen`s rules [9], which explained the structure of oxide glasses, the doped Sm ions, depending on its size and its high activation energy, can not substitute the silicon atoms and thus can not form any ligands in the silica network. FTIR measurements in the present work proved this suggestion.

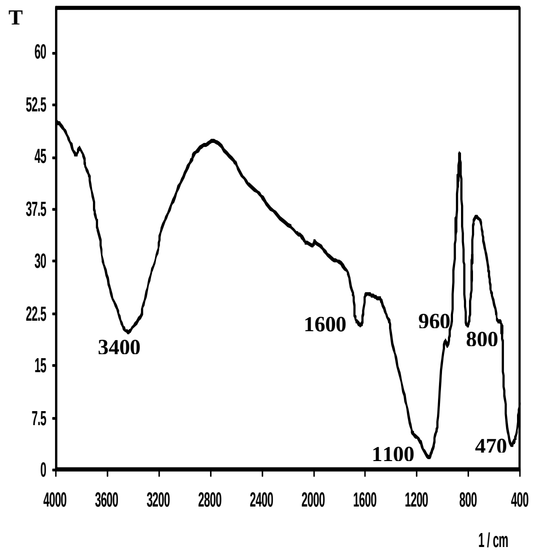

Fig.4: FTIR spectrum of a monolith containing 0.5 M Sm^{3+}.

UV/Vis absorption spectra, at room temperature, of Sm^{3+} doped monoliths are presented in figure (5). The spectrum of pure SiO_2- monolith is given for comparison. It can be seen that the broad peak at 280 nm due to charge transfer transition $O^{2-}\rightarrow Sm^{3+}$ in samarium doped monoliths [10,11]. The absorption band of the 280 nm transition depends on the concentration of the Sm^{3+} ions incorporated in the monoliths.

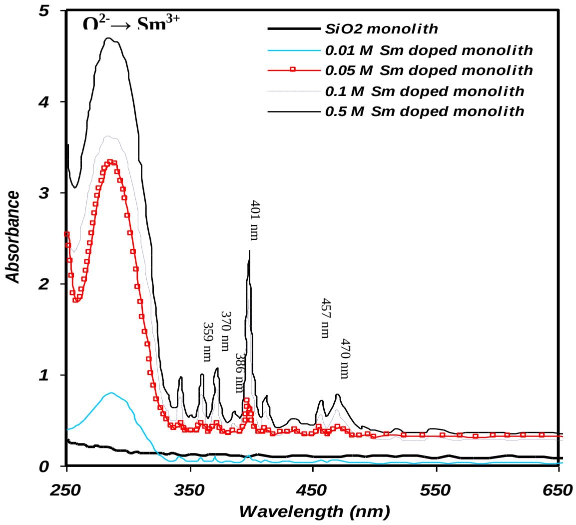

Fig. 5: Absorption spectra of Sm^{3+} non-doped and doped monoliths at different concentrations.

The absorption bands, due to Sm^{3+} transitions of ${}^6H_{5/2}\rightarrow {}^4D_{7/2}$ ~ 343 nm, ${}^6H_{5/2}\rightarrow {}^4K_{15/2}$ ~ 359 nm, ${}^6H_{5/2}\rightarrow {}^6P_{7/2}$ ~ 370 nm, ${}^6H_{5/2}\rightarrow {}^4L_{15/2}$ ~ 386 nm, ${}^6H_{5/2}\rightarrow {}^6P_{3/2}, {}^4F_{7/2}$ ~ 401 nm, ${}^6H_{5/2}\rightarrow {}^6P_{5/2}$ ~ 412 nm, ${}^6H_{5/2}\rightarrow {}^4I_{13/2}$ ~ 457 nm and ${}^6H_{5/2}\rightarrow {}^4I_{9/2}, {}^4M_{15/2}$ ~ 470 nm [10,11]. These transitions indicate the presence of Sm^{3+} ions and its spectroscopic activity within the monoliths structure. The Sm^{3+} 4f-4f transitions, seen in the spectra, are in good agreement with existing data[--]. It can be also seen from in figure (5) that the intensity of the peak absorption bands is increased as a result of a corresponding increase of Sm^{3+} concentration. This is due to that the probability of absorption process is increased as the Sm^{3+} ions contribution in the silica network increases, according to Beer's law.

In figure (6), the integral absorption for some Sm^{3+} 4f-4f transitions: ${}^6H_{5/2}\rightarrow {}^4K_{15/2}$ ~ 359 nm, ${}^6H_{5/2}\rightarrow {}^6P_{7/2}$ ~ 370 nm and ${}^6H_{5/2}\rightarrow {}^6P_{3/2}, {}^4F_{7/2}$ ~ 401 nm, depends linearly on the samarium concentration (mol/l). This indicates that the prepared sol-gel materials can be used for optical application such as optical filters for UV and 401 nm light. Depending on Beer's law and from the slope of the lines given in figure (6), the oscillator strengths of these Sm^{3+} transitions in the monoliths have been determined. The oscillator strength of Sm^{3+} ions incorporated in silica Xerogel matrices (assuming the absorption curve to be Gaussian) can be calculated using the relation[11]:

$$f = 4.32 \times 10^{-9} \int \xi(v)\, dv. \qquad (1)$$

Where v is the wavenumber (cm^{-1}), $\xi(v)$ is the molar extinction coefficient and is equal to $1/Cd$ ($\log I_0/I$). C the molar concentration, d the thickness of the prepared monoliths in cm and $\log I_0/I$ is the optical density or absorptivity. The results are presented in table 1. The values of oscillator strength of Sm^{3+} are connected with hypersensitive electric-dipole transitions [11] and give an indication that there is non-centosymmetrical surrounding of Sm^{3+} ions in the silica network.

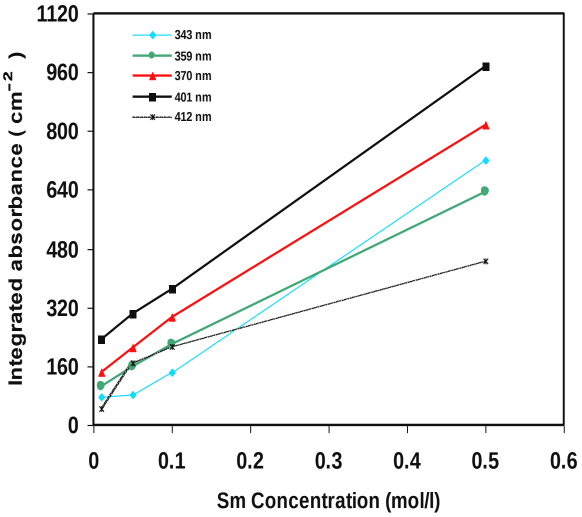

Fig. 6: The integrated absorbance as a function of Sm^{3+} concentration for some Sm^{3+} transitions.

Table 1: The results of the oscillator strength of some Sm^{3+} transitions for the sol-gel monoliths

$\nu_{max.}$ (cm^{-1})	Sm^{3+} Transitions	f $\times 10^{-6}$
29154.5	$^6H_{5/2} \rightarrow {}^4D_{7/2}$	1.02
27855.1	$^6H_{5/2} \rightarrow {}^4K_{15/2}$	1.08
27027	$^6H_{5/2} \rightarrow {}^6P_{7/2}$	1.19
24937.6	$^6H_{5/2} \rightarrow {}^6P_{3/2}, {}^4F_{7/2}$	3.82
24271.8	$^6H_{5/2} \rightarrow {}^6P_{5/2}$	0.84

Conclusions

Cylindrical and transparent silica monoliths, containing up to 0.5 M of Sm^{3+}, are reproducibly made by sol-gel technique. Formation of randomly distributed Sm^{3+} ions in the monoliths up to 0.1 M Sm^{3+} doping concentration, and these ions can not form any ligands in the silica network. At 0.5 M Sm^{3+} doping concentration, there is a probability of formation of Sm^{3+} clusters in the structure of silica monoliths. A linear concentration dependence of some of the Sm^{3+} absorbance is observed. The values of oscillator strength of Sm^{3+} suggest a non-centosymmetrical surrounding of Sm^{3+} ions.

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