The Effect of Ce-doping Molar Concentration with Silica Xerogel on the Materials Optical Properties

Abdul-Jabbar Abbas Oudh, Asia H. Al-Mashhadani* and Wesam A.A. Twej

Department of Physics, College of Science, University of Baghdad, Iraq.

*assia19662006@yahoo.com

Abstract: Ionic cerium-doped pure silica glass with high photoluminescence, has been prepared using the sol–gel technique and densification of the porous xerogel under inert and air atmosphere. The present study shows the effect of densification atmosphere and molar concentrations on the optical properties of ionic cerium-activated silica glasses. Moreover, the PL intensity increased with increasing the molar concentration of ionic Ce+3. The PL is composed of two sub-bands ascribable to tetragonal distortion of the matrix and spin–orbit coupling but these sub-bands are closer to each other when the core rod is densified under inert atmosphere.

1 Introduction

The term sol-gel was first coined in the late 1800s. Sol-gel chemistry for the synthesis of new materials is becoming increasingly popular because of its relatively simple components and the variety of applications to which it can be applied [1]. It generally the term sol-gel refers to a low-temperature method using inorganic precursors that can produce ceramics and glasses with better purity and homogeneity than through high temperature conventional processes [2]. Two most attractive features of the sol-gel process are that it can produce compositions that cannot be created with conventional methods, and that the mixing level of the solution is retained in the final product, often up to the molecular scale.

Sol-gel method has been successfully used to manufacture a variety of products, viz., bulk glasses [3], optical fibers [4], special coatings, ultra-pure powders, and multifunctional materials [5]. Sol-gel processed transparent porous matrix offers the possibility of doping various organic and inorganic molecules [6]. Sol-gel process has been used to fabricate materials, which can be used as new laser materials, dosimetry application, Nano composites, biomimetic systems, and so on. Because of potential in fabrication of a wide variety of new materials, understanding of sol-gel processes has become the center of interdisciplinary research, viz., physics, chemistry, biology, biotechnology, biochemistry, electronics, and related engineering branches. Sol-gel materials have a wide range of applications, from environmental monitoring, biosensors for healthcare, to nanotechnology for sensing clinically important analytes [7].

Silicate glasses are commonly used as optical materials in a broad range of applications due to their ready availability, relatively simple fabrication and large panel of properties (transparency, chemical durability, etc.) [8]. Their luminescent properties are usually modulated by doping with rare-earth ions. Since their discovery in the last years of the 18th century, rare earth elements have displayed wide applications, especially in photoluminescence [9]. Their exceptional spectroscopic properties coming from their 4f intra-configurationally electronic transitions lead to high quantum efficiencies and narrow emission bands [10].

The simplicity of the sol-gel route in glass fabrication, the low temperature processing conditions, the large number of possibilities in material design and the highly concentrated and homogenous doping levels, make it...
more applied than conventional melt processing [11]. Then, rare-earth ion-doped sol-gel silicate glasses are
consider promising materials for photonics applications such as lasers, photonics or fiber optics [12]. For
decades, Ce$^{3+}$ doped and co-doped sol-gel silica glasses have attracted particular interest for their optical
properties. In particular, this rare-earth ion exhibits an intense blue luminescence of interest for phosphors [13].
This ion is also well known in structural probes used to analyze materials’ matrix structures [14].

2 Experimental

2.1 Samples preparation and treatments
The first step of the fabrication consists in the synthesis of a cylindrical rod by the sol-gel route. This technique
was chosen because it enables to achieve transparent glasses at low temperatures, that is to say several hundred
degrees below the reaction temperature required in this process [15]. In this present work, the synthesis of silica xerogel, which contains cerium chloride (CeCl$_3$$\cdot$7H$_2$O). The experimental conditions have been adapted so that the samples formation via the sol gel route can be performed
at neutral pH. The kind of rare-earth element (Ce) has been chosen because it have best luminescent. The prepared samples have different molar concentrations ($1\times10^{-3}$, $4\times10^{-2}$, $1\times10^{-1}$, $5\times10^{-1}$, $8\times10^{-1}$,
and$9.5\times10^{-1}$mol/liter) and different densification air atmospheres and inert gas (Argon).
Nanoporous silica monoliths were prepared using a polymeric sol–gel technique from tetraethylorthosilicate
(TEOS) precursor [16]. The obtained xerogel were stabilized at 900$^\circ$C and soaked in alcoholic solutions
containing a cerium salt (CeCl$_3$$\cdot$7H$_2$O). Then, the samples were withdrawn from the doping solutions and dried
at 50$^\circ$C for several hours in order to remove solvents and to retain cerium element within the Nano-pores.
The doped matrices were then densified in air atmospheres and inert gas (Argon) under the conditions described
[17]. For comparison, non-doped and Ce-doping silica xerogel have also been fabricated using the same
technique. By this route, four kinds of silica xerogel samples were elaborated and labeled SiO$_2$CeAir,
SiO$_2$Air, SiO$_2$CeAr, and SiO$_2$Ar. Once carefully cut and polished, the obtained glasses present no cracks and
exhibit a very high transparency, as shown in Figure 1.

![Figure 1: Digital photographs (a) SiO$_2$Ar, (b) SiO$_2$CeAr,(c) SiO$_2$Air,(d) SiO$_2$CeAir.](image)

2.2 Characterization methods
The prepared samples densification under inert gas (Argon) and have been analyzed using different measuring
instruments such as UV-visible spectrophotometer,FluorescenceSpectrophotometer,Fourier Transformation
Infrared (FTIR) spectroscopy, and all these items have been presented in this paper as shown in Table1.

| Table 1: The apparatus and equipment's used in this study. |
|----------------------------------------------------------|
| Equipment                          | Company          | Origin |
|------------------------------------|------------------|--------|
| spectrophotometer                  | EMC-LAB          | Germany|
| scientific furnace                 | Barnstead       | U.S.A  |
| pH-meter                           | Sartorius        | Germany|
| Stirrer                            | Stuart           | UK     |
| scientific furnace                 | Nabertherm       | Germany|
| Oven                               | Memmert          | Germany|
| FTIR-spectrophotometer             | SHIMADZU         | Japan  |
| Analytical Balance                 | Sartorius        | Germany|
| Fluorescence Spectrophotometer     | Shanghai Drawell | China  |
| spectrophotometer                  | Instrument Co.Ltd. | China  |
3 Results and discussion

3.1 Fourier transforms IR spectroscopy

There exists many ways of modifying the pore size distribution in a xerogel. The easiest parameter to manipulate in order to decrease the pore diameter is the heat-treatment temperature (or the heat-treatment time) [18].

The FTIR spectroscopy provides extensive in information about the vibrational, chemical and structural properties of different materials [19].

It has been particularly used in the characterization of sol-gel materials, leading to an extensive knowledge of the relationship between IR spectra, molecular level structure and properties. Figure 2 as shown the IR transmission spectrum of non-doped silica xerogel sample, which was prepared under synthetic recipe condition of pH=7 and 900°C.

Figure 2: FTIR spectrum of non-doped sample silica sol-gel xerogel under 900°C.

The absorption band centered at 460.2 cm⁻¹ is due to the bending vibrations of (Si-O-Si) groups, and the absorption band peaking at 810.1 cm⁻¹ is attributed to the symmetric stretching (Si-O-Si) groups, while the wide band at around 1103.8 cm⁻¹ is the characteristic Si-O-Si asymmetric stretching vibrations [20]. The weak band at 964.8 cm⁻¹, which is ascribed to stretching vibration of silanol (Si-OH) groups [20], indicates the limited number of these groups in the silica network, which means that the condensation reaction is nearly complete. Because of the drying process at 110 °C, dose not completely trap the water molecules from the pores of silica xerogel, therefore two absorption bands appeared. The first one is at 1640.7 cm⁻¹ and due to bending vibrations of (O-H) bond in H₂O molecules, while the second band peaking at 3440 cm⁻¹ is ascribed to stretching vibrations of this bond [21]. However, the intensity of the first band became very weakly and the second band disappeared for the pure glass sample, which is sintered at 500°C, meaning, that the most H₂O molecules are driven out after the sintering process.

3.2 Absorption spectroscopy measurements

In this present work, the UV-Visible spectrophotometer model (UV-6100PC) from EMC-LAB it has been used to obtain absorption spectra of non-doped or doped silica xerogel. Fig. 3 shows the optical absorption spectra of Ce-doped and non-doped silica xerogel with different concentrations obtained under air atmosphere. The absorption coefficient (α) in Cm⁻¹ units as a function to wavelength (λ) in nanometer units [22].
Figure 3: Optical absorption spectra of non-doping SiO$_2$Air and Ce-doped silica xerogel SiO$_2$CeAir with different concentrations obtained by densification under Air atmosphere.

We can notice that non-doped (SiO$_2$Air) silica xerogel presents no absorption signal in the UV–visible domain. Whereas, the doped samples (SiO$_2$CeAir) densified under air (SiO$_2$CeAir) shows an absorption band peaking around 248.127nm(4.997eV), 256.175nm(4.84eV), and 258.539nm(4.796eV) with concentration $1 \times 10^{-3}$, $4 \times 10^{-2}$, and $1 \times 10^{-1}$ mol/liter, respectively, which could be attributed to charge transfer transitions from ligands to the quadruple-charged cerium cat ions (Ce$^{+4}$)[22].

Figure 4 shows the optical absorption spectra of non-doping and Ce-doping silica xerogel samples at different concentrations and densification these samples under inert gas (Argon).

Figure 4: Optical absorption spectra of Ce-doped and non-doped silica xerogel with different concentrations obtained by densification under Argon gas.

From the results above the SiO$_2$CeAr xerogel exhibits two absorption bands for each concentrate except the sample have non-doping (glass). The first band centered about 249.549nm - 262.789 nm (4.969 eV - 4.72 eV) and second band about 317.555 nm – 334.215 nm (3.9 eV – 3.71 eV), which are assigned to Ce$^{+4}$ and to 4f→5d transition of Ce$^{+3}$ ions, respectively [23].

The most important from above results, the intensity of absorption bands for all samples has increased with increasing of their molar concentrations, and this is due to the increasing of ions contribution in the absorption process so much as the increasing of their concentrations.

Moreover, we used these spectra to estimate the cerium ions concentrations and the corresponding absorption cross sections in both samples. Firstly, the absorption cross section ($\sigma$) for Ce$^{+4}$ was evaluated about $213.33 \times 10^{-23}$ cm$^2$ to 294.94 x $10^{-23}$ cm$^2$ by using the measured maximum absorption coefficient in the case of SiO2CeAir (no significant contribution of Ce$^{+3}$ in this case; see previous figure, and the concentration of Ce species determined by UV-Visible spectrophotometer. Secondly, from the maximal absorbance of Ce$^{+4}$ in SiO$_2$CeAr sample, the Ce$^{+4}$ concentration was deduced using the already obtained cross section for Ce$^{+4}$. Finally, the Ce$^{+3}$ concentration was calculated and using the maximal absorbance of a Ce$^{+3}$, an absorption cross section ($\sigma$) for
Ce$^{3+}$ of about 10.54 x 10$^{-23}$ cm$^{-2}$ to 55.53 x 10$^{-23}$ cm$^{-2}$ was determined. Hence, the obtained ratio $\sigma(\text{Ce}^{4+})/\sigma(\text{Ce}^{3+})$ is of about 20.24, 8.5, 8, 5.64, 5.37, and 5.31 for 1 x 10$^{-3}$, 4 x 10$^{-2}$, 1 x 10$^{-1}$, 5 x 10$^{-1}$, 8 x 10$^{-1}$, and 9.5 x 10$^{-1}$ mol/liter molar concentrations, respectively. The ratios (8.5, 8) and the obtained absorption cross sections are close to the ones reported in the case of a Ce-doped silica xerogel prepared by plasma torch chemical vapor deposition [22-24]. On the opposite, lower values of the cross section ratio were obtaining for cerium-activated alkali silicate glasses [25]. Besides, a concentration molar ratio ([Ce$^{3+}$]/[Ce$^{4+}$]) it has found a large value for SiO$_2$CeAr sample. This clearly shows that in air oxidizing conditions, cerium is preferably stabilized as Ce$^{4+}$ inside the silica matrix while the trivalent state (Ce$^{3+}$) is favored by inert atmosphere conditions. Indeed, during glass densification, Ce$^{3+}$ and Ce$^{4+}$ ions are in equilibrium [26] with dissolved oxygen inside the matrix, according to the equation:

$$4\text{Ce}^{4+} + 2\text{O}^2\rightarrow 4\text{Ce}^{3+} + \text{O}_2$$

Under inert atmosphere, the absence of oxygen most likely shifts the thermodynamic equilibrium and favors the Ce$^{3+}$ formation.

From the previous results, we can notice the intensity of absorption bands under Argon for all samples has increased with increasing of their molar concentrations, and this is due to the increasing of ions contribution in the absorption process so much as the increasing of their concentrations. But the intensity for sample have concentration 9.5 x 10$^{-1}$ mol/liter started decrease because the state of ionic saturation in this sample as shown in Figure 4.

The absorption coefficient, cross-section, and the ratio of cross-section as a function of concentration for SiO$_2$CeAr were studied. Figure 5(a,b) shows the relationship the absorption coefficient ($\alpha$) and cross-section ($\sigma$) as a function of concentration, we can notice the values ($\alpha$) and ($\sigma$) increased with increasing of the molar concentrations of both Ce$^{3+}$ and Ce$^{4+}$ until reaches 9.5 x 10$^{-1}$ mol/liter concentration then starting decreasing due to the ionic saturation. Whereas, the ratio of cross-section decreased with increasing the molar concentration as shown in figure 6.

![Figure 5](image-url)

**Figure 5:** (a) Absorption coefficient as a function of concentration of Ce$^{3+}$ and Ce$^{4+}$; (b) Cross-section as a function of concentration of Ce$^{3+}$ and Ce$^{4+}$.
3.3 Fluorescence spectroscopy measurements

In this present work, the fluorescence spectrum at room temperature, was measured using Fluorescence Spectrophotometer from Drawell Scientific Instrument, it has been used to obtain emission spectra of non-doped or doped silica xerogel. Fig. 7 shows optical emission spectra of Ce-doped silica xerogel obtained under argon gas. The intensity in arbitrary units as a function to wavelength (λ) in nanometer units.

Figure 7 presents the optical photoluminescence (PL) spectra of SiO$_2$CeAr recorded under excitation at wavelength (λ= 365 nm) have energy (E=1240/365 nm =3.39 eV). The emitted luminescence is dominated by a broad band peaking 446 nm (2.78 eV), 456 nm (2.72 eV), 468 nm (2.65 eV), 474 nm (2.62 eV), 478 nm (2.59 eV), and 476 nm (2.6 eV) for 1×10$^{-3}$, 4×10$^{-2}$, 1×10$^{-1}$, 5×10$^{-1}$, 8×10$^{-1}$, and 9.5×10$^{-1}$ molar concentrations, respectively, with a full width at half maximum (FWHM) from 82 nm to 138 nm. These bands can be ascribed to the allowed 5d→ 4f optical transition of Ce$^{3+}$ ions [27]. We should point out that only the samples treated under inert conditions presents a PL excitation spectrum related to the visible emission, with a relatively broad excitation band ranging from 249.549 to 446 nm and a high optical efficiency [see Figures 4 and 7].

Spectral characteristics of these samples are found similar to those of the glass. Indeed, its absorption spectrum exhibits the 249.549 nm - 262.789 nm and 317.555 nm – 334.215 nm bands associated with to Ce$^{4+}$ and Ce$^{3+}$ ions, respectively. Moreover, upon 351 nm excitation, the room temperature luminescence is dominated by a visible emission located around 446-478 nm (2.78 - 2.59 eV); FWHM from 82 to 138 nm) and attributed to Ce$^{3+}$ ions. As a result, the covalency of Ce–O bond increases, which reduces the energy difference between the ground and the excited states.

Figure 8(a,b), show the logarithmic relations FWHM, intensity, and position (λ) as a function of concentration.
4 Conclusions

The present study shows the effect of molar concentration and different densification inert gas (Argon) and air atmosphere on the optical properties of ionic cerium-activated silica xerogel. Radiosensitive cerium-doped silica xerogel have been obtained with low doping concentration using the sol–gel technical. These sol–gel materials contained a higher Ce$^{3+}$/Ce$^{4+}$ atomic ratio when densified under inert gas (Ar) and air atmosphere, resulting in a much higher PL emission quantum efficiency in the visible range. This Ar-treated glass was successfully used as starting material to draw a millimeter-sized rod that could be used in many applications. Whereas, air-treated silica glass have problem due to oxygen atmosphere is exist. Moreover, we can notice the fluorescence increased with increasing the molar concentrations of Ce$^{3+}$ ions in silica glass samples. For the first time, we investigated the PL signal of such a cerium-doped rod with different concentrations. Finally, we conclude the intensity of PL signal it has been increased with increasing concentration until reaches $9.5 \times 10^{-1}$ mol/liter.

References

[1] M.P. Ferreira and L.O. Defaria, Journal of Sol-Gel Science and Technology, vol. 21, pp. 173-176, 2001.

[2] L.L. Hench and J.K. West, J. of Chemical Reviews, vol.90, no 1, pp.33-72, 1990.

[3] F. Kirkbir, H. Murata, D. Mayers, S.R. Chaudhari and A.Sarkar, J. of Sol-gel Sci. Technol., vol.6, no.3, pp.203-217, 1996.

[4] K. Susa, S.I. Matsuyama, S. Satoh and T. Suganuma, J. of Electronic Letters, vol.18, issue 12, pp.499-500, 1982.

[5] J.M. Zeigler and F.W. Gordon Fearon, Advances in Chemistry Series No.224, American Chemical Society, Washington DC, pp. 227-240, 1989.

[6] J.L.R. Nogues and M.V. Moreshead, J. of Non-Cryst. Solids, vol 121, pp.136-42, 1990.

[7] N. K. Chaudhury, R. Gupta and S. Gulia, Defence Science Journal, vol. 57, no. 3, pp. 241-253, 2007.
[8] J. Zarzycki, Wiley-VCH: Weinheim, New York, NY, USA, vol. 9, pp. 798, 1991.

[9] Y. Dwivedi and S.C. Zilio, J. of Nanosci. Nanotechnol, vol. 14, pp. 1578–1596, 2014.

[10] K. Binnemans, Chem. Rev., vol. 109, pp. 4283–4374, 2009.

[11] M. Yamane and Y. Asahara, Cambridge University Press, Cambridge, UK, p. 283, 2000.

[12] H. C. Vasconcelos and A. S. Chandra, U., Ed., InTech: Rijeka, Croatia, pp. 81–107, 2017.

[13] G. Blasse, B. C. Grabmaier, Springer-Verlag, Berlin, Germany, p. 242, 1994.

[14] G. Alombert-Goget, N. Gaumer, J. Obriot, A. Rammal, S. Chausse dent, A. Monteil, H. Portales, A. Chiasera and M. Ferrari, J. of Non-Cryst. Solids, vol. 351, pp. 1754–1758, 2005.

[15] P. S. J. Russell, J. of Light wave Technol., vol. 24, issue 12, pp. 4729–4749, 2006.

[16] H. El Hamzaoui, L. Courthéoux, V. N. Nguyen, E. Berrier, A. Favre, L. Bigot, M. Bouazaoui, B. Capoen, J. of Materials Chemistry and Physics, vol. 121, pp. 83–88, 2010.

[17] H. El Hamzaoui, G. Bouwmans, B. Capoen, Y. Ouerdane, G. Chadeyron, R. Mahiou, S. Girard, A. Boukenter and M. Bouazaoui, J. of Materials Research Express, vol. 1, pp. 1–10, 2014.

[18] Y. Xi, Z. Liangying, W. Sasa, J. of Sens. Actuators B: Chemical, vol. 25, issues 1–3, pp. 347-352, 1995.

[19] B. C. Smith, Boca Raton, FL: CRC Press, 1996.

[20] L. Yang, ph. D. Thesis, California Institute of Technology, pp. 43-47, 2005.

[21] C. Carla., C. Mariano, L. Roberta and M. Ama, "Eu+3 Doped Y2O3-SiO2 Nano-composite Obtained by a Sol-Gel Method", J. of Mat. Res. Soc. Sym. Proc., vol. 676, pp. 181-186, 2001.

[22] Y. Ishii, K. Arai, H. Namikawa, M. Tanaka, A. Negishi and T. Handa, "Co doping effects on absorption and fluorescence properties", J. of Am. Ceram. Soc., vol. 70, pp. 70-72, 1987.

[23] Khodair, Z. T., Al-Jubbori, M. A., Hassan, A. M. et al. Journal of Elec Materi (2019) 48: 669.

[24] R K Mohammad, R A Madlol, N M Umrnan and F I Sharrad Structure and electronic properties of substitutionally doped cycloheptane molecule using DFT, Results Phys. 6 (2016) 1036.

[25] M-L. Brandily-Anne, J. Lumeau, L. Glebova and L.B. Glebov," Specific absorption spectra of cerium in multicomponent silicate glasses", J. Non-Cryst. Solids, vol. 356, p. 2337, 2010.

[26] A. Herrmann, H.A. Othman, A.A. Assadi, M. Tiegel, S. Kuhn and C. Rüssel,"Spectroscopic Properties of Cerium-Doped Aluminosilicate Glasses", J. of Opt. Mater. Express, vol. 5, p 720, 2015.

[27] C. Canevali, M. Mattoni, F. Morazzoni, R. Scotti, M. Casu, A. Musinu, R. Krmanovic, S. Polizzi, A. Speghini and M. Bettinelli, J. of Am. Chem. Soc., vol. 127, pp. 14681-14691, 2005.