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Study of the light emission from Eu^{3+} doped nanoporous organosilicate films*

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***Abstract*— Rare earth doped Nanoporous organosilicate are promising for luminesce materials application because of their unique structural and large internal surface area. In this paper, we have systematically investigated the photoluminescence characteristics of the silica based materials. In this study, the Eu^{3+} were assembled into the pores of nanoporous organosilicate glass (OSG) by sol-gel method. In addition there are obvious red luminescence peak of the films. However the doping of Eu^{3+} can change the porosity of the films. The photoluminescence characters of different Eu^{3+} ions doped OSG films have been studied. And all the prepared films have showed a stronger emission of Eu^{3+} at 615nm. The optimal content of Eu^{3+} has been confirmed according to the sample with strongest emission.**

I. INTRODUCTION

Strong luminescence from silicon based light emitters is detected at room temperature. This discovery is very attractive. Because this indicates potential applications in Si-based optoelectronic devices, especially blue and UV luminescence devices, which means these devices are easy to manufacture or integrate with CMOS. So luminescent silica based materials attracted enormous research attention in recent years[1]. There are many kinds ways to make luminescent silica based materials. Studies have shown that sol-gel method is an appropriate method for the preparation of new luminescent nano-materials[2-4]. Porous organosilicon glass films have the advantages of high hydrophobicity, large internal surface area and uniform micropores, and are an excellent rare earth ion carrier material[5,6]. Therefore Luminescent silica based materials prepared by sol-gel technology have broad application prospects in various kinds of fields such as optics, luminescent solar collectors, intelligent window photochromic panels, environmental and biological impurities sensors, tunable lasers, active waveguides, linear and nonlinear optical materials, and biomarkers[7-10].

To improve the luminescence intensity of silica-based materials, many kinds of chemical elements are added into the silica-based materials. One kind of the doped elements is rare earth element. This kind of chemical element can provide the luminous center. It is well known that the most common valence state of rare earth ions is the trivalent state. Different trivalent rare earths (such as Sm^{3+}, Ce^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+}) are doped into silica gel, and different sensitizers (such as Al ion) are added to obtain the luminescence performance of strong emission, which has been widely reported[11-14]. Recently reports on the luminescence of europium trivalent (Eu^{3+}) doped in silica keep increasing[15,16]. These results show that the rare earth alone cannot emit light in the silica matrix without any energy transfer activator[17]. Therefore, it is of great significance to study photoluminescence of porous OSG films doped only with rare earth ions.

In this work, we report the synthesis and properties of Eu^{3+} doped porous OSG films. The porosity dependence, the concentration dependence and the antenna effect of Eu^{3+} doped OSG films are analyzed respectively.

II. EXPERIMENT

The nanoporous OSG films were prepared by acid-catalyzed hydrolysis and polycondensation of 1,2-bis(trimethoxysilyl)ethane(BTMSE) and Methyltrimethoxysilane (MTMS) with deionized water. Tetrahydrofuran (THF) was added to produce a homogeneous solution. Brij 30 (C_{12} $H_{25}(OCH_2OCH_2)_4OH$ with molar mass 362 g/mole) was used as a surfactant to obtain porous structure by a self-assembly process[18]. The molar ratio of BTMSE:MTMS:H2O was 0.47:0.53:3.087, and a small amount of a 0.0053M HCl was added as a catalyst. The prepared solution was stirred continue for 10~12h at 60 ℃, and then the gel was stand for 24h. Different content of $Eu(NO_3)_3 \cdot 6H_2O$ was added into the prepared precursor mixture and remarked as #1, #2, #3, and #4, as shown in Table 1.

The films were deposited on 150mm diameter silicon wafers (1 – 10 Ω •cm) at the rotation speed of 4500 rpm and cured on the hot plate at 150℃, 40 min to remove solvents (soft bake), and final curing at 400℃, 20 min remove NO_3- and to obtain Eu ions-doped OSG films (hard bake).

The Eu^{3+} doped OSG films were treated by O_2 plasma in ICP-8000, then soaking them in 2% v/v 3-aminopropyltriethoxysilane solution for 1.5h. To measure the chemical components of the samples, Fourier Transform Infrared Spectroscopy (FTIR, JASCO FT/IR-6300) was used. The measurement settings are 64 times scan, 4 cm^{-1} resolution and 4000-400 cm^{-1}wavenumber range of. The luminescence of the film was measured by photoluminescence (PL) on JASCO FP-8300. The Xe lamp was used as a light source, and the excitation and emission

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spectra range in wavelength is from 200nm to 750nm, and the slit width is 5nm. The porosities of OSG films were characterized by using heptane adsorption isothermsmeasurement on ellipsometry(EP) based apparatus at 21℃.

III. Result and Discussion

Fig. 1 shows the FT-IR spectra of the pristine OSG films with a porosity of 20%. Curve a and Curve b in Fig. 1 represents the FTIR spectra of Soft Bake film and Hard Bake film, respectively. The band range from 3700 to 3000 cm^{-1} in curve a(Fig. 1) can be attributed to the Si-OH vibration, the band range from 3000 to 2750cm^{-1} and 1400 cm-1 can be attributed to the CHx group, the absorption peak at 1750cm^{-1} can be attributed to the silanol groups O-H absorption, the band range from 1280 to 1270cm^{-1} can be attributed to the terminal Si-CH_3 bonds that are important components of OSG films, the range from 1300 to 1000cm^{-1} corresponds to the Si-O-Si skeleton, these were the characteristic absorption peaks of porous OSG matrix[19]. The result shows that Hard Bake removes amounts of CHx group and all of the Si-OH, whose existence will increase the adsorption of water molecules. This can effectively reduce the PL quenching of water molecules[20].

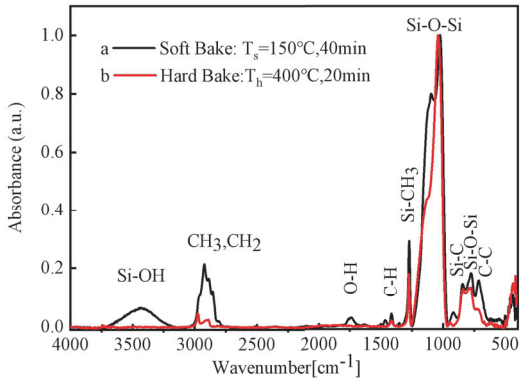

Fig. 1. FT-IR spectra of the pristine OSG films with a porosity of 20% Soft Bake (curve a) and Hard Bake (curve b).

Table 1 shows the EP results of Eu^{3+} doped OSG films. The results indicates that the porosity of the films decrease with the increase of Eu^{3+} content. It is inferred that for the low content of Eu^{3+}(e.g. sample #2), only small amout of Eu^{3+} was deposited on the wall of the pall. As for the high content of Eu^{3+}(e.g. sample 4), Eu^{3+} first fills small pores. Therefore, the pores closed very fast at the neck because of the filling, leading to that some pores became unaccessible. So that for sample #4, RI doesn't change much, but the change of full porosity is significant. Without Eu^{3+} doping, the pores are completely open. For sample #2, small amount of Eu^{3+} deposited on the neck of the pore. For sample #3, more Eu^{3+} was deposited on pore neck. For sample #4, many pores closed very fast at the opening and then the porosity as shown in Fig. 2. reduced. It indicates that doping Eu^{3+} ions make pore size smaller and pore filling is becoming diffusion limited.

Table 1. Effect of Eu^{3+} content on EP

Sample No.	Effect of Eu^{3+} content on EP			
	Eu^{3+} content (wt%)	*Thickness (nm)*	*Refractive index(RI)*	*Porosity (%)*
#1	0	478.0	1.325	25
#2	1.7	493.6	1.329	25
#3	12.1	485.2	1.333	21
#4	25.8	465.7	1.320	13

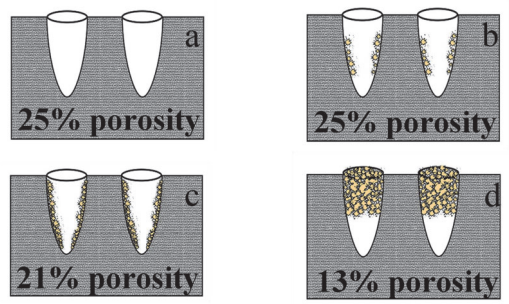

Fig. 2. The possible model of porosity with different concentration of Eu^{3+} ions. (a) Eu^{3+} ions content is 0.0 wt%; (b) Eu^{3+} ions content is 1.7 wt%; (c) Eu^{3+} ions content is 12.1 wt%; (d) Eu^{3+} ions content is 25.8 wt%.

Fig 3 Shows the PL excitation spectra of sample #3. The excitation spectra of the sample were obtained by monitoring the emission wavelength of 615nm. This peak was the strongest emission wavelength in the sample, which are attributed to the f–f transitions within the $Eu^{3+}4f^6$ electron configuration[21]. This excitation spectra contains of a broad band and a narrow peak. The broad band at about 230nm is due to the charge-transfer band of Si-O-Si deficient centers-Eu^{3+}[22]. Fig 4 shows the emission spectra of films with different Eu^{3+} content. All of these emission spectrum showed the narrow peaks assigned to the f–f transitions of the Eu^{3+}, which is due to the shielding of the 4f orbitals by the outer $5s^2$ and 5^{p6} orbitals. There are three emission peaks including 590nm, 615nm and 689nm of all the samples. The emission band at 590nm could be attributed to the typical $^5D_0$-$^7F_1$ transition of Eu^{3+}. The strongest emission band appeared near 615nm could be attributed to the typical $^5D_0$-$^7F_2$ transition of Eu^{3+}. The emission band at 689nm could be attributed to the $^5D_0$-$^7F_4$ transition of Eu^{3+}. The emission peak at 615nm belongs to the electric dipole transition, and the fluorescence intensity is greater than the magnetic dipole transition at 590nm. It indicates that europium ion is in the inversion position of symmetry center and is strongly dependent on the local symmetry environment[23]. The strongest red emission occurs when Eu^{3+} content is 12.1wt%. High concentration with Eu^{3+} doping will close the hole of the film leading to luminescence intensity quenching.

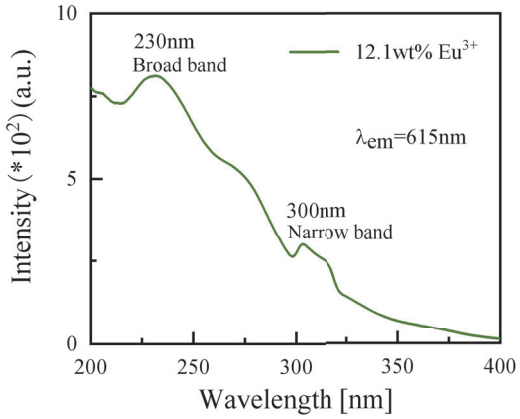

Fig 3 Excitation spectra of 12.1wt% Eu^{3+} doped OSG films.

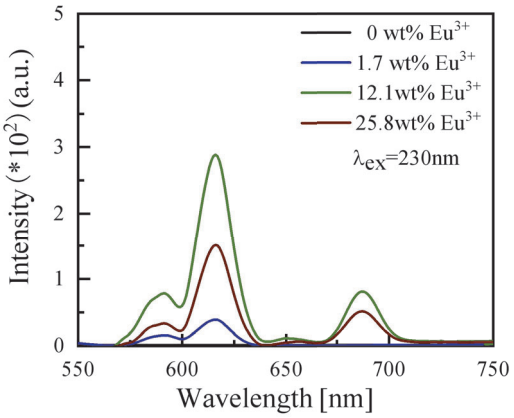

Fig. 4 Emission spectra of different content of Eu^{3+} doped OSG films.

APTES treatment of 12.1wt% Eu^{3+} doped OSG films increase the energy transfer efficiency by the antenna effect as shown in Fig.5. Fig 5 (b) shows the FTIR spectrum of APTES treatment of Eu^{3+} doped OSG films the bands at around 900-1250 cm^{-1} originating from the Si – O – Si asymmetric/symmetric stretching, which shift towards higher binding energy/wavenumber due to the increase of CHx groups and this suggests the formation of more Si–O–Si cage type structures[24]. Fig4 (c) shows that the band at 615 cm^{-1} are attributed to the Short-wave level- ≡C-H deformation vibration. The increased spectral intensity by the treatment with the antenna molecules indicates that supply the small absorption coefficient of rare earth ions in the UV-visible region, and the non-radiation transition enhances the characteristic emission of Eu^{3+} at 615nm Fig 4 (d).

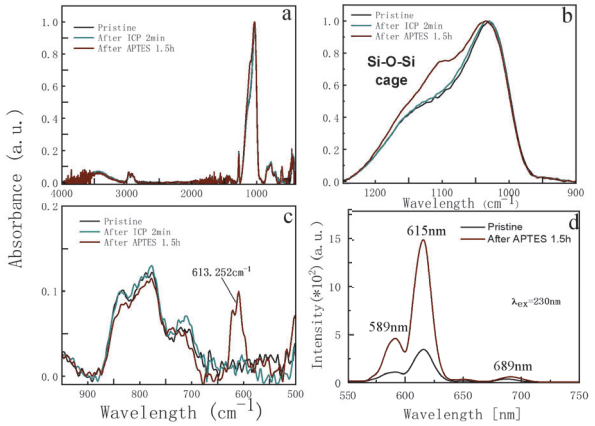

Fig. 5. FTIR spectrum of APTES treatment of 12.1wt% Eu^{3+} ions doped OSG film (a) and in large of 1250-950cm^{-1} (b), 950-500cm^{-1} (c). PL emission spectrum of APTES treatment of 12.1wt% Eu^{3+} ions doped OSG films (d).

IV. Conclusion

The luminescence film can be prepared by sol-gel method with doped Eu^{3+}. Comparing the PL result of the films with different Eu^{3+}, it can be found that the film with Eu^{3+} of 12.1wt% has the strongest luminescent intensity at 615nm. The doped Eu^{3+} ions replaces Si-CH_3 of the film and forms the Si-Eu band, which makes pore size smaller and pore filling becoming diffusion limited. In addition, high concentration doping leads to PL quenching. Finally the antenna effect without radiative transition enhances the characteristic emission of Eu^{3+}.

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References

[1] Zhi-Yong W, Ke-Xin L and Xiao-Tang R 2010 Mechanism and enhancement of photoluminescence from silicon nanocrystals implanted in SiO_2 matrix Chinese Phys. B191–5

[2] Miyata H, Fukushima Y, Okamoto K, Takahashi M, Watanabe M, Kubo W, Komoto A, Kitamura S, Kanno Y and Kuroda K 2011 Remarkable birefringence in a TiO_2-SiO_2 composite film with an aligned mesoporous structure J. Am. Chem. Soc. 13313539–44

[3] De la Cruz J, Palomino Merino R, Trejo-García P, Espinosa J E, Aceves Torres R, Moreno-Barbosa E, Gervacio-Arciniega J J and Soto E 2019 Luminescent properties of a hybrid SiO_2-PMMA matrix doped with terbium Opt. Mater. (Amst). 8742–7

[4] Liu J, Wang X, Xuan T, Li H and Sun Z 2014 Photoluminescence and thermal stability of Mn^{2+} co-doped $SrSi_2O_2N_2$:Eu^{2+}green phosphor synthesized by sol-gel method J. Alloys Compd. 593128–31

[5] Dutt A, Matsumoto Y, Godavarthi S, Santana-Rodríguez G, Santoyo-Salazar J and Escobosa A 2014 White bright luminescence at room temperature from TEOS-based thin films via catalytic chemical vapor deposition Mater. Lett. 131295–7

[6] Rani N and Ahlawat R 2019 Role of Ceria Nanocrystals on Morphology and Luminescence of Eu^{3+} doped SiO_2 nanopowder J. Lumin. 208135–44

[7] Nayef U M, Hussein H T and Abdul Hussien A M 2018 Study of photoluminescence quenching in porous silicon layers that using for chemical solvents vapor sensor Optik (Stuttg). 1721134–9
[8] Van Der Voort P, Esquivel D, De Canck E, et al. Periodic mesoporous organosilicas: from simple to complex bridges; a comprehensive overview of functions, morphologies and applications[J]. Chemical Society Reviews, 2013, 42(9): 3913-3955.
[9] Wen D and Shi J 2013 A novel narrow-line red emitting $Na_2Y_2B_2O_7$:Ce^{3+},Tb^{3+},Eu^{3+} phosphor with high efficiency activated by terbium chain for near-UV white LEDs Dalt. Trans. 42 16621–9
[10] Wirnsberger G, Yang P, Scott B J, Chmelka B F and Stucky G D 2001 Mesostructured materials for optical applications: From low-k dielectrics to sensors and lasers Spectrochim. Acta-Part A Mol. Biomol. Spectrosc. 572049–60
[11] Jin L, Li D, Xiang L, Wang F, Yang D and Que D 2013 Energy transfer from luminescent centers to Er^{3+} in erbium-doped silicon-rich oxide films Nanoscale Res. Lett. 81–6
[12] Sun J, Zhang X S, Yuan L L, Feng Z J, Ling Z and Li L 2014 White emission from Tm^{3+}/Tb^{3+}/Eu^{3+} co-doped fluoride zirconate under ultraviolet excitation Chinese Phys. B 232–6
[13] Pawlik N, Szpikowska-Sroka B, Sołtys M and Pisarski W A 2016 Optical properties of silica sol-gel materials singly- and doubly-doped with Eu^{3+} and Gd^{3+} ions J. Rare Earths 34 786–95
[14] Wu-Chang D, Yan L, Yun Z, Jian-Chuan G, Yu-Hua Z, Bu-Wen C, Jin-Zhong Y and Qi-Ming W 2009 A comparison of silicon oxide and nitride as host matrices on the photoluminescence from Er^{3+} ions Chinese Phys. B 183044–8
[15] Zhang Q, Sheng Y, Zheng K, Qin X, Ma P and Zou H 2015 Novel organic-inorganic amorphous photoactive hybrid films with rare earth (Eu^{3+}, Tb^{3+}) covalently embedded into silicon-oxygen network via sol-gel process Mater. Res. Bull. 70379–84
[16] Zhang W long, Liu Y, Yu H and Dong X ting 2019 Eu and Tb co-doped porous SiO_2 aerogel composite and its luminescent properties J. Photochem. Photobiol. A Chem. 37947–53
[17] Khan A F, Yadav R, Singh S, Dutta V and Chawla S 2010 Eu^{3+} doped silica xerogel luminescent layer having antireflection and spectrum modifying properties suitable for solar cell applications Mater. Res. Bull. 451562–6
[18] Whitesides G M and Grzybowski B 2002 Self-assembly at all scales Science (80-). 2952418–21
[19] Nenashev R, Wang Y, Liu C, Kotova N, Vorotilov K, Zhang J, Wei S, Seregin D, Vishnevskiy A, Leu J (Jim) and Baklanov M R 2017 Effect of Bridging and Terminal Alkyl Groups on Structural and Mechanical Properties of Porous Organosilicate Films ECS J. Solid State Sci. Technol. 6 N182–8
[20] Tagaya M, Ikoma T, Yoshioka T, Motozuka S, Minami F and Tanaka J 2011 Efficient synthesis of Eu(III)-containing nanoporous silicas Mater. Lett. 652287–90
[21] Chen W, Sammynaiken R and Huang Y 2000 Photoluminescence and photostimulated luminescence of Tb^{3+} and Eu^{3+} in zeolite-Y J. Appl. Phys. 881424–31
[22] Lu Q, Wang Z, Wang P and Li J 2010 Structure and luminescence properties of Eu^{3+}-doped cubic mesoporous silica thin films Nanoscale Res. Lett. 5761–8
[23] Binnemans K, Lenaerts P, Driesen K and Go C 2004 A luminescent tris (2-thenoyltrifluoroacetonato) europium (III) complex covalently linked to a 1 , 10-phenanthroline- functionalised sol–gel glass 191–5
[24] Redzheb M A 2018 Synthesis and Characterization of Mesoporous Organosilica Films for Low-k Dielectric Application 1–177