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Spectroscopic investigations on Se/RE doped sol gel derived silica matrices

Tessy Paul, K. Anupama, P.O. Jibin, K.A. Ann Mary *

Department of Physics, St. Thomas' College, Thrissur, Kerala 680001, India

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ABSTRACT

Selenium and rare earth ions co-doped inorganic luminescence silica matrices are synthesized through sol gel route. The incorporation of cubic Se quantum dots within the porous silica frame is confirmed from TEM analysis. The successful entrapment of green as well as blue color emitters within the silica frame generates evident luminescence bands in the visible region. Obtained Se/Tb^{3+} ions doped silica glasses give characteristic sharp emission peaks of terbium ions at 488 nm, 543 nm, 584 nm, 619 nm wavelength under UV excitations. A broad blue emission band from selenium nanodots centered at 421 nm wavelength is observed in the emission spectrum. Colorimetric studies are done with the aid of 1931 chromaticity diagram. CIE indices of the co-doped glasses are found to lie in between the CIE indices of selenium doped silica glasses (0.18, 0.21) and terbium doped silica glasses (0.28, 0.46). For a fixed concentration of Se and terbium in silica glasses, tunable luminescence without shift in peak wavelength is observed under the excitation wavelength of 340 nm to 380 nm. Varying blue to green luminescence intensity ratio (B/G) with the excitation wavelength reveals the possibility of tunable emission of the glassy matrix for their applicability in solid lighting systems.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Photochemistry and Sustainable Energy (ICPSE 2019).

1. Introduction

Solid state lighting devices have got much significance in recent times due to their numerous applications like advanced lighting systems, efficient sensing platforms and fluorescence based biomedical tools [1]. Luminescent glass based devices have played a significant role in the energy saving field and showed a remarkable progress over the conventional lighting systems in cost-effectiveness, efficiency as well as durability [2]. Glasses can be fabricated with desired optical quality by the compositional modifications. By incorporating multi color emitters within the mesoporous silica network, luminescent glasses can be fabricated successfully. Till date, many efforts have already been done in developing solid state lighting systems by the integration of fluorescence from RGB tri chromatic emitters [3–5]. Trivalent rare earth ions are widely utilized as reliable candidates for sharp visible emission peaks due to their abundant energy levels [6]. The luminescence properties of rare earth ions in various host lattices are also studied much for several years [7,8]. Many tri-doped systems are reported in the last few years for the successful fabrication of luminescent glasses under a single UV excitation wavelength. There has been vigorous research works reported in the areas of organic as well as inorganic components for solid emissions from portable matrices. Li and Da Cunha Androde et al. reported that Eu^{2+} doped low-silica calcium aluminosilicate (LSCAS) glass have broad and intense orange light emission [9]. Characteristic blue emissions from cubic selenium in the strained glassy matrix are already studied recently [10]. Additionally, Er^{3+} and Yb^{3+} ions co-doped oxyfluoride tellurite glasses having significant reddish emission color are successfully synthesized by melt quenching method [11]. Moreover, efficient luminescence bands from other rare earth ions can be successfully tailored for potential applications in multi color emitting glasses [12,13].

Herein, we fabricated a mesoporous silica frame by the successful entrapment of optimized concentration of luminescent selenium quantum dots and trivalent terbium ions. HRTEM images as well as SAED pattern reveal the crystalline nature of the incorporated selenium nanodots within the glassy matrix. Luminescence properties and the colorimetric studies indicate the

* Corresponding author.
E-mail address: ann@stthomas.ac.in (K.A. Ann Mary).

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applicability of samples for artificial lighting systems and high definition display systems.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 98%), Selenous acid (98%), Terbium(III) nitrate pentahydrate (99.9%), Distilled water and Ethanol were purchased from Sigma-Aldrich and all the reagents are used as received without further purification.

2.2. Synthesis of selenium–europium-terbium doped silica glasses

Silica glasses are prepared via sol gel route with tetraethyl orthosilicate (TEOS) as precursor under room temperature. A suitable wt% of terbium(III) nitrate pentahydrate (3 wt%) is dissolved in ethanol and added to the tetraethyl orthosilicate (TEOS) solution. The resulting mixture is stirred continuously for about an hour at room temperature till became a clear solution. Then selenous acid of suitable wt% dissolved in distilled water is added to the primary clear solution. A few drops of concentrated nitric acid are added as the catalyst. TEOS/H_2O/HNO_3 molar ratio is kept as 1:12:0.01. The final clear solution is poured into small poly propylene containers, sealed using paraffin wax and kept for about a month to form a stiff gel. Samples are then heated in the hot air oven at 60 °C for one week to eliminate water and other organics present [11].

2.3. Characterization

Multi doped silica glass samples are subjected to optical and morphological characterization. The morphological characterization and SAED pattern are done using Transmission Electron Microscopy (JEM 2100 model electron microscope) operated at 200 kV. Fluorescence emission spectra of the samples are recorded using Shimadzu RF-5301pc Spectroflurometer. The color of the emission from the obtained matrix is quantified using CIE 1931 chromaticity diagram.

3. Results and discussions

The transparent Se/RE doped silica glasses are prepared via sol gel route with tetraethyl orthosilicate (TEOS) as the precursor under room temperature. HRTEM image shown in Fig. 1(a) reveals the crystalline nature of Se within the amorphous silica matrices.

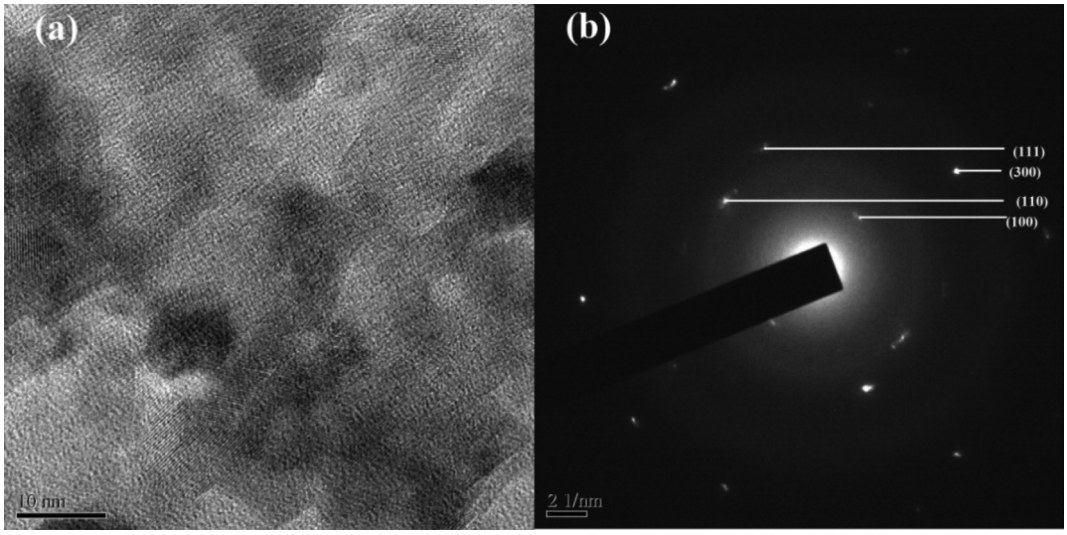

Fig. 1. (a) HRTEM image and (b) SAED pattern of cubic selenium doped silica glasses.

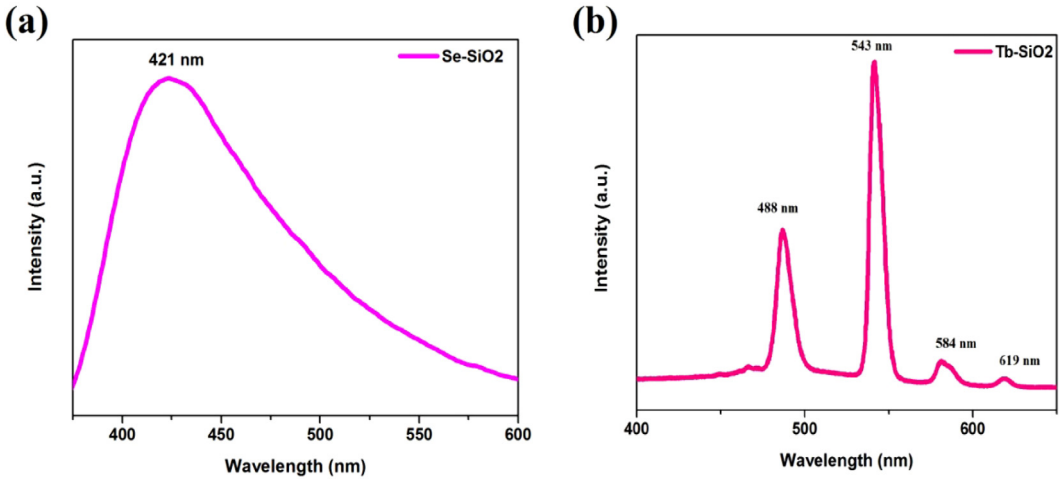

Fig. 2. The room temperature photoluminescence spectrum of (a) 3 w% Se doped silica glasses (b) 3 w% Tb^{3+} doped silica glasses with excitation wavelength 340 nm.

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The d-spacing obtained from SAED pattern (as in Fig. 1(b)) can be assigned to (1 0 0), (1 1 0), (1 1 1), (3 0 0) lattice planes of cubic selenium (ICDD no. 38-0768) [11]. Also the d-spacing from HRTEM (3.09Å) closely matches with the values obtained from SAED pattern which corresponds to (1 0 0) plane.

Under UV excitation with corresponding 4f-4f transitions [14], multiple emission peaks are observed in visible range. Selenium doped glasses have a broad blue luminescence band with peak maximum at 421 nm (shown in Fig. 2(a)). For terbium doped samples, multiple emission bands occurs at 488 nm (blue), 543 nm (green), 584 nm (yellow) and 619 nm (red) wavelength. The dominant peak at 543 nm (as in Fig. 2(b)) can be assigned as magnetic dipole transition which lies in the green region. This can be attributed to $5D_4 \rightarrow 7F_6$, $5D_4 \rightarrow 7F_5$, $5D_4 \rightarrow 7F_4$, $5D_4 \rightarrow 7F_3$ transitions in Tb^{3+} ions. Se/RE doped glasses comprise of both emission peaks of selenium and trivalent terbium ion (as in Fig. 3) with enhanced emission intensities [15]. By the addition of dopants into the silica frame, cleavage of Si-O-Si bonds occur within the glassy matrix and led to the compositional modifications in the network [16]. As the excitation wavelength varies, no significant peak shift is observed in the room temperature photoluminescence spectra.

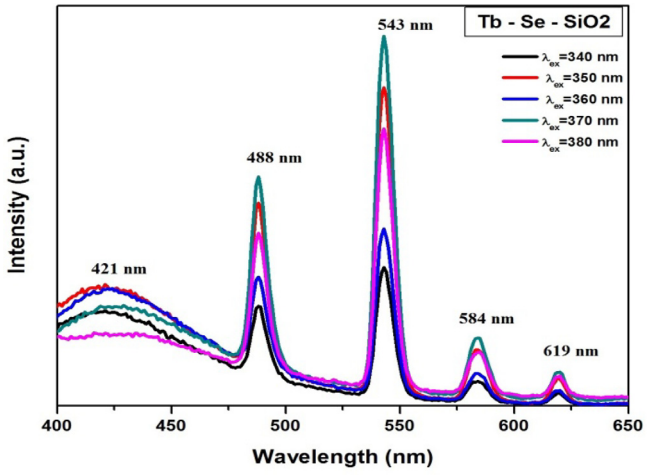

Fig. 3. The room temperature photoluminescence spectra of Se–Tb^{3+} doped silica glasses at different excitation wavelength.

Table 1
CIE indices, color region and B/G ratio obtained for the Se/RE doped glasses with excitation wavelength of 340–380 nm.

Sl. No.	λ_{ex} (nm)	CIE indices	Color region	B/G ratio
1	340	(0.20, 0.25)	Light blue	0.68
2	350	(0.21, 0.31)	Cyan	0.38
3	360	(0.20, 0.25)	Light blue	0.66
4	370	(0.23, 0.35)	Light green	0.27
5	380	(0.24, 0.36)	Light green	0.26

The color coordinates of bare Se (0.18, 0.21) and Tb (0.28, 0.46) glasses are marked in the Fig. 4(a) in blue and green region respectively. The gradual change in the CIE indices along with excitation wavelength is shown in Fig. 4(b). Thus the color emission can be altered from blue, blue-green and to green by adjusting the excitation wavelength (Table 1).

4. Conclusions

Se quantum dots are incorporated into Tb^{3+} doped transparent silica glasses via sol–gel route. HRTEM & SAED data confirms the crystallinity of selenium nanoparticles embedded within the amorphous glassy matrix. Luminescence properties of the obtained matrices are studied under UV/near UV light excitation. Selenium and terbium ions played the role of network modifiers within the matrices which led to the significant enhancement in the emission intensity. Emission spectra of the Se/RE silica matrices exhibit prominent emissions from both selenium nanoparticles and terbium ions. A study on multicolor emissions from Se/Tb silica glasses are done with the aid of CIE 1931 chromaticity diagram. Variation in blue to green intensity (B/G) ratio for Se/Tb glasses results in a remarkable change in the CIE indices that lies between the chromaticity points of bare Tb and Se glasses. The emitting color can be gradually altered from blue to green by the changing the excitation wavelength. The synthesized Se/RE doped glasses show excitation dependent color tunability and hence it can be applicable for artificial lighting systems, solid muticolor emitting matrices and high definition display systems.

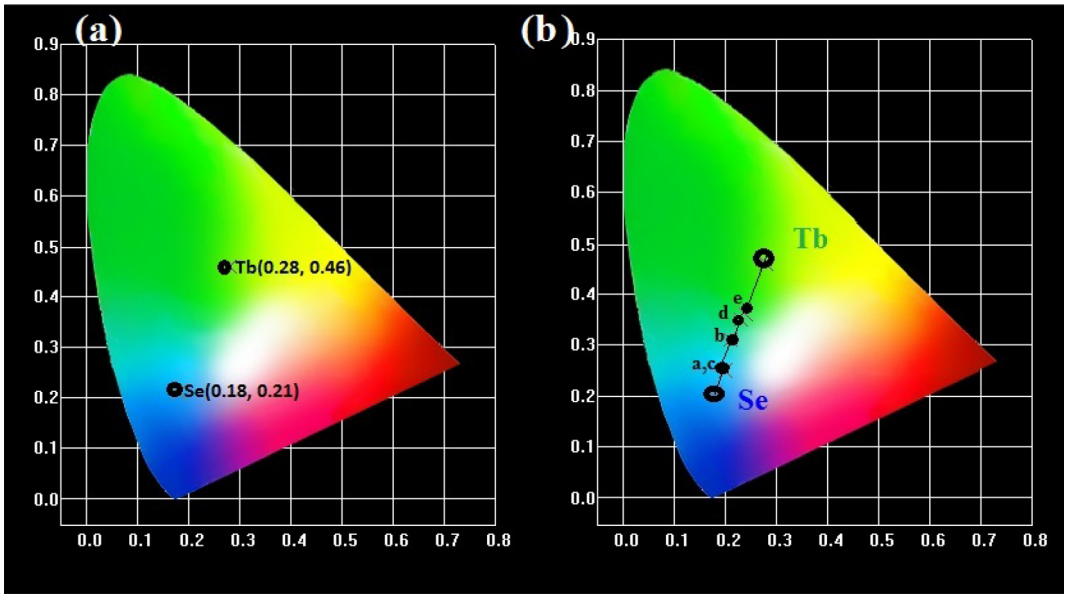

Fig. 4. CIE chromaticity diagram of (a) bare selenium and terbium doped silica glasses (b) Se/Tb doped silica glasses.

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CRediT authorship contribution statement

Tessy Paul: Conceptualization, Methodology, Writing - original draft, Investigation. **K. Anupama:** Formal analysis, Visualization. **P. O. Jibin:** Validation, Resources. **K.A. Ann Mary:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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