Volume 1 Issue 1 September 2023

REFLECTION

Journal home page: https://www.sdcjournal.in/index.php/reflection

Research Article

Plasmonic and Colorimetric Characteristics of Terbium ions in Sol-Gel derived Titanosilicate Glass

Athira Maria Johnson [1, 2], Greeshma Sara John [1, 2], Arjun Suresh. P[1, 2] & Arun Kumar K V[1, 2] *

[1]*Department of Physics, CMS College (Autonomous), Kottayam 686001, Kerala, India*

[2]*Nanotechnology and Advanced Materials Research Centre, CMS College (Autonomous), Kottayam 686001, Kerala, India.*

*Corresponding author (*E-mail address*: arunkumar@cmscollege.ac.in)

Received: 18/10/2022, Received in revised form: 22/03/2023, Accepted: 03/04/2023

Abstract

Terbium is one of the rare earth elements exhibiting emission in the visible range, which accounts for several optical applications. The effect of plasmonic nanoparticles of silver on the fluorescence enhancement of terbium ions doped titanosilicate matrix is investigated in the present work. The non-hydrolytic sol-gel method is used to synthesize Ag nanoparticles doped Tb^{3+}: $SiO_2 – TiO_2$. XRD does the structural characterisation, and TEM analysis confirms the presence of nanocrystals. FTIR spectroscopy is done to verify the matrix formation. Photoluminescence characteristic studies are performed to analyse the effect of silver nanoparticles in the fluorescence enhancement of the terbium ions, which is discussed as the consequence of the energy transfer phenomenon and localised surface plasmon resonance. Colorimetric characterisation confirms the colour-tunable capability of silver nanoparticles

Keywords: sol-gel, silver, color tunability, rare earth

1. Introduction

Rare earth ions comprise a class of elements potential enough to develop optical applications. They can be used as light emitters, optical fibres, tunable waveguides, sensors etc. [1]. The optical applications owed to the rare earth ions are due to the intra f-f transitions [2]. The rare earth ions incorporated with doubly doped solid matrices account for a tremendous increase in optical properties, specifically luminescent properties [3]. Research is being done to include both the rare earth ion and solid matrices to result in fluorescence enhancement [3]. Most of the rare earth ions have been employed as phosphor materials, of which an interesting and exciting rare earth employed in the present study is terbium, a key element in the fabrication of visible LEDs [2]. It holds important due to the strong and intense intra 4f transition in the visible range accounting for a very high intrinsic lifetime [2]. The low sensitivity of Tb ions to the non-radiative de-excitation process makes it capable of intense photoluminescence (PL) emission in lanthanides [2]. The host employed is a glass matrix owing to the advantages of low cost and easy fabrication [1]. They also account for the benefit of being the most reliable dense media for optoelectronic devices [1].

Introducing nanoparticles in rare earth ion doped glass matrix is an area of interest, as the plasmonic nanoparticle can enhance the fluorescence intensity [3]. This enhancement is a consequence of the energy transfer between the rare earth ion and the nanoparticle [3]. This effect could also be attributed to the localised surface plasmon resonance exhibited by the plasmonic nanoparticles. The f-f electronic dipole transitions are theoretically forbidden by the parity rule, which results in a weak absorption cross-section [4]. But the observed intensification in the fluorescence could be ascribed to the enhancement of the f-f absorption cross section by the plasmonic effect. Two primary reasons to utilise Plasmonic nanoparticles of silver are, one being the plasmonic effect owned by the metal nanoparticle and the energy transfer between the Ag ions to rare earth ions or the host defects [4]. The plasmon resonance exists due to the peculiar properties of metallic nanoparticles, such as the small size effect and quantum size effect [5]. An overlap of plasmon absorption band over the f-f absorption lines is expected to occur, thus responsible for the enhanced emission of rare earth ions [4].

Terbium ions are considered essential rare earth for green phosphors since they exhibit strong PL characteristics due to the intense $^5D_4$- $^7F_1$ transition [4]. This green emission could account for different applications, including display devices, biological probes, scintillators etc. [1]. Introducing metallic nanoparticles is the most effective method to control the quenching experienced in the luminescence spectrum of rare earth ions [1]. The silicate host experiences an enhancement in the luminescence spectrum, even though it tends to quench at higher concentrations of metallic nanoparticles due to the transfer of energy from rare earth ions to the metallic nanoparticle [1].

Various synthesis methods exist to incorporate metallic nanoparticles into a multicomponent glass composite, including the sol-gel method [3]. The sol-gel synthesis method dominates over other methods due to their advantages of high purity, increased homogeneity and low processing temperature [3]. Thus, this work emphasises the enhancement of luminescence properties of terbium-doped multicomponent titanosilicate glass matrix with the introduction of plasmonic nanoparticles of silver by the most economical and simple sol-gel method. Our studies give an insight into the colour tunability of the prepared sample, which could be attributed to the plasmon resonance effect of silver nanoparticles.

2. Experimental

2.1 Sample Preparation

The multicomponent titanosilicate glass matrix was synthesised by the non-hydrolytic sol-gel method [3]. Two precursors used were tetraethyl orthosilicate for SiO_2 and titanium isopropoxide for TiO_2, respectively [3]. The solvent employed was ethanol. The precursor used to introduce the dopants was terbium nitrate and silver nitrate. The catalyst used to enhance the reaction was 1 mol/L HNO_3. The gelation process experienced a longer time as H_2O/alkoxide ratio was maintained very low [3]. The alcoholysis process was done by ethanol, which produced water as a by-product [3].

Studies were done on the two prepared samples

Sample A: SiO_2-TiO_2 + Tb^{3+}

Sample B: SiO_2-TiO_2 + Tb^{3+} +Ag

The precursors were stirred on a magnetic stirrer with ethanol as the solvent. The dopants, such as terbium nitrate and silver nitrate, were stirred with ethanol separately and added to the final mixture to produce a homogenous mixture. The samples were prepared at room temperature. The final mixture was then transferred to clean polypropylene dishes and kept for drying under ambient conditions in a dark place to form a hard gel. The sample was then annealed at 750 ^{o}C to obtain the final product.

2.2 Characterisation techniques

Structural characterisation was done employing the XRD measurements. Matrix confirmation was done by FTIR analysis. A morphological study was carried out using a high-resolution transmission electron microscope. The emission study was done by doing the Photoluminescence measurements. Finally, the colorimetric calculation was done to obtain the CIE coordinates.

3. Results and Discussions

3.1 Structural Characterisation

The XRD measurements of the titanosilicate glass matrix doped with terbium and plasmonic nanoparticles of silver annealed at 750 ^{o}C are shown in figure 1. All the peaks are in agreement with the reference data. XRD result confirms the nanophase formation of TiO_2 and the presence of silver nanoparticles. Three prominent peaks are found in the pattern at 2θ ~ 25º, 38º and 75º corresponding to (1 0 1), (1 1 1) and (3 1 1), respectively. The characteristic peak of amorphous SiO_2 can be seen in the XRD diffraction pattern, which is broad and centred at 25º [3]. The broad peak represents the amorphous silica present in the matrix. The peaks at 25º, 48º, 54º, and 62º correspond to (1 0 1), (2 0 0), (2 1 1), (2 0 4) planes, which corresponds to the anatase TiO_2 (JCPDS file 21-1272) while the peaks at 38º, 44º, 75º corresponds to the plane (1 1 1), (2 0 0), (3 1 1) which are the characteristics peaks of silver (JCPDS file 04-0783) [6].

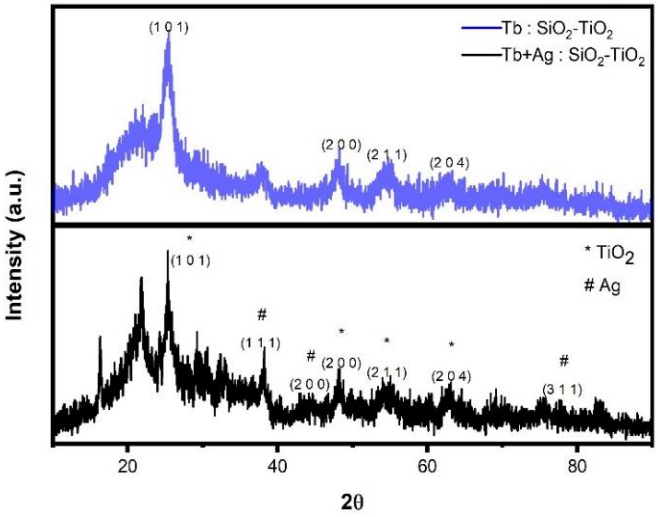

Figure. 1: XRD patterns of the sample with and without silver

Crystallite Size (t) is determined using the Debye-Scherrer Formula,

$$t = \frac{0.89\lambda}{\beta \cos\theta}$$

Where λ corresponds to the X-Ray wavelength used, β denotes the full width at half maximum (FWHM), θ is the corresponding angle of diffraction. The crystallite size is calculated as 17 nm.

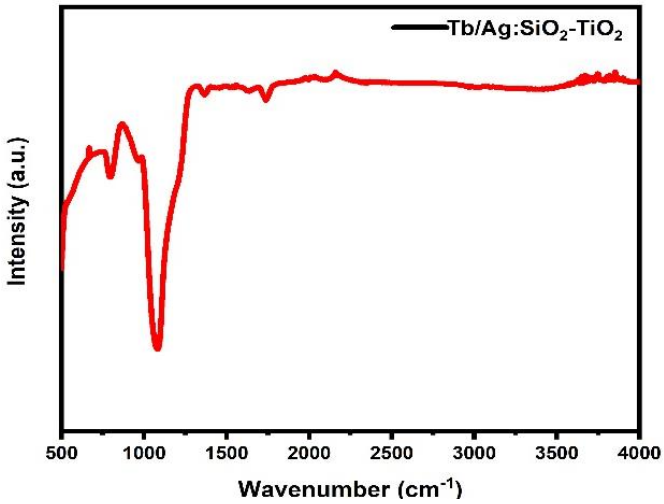

Figure. 2: FTIR Spectrum of the sample

The matrix confirmation was done using the FTIR spectroscopic studies. Figure 2 shows the FTIR spectrum of the sample. Peaks at 3500 cm^{-1} for room temperature sample correspond to water which vanishes for the annealed sample. The peak at 953 cm^{-1} corresponds to the Si-O-Ti bond, which confirms the formation of the titanosilicate matrix [7]. The peak at 1214 cm^{-1} is associated with asymmetric Si-O-Si stretching.

Si-O-Si symmetric stretching is responsible for the peak at 667 cm^{-1}. The peak at 519 cm^{-1} corresponds to Si-O bending vibration. The peak at 1416 cm^{-1} is associated with the Ti-O-Ti stretching vibration. The peak at 860-990 cm^{-1} is the typical range of SiO_2-TiO_2.

The morphological analysis, as well as the confirmation of the formation of silver nanoparticles, was done by the TEM analysis. TEM images of the annealed sample are given in figure 3. TEM images confirm the presence of silver nanoparticles seen as spherical particles [4].

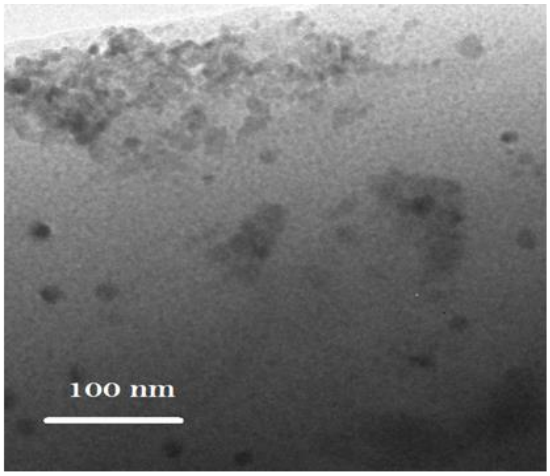

Figure. 3: TEM image of sample doped with silver

3.2 Optical studies

Photoluminescence (PL) is used to study photogenerated electron-hole pairs in semiconductors. Figure 4 shows the emission spectra of the prepared sample without and with plasmonic nanoparticles of silver annealed at 750°C, respectively, within the wavelength range of 400-700 nm. The characteristic peaks of terbium are obtained at 485 nm and 545 nm [4]. The transition corresponding to 545nm is $^5D_4$ - $^7F_5$, and the transition corresponding to 485 nm is $^5D_4$ - $^7F_6$ [5].

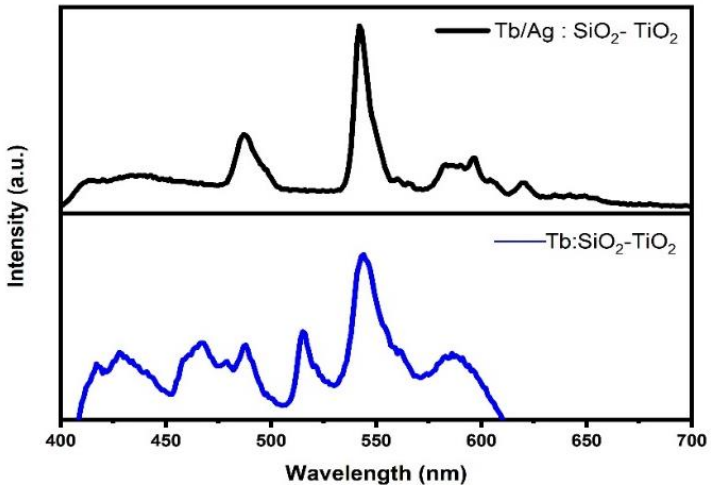

Figure. 4: Emission spectra of the sample with and without silver

The strongest peak is the one at 545 nm [5]. There is an enhancement in the emission intensity in the presence of silver nanoparticles, which could be attributed to the Local surface plasmon resonance [1,8]. This increase in intensity is a consequence of the energy transfer between silver nanoparticles and terbium ions [1,8], which, in turn, increases the electron density in the excited state of terbium ions [5]. Colorimetric analysis shows the colour tunability in the presence of the plasmonic nanoparticles of silver. The enhancement in the fluorescence intensity can be observed in the colorimetric analysis given in figure 5. The chromaticity coordinates in the CIE plot are shifted from (0.31, 0.35) to (0.31, 0.38) due to the presence of Ag nanoparticles. This shows the capability of Ag nanoparticles to tune the emission to a desired intensity.

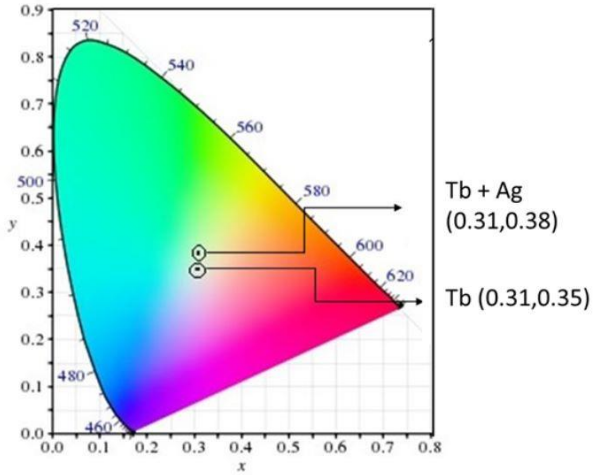

Figure. 5: CIE plot analysis of Ag/Tb^{3+} doped titanosilicate glass

4. Conclusion

The titanosilicate glass matrix doped with terbium ions and plasmonic nanoparticles of silver was synthesised successfully by the non-hydrolytic sol-gel technique. The obtained sample was then annealed at 750 ºC. The sample was characterised using techniques such as FTIR, XRD, TEM, UV-Vis studies, and PL analysis. XRD analysis confirms the presence of silver nanoparticles. The detected peaks of the silver nanoparticle in the XRD spectrum are in good symmetry with reference data. The size of silver nanoparticles is calculated by Debye–Scherrer equation and is found to be 17 nm. FTIR studies confirm the presence of the Si-O-Ti stretching bond, which confirms the formation of titanosilicate glass. The TEM analysis does further confirmation of the plasmonic nanoparticles of silver. The PL analysis shows a strong emission in the green region due to the presence of terbium ions which is colour tunable by the presence of the plasmonic nanoparticles of silver. It is a consequence of the interaction of terbium ions with silver nanoparticles. Thus, this work successfully depicts the effect of plasmonic nanoparticles in the colour tunability of the terbium doped titanosilicate glass.

References

1. Dousti M R, and Raja J A. Enhanced green emission of terbium-ions-doped phosphate glass embedding metallic nanoparticles. *Journal of Nanophotonics* **9** (2015) 093068.
2. Pivin J C., Gaponenko N V., Molchan I., Kudrawiec R., Misiewicz J, Bryja ., Thompson G E, and Skeldon P. Comparison of terbium photoluminescence from ion implanted and sol–gel-derived films. *Journal of alloys and compounds* **341** (2002) 272-274.
3. Kumar K V A, Revathy K P., Prathibha V, Sunil T, Biju P R., and Unnikrishnan N V. Structural and luminescence enhancement properties of Eu^{3+}/Ag nanocrystallites doped SiO_2-TiO_2 matrices. *Journal of Rare Earths* **31** (2013) 441-448.
4. Abbass A E, Hendrik C S, Elizabeth C, and Robin E K. Enhanced terbium emission due to plasmonic silver nanoparticles in bismuth silicate. *Journal of the American Ceramic Society* **99** (2016) 876-880.
5. Zhou D, Xuemei L, Ailing W, Jingjing L, Yanrong Q, Haibin C, and Yongliang Z. Fluorescence enhancement of Tb^{3+} complexes by adding silica-coated silver nanoparticles. *Science China Chemistry* **58** (2015) 979-985.
6. Kim Y H, Young S K, and Beong G J. Preparation and Characterisation of Ag-TiO_2 Core-Shell-Type Nanoparticles. *Journal of Industrial and Engineering Chemistry* **10** (2004) 739-744.
7. Fernandez T, Gijo J, Siby M, and Rejikumar P R. An ultra-low hydrolysis sol-gel route for titanosilicate xerogels and their characterisation. *Journal of sol-gel science and technology* **41** (2007) 163-168.
8. Alam Al-M, Kamruzaman M, Lee S H, Young H K, Hae J J, Yeoun S S, and Sung H K. Silver nanoparticles enhanced luminescence of terbium complex in solution for L-dopa determination. *Journal of Nanoscience and Nanotechnology* **12** (2012) 6005-6010.