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RESEARCH ARTICLE

Structural and Spectroscopic Studies of Sm^{3+} Ions Doped ZnS Nanoparticle in Silica Glass Matrix

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Abstract

Objective: This report intends to study the structural and spectroscopic properties of Sm^{3+} doped with ZnS nanoparticles in silica glass. **Methods:** The research adopted the sol-gel technique for preparing the sample. The physical property of the studied glass sample is examined by different characterization techniques such as Abbe refractometer, X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) and Photoluminescence (PL) spectroscopy. **Findings:** XRD studies confirmed the formation of glassy amorphous nature and TEM studies confirmed that the studied nanoparticles are polycrystalline in nature with a particle size lies between 10-50 nm after annealing at 300 °C. The PL spectra have three emission bands that correspond to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ correspondingly at 565 nm, 603 nm and 650 nm with most prominent bands in the orange-red region. **Novelty:** This research proves that the rare earth element can be successfully doped with semiconductor nanoparticle by using sol-gel technique in silica glass. Consequently, the doped glass can be utilised for producing nearly pure white hue when triggered at 370 nm.

Keywords: Samarium; ZnS; XRD; TEM; PL; CIE Chromaticity

1 Introduction

Silicate glasses are among the optical glasses that are inexpensive and have a strong optical transmission in the visible and near-infrared spectrum. Numerous researchers have recently focused on memory and switching devices for glasses, as well as improved insulators and dielectrics. Due to its superior physical and optical characteristics, outstanding chemical stability, low non-linear refractive index, and high durability, silica glass is typically a desirable host matrix for transition metal ions [(1)]. Silicon oxide (SiO_2) has been utilized as substrates for electronic displays, optical fibers, optical discs, dental and medical implants, and radiation shielding in order to attain mechanical quality [(2)]. Study of silica glass doped with rare earth (RE) have numerous applications as a result of their unique spectroscopic properties which is due to various transitions among the 4f energy states. Among the RE ions, Sm^{3+} doped silica glasses have been greatly studied due to its emission bands in the orange-red light region generated from the characteristic emissions $^4G_{5/2} \rightarrow$ ^{6}Hj (j = 5/2, 7/2, 9/2), they have frequently been used to create nanomaterials that can be used in a variety of fields, including color displays, high-density memory, and underwater communications.[3–5]. The $^4G_{5/2}$ emitting level of Sm^{3+} ions also exhibit significant quantum efficiency and is sort of the efficient lanthanide ions to anticipate fluorescence properties. As a result, hosts with high phonon energies (~1100 cm^{-1}), silicate glasses, have a low probability of experiencing nonradiative decay. Additionally, Sm^{3+} ions have a lot of emission peaks in the visible spectrum. Furthermore, compressed fiber lasers and planner wave guides are made of using Sm^{3+} ion-doped materials[6]. Due to the size dependent the photo physical properties can be varied as per requirement by changing the size, such as CdS, TiO_2, Al_2O_3, ZnS[7–10] that are implanted in a solid matrix have drawn a lot of attention in a variety of fields, including optics and biology. ZnS nanoparticle are interesting due to their novel electronic and optical properties originating from size quantization. ZnS is a wide gap II-VI compound semiconductor and is commercially used as phosphors in many devices[10]. It is observed that the energy exchange is more efficient in ZnS nanocrystals among the nanoparticles. Semiconductor doping is the requisite and successful approach for enhancing the structural, morphological, optical, luminescence, magnetic and photocatalytic properties, by which enlarging their applicability to various fields[10]. Among the $A_{II}B_{IV}$ group semiconductors, ZnS is a nontoxic semiconductor, which is of considerable interest as long as it has very wide band gap (Eg ~ 3.6 eV), high fluorescence efficiency, good stability, and good optoelectronics properties[10]. Recent years have seen considerable research on ZnS based semiconductor quantum dots making advances in the fields of electronics, optoelectronics, fundamental sciences and cutting-edge technologies[11]. RE ion doped ZnS are excellent lighting and display component candidates because they act as efficient luminescence centers. In the past, we have presented significant findings regarding semiconductor nanoparticles doped with rare earth ions in silica glass. Our investigation focused on the impact of semiconductor nanoparticles on PL spectra as a means of network modification. In this work, we have employed ZnS nanoparticles to examine alterations in structural and spectroscopic analyses. We have proved that the ZnS nanoparticle doped Sm^{3+} ions can be utilized for producing nearly pure white hue for optoelectronic applications.

2 Methodology

2.1 Chemicals

The following chemicals were purchased from Sigma-Aldrich: distilled water, tetraethyl orthosilicate (TEOS, 99.9%), zinc sulphide (99.9%), ethanol (99.9%), and samarium (III) nitrate hexahydrate (HNO_3). All chemicals and solvents were used directly without being further purified.

2.2 Preparation

The sol-gel process for the preparation of samples relies on the hydrolysis and condensation of tetraorthosilicate (TEOS) in the presence of H_2O to form the SiO_2 network[10] has been utilized for preparing ZnS (1 mol%) doped Sm^{3+} ions (2 mol %) in silica glass. In the presence of distilled water and HNO_3, TEOS is utilised as the primary precursor. In order to keep the molar ratios of TEOS, ethanol, water, and nitric acid at 1:4:4:0.00165, 0.00165 was added to this solution. For the preparation of ZnS nanoparticle, ZnS powder was first dissolved in ethanol, distilled water and HNO_3 and stirred for 2 hrs. To create sol, the mixture is now agitated for two hours. After a few days at room temperature, the sol is placed in a plastic container with a tight-fitting lid to form a hard gel. To create a solid glass sample, a few pinholes are made for evaporation and left for three weeks. Then the sample was transferred into muffle furnace for an hour at 900 °C respectively. Later, the prepared glasses were characterized for different measurement technique. All sample preparation and data recording were done at room temperature.

2.3 Sample Characterization

The glass sample under study was coated with 1-bromonaphthalene ($C_{10}H_7Br$) as an adhesive coating and its refractive index was determined using an Abbe refractometer. Using xylene (C_8H_{10}) as an immersion liquid, the density of the solid glass sample under study was calculated using the Archimedes principle. PL spectra of the glass samples were recorded using iHR320 imaging spectrometer using Syner JYTM software from Horiba Scientific by using excitation wavelength of diode laser, λ_{ex} = 450 nm. The crystal structure was analysed using X-ray Diffractometer (Panalytical Empyrean) equipped with a Cu-Kα radiation source. Additionally, using FEI Tecnai high-resolution transmission electron microscopy (HR-TEM) with a 300 kV acceleration voltage, the particulate nanostructure patterns of the nano-composites were investigated

3 Results and Discussions

3.1 XRD Study

Figure 1 shows the XRD spectra of Sm^{3+} doped ZnS nanoparticle in silica glass matrix annealed at 300 °C. It is observed that the distinct broad hollow peak is formed rather than intense crystalline peaks which established the glassy amorphous nature of the glass sample. The intense peak at $2\theta = 23°$ is attributed to the amorphous nature of silica glass. ZnS nanoparticle shows trigonal structure even at room temperature[12] while doped sample only shows amorphous nature even when the annealing temperature is 300 °C. For doped sample from 500 °C onward crystalline peaks can be seen which was reported in our previous result[10].

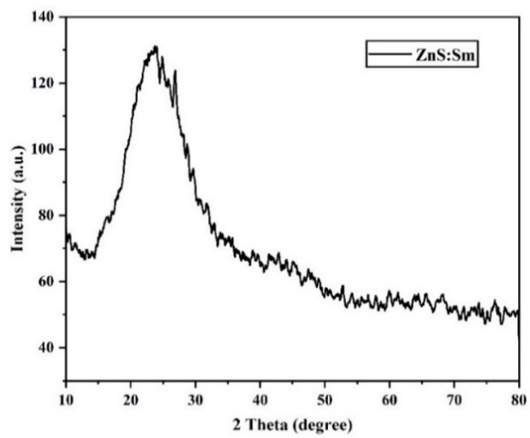

Fig 1. XRD spectra of Sm doped ZnS nanoparticle annealed at 300 ° C

3.2 TEM Study

The TEM micrograph of the studied doped sample was recorded to study the presence of Sm as well as the confirmation of ZnS in doped SiO_2 matrix as shown in Figure 2(**a**-**b**). It is feasible to state that the range of particle sizes after annealing at 300°C is between 10 and 50 nm by studied through Image J software. The investigated ZnS nanoparticles are polycrystalline in nature as shown by the SAED image which displays a set of ring structures as depicted in Figure 2 (**b**).

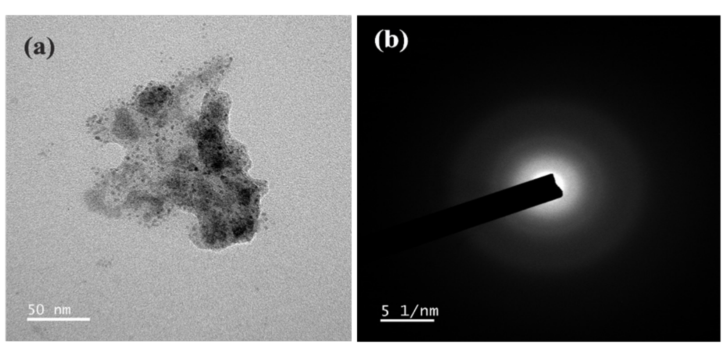

Fig 2. (a) TEM image of Sm^{3+} doped ZnS nanoparticle in silica glass matrix (b) Selected Area Electron Diffraction image

3.3 Physical properties

The density of Sm^{3+} ions doped with a fixed amount of ZnS nanoparticle (1 mol %) in silica glass matrix was determined by using Archimedes principle where the sample was immersed in xylene. The refractive index was measured by Abbe's refractometer. These two measured values are used for calculating another physical property such as Average molecular weight (M_T), Ion's concentration (N_i), Dielectric constant (ε_d), Optical dielectric constant (ε_d-1), Molar volume (V_m), Reflection Losses (R_L), Molar Refractivity (R_M), Energy gap (E_g), Polaron Radius (R_p), Interionic distance (R_i), Field strength (F_s), Molar polarizability (α_m) and Metallization Criterion (M_c) by using appropriate expressions[13] and represented in Table 1. The non-linear dynamics of the materials are determined by the sample's electronic polarizability. Exposure to intense light causes the material to exhibit electronic polarizability. Volt Lorentz-Lorentz theory[14,15] are utilised for deriving electronic polarizability (α_e) as follows

$$\frac{(n^2-1)}{(n^2+1)}V_m = \frac{4}{3\pi}N\alpha_e \tag{1}$$

where n is refractive index, V_m is molar volume and N is Avogadro's number.

Table 1. Various physical properties of Sm^{3+} ions doped with a fixed amount of ZnS nanoparticle

Physical properties	Sm (2.0 %)
Refractive index (ni)	2.353
Density (ρ) (g/cm^3)	2.203
Thickness (Zt)	0.171
Average molecular weight M_T (g)	68.14
Ion's concentration (Ni x 10^{20})	3.89
Dielectric constant (ε_d)	5.54
Optical dielectric constant (ε_d-1)	4.54
Molar volume (V_m) (cm^3/mol)	30.93
Reflection Losses (R_L)	0.163
Molar Refractivity (R_M)	21.47
Energy gap (E_g)	1.86
Polaron Radius (R_p x 10^{-8}) (cm^{-3})	2.23
Interionic distance (R_i x 10^{-7}) (cm^{-3})	0.856
Electronic polarizability (α_e x 10^{21})	2.38
Field strength (F_s x 10^{13})	34.4
Molar polarizability (α_m)	8.52
Metallization Criterion (M_c)	0.306

3.4 PL Spectra

The PL spectra of Sm^{3+} ions doped with a fixed amount of ZnS (1 mol %) nanoparticle in silica glass matrix prepared by sol-gel technique annealed at 900 °C is shown in Figure 3. The PL spectra have three emission bands that correspond to $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ correspondingly at 565 nm, 603 nm and 650 nm. The luminous band's peak at 650 nm being the most prominent. The most prominent emission peaks were observed in the green and orange-red region. All assignments of transition bands are done with lanthanide spectra transition reported by Dieke[16] and Carnal et al.[17]. The peak at 565 nm results from transition between a magnetic field ($\Delta J = 0$ and ± 1) and an electric field ($\Delta J = \pm 2$). The peak observed at 603 nm satisfies the selection rule for magnetic dipole transition, it is ascribed to the transitions between partially electric and partially magnetic dipoles, with the electric dipole transition being more prevalent, while the peak at 650 nm results from an electric dipole transition.

3.5 CIE Chromaticity

Examining the color coordinates shown on a traditional chromaticity diagram is necessary to determine the actual nature of the material's color emissions. A tool for measuring the tunability of the emission wavelength and the intensity variation in the

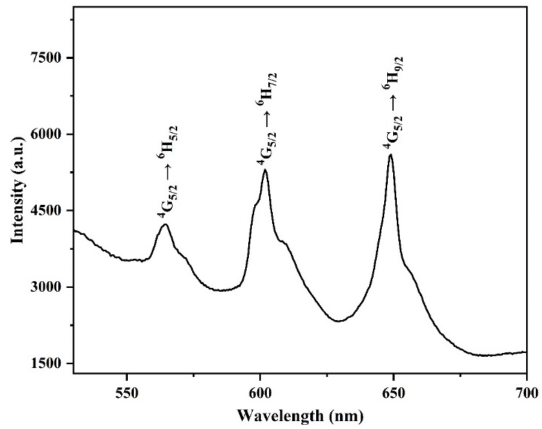

Fig 3. PL Spectra of Sm^{3+} ions doped with a fixed concentration of ZnS nanoparticle in silica glass matrix

emission band is the CIE 1931 (Commission International d'Eclairage) diagram. It is a universal method of representing every color by combining three primary colours. Figure 4 shows the CIE Chromaticity diagrams of ZnS doped Sm^{3+} ions in silica glass matrix. This diagram demonstrated that the studied samples emit a nearly pure white hue when triggered at 370 nm. The following equations are used to derive the chromaticity coordinates from the tri-stimulus values [12].

$$x = \frac{X}{X+Y+Z} \quad (2)$$

$$y = \frac{Y}{X+Y+Z} \quad (3)$$

$$z = \frac{Z}{X+Y+Z} = 1 - x - y \quad (4)$$

It is also possible to compute the phosphors' correlated colour temperature (CCT) to see if they are suitable for use as a practical white light source. The colour appearance of the light output by a light source is specified by its CCT (in Kelvin), which compares the colour of the light to that of a reference light source at a particular temperature. The CCT value, a measurement of the overall warmth or coolness of the look, is useful when designing illuminating devices [18]. Using the McCamy empirical formula, the relevant CCT values can be determined from the CIE chromaticity coordinates [19]

$$CCT = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (5)$$

Where, $n = (x - x_c)\ (y - y_c)$ is the inverse slop line and $x_c = 0.3320$ and $y_c = 0.1858$ is the epicentre of the chromaticity coordinates. The colour coordinates for the studied glass sample were x= 0.297 and y= 0.333 which falls within the white light region and the corresponding CCT value was 7358 K. Generally, CCT values less than 5000 K imply warm white light used for home appliances while those above 5000 K suggest cool white light utilised for commercial lighting purposes [20]. The result indicates that the studied glass sample are quite suitable for making nearly pure white hue light source for commercial lighting purpose.

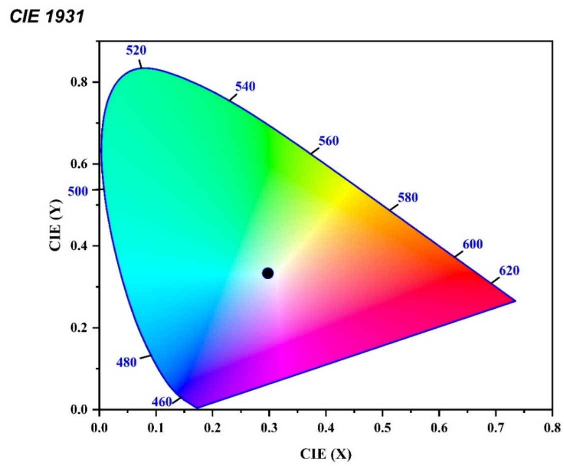

Fig 4. CIE Chromaticity of Sm^{3+} ions doped fixed concentration of ZnS nanoparticle in silica glass matrix

4 Conclusions

Sm^{3+} ions doped with a fixed amount of ZnS (1 mol %) nanoparticle in silica glass matrix have been synthesized successfully using a sol-gel technique. Therefore, sol-gel methods are recommended for synthesizing the glass sample since it is a very low-cost method compared to other technique. The density, refractive index and various physical properties were calculated. SAED studies confirmed the development of hexagonal polycrystalline structure, while XRD studies the formation of amorphous nature. TEM image confirmed that the particles size varies from 10 to 50 nm. The PL spectra have three emission bands that correspond to ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$, ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ and ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ correspondingly at 565 nm, 603 nm and 650 nm with most prominent bands in the green and orange-red region. The examined glass can produce a nearly pure white hue when triggered at 370 nm, according to the CIE color chromaticity and CCT measurements.

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