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Photoluminescence Characteristics of Ag:Sm^{3+} Co-doped PVA Composites Synthesized by Chemical Reduction Method

Films of silver-samarium (Ag-Sm^{+3}) co-doped in PVA have been synthesized via chemical method. Silver nanoparticles have been synthesized at a specific consternation and redaction period via chemical reduction method, while samarium nitrate ($SmCl_3.6H_2O$) solutions as a source of Sm^{+3} ions. Photoluminescence (PL), Fourier-transform infrared (FTIR), UV-visible spectroscopy, and x-ray diffraction (XRD) have all been used to analyze the doped matrices as a function of Sm^{+3} ion concentration. The structural behavior of Sm^{+3} ions and silver nanoparticles has been investigated and showed randomly dispersed in the PVA network structure. The spectral diagnosis of synthesized samples demonstrated green, orange and red emission bands and these transitions arising from $^4G_{5/2} \rightarrow {}^6H_J$ on 400 nm excitation. The influence of Ag co-doping has been clearly observed on the photoluminescence of Sm^{+3} ions compared with the case of without Ag co-doped, resulting from the surface plasmon resonance (SPR) of Silver nanoparticles (Ag NPs). The CIE chromaticity diagram has been used to recognize the luminescence colors of film samples.

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1. Introduction

Lanthanide ions are commonly used as dopants for the active media of solid-state lasers because they seem to have an abundance in fluorescence emission lines that cover all ranges of visible and near-infrared (NIR) regions of the electromagnetic spectrum [1]. Recent studies have highlighted significant interest in the distinctive optical properties of lanthanides (Ln^{3+}), including their exceptional color purity, extended excited-state lifetimes, minimal disturbance of excited states by the crystal field environment, and straightforward spectral conversion of wavelengths through up conversion and down conversion processes. [2,3]. Ln^{3+}-doped materials display distinctive optical properties stemming from intra 4f→4f transitions, making them particularly intriguing. Although these transitions are prohibited by the Laporte rule, Ln^{3+} luminescence remains detectable [4,5]. Functional materials containing Ln ions have potential for use in the fabrication of displays, light-emitting diode (LED) phosphors, and white light sources [6]. Observations indicate that the interaction of rare earth ions with noble metals, like silver (Ag) or gold (Au), in different glasses has demonstrated effectiveness in enhancing the photoluminescence of lanthanide ions within these materials [7]. The enhanced photoluminescence (PL) performance can be linked to the nanoparticles' localized surface plasmon resonance (SPR) effect, which exhibit absorption at approximately 420 nm [8]. This optical phenomenon is defined by a collective excitation of conduction band electrons, leading to increased electromagnetic fields near the silver nanoparticles. This process enhances the excitation efficiency and radiative decay rate, leading to an increased absorption coefficient of the rare earth (RE) ions. Different viewpoints have clarified the reasoning for this improvement in photoluminescence by citing traditional energy transfer from very small non-plasmonic silver particles that resemble molecules or isolated silver (Ag^+) ions to the rare earth (RE) ions [9,10].

Polymeric materials have attracted considerable attention in various scientific and technological fields, as they can be customized to meet specific requirements across a wide range of applications, owing to their lightweight nature, impressive mechanical strength, and favorable optical characteristics. Poly (vinyl alcohol) (PVA) stands out as a significant polymeric material, owing to its diverse industrial applications and comparatively low production costs. This material operates effectively as a solid electrolyte polymer when doped with phosphoric acid, making it appropriate for application in solid-state photovoltaic displays (ECDs) and solid-state photovoltaic cells, or as a static stabilizer in the formulation of conductive polymer dispersions. A notable feature of semicrystalline PVA is the presence of both crystalline and amorphous regions, as well as the physical properties that emerge from the interactions at the crystalline-amorphous interface. In recent years, doped polymers have garnered significant attention due to their unique physical and chemical properties, which render them advantageous for particular applications [11,12].

This study focuses on the spectroscopic behavior of samarium ions (Sm^{3+}) within an Ag^+-Sm^{3+} co-doped polymer structure matrix. The aim is to explore how the

surface plasmon resonance of Ag NPs influences the photoluminescence properties of these active ions.

2. Experimental Work

First, a chemical reduction method has been employed to synthesize silver nanoparticles (Ag NPs) with specific characteristics. Silver nitrate ($AgNO_3$, supplied by Kandel, Germany) has been used as a precursor and Sodium citrate tribasic dehydrate ($C_6H_5Na_3O_7.2H_2O$, supplied by Sigma-Aldrich) as a reducing agent. A 25mL of $AgNO_3$ solution has been added to 100 mL of H_2O. A solution of 1% sodium citrate (0.5 g in 50 mL of H_2O) has been prepared, then heating 125 mL solution of $AgNO_3$ until it reaches a boiling point of 97°C. A 2.5 mL of a 1% sodium citrate solution is added drop by drop within the boiling step. The colour of colloids is changed to pale yellow and this gives primary evidence of silver nanoparticles (Ag NPs) formation. The reaction mechanism can be articulated in the following manner [13]

$$4Ag^{+} + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^{0} + C_6H_5O_7H_3 + 3Na + H + O_2\uparrow$$

The Ag colloids were synthesized at a specific concentration of 5×10^{-3} mol/L and a reduction period of 5 minutes that gives particle size, averaging between 20.40 to 31.52 nm [14].

Samarium chloride hexahydrate ($SmCl_3.6H_2O$, 99.9% from Aldrich) is used as a source of Sm^{+3} ions. $SmCl_3.6H_2O$ solutions have been prepared at different concentrations (1.5, 0.55, 0.25, 0.1, 0.05 $\times10^{-1}$ mol/L) by dissolving a specific weight of this salt in a specific volume of deionized water and kept the final solution under magnetic stirrer for 30 minute in order to obtain a homogenous solution.

The film samples were prepared utilizing PVA with a molecular weight of 10000 g/mol (BDH Chemicals, England) as the main polymeric material for this study. PVA films solution were synthesized using exact amounts of $AgNO_3$ and $SmCl_3.6H_2O$ as dopants via the solution casting technique. 1.5 g of PVA powder was added into 10 mL of distilled water and let to swell for a duration of 24 hours at ambient temperature. 2 mL of both silver (Ag) colloids and $SmCl_3.6H_2O$ solution were added to the polymeric solution with ensuring continuous stirring was maintained during the entire process. The final solution was meticulously dispensed into flat glass plate dishes. The procedure was conducted multiple times using varying concentrations of samarium solutions. Homogenous films were achieved following a 36-hours drying period in an air oven at 40°C as illustrated in Fig. (1). The films thicknesses were measured to be in the range of 25±5μm.

3. Results and Discussion

Figure (2) illustrates the x-ray diffraction (XRD) pattern (XRD) of Ag^{+}-Sm^{3+} co-doped PVA, acquired using a PHILIPS micro X-ray Diffractometer operating at PW1730. A distinct diffraction peak is noted at 2θ=20.25°, attributed to the semi-crystalline characteristics of the PVA polymer, resulting from robust intermolecular interactions among the PVA chains facilitated by hydrogen bonding between the molecules [15,16]. The crystallization of silver nanoparticles (Ag NPs) has been revealed and it has been proven through the peak at 2θ = 37.9°, and will be compared according to ASTM standards [17].

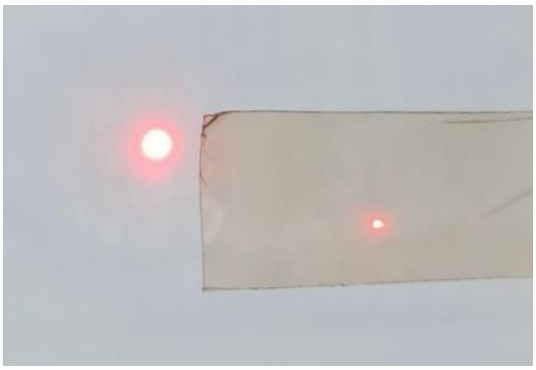

Fig. (1) Photograph of one of Ag-Sm^{3+} co-doped PVA film prepared at 0.117% Sm^{3+} concentration and after 36 hour drying an oven at 45°C

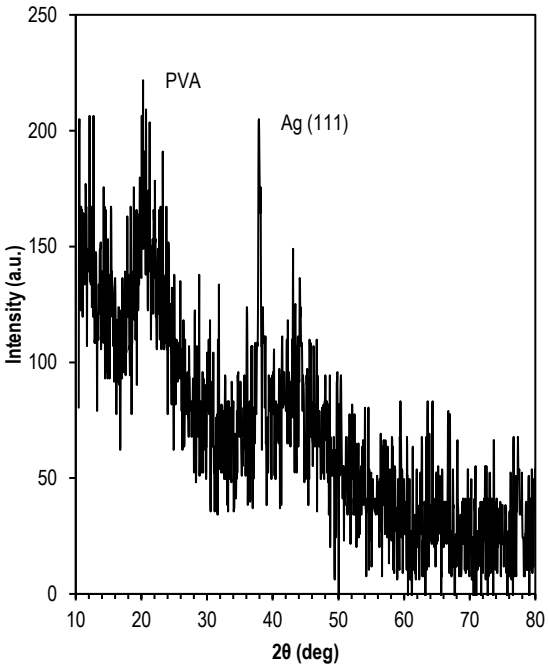

Fig. (2) XRD pattern of the optimum prepared Ag^{+}-Sm^{3+} co-doped PVA film

The FTIR spectra were recorded using a Shimadzu FTIR spectrometer on KBr pellets of pure PVA and Ag^{+}-Sm^{3+} co-doped PVA film samples to characterize

their functional groups, as illustrated in Fig. (3). The stretching vibrations start from the O-H bonding which is observed at around 3300 cm^{-1}. On the other side the bands observed at approximately 2915, 1700, and 1085 cm^{-1} were attributed to C-H, C=C, and C-O, respectively [16]. In addition, vibration bands of silver nanoparticles (Ag NPs) can arise at about 1322 and 1642 cm^{-1} [18]. These results give primarily indication that the silver nanoparticles (Ag NPs) and Sm^{3+} ions do not form any ligands in the PVA network structure, but rather than it may tend to be positioned at interstitial sites within the structure.

Figure (4) illustrates the absorption spectra, obtained using a Centra 5 UV-VIS spectrometer; GBC Scientific Equipment Pty Ltd., of the prepared $SmCl_3.6H_2O$ solution samples at different molar concentrations. It can be observed many absorption bands located at about 305 and 317, 332, 344, 362, 374, 390, 401, 415, 441, 463, 479 and 499 nm which are associated with the transitions $^6H_{5/2}\rightarrow{}^3H^{9/2}$, $^4F_{11/2}$, $^4D_{7/2}$, $^3H_{7/2}$, $^4F_{9/2}$, $^4D_{5/2}$, $^6P^{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4I_{11/2}$, $^4G_{7/2}$, respectively [19]. These transitions give principle evidence about the spectroscopic activity of Sm^{3+} ions. The absorbance increases with concentration, as described by the Beer-Lambert law.

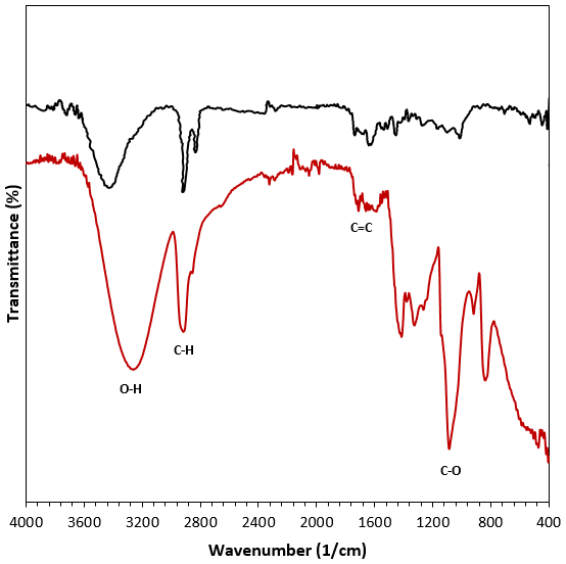

Fig. (3) FTIR spectra of pure PVA and Ag+Sm^{3+} co-doped PVA film samples

The positions of the absorption bands in Sm-doped PVA films are similar to that of $SmCl_3.6H_2O$ solutions as shown in Fig. (5), indicating the presence of Sm^{3+} ions within the polymer structure. Also, the absorbance increased as the Sm^{3+} ions concentration increases the photoluminescence spectra of Sm-doped PVA films at different Sm^{3+} ions concentrations are clarified in Fig. (5) and it performed using the 400 nm excitation wavelength using Fluoro Mate FS-2 Spectrometer. The emission bands observed at 532, 582, and 654 nm correspond to the intra-4f transitions of Sm^{3+} from excited levels to lower levels, specifically the transitions $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$, respectively [17]. It can be clearly observed that the emission intensity is increased with the concentrations at the low doping levels (0.117-0.017%) and this corresponding increases can be attributed to the increase of absorbance, i.e., increase the concentration of excited ions. While the emission intensity decreased at the high doping levels (0.412-0.391%) that are due to concentration quenching and the tendency of these ions to clusters and subsequently non-radiative relaxations.

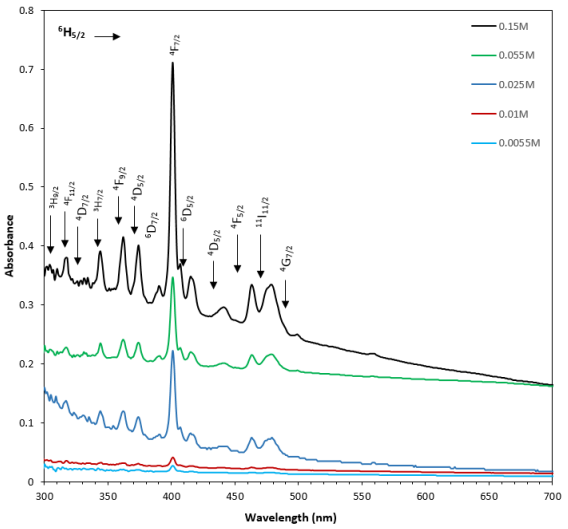

Fig. (4) Absorption spectra at different concentrations of the samarium chloride hexahydrate in the deionized water

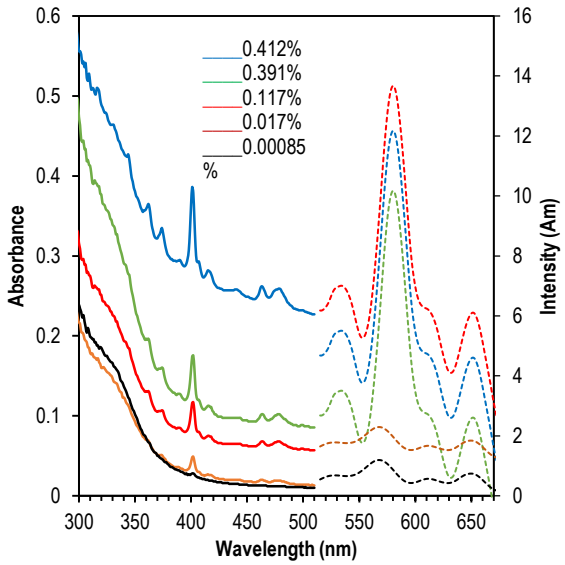

Fig. (5) Absorption and photoluminescence spectra of different concentrations Sm^{3+} doped PVA, excited by 400 nm

Figure (6) illustrates the absorption spectra of Ag-Sm^{3+} co-doped PVA films at all concentrations of Sm^{3+} ions. The surface plasmon resonance (SPR) band of silver nanoparticles (Ag NPs) was noted at 420 nm,

with additional absorption bands associated with 4f–4f transitions in the configuration of Sm^{3+} ions. Theses spectra show clearly the spectroscopic activity of Sm^{+3} ions and silver nanoparticles (Ag NPs) within the structure of polymer films. It is also clear that the range of prepared concentrations of active Sm ions led to an increase in absorbance as the concentration increases without reaching the saturation limit.

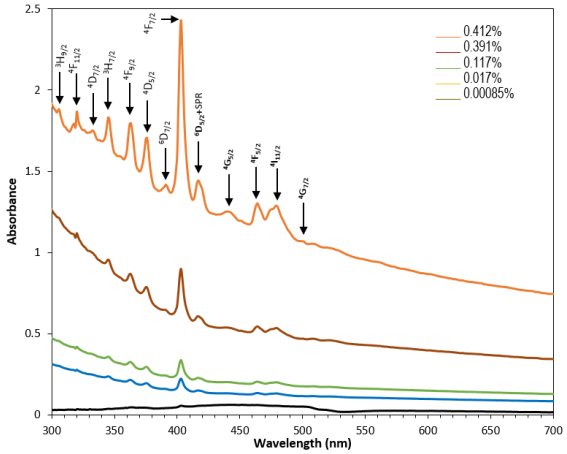

Fig. (6) Absorption spectra of Ag-Sm^{3+} co-doped PVA polymer films at different concentrations of Sm^{3+} ions

The photoluminescence (PL) spectra of Ag^{+}-Sm^{3+} co-doped PVA films were obtained as a function of Sm^{3+} concentrations, as shown in Fig. (7). Three emission bands are distinctly observed at approximately 525, 610, and 663 nm, corresponding to the transitions $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (in the green region), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (in the orange region), and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (in the red region). It can be also recognized a concentration quenching of the emission bands for high doping levels of Sm^{3+} ions, while the PL intensity increases with increasing the concentrations up to 0.391%. On the other side, silver nanoparticles (Ag NPs) as a co-dopant enhanced the photoluminescence (PL) properties in which, for optimum concentration (0.391%), the full-width at half maximum (FWHM) of the mentioned transitions (525, 610, and 663 nm) are reduced to 35, 33.5, 25 nm compared with the corresponding values (39.7, 44.8, 28 nm) of Sm^{3+}-doped PVA films. The decrease in FWHM correlates with the rise in PL intensity and can be linked to the local field effect (LFE), stemming from the surface Plasmon resonance (SPR) of silver nanoparticles (Ag NPs) in the Ag^{+}-Sm^{3+} co-doped PVA [19,20]. In summary, incorporating silver (Ag) will enhance the emissivity, thereby increasing the potential for achieving white light.

In order to enhance this possibility, the experimental results of photoluminescence (PL) spectra of co-doped samples are combined into the specification of the CIE 1931 chromaticity diagram in order to determine all light colors in an x, y coordinate system. The inset of Fig. (7) illustrates the chromaticity coordinates of one of Ag-Sm^{3+} co-doped PVA film at -0.391% of Sm. The emitted light appears white, as the coordinates fall within the white range (0.353, 0.340) on the chromaticity chart, with pure white light coordinates being (0.333, 0.333).

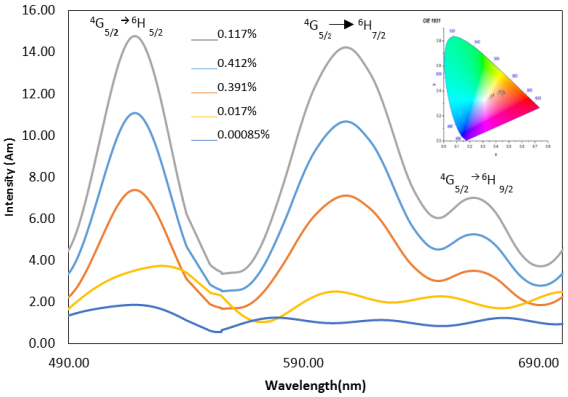

Fig. (7) Photoluminescence (PL) spectra of PVA polymer films co-doped with Ag^{+}-Sm^{3+} ions excited by 400 nm

4. Conclusions

Poly (vinyl alcohol) (PVA) has demonstrated its effectiveness as an organic host material for active ions like Sm^{3+} ions and silver nanoparticles, displaying various advantageous characteristics including high transparency and thermal stability. The structural behavior of Sm^{3+} ions and silver nanoparticles within this host is characterized by random dispersion. The spectroscopic activity of Sm^{3+} ions doped polymer films is clearly evident, showing luminescence quenching at higher doping concentrations. Additionally, the influence of the SPR of silver nanoparticles shows an enhancement in the photoluminescence properties. The analysis of photoluminescence spectra and the CIE 1931 chromaticity diagram suggest that a suitable mixture of color emissions is generated from Ag-Sm^{3+} co-doped PVA films, indicating their potential use as white light emitting media.

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