Preparation and Photoluminescence Characteristics of Samarium Ions Imbedded in Poly(Vinyl-Alcohol) Films

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Abstract
Films of samarium (Sm^{3+})-doped polyvinyl alcohol (PVA) have been synthesized via chemical method, starting from samarium nitrate ($SmCl_3.6H_2O$) solutions as a source of Sm^{3+} ions. Photoluminescence (PL) and UV-visible spectroscopy were used to investigate the spectroscopic activity of Sm^{3+} ions doping in PVA. Prominent emission bands of Sm^{3+}-doped PVA have been observed for the transitions $4G_{5/2}\rightarrow 6H_{5/2}$, $4G_{5/2}\rightarrow 6H_{7/2}$ and $4G_{5/2}\rightarrow 6H_{9/2}$ at 532, 582 and 654nm, respectively, using 400nm radiation source for excitation.

Keywords: Photoluminescence; Lanthanide ions; Spectroscopy; Chemical reduction
Received: 01 January 2025; **Revised:** 02 February 2025; **Accepted:** 09 February 2025; **Published:** 1 April 2025

1. Introduction

Modern society has come to rely on the incredible technological utility of lanthanide elements [1], they are renowned for their unique electronic properties and widespread applications in various fields of science and technology [2]. Lanthanide ions possess similar chemical characteristics, making them challenging to separate and distinguish from one another [3]. However, their distinctive electronic configurations and remarkable magnetic, optical, and luminescent properties set them apart from other elements. These characteristics make lanthanide ions indispensable in numerous industrial and scientific applications, including catalysis, electronics, optics, and medicine [4,5]. They provide the basis for many clean energy technologies. Lanthanide elements are not only ubiquitous in modern society; they will be of great importance in achieving a sustainable and carbon-free global energy supply. They make modern technologies perform their work with weight emissions, and less energy consumption. In other words, they make them more efficient, smaller, faster, more bearable and thermally stable. Products and technologies powered by these elements and their advantages help in global economic growth and the improvement of the standard of living [6-8].

Polymers are big macromolecules composed of repeating structural devices referred to as monomers that are covalently bonded. They are categorized into natural polymers and artificial polymers. Polymers show off numerous bodily and chemical properties, which make them important in diverse industries, consisting of medicine, electronics, construction, and packaging [9,10]. PVA, additionally termed polyethene, is the most often utilized as a polymer as an adhesive product and in manufacturing various polymers. PVA is an inexpensive and easily accessible polymer that comes in white powder form and he is a synthetic biodegradable thermoplastic polymer that is safe and useful in a variety of industries, including resins, medicine, construction, packaging, and more [11,12].

In this study, the chemical method was employed to embed Sm^{3+} ions in PVA films as hosts for severe emissions withinside the seen area so as to analyze the outcomes of ion concentrations on the luminescence properties.

2. Experimental Work

Sm^{3+}-doped PVA films were prepared using samarium chloride hexahydrate ($SmCl_3.6H_2O$, 99.9% from Aldrich) as a source of Sm^{3+} ions. A different concentration of Sm^{3+} solution was prepared by dissolving 1.5, 0.55, 0.25, 0.1, or 0.05×10^{-1} mol/l of $SmCl_3.6(H_2O)$ solution in deionized water and leaving it for 30 min on a magnetic stirrer to obtain homogenous solutions.

Using a chemical reaction, the PVA film samples were prepared with a molecular weight of 10000 g/mol (BDH Chemicals, England); a 1.5 g of PVA was dissolved in 10 mL of distilled water and left on a magnetic stirrer for 24 hours at ambient temperature. $SmCl_3.6H_2O$ solutions were added to the polymer mixture in a ratio of 2:4 and left on a magnetic stirrer for 30 min to get final homogeneous solution, then poured into a plastic Petri dish and left for 36 hours to dry in an air oven at a temperature of 45°C. Figure (1) illustrates a prepared sample of Sm^{3+}- doped PVA film.

3. Results and Discussion

In Fig. (2), the absorption and transmission spectra of PVA film are shown. It can be shown that there is a high transparency of up to 89% and also no spectral activity in the spectral range of 400-800 nm. This high transparency is assumed to be a suitable property for the PVA films as a host matrix for lanthanide ions. Because of its semicrystalline structure and strong intermolecular interaction between PVA chains via intermolecular hydrogen connections, the XRD pattern of synthesized pure PVA (Fig. 3) displays high peaks at about 2θ = 19.49° and 40.47°, which may result in a partial ordering of the polymer chains [13,14].

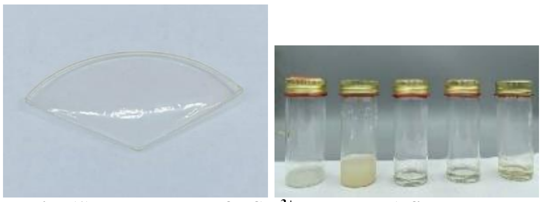

Fig. (1) Photograph of a Sm^{3+}-doped PVA film sample prepared at 0.117% and Sm in water solutions at different concentrations

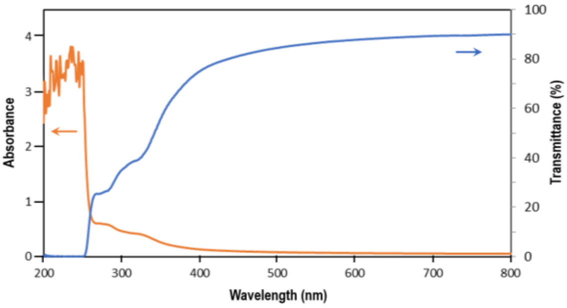

Fig. (2) Absorption and transmission spectra for pure PVA polymer prepared with a weight of 1.5 g PVA and 10 ml of deionized water

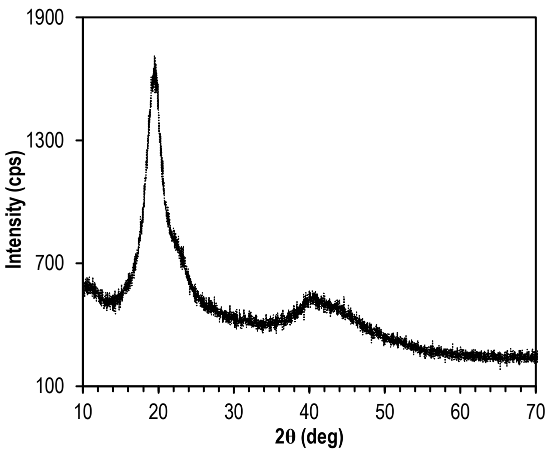

Fig. (3) XRD pattern of pure PVA sample

A Shimadzu UV-visible spectrophotometer was used to record the UV-visible absorption spectra of Sm^{3+} ions in deionized water solutions, as shown in Fig. (4). It can be observed that there are thirteen absorption bands of Sm^{3+} in $SmCl_3.6H_2O$ solution caused by electronic transitions of energy level 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 $^6H_{5/2}\rightarrow{}^3H_{9/2}$, $^4F_{11/2}$, $^4D_{7/2}$, $^3H_{7/2}$, $^4F_{9/2}$, $^4D_{5/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4I_{11/2}$, and $^4G_{7/2}$, respectively [15]. These transitions give principal evidence about the spectroscopic activity of Sm^{3+} ions. The absorbance increases with concentration, as described by the Beer-Lambert law.

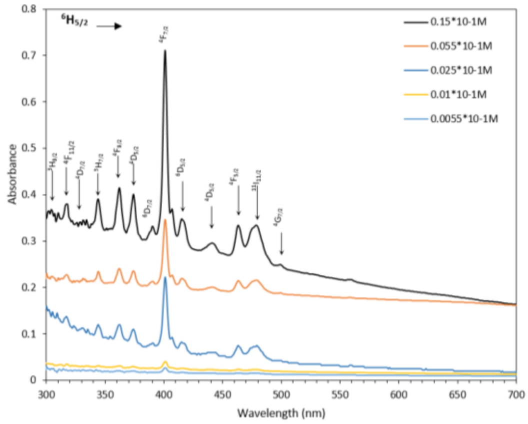

Fig. (4) The absorption spectra at different concentrations of the samarium chloride hexahydrate in the deionized water

Figure (5) illustrates the emission spectra of $SmCl_3.6H_2O$ solution using FluoroMate FS-2 spectrometer using the 400nm excitation wavelength for different concentrations. The transformation from the excited state of Sm^{3+} ions $^4G_{5/2}\rightarrow{}^6H_J$ (J=5/2, 9/2, and 11/2) is responsible for the emission peaks that are clearly visible at 560, 636, and 692 nm, respectively [16]. As the concentration is increased, the emission intensity increases too.

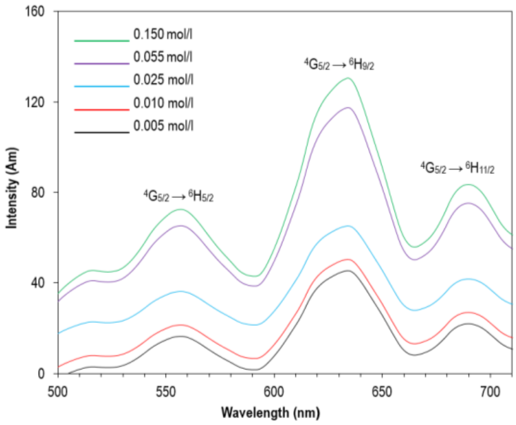

Fig. (5) Emission spectra of $SmCl_3.6H_2O$ in deionized water solutions at various molar concentrations (excited by 400nm)

The absorption spectra of Sm^{3+}-doped PVA at various concentrations are shown in Fig. (6). It is evident that the $^6H_{5/2}\rightarrow{}^4F_{7/2}$ transition is represented by the basic band at around 400nm. As seen in Fig. (6), the locations of the absorption bands in Sm^{3+}-doped PVA films are comparable to those in $SmCl_3.6H_2O$ solutions, suggesting that Sm^{3+} ions are present in the polymer structure. Additionally, when the concentration of Sm^{3+} ions is increased, the absorbance accordingly increases. These figures demonstrate that the concentration of Sm^{3+} ions is diluted in the liquid phase, resulting in lower absorbance than in the bulk phase. In contrast, the bulk phase shows noticeable absorbance due to the effect of solvent evaporation, which causes the Sm^{3+} ions to be concentrated in a smaller volume than the PVA volume.

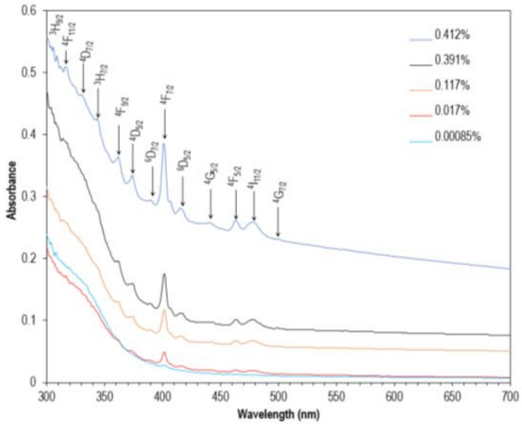

Fig. (6) Absorption spectra of Sm^{3+}-doped PVA at various concentrations

The photoluminescence (PL) spectra of Sm^{3+}-doped PVA films at different concentrations are clarified in Fig. (7) using 400nm excitation wavelength. The emission bands can be observed at 532, 582, and 654 nm corresponding to the intra-4f transitions of Sm^{3+} from excited level $^4G_{5/2}$ to lower levels; $^4G_{5/2}\rightarrow{}^6H_{5/2}$,$^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$, respectively [13]. It can be seen that the PL intensity increases with the concentrations at the low doping levels (0.117-0.017%), and this corresponding increase can be attributed to the increase of absorbance, i.e., an increase in the concentration of excited ions. On the other side, the concentration quenching occurs at the high doping levels (0.412-0.391%) through the decreasing of PL intensity with the concentration due to the tendency of these ions to clusters and subsequently non-radiative relaxations.

4. Conclusions

Polyvinyl alcohol (PVA) has demonstrated its effectiveness as an organic host material for active ions like Sm^{3+} ions displaying various advantageous characteristics including high transparency. At higher doping concentrations, luminescence quenching is readily visible in the spectroscopic activity of Sm^{3+} ion-doped polymer films. In order to improve the visual emissions of such ions, the current results are regarded as a promising beginning for study into the possibilities of co-doping with metal nanoparticles like gold and silver that are beneficial in the applications of white light-emitting diodes.

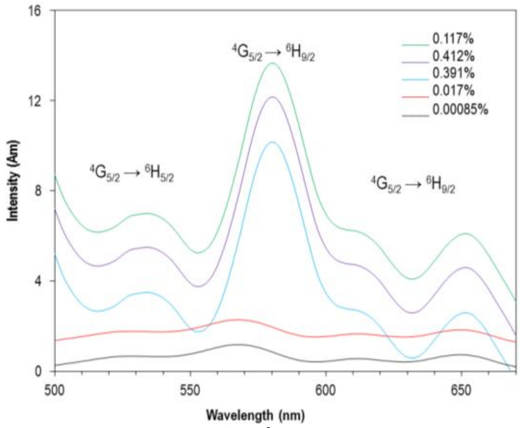

Fig. (7) PL spectra of Sm^{3+}-doped PVA at varying concentrations, excited by 400nm

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