

Successful Synthesis and Characterization of Luminescent (4:1wt.%) PMMA: SrAlO₇Eu²⁺Dy³⁺ Polymer Composite Fiber

Amrapali B. Patil¹, R. J. Dhokne (Pathare)², A. S. Daryapurkar³

¹ Department of Physics, Mahatma Fule Arts, Commerce & Sitaramji Chaudhari Science Mahavidyalaya, Warud, Amravati-444906, Maharashtra, India
Email: amrapalisukhadeve03[at]gmail.com

²Shri Shivaji Education Society Amravati's Science College, Congress Nagar, Nagpur, Maharashtra, India
Email: raginidhokne[at]gmail.com

³Department of Basic Sciences, Indian Institute of Information Technology, Nagpur, Maharashtra, India
Email: asdaryapurkar[at]iiitn.ac.in

Abstract: PMMA/SrAlO₇Eu²⁺Dy³⁺ fibres were produced via electrospinning. First, 2.4grams of PMMA was liquified in 10 ml of DMF to create 4:1wt.% solution, stirred for 5 hours at 120-200 rpm. Then, 0.6grams of SrAlO₇Eu²⁺Dy³⁺ was added and slowly stirred for 14 hours to form a unique mixture. This solution was carried to a syringe for electrospinning, with a 15-16 cm distance to the collector, a feed rate of 3 ml/h, and a high voltage of 18-20 kV. The collector rotated at 1200-1400 rpm to form a uniform sheet of fibres. Analyses using SEM, FTIR, and XRD confirmed the morphology of the fibers, which contained SrAlO₇Eu²⁺Dy³⁺ nanoparticles in a tetragonal structure. Photoluminescence studies revealed that excitation at 380 nm resulted in a 530 nm emission, indicating vibrant sea-green luminescence. These fibres are suitable for applications in smart textiles, wound dressings, and luminescent fabrics.

Keywords: Polymer, phosphors, electrospinning, etc.

1. Introduction

Photoluminescent materials incorporated into polymers are becoming increasingly popular across multiple industries, such as fashion for nightclub clothing and UV-reactive labels utilized for counterfeit detection and security [1,2]. The smart clothing industry, particularly in the realm of protective textiles, demonstrates considerable commercial promise. Functional textiles equipped with antibacterial, superhydrophobic, and flame-retardant characteristics prioritize practical applications over aesthetic considerations [3,4]. Divalent Europium (Eu²⁺)-doped strontium aluminate phosphors show extended sea green phosphorescence caused by the 5D to 4F quantum jump in Eu²⁺ ions. Their phosphorescent properties might be intensified by co-doping with rare earth ions like Dy³⁺ or adding excess AlO₇ [5]. These phosphors are used in luminous paints for highways, airports, and buildings, as well as in ceramics, textiles, outdoor displays, glowing clocks, and safety signals. These materials are ideal for use in vibrant timepieces, essential emergency equipment, and various warning signals. They are well-regarded for their exceptional chemical stability, ensuring safety during use, as well as their impressive brightness. Additionally, they exhibit long-lasting photoluminescence, making them a reliable choice for applications that require consistent visibility [6].

Electrospinning is a simple and economical method used to create fibres that range in size from the microscale to the nanoscale. This technique employs an electrostatic field to stretch and elongate a polymer solution, resulting in the formation of fine fibres [7]. Polymer-Phosphor composite electro spun fibres offer benefits like a high shape

compactness, large specific surface area, tuneable porosity, flexibility, and customizable fibre composition for enhanced performance [8]. This research paper presents a successful synthesis and characterization of a luminescent phosphor polymer composite, specifically (4:1wt%) PMMA/SrAlO₇Eu²⁺Dy³⁺ fiber. The fibers created display considerable brightness along with a lengthy afterglow decay. Following a few minutes of exposure to visible light, these fibers are capable of emitting light for over ten hours in the absence of light.

2. Experimental Work

2.1 Materials

PMMA (Polymethyl methacrylate) average MW120000 by GPC Sigma-Aldrich, Eu²⁺, Dy³⁺ Doped Strontium Aluminate MW 209.11g/mol Sigma-Aldrich, Dimethyl formamide anhydrous DMF(MW73.09) Sigma-Aldrich. All materials used were of high quality and sourced from Central Scientific Company, situated in Nagpur, Maharashtra.

2.2 Preparation of PMMA/SrAlO₇Eu²⁺Dy³⁺ solution

2.4gm PMMA was dissolved in 10ml of DMF solvent to give a mass percent composition of 4:1wt% and magnetically stirred (120 to 200 rpm) for 5hr at room temperature. Then 0.6gm of Eu²⁺Dy³⁺ doped Strontium Aluminate was added to PMMA solution and slowly stirred for 14 Hrs. with a magnetic stirrer till homogeneous at room temperature.

2.3 Preparation of PMMA/SrAlO₇Eu²⁺Dy³⁺ fiber

The PMMA/SrAlO₇Eu²⁺Dy³⁺ uniform mixture was loaded into a 5 ml syringe and delivered to the tip at a flow rate of 3 ml/hr utilizing a syringe pump. A high voltage of 20 kV was applied to the needle, while a stranded electrode was attached to a metallic collector plate covered with aluminum foil, positioned 16 cm away. The fibres were collected on foil and dried in a preheated void furnace for 10 hours to remove residual solvent.

3. Characterization Techniques

X-ray diffraction (XRD) study was done using a D8-Discover diffractometer (Bruker, USA) with Cu-K α radiation (1.5405 Å) over a 2 θ range of 14.20° to 90.30°, at 40 kV and 40 mA. A scanning electron microscope (SEM) model ZU SSX – 550 Super scans from Shimadzu was used to analyze the morphology. FTIR spectral study was done with a Shimadzu FTIR Tracer-100 spectrometer using a Diamond ATR. Photoluminescence (PL) spectra were obtained using a Cary-Eclipse Spectrofluorometer.

4. Results and Discussion

4.1 SEM

The magnified SEM images with scale bars corresponding to 1 μ m, and resolutions of x5000 revealed the fibre diameter ranges from 0.79 μ m to 1.64 μ m. The varying diameters of the electrospun fibres indicate that the choice of polymer affects the viscosity of the PMMA/SrAlO₇:Eu²⁺, Dy³⁺ solution. This modification is due to the enhanced conductivity of the electrospinning solution from adding SrAlO₇:Eu²⁺, Dy³⁺. The SEM analysis shows that smooth, symmetrical, homogeneous fibres of (4:1wt%) PMMA/SrAlO₇:Eu²⁺, Dy³⁺ were fabricated.

Homogeneous fibres are formed by carefully controlling key electrospinning parameters, including solution viscosity, electric field strength, sample feed rate, etc. Each factor is crucial for producing uniform and symmetrical composite polymers.

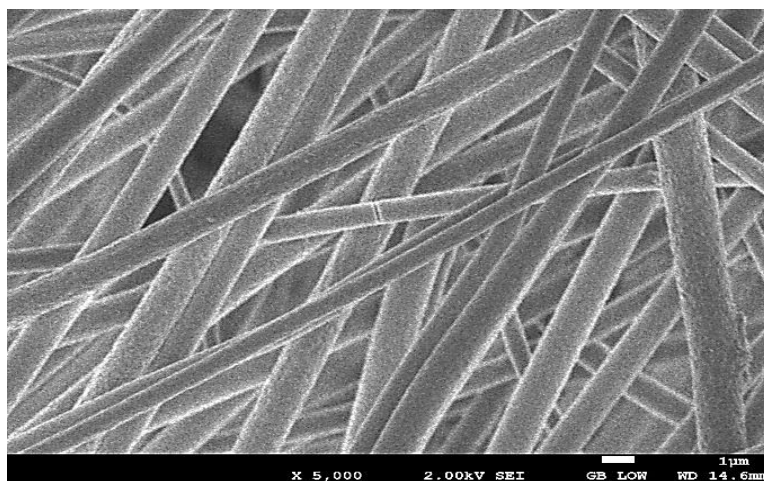


Figure 1(a): SEM image of (4:1wt%) PMMA/SrAl₂O₄:Eu²⁺, Dy³⁺ fiber

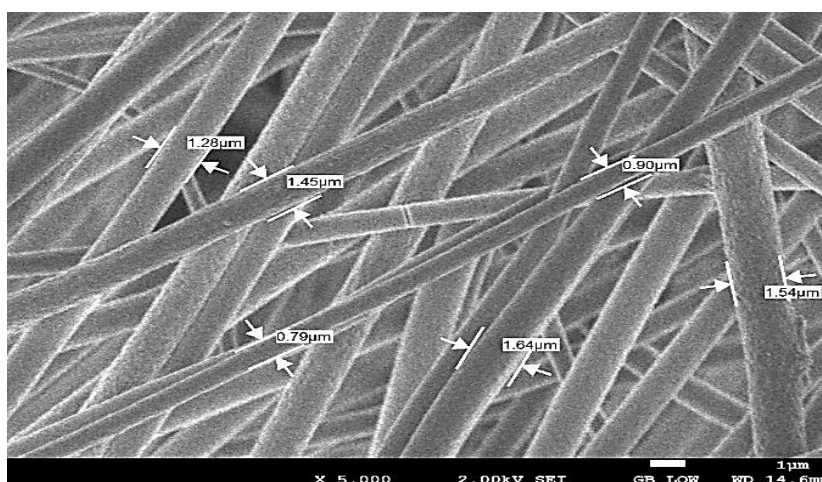


Figure 1(b): SEM image of (4:1wt%) PMMA/SrAl₂O₄:Eu²⁺, Dy³⁺ fibre showing the diameter of fibre

4.2 XRD

The XRD analysis of PMMA/SrAlO₇:Eu²⁺, Dy³⁺ strongly correlates with JCPDS PDF card No. 1008842, confirming a tetragonal phase with two equal axes and angles of $\alpha=90^\circ$,

$\beta=90^\circ$ and $\gamma=90^\circ$. The mean particle size, calculated using the Debye-Scherrer equation, ranges from 40 to 45 nm, which is consistent with the pure phosphor characteristics. Lattice parameters obtained from POWD software are $a=3.7560$ Å, $b=3.7560$ Å, and $c=6.2340$ Å. The absence of supplementary

peaks in the XRD pattern indicates that PMMA effectively serves as a matrix for the $\text{SrAlO}_7\text{:Eu}^{2+}$, Dy^{3+} phosphor, confirming the phosphor retains its phase in PMMA.

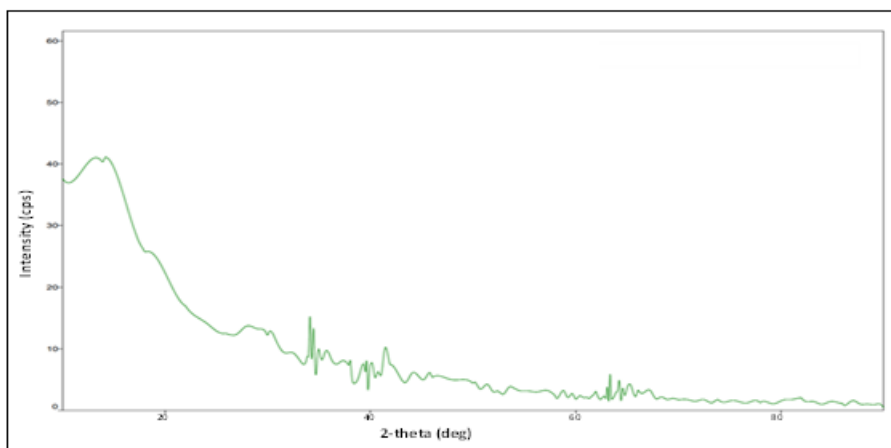


Figure 2: XRD graph image of (4:1wt%) PMMA/SrAl₂O₄:Eu²⁺, Dy³⁺

4.3 FTIR study

FTIR study confirmed the functional groups and chemical bonds in the synthesized PMMA/SrAlO₇:Eu²⁺+Dy³⁺ fiber. A peak at 1732 cm⁻¹ indicates carbon-oxygen double bond stretching in the carbonyl group, while a peak at 3434 cm⁻¹

corresponds to C=C and O-H bond elasticity. The spectral bands from 350 to 1000 cm⁻¹ are due to the IR-active vibrations of the SrAlO₇:Eu²⁺+Dy³⁺ phosphor. The appropriate dispersion is validated, since the PMMA/SrAlO₇:Eu²⁺+Dy³⁺ fibre exhibits all the distinct bands associated with the composite.

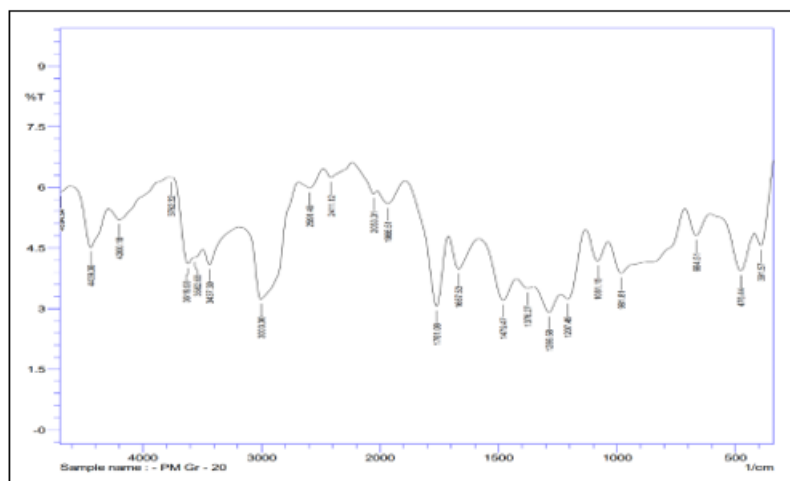


Figure 3: FTIR image of (4:1wt%) PMMA/SrAl₂O₄:Eu²⁺, Dy³⁺

4.4 Photoluminescence Study

The photoluminescence (PL) spectrum of PMMA/ SrAlO₇: Eu²⁺, Dy³⁺ fibre revealed a wide emission peak at 530 nm, indicating a sea green hue. The high point peak at 530 nm is due to the quantum jump from 4f⁶ 5d¹ to 4f⁷ of the Eu²⁺ ion co-doped with Dy³⁺ ion in the SrAlO₇:Eu²⁺,Dy³⁺ phosphor. Emission spectra were obtained at $\lambda_{ex} = 380$ nm, and excitation spectra were captured at $\lambda_{em} = 530$ nm. 380nm peak is the characteristic 4f⁷ → 4f⁶ 5d¹ quantum jump of the divalent europium ion (Eu²⁺) co-doped with Dy³⁺ in the SrAlO₇:Eu²⁺,Dy³⁺ phosphor.

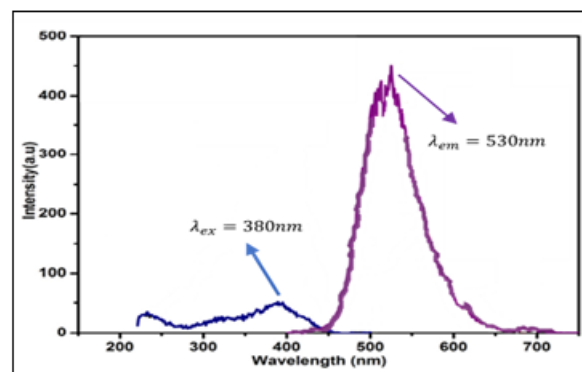


Figure 1: FTIR graph image of (4:1wt%) PMMA/SrAl₂O₄:Eu²⁺, Dy³⁺

5. Conclusion

An electrospinning technique has been successfully employed to fabricate 4:1wt% of PMMA/SrAlO₇:Eu²⁺, Dy³⁺ electrospun fibers, which exhibit an average diameter of 1.2μm. Scanning electron microscopy (SEM) images demonstrate that the Eu²⁺ & Dy³⁺ ions of SrAlO₇:Eu²⁺, Dy³⁺ phosphor are uniformly integrated within the PMMA molecular chain. The resulting fibres significantly influence the photoluminescent (PL) properties of Eu²⁺ ions enhanced by cooping Dy³⁺-ion, attributed to the robust coordination interactions between the Eu²⁺ ions and the polymer matrix. These fibers are suitable for applications in smart textiles, wound dressings, and luminescent fabrics.

References

- [1] S. B. Mishra, A. K. Mishra, N. Revaprasadu, "Strontium Aluminate/Polymer Composites: Morphology, Luminescent Properties, and Durability," *Journal of Applied Polymer Science*, Vol. 112, 3347–3354, 2009. (journal style)
- [2] Manjusha P. Dandekar, "fabrication of electrospun nanofibers of europium complex Eu(TTA)₃phen using electrospinning technique", *Procedia Materials Science* 10:580-587, 2015. (book chapter style)
- [3] Sumara Khursheed, "Phosphor Polymer Nanocomposite: SrAl₂O₄:Eu²⁺, Dy³⁺ Embedded PMMA for Solid-State Applications", *Materials Today: Proceedings* 21 2096–2104, 2020. (book chapter style)
- [4] Hui-Yi Chang, "Preparation of hydrophobic nanofibers by electrospinning of PMMA dissolved in 2-propanol and water.," *MATEC Web of Conferences* 264, 03004, 2019. (book chapter style)
- [5] Feng Ye, Shengjie Dong, "Fabrication and characterization of long-persistent luminescence/polymer (Ca₂MgSi₂O₇:Eu²⁺,Dy³⁺/PLA) composite fibers by electrospinning", *Optical Materials*, 2015. (journal style)
- [6] Manjusha P. Dandekar, " fabrication of electrospun nanofibers of europium complex Eu(TTA)₃phen using electrospinning technique," *Procedia Materials Science* 10:580-587, 2015. (book chapter style)
- [7] Manjusha Dandekar, "Synthesis and Photoluminescence Study of Electrospun Nanofibers of Eu(TTA)₃Phen/PMMA-PVDF Composite for Photoluminescent Fabric Designing", *AIP Conference Proceedings* 2104, 020011, 2019. (book chapter style)