



OPTICAL ENERGY GAP OF $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ ORGANIC COMPLEXES IN POLYMER MATRIX

N. THEJO KALYANI¹, DHOBLE S.J.² AND PODE R.B.³

¹Department of Applied Physics, Priyadarshini College of Engineering, Nagpur, MS, India

²Department of Physics, RTM Nagpur University, Nagpur, MS, India

³Department of Physics, Hung Hee University, Seoul, South Korea.

*Corresponding Author: Email- thejokalyani@rediffmail.com

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Abstract- Three kinds of Europium β -diketonate complexes $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ (Eu: Europium, Ln: Y/Tb, Y: Yttrium, Tb: Terbium, TTA: Thenoyl TrifluoroAcetone, Phen: 1-10 Phenanthroline; $x=0.5$) were dispersed in Poly Methyl Metha Acrylate (PMMA) and Polystyrene (PS) matrices. The resulting systems were studied using optical absorption spectroscopy and optical energy band gap of the complexes were determined in these matrices. Absorbance spectra of blended films in PMMA is characterized by a strong absorbance peak centered at 334 nm with a shoulder at 280 nm while the absorbance spectra of blended films in PS is characterized by a strong absorbance peak centered at 336 nm with a shoulder at 280 nm. Energy gap of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ in PMMA and PS matrices was found to be 3.42 and 3.36 eV, 3.345 and 3.29 eV, 3.45 and 3.41 eV for respectively. As these complexes are compatible in different polymers, OLED devices of these materials can be fabricated by solution techniques also.

Keywords- β -diketonate, PMMA, PS, Matrix, luminescence, ligand, OLED.

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Introduction

The growing importance of polymer thin film in integrated optical technology motivated to study the incorporation of rare earth complexes in polymers [1]. RE complexes doped in polymers are important because of their owing properties such as solution processing and mechanical flexibility. Hence they could be easily spin coated and thermally converted into uniform films. Especially, Europium β -diketonates have good luminescent properties due to the unique electronic structure of Eu^{3+} and the antenna effect of the ligands [2-5], which have important applications in laser, phosphor and electro-optical devices. Luminescence from trivalent lanthanide ions arises from electronic transitions between the 4f orbitals which are forbidden on symmetry grounds, leading to poor absorption cross-sections and relatively long-lived excited states [6]. An approach to increase the luminescent efficiency is to modify the complexes with different kinds of ligands characterized by broad and intense absorption bands [7-8]. Some fluorescent lanthanides can accept energy from the ligand in close proximity,

provided that the excited state of the donor is above the emitting level of the ions. Within the donating complex, the rare-earth ion cannot accept energy from the level of the ligand, but the energy is transferred to the respective fluorescent complex, provided that the complexes are in close proximity, e.g., in an aqueous suspensions, co-precipitates and LB films, containing a large excess of the donating complex [9-11]. This phenomenon was called co-fluorescence or enhanced luminescence [12-14].

In the present work, we have considered one such phenomenon (LB films) as polymer thin films have growing importance in integrated optic technology. We have chosen PMMA [15-17] and polystyrene (PS) as model polymers in this study as they are optically and electronically inert, also has good film forming properties with a high glass transition temperature of 114°C and 100°C respectively. PMMA and PS are common polymers, which have their physical, chemical and optical properties extensively investigated. The molecular structure of PMMA and PS are as shown in fig.1 (a) and (b) respectively.

Optical Energy Gap of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ Organic Complexes in Polymer Matrix

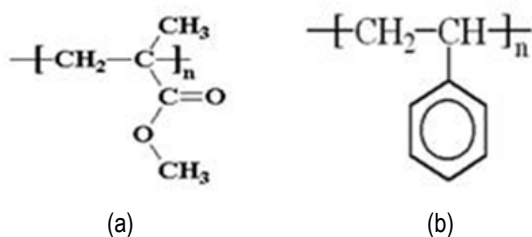


Fig.1- Molecular structure of (a) PMMA and (b) Polystyrene

Moreover, these polymers are stable in air with a high formability, and have no absorption and fluorescence in the visible region. As both polymers have good film forming properties with a high glass transition temperature the synthesized Eu complexes are doped in PMMA and PS.

Experimental

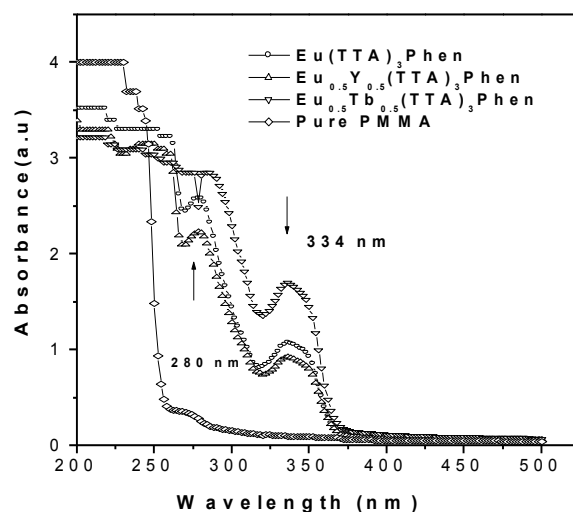
Preparation and characterization of Blended Films

Commercially available polymers PMMA/PS were used for making blended films of the synthesized complexes. As they are optically and electronically inert, low molecular weight organic materials having charge transport properties were doped into these polymers. Polymer (PMMA/PS) matrix was prepared by dissolving 0.5 grams of polymer (PMMA/PS) in 15 ml of chloroform at room temperature with vigorous stirring for 15 minutes at room temperature. Later 0.05 gms of the synthesized complex of pure $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$, taken individually were dissolved in the same solvent in another beaker by wt. as 10%. Now the complex solution is mixed with PMMA/PS matrix at room temperature under vigorous stirring for 15 minutes so as to obtain homogeneous mixture. The resulting homogeneous mixture was poured on to a good quality stainless steel substrate to spread it up. The solvent was allowed to evaporate in air for 2 to 3 hrs at room temperature and then pilled up from the substrate. Later the samples were placed in vacuum dry oven at room temperature overnight to remove any residual solvent left if any. Blended films so obtained were homogeneous and showed excellent optical transparency. No visible phase separation was detected. Absorption and photo luminescence measurements were made on SPECORD 50 at RTM Nagpur university.

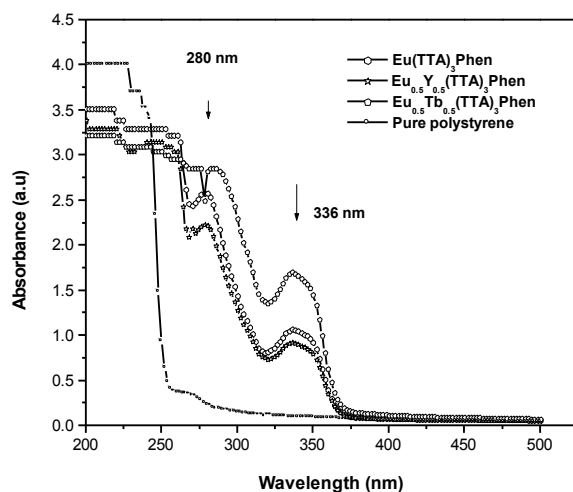
Results and discussion

Optical Absorption Spectra of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ complexes in PMMA and PS

Fig.2(a) and 2(b) shows the absorption spectra of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ blended film in PMMA and PS at room temperature respectively. Absorbance spectra of blended films in PMMA is characterized by a strong absorbance peak centered at 334 nm with a shoulder at 280 nm while the absorbance spectra of blended films in PS is characterized by a strong absorbance peak centered at 336 nm with a shoulder at 280 nm. The peak in the UV region is attributed to the n- π transition while the other peak is observed in visible region is attributed to the $\pi-\pi^*$ transition. For all the doped complexes the absorption peak is same because the ligand used is same in all the cases. As the absorption wavelength is the characteristic of aromatic group of β -diketonate (TTA) and hence there was no accountable shift in λ_{max} except the change in the optical density, which depends on the metal ions and their concentration.



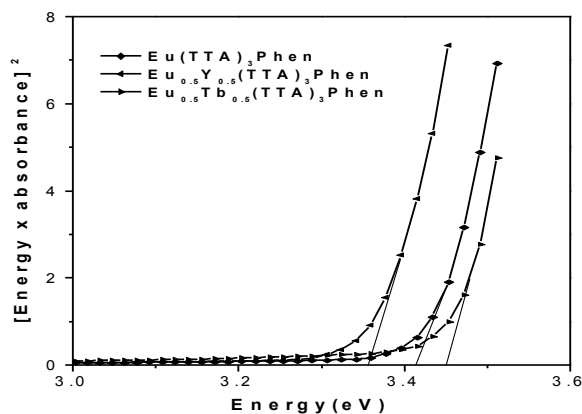
(a)



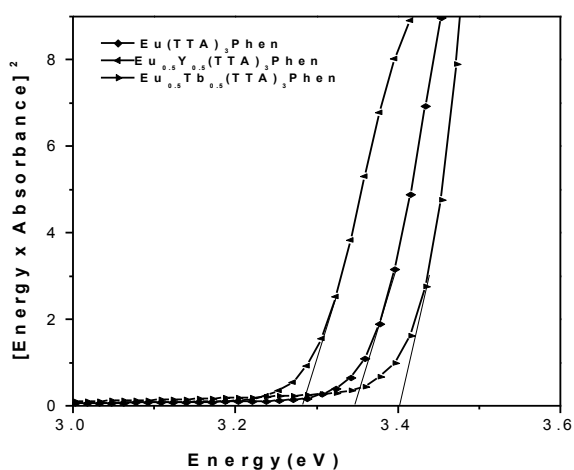
(b)

Fig. 2- Absorption Spectra of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ complexes in (a) PMMA (b) PS

Using the procedure described by Morita et al [18] for energy gap determination, we obtained energy gap E_{g} 3.42 and 3.36 eV, 3.345 and 3.29 eV, 3.45 and 3.41 eV for the blended films of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ in PMMA and PS respectively



(a)



(b)

Fig. 3- Determination of energy gap of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ in (a) PMMA and (b) PS

Conclusions

The energy gap of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ organic complexes in polymer matrix were determined by optical absorption studies. Absorbance spectra of blended films in PMMA is characterized by a strong absorbance peak centered at 334 nm with a shoulder at 280 nm while the absorbance spectra of blended films in PS is characterized by a strong absorbance peak centered at 336 nm with a shoulder at 280 nm. Energy gap of $\text{Eu}_x\text{Ln}_{(1-x)}(\text{TTA})_3\text{Phen}$ in PMMA and PS matrices was found to be 3.42 and 3.36 eV, 3.345 and 3.29 eV, 3.45 and 3.41 eV for respectively. Thus the optical studies revealed that the energy gap of these rare earth complexes (emission materials), which is an essential factor that decides the selection of other materials for different layers during OLED device fabrication. Thus blending the organic complexes in the polymers lead a way to determine the energy gap of the complexes. As these complexes are compatible in different polymers, OLED devices of these materials can be fabricated by solution techniques also.

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