



Photoluminescent effect of Sm on the intensity of Europium complexes

R.M.Meshram

M.B.Patel College, Sakoli

Abstract:

In the recent trends multidisciplinary scenario exhibits so many uses. In this paper materials are synthesized on the based chemistry, characterized on the basis of physics and used as well as applied in the field of electronics. The main application of Electroluminescent device are in the area of light emitting displays which is of great interest.. In this paper, the quaternary rare-earth complex $\text{Eu}_x(\text{Sm}_{1-x})(\text{TTA})_3\text{phen}$ and $\text{Eu}_x(\text{Sm}_{1-x})(\text{TTA})_3\text{phen}$ were successfully prepared by using the method of chemical Co-precipitation. According to the general formula $\text{Eu}_x\text{A}_{1-x}(\text{TTA})_3\text{Phen}$ (A denotes Sm, Gd, Bi and x denotes mole fraction of doping ion) a series of samples were prepared. The doping ions Sm^{3+} , Gd^{3+} and Bi^{3+} can enhance luminescent intensity of the complexes. The Eu^{3+} ion emission line at 613nm due to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is observed in red region. This enhancement in the emission intensity supposed to be due to energy transfer from Sm^{2+} to Eu^{3+} ion. The emission intensity of fluorescence is enhanced by adding the doping ions. Among all the complexes in EuSm combination, $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$ complex has the strongest fluorescent intensity while $\text{Eu}_{0.4}\text{Sm}_{0.6}(\text{TTA})_3\text{Phen}$ has the strongest fluorescent intensity in EuSm Combination. Characterizations of these complex were performed by using photoluminescence, XRD. This complex show very better results than common ternary complexes for light-emitting performance and luminescence properties.

Keywords: Luminisence, Europium, Samarium, XRD

1.Introduction:

The main advantages of Rare earth Luminescent materials is due to narrow emission band, high light absorption ability and conversion efficiency [1, 2],

Some rare-earth them have excellent optical properties and hence are widely used in high-performance luminescence devices and as catalyst supports. Trivalent rare-earth ions such as

Eu^{3+} , Tb^{3+} , and Tm^{3+} -doped in a suitable host material show strong emission based on electron transition between the $4f$ orbitals (3). Europium ternary chelates have been well known for their enhanced luminescence characteristics based on $4f$ electronic transitions of Eu^{3+} ion(4).

Using two types of ligands and the technique of co-luminescence, a new type of ternary rare earth complexes with emitting strong fluorescence under ultraviolet was synthesized(5)

The luminescence properties depend strongly on the chemical composition and crystal structure of the host material. Some reports on red-emitting OLEDs using Eu^{3+} organic complexes are also available. Earlier, Kido et al. reported the fabrication of Electroluminescence (EL) cell by using an evaporation process with the $\text{Eu}(\text{TTA})_3\text{phen}$ as an emitting material [6,7].

The synthesis process is based on the concept of a synergistic effort. Synergism, which is known in analytical chemistry, is the effect of introducing a second ligand into metal complexes to neutralize and saturate the coordination number of metal complexes.

2. Experimental:

2.1 Synthesis of $\text{Eu}(\text{TTA})_3\text{Phen}$:

3 mmol of ligand TTA and 1 mmol of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL of anhydrous ethanol, and the mixture was stirred constantly until a homogeneous solution was obtained. The 3 mmol of triethylamine was added dropwise to the above solution and then 1 mmol of phen ethanol solution was added, with constant stirring, white precipitates of $\text{Eu}(\text{TTA})_3\text{Phen}$ were generated. The precipitates were suction filtered and washed several times with ethanol, dried in air and then placed in a desiccators for use. To prepare Sm-doped lanthanide complexes $\text{Eu}_x\text{Sm}_{1-x}(\text{TTA})_3\text{Phen}$, 1 mmol of the reaction material of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was changed as x mmol of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and $(1 - x)$ mmol of $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, where $x = 1.0, 0.8, 0.6, 0.4, 0.2$. The other steps were the same as those used to prepare the pure $\text{Eu}(\text{TTA})_3\text{phen}$.

2.2 Synthesis of quaternary complex $\text{Eu}_x\text{Sm}_{x-1}(\text{TTA})_3\text{Phen}$:

For preparation of $\text{Eu}_x\text{Sm}_{x-1}(\text{TTA})_3\text{Phen}$, $\text{Eu}_2\text{O}_3, \text{Sm}_2\text{O}_3$ was weighted precisely and dissolved in concentrated hydrochloric acid, then excessive hydrochloric acid was vaporized, finally solutions with concentration 0.2 and 0.5 mol were obtained. According to the general

formula $\text{Eu}_x\text{Sm}_{x-1}(\text{TTA})_3\text{Phen}$ (x denotes mole fraction of doping ion) a series of samples were prepared. Thenoyltrifluoroacetone and phenanthroline were weighed precisely and dissolved in ethanol and added to a 150 mL three-necked flask with drop-funnel and thermometer. The flask was placed in water-bath and kept definite temperature, 20 mL ethanol solution containing 4.0 mmol europium chloride and 1.0 mmol samarium chloride were added in dropwise, the solution was stirred and refluxed for 2.5 h. White deposit was filtered, washed with distilled-water and ethanol successively, and then dried in vacuum oven.

3. Result and Discussion:

3.1 PL Measurements:

The excitation and emission spectra of powder were recorded at room temperature by using spectrofluorometer. All excitation spectra were recorded by monitoring the Eu^{3+} fluorescence centered at 613 nm, similarly all emission spectra of complexes were obtained by exciting these complexes using 378 nm ultraviolet.

The excitation and emission spectra of all complexes with different doping ions and different content have observed as shown in comparisons graph in fig 1,2. This observed from the Fig.1, Among all the complexes, $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$ complex has the strongest fluorescent intensity. Five typical Eu^{3+} fluorescence shoulder peaks appear at 581nm,591nm,598nm,613nm,619nm respectively, which belong to $5\text{D}_0 \rightarrow 7\text{F}_0$, $5\text{D}_0 \rightarrow 7\text{F}_1$, $5\text{D}_0 \rightarrow 7\text{F}_2$, $5\text{D}_0 \rightarrow 7\text{F}_3$ and $5\text{D}_0 \rightarrow 7\text{F}_4$, respectively. Of all the fluorescent emissions, the relative intensity of $5\text{D}_0 \rightarrow 7\text{F}_2$ is the strongest. Moreover, the positions of emission peak of all doping complexes are the same as those of $\text{Eu}(\text{TTA})_3\text{Phen}$ basically, which indicates that there is typical Eu^{3+} fluorescent emission. All complexes with general formula $\text{Eu}_x\text{Sm}_{1-x}(\text{TTA})_3\text{Phen}$ show strong excitation peaks corresponding to absorption of ligands, indicating that only ligand is excited in the complexes under ultraviolet excitation because absorption of rare earth ions is weak. The similarity of the fluorescence excitation and emission spectra between doping complexes and no-doping complexes shows that the addition of doping elements has no influence on the process of energy transfer.

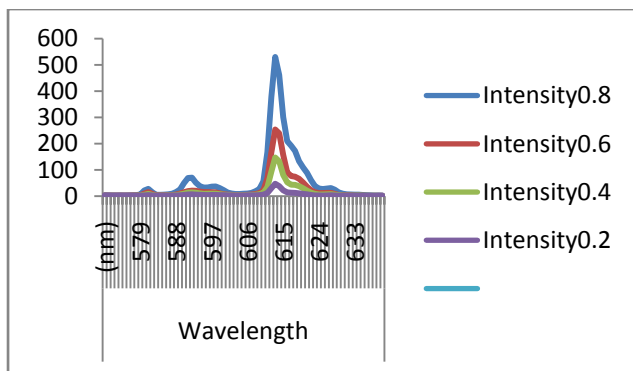


Figure1: Emission spectra of $\text{Eu}_x\text{Sm}_{1-x}(\text{TTA})_3\text{Phen}$

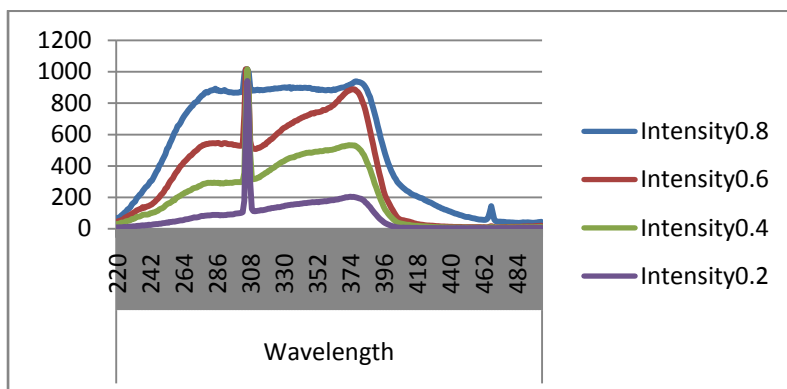


figure2: Excitation spectra of $\text{Eu}_x\text{Sm}_{1-x}(\text{TTA})_3\text{Phen}$

3.2 XRD Measurement:

XRD pattern of $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$ powders were recorded on omega PW3071 Powder Diffractometer as shown in figure3. The XRD spectrum shows many well resolved peaks for $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$ powder. Observance of many distinct peaks confirms the crystalline behaviour of $\text{Eu}(\text{TTA})_3(\text{phen})$ powder.

The d-values and peak intensity in XRD measurement are given in table1. It observed that 100% relative intensity corresponds to d- value of 2.82251\AA .

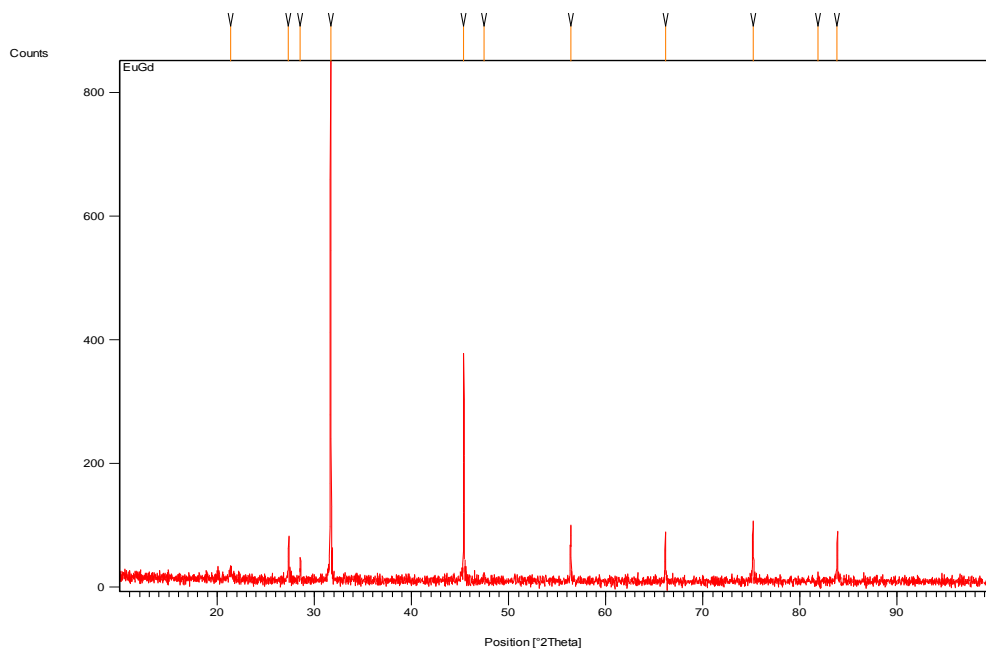


Figure3: XRD of $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$

Pos. [$^{\circ}2\text{Th.}$]	Height [cts]	FWHM [$^{\circ}2\text{Th.}$]	d-spacing [\AA]	Rel. Int. [%]
21.4042	12.84	0.4896	4.14803	2.54
27.3391	59.86	0.1224	3.25953	11.86
28.5542	32.18	0.1224	3.12353	6.37
31.6753	504.96	0.2448	2.82251	100.00
45.3871	321.49	0.1224	1.99662	63.67
47.4829	10.73	0.1224	1.91326	2.13
56.3807	74.74	0.1632	1.63060	14.80
66.1217	59.02	0.1224	1.41202	11.69
75.1554	96.81	0.1224	1.26312	19.17
81.8655	5.93	0.2448	1.17572	1.18
83.8251	50.39	0.2448	1.15315	9.98

Table1: d-value and peak intensity in XRD measurement

4. Conclusion:

- 1) Using co-precipitating method, a series of $\text{Eu}_x\text{Sm}_{1-x}(\text{TTA})_3\text{Phen}$ s complex light-conversion agents with emitting red strong fluorescence by doping relative cheap fluorescent inert ions can be synthesized.
- 2) The doping ions Sm^{3+} can enhance luminescent intensity of the complexes.

- 3) The Eu^{3+} ion emission line at 613nm due to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is observed in red region.
- 4) The properties of quaternary complexes of Eu^{3+} are significantly better than their ternary complexes.
- 5) Emission wavelength was found to be maximum for $\text{Eu}_{0.2}\text{Sm}_{0.8}(\text{TTA})_3\text{Phen}$ among all the synthesized complexes.

References:

1. Felinto MCF, Tomiyama CS, Brtio HF, Teotonio ES, Malta OL. *Synthesis and luminescent properties of supramolecules of β -diketonate of Eu(III) and crown ethers as ligands. J Solid State Chem, 2003, 171: 189–194*
2. Owen R, Lin W. *Crystal engineering of NLO materials based on metal-organic coordination networks. Acc Chem Res, 2002, 35: 511– 515*
3. Hiroaki Samata¹, Daisuke Itakura¹, Shungo Imanaka¹, Tadashi C. Ozawa² *Journal of Materials Science and Chemical Engineering, 2014, 2, 23-29*
4. G.D. Qian, M.Q. Wang, *J. Am. Ceram. Soc.* 83 (4) (2000)703.
5. ZHOU Zhong-cheng, SHU Wan-yin, WANG Zheng-xiang. *Spectra analysis and fluorescence sensitization of solid complexes Tbl-~ Gd, As (A = o-Aminobenzoic acid, x = 0-1) f-J]. Chinese Journal of Spectroscopy Laboratory, 2002, 19(5) : 569-572. (in Chinese)*
6. J. Kido, K. Nagai, Y. Okamoto and T. Skotheim, *Chem. Lett.* 235, 1267 (1991).
7. J. Kido, K. Nagai and Y. Okamoto, *J. Alloys Compd.* 192, 30 (1993).