Enhanced luminescence of rare-earth Tb (III) obtained by mixing of Gd (III) in a fumarate complex and intra-molecular energy transfer

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Trivalent lanthanide ions display fascinating optical properties. Therefore, the rare-earth complexes of terbium fumarate heptahydrate and GdTb fumarate heptahydrate were grown by using a single gel diffusion technique. The crystals were characterized by different physicochemical techniques of characterization. UV-Vis and photoluminescence spectrophotometric experiments were carried out to study the optical properties of the grown crystals. Under various excitations (339 nm, 350 nm or 368 nm) the terbium fumarate complex emitted characteristic (4f-4f) green emission of Tb³⁺ (⁵D₄-⁷F_J, J = 6, 5, 4 and 3, respectively). Luminescence spectra showed that Gd³⁺ ions in the mixed complex have not affected the luminescence emission peak positions, but remarkably increased the luminescent intensities of the terbium complex. The energy-transfer mechanism between the ligand and the central Tb³⁺ ions and from the Gd³⁺ to the Tb³⁺ was discussed.

Keywords: rare-earth coordination compounds; luminescence; energy transfer

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1. Introduction

Luminescence is a term used to describe the process in which light is produced by absorption of energy. Luminescence contains two basic forms, fluorescence and phosphorescence, depending on multiple spin state during the radiative relaxation process. Fluorescence refers to the emitting of light between energy states of the same spin multiplicity, and the process generally lasts not more than about 10 ns. On the other hand, phosphorescence refers to the emitting of light between states with different spin multiplicity and the process lasts a microsecond to seconds. Luminescence can arise from direct organic ligands excitation (particularly from the highly conjugated ligands), metal-centered emission (widely observed in lanthanide MOFs through so-called antenna effect), and charge-transfer, such as ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT). Furthermore, the guest molecules can also result in luminescence of MOFs. Rare-earth

ions not only serve as hosts of lighting materials but also sensitizers and activators because of their abundant emission colors due to their 4f-4f or 4f-5d transitions [1]. The unique characteristics of luminescence of rare-earth elements are attributed to the narrow emission and high color purity generated from these ions. Luminescent rare-earth complexes have potential technological applications in fluorescence devices [2–4]. Their application has also been reported in electroluminescent devices [5–8] and as fluorescence probes and labels in a variety of biological systems [9–12]. The process was first demonstrated by Wiessman [13] to present the strong luminescence of certain organoeuropium compounds and was later observed and studied by several other authors [2, 14, 15]. Some studies have also indicated that the addition of the certain second rare-earth ions, such as Gd (III) and La (III), could change the fluorescence properties of the rare-earth complexes [16, 17], as well. It is well-known that the luminescence mechanism is an intra-molecular energy transfer from the ligands to the metal ions under excitation by near ultraviolet light, that is called “antenna effect” [18]. In this

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paper, second rare earth ion Gd^{3+} was found helpful in improving terbium emission. Therefore, numerous complexes containing second rare-earth ions are expected to be introduced into the complexes to obtain materials with higher luminescence.

2. Experimental

Terbium nitrate hexahydrate (99.9 %) and gadolinium chloride hexahydrate (99.9 %) were purchased from Chengdu Haoxuan Technology Co., Ltd., China, while the fumaric acid (99.5 %) and sodium meta-silicate (99.5 %) were purchased from Thomas Baker Mumbai, India. The chemicals were used in the process without any further purification. Both pure terbium fumarate heptahydrate (TFH) and mixed gadolinium terbium fumarate heptahydrate (GTFH) single crystals were grown by single gel diffusion technique in the crystallizers consisting of glass test tubes of the length of 200 mm and the diameter of 25 mm. The details of the experiment have been published by Want *et al.* [19]. An energy dispersive spectrometer (OXFORD ISIS-300 System) was used to identify the presence of terbium, gadolinium, carbon and oxygen in the grown crystals. The UV-Vis spectrum for both TFH and GTFH crystals was measured with a Cary 5000 spectrometer in the range of 200 to 1000 nm. The photo luminescence spectra of these crystals were obtained by using a Varian Cary Eclipse spectrophotometer and recorded under the same experimental conditions.

3. Results and discussions

3.1. Powder XRD diffraction results

Fig. 1 shows the powder XRD pattern of GTFH crystals. The powder X-ray data were indexed using CRYSFIRE program [20]. The structure of as-grown GTFH crystals was evaluated to be monoclinic belonging to the space group $P2_1/n$ with the cell parameters: $a = 9.2705 \text{ \AA}$, $b = 14.3701 \text{ \AA}$, $c = 14.3602 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 91.41^\circ$ and $\gamma = 90^\circ$. These cell parameters were found very close to the cell parameters of terbium fumarate

heptahydrate belonging to $P2_1/n$ space group as obtained from its single crystal XRD reported by Shah *et al.* [21]. The mixed fumarate complex is, therefore, isomorphous with terbium fumarate complex and may also contain four coordinated and three lattice water molecules as shown by an ORTEP diagram for terbium fumarate heptahydrate reported by Shah *et al.* [21]. The presence of seven water molecules in the complex was also substantiated by the dehydration step of TGA graph as shown in Fig. 2, where the calculated loss of seven water molecules = 16.04 % equals to the experimental loss of 15.5 %.

Fig. 1. Powder XRD pattern of mixed Gd Tb fumarate heptahydrate.

3.2. Elemental analysis

In order to confirm the content of gadolinium and terbium in the grown crystals, an energy dispersive X-ray analysis (EDAX) was carried out for the grown complexes. Fig. 3 shows the EDAX spectrum of the mixed GTFH crystals which confirms the presence of both gadolinium and terbium in the complex. Table 1 shows the atomic and mass percentages of the elements, like oxygen, carbon, gadolinium and terbium as obtained from EDAX of the compound. From the EDAX analysis, the qualitative and quantitative content of Gd and Tb in the complex is in the ratio of 1:1, which is also in total agreement with the empirical formula of the compound $\text{Gd Tb}(\text{C}_4\text{O}_4\text{H}_2)_3$ as established from CHN

Table 1. EDAX analysis of GTFH complex.

Element	Mass % (Calculated)	Mass % (Experimental)	Atomic % (Calculated)	Atomic % (Experimental)
Carbon	18.50	19.98	36.00	37.75
Oxygen	39.02	40.57	57.60	56.52
Terbium	20.40	20.09	3.02	2.84
Gadolinium	19.50	19.36	3.02	2.87

Fig. 2. TGA of mixed GTFH crystals showing the dehydration stage.

Fig. 3. EDAX spectrum of GTFH crystals showing the presence of gadolinium, terbium, oxygen and carbon in the grown compound.

analysis. The percentage of carbon and hydrogen present in the complex is shown in Table 2.

Table 2. CHN analysis of GTF crystals.

Element	Mass % calculated	Mass % experimental
Carbon	18.37	18.45
Hydrogen	2.57	2.02
Nitrogen	0	0

3.3. UV-Vis spectral analysis of terbium fumarate and gadolinium terbium fumarate heptahydrates

The UV-Vis spectrum of terbium fumarate heptahydrate (TFH) crystal is shown in Fig. 4. The spectrum shows maximum absorption in the near-UV range (200 to 350 nm) at 266 nm for which the reflectance of 14.426 % was observed owing to $n \rightarrow \pi^*$ transition. This transition might be due

to the lone pair of electrons present in oxygen and antibonding π orbital of $C=C$ of fumarate ligand. At 489 nm, another dip with reflectance of 67.470 % is found in the UV-Vis spectrum. This wavelength is attributed to $\pi \rightarrow \pi^*$ transition and is caused by $C=C$ of fumarate part of terbium coordination complex. At 586 nm, the UV-Vis spectrum shows another dip which may be due to d-f transition of terbium. From the spectrum, it has been inferred that TFH crystals have sufficient transmission nearly in the entire visible and IR region. The absorption coefficient at low wavelength and the transparency in the visible part of the spectrum from 500 nm are high, suggesting their suitability for laser and luminescent materials. The band gap energy of terbium fumarate heptahydrate crystals with the maximum wavelength of absorption (266 nm) has been calculated by using the simple conversion equation, $E = hc/\lambda_{\max}$ as 4.65 eV.

The UV-Vis spectrum of gadolinium terbium fumarate heptahydrate (GTFH) crystal is shown in Fig. 5. The spectrum showing maximum absorption in the near-UV range (200 to 350 nm) at 263 nm for which reflectance is 6.057 % was observed owing to $n \rightarrow \pi^*$ transition. This transition may be due to the lone pair of electrons present in oxygen and antibonding π orbital of C=C of fumarate ligand. The absorption coefficient is high at low wavelength and the graph is smoother for the mixed fumarate complex, hence, the transparency in the visible part of the spectrum from 540 nm suggests its high suitability for laser and luminescent materials. There is hardly any change in the band gap energy of the GTFH crystal in comparison to that of TFH crystal. For the maximum wavelength of absorption (263 nm) the band gap energy is calculated by using the simple conversion equation $E = hc/\lambda_{\max}$ as 4.66 eV.

Fig. 4. UV-Vis spectrum of terbium fumarate heptahydrate complex.

3.4. Photoluminescence (PL) spectrum of TFH and GTFH crystals

The lanthanide ions suffer from weak light absorption due to the forbidden f-f transitions, making the direct excitation of the metals very inefficient unless high-power laser excitation is utilized. This problem can be overcome by coupling species that can participate in energy transfer processes, known as “luminescence sensitization” or “antenna

Fig. 5. UV-Vis spectrum of GdTb fumarate heptahydrate complex.

effect” [3, 22, 23]. Fig. 6 shows the emission spectrum of TFH single crystals recorded at room temperature.

The emission spectrum of terbium fumarate complex excited at 339 nm, 350 nm or 368 nm reveals well resolved strong luminescence of the f-f transitions of Tb^{3+} ions. Fig. 6 exhibits the characteristic transitions of Tb^{3+} ions at 491 nm, 546 nm, 587 nm and 621 nm ascribed to the $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4$ and 3 , respectively) which are characteristic of 4f-4f transitions of Tb^{3+} ions in the host lattice [24]. The luminescence spectrum of terbium fumarate is dominated at 546 nm in the green region, which is attributed to the $^5D_4 \rightarrow ^7F_5$ transitions of Tb^{3+} ions. Because of the intense absorption bands of organic chromophores, much more light can be absorbed by the organic ligands than by the lanthanide ion itself. Strong emission intensities indicate that the ligand is able to absorb energy and transfer it to Tb^{3+} ion, emitting the characteristic fluorescence of the Tb^{3+} ion. However, the presence of water molecules in the grown crystals may quench the luminescence. Indeed, it has been reported that vibrations of water molecules could effectively reduce the electronic energy of excited rare-earth ions, and the extent of the quenching is directly related to the number of the coordinated water molecules [25].

Fig. 7 shows the emission spectrum and the inset shows the excitation spectrum of the mixed

GTFH complex. From this spectrum, it can be seen that the introduction of Gd^{3+} ions has not affected the characteristic emission peak positions of Tb^{3+} , but increased the luminous intensity of the complex. Energy transfers from one lanthanide to another lanthanide ion have also been observed to enhance the luminescence intensity in heterolanthanide MOFs. For instance, the Eu^{3+} emissions at 595 and 615 nm in the heterolanthanide MOF $[(\text{Eu},\text{Tb})-(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2]\cdot(\text{C}_{10}\text{H}_8\text{N}_2)$ ($\text{C}_6\text{H}_8\text{O}_4$ = butane-1,4-dicarboxylate, $\text{C}_{10}\text{H}_8\text{N}_2$ = 4,4-bipyridine) are much stronger than those in $[\text{Eu}(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2]_3\cdot(\text{C}_{10}\text{H}_8\text{N}_2)$, while the Tb^{3+} emission at 545 nm in the heterolanthanide MOF $[(\text{Eu},\text{Tb})-(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2]_3\cdot(\text{C}_{10}\text{H}_8\text{N}_2)$ is completely quenched [26]. Within heterolanthanide MOF $[(\text{Eu},\text{Tb})-(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2]_3\cdot(\text{C}_{10}\text{H}_8\text{N}_2)$, the Tb^{3+} centers sensitize the Eu^{3+} , leading to effectively enhanced Eu^{3+} emission. Such energy transfer from Tb^{3+} to Eu^{3+} has also been observed in the MOFs $(\text{Eu}_{0.2}\text{Tb}_{0.8})_2(2,5\text{-pdc})_2(1,4\text{-pda})(\text{H}_2\text{O})_2$ and $(\text{Eu}_{0.1}\text{Tb}_{0.9})_2(2,5\text{-pdc})_2(1,4\text{-pda})(\text{H}_2\text{O})_2$ (H_2pdc = 2,5-pyridinedicarboxylic acid, H_2pda = 1,4-phenylenediacetic acid) [27]. In the heteronuclear GTFH complex, there is no obvious shift in the wavelength of the luminescent emission peaks. However, the luminous intensity in case of the heteronuclear complex has unprecedentedly increased. The increase in luminous intensity in mixed GdTb complex as compared to pure Tb fumarate complex may be caused by the energy transfer probability of electric dipole transitions. Gd may have transferred energy by means of intramolecular/intraionic energy transfer mechanism, which accounts for the increase in the luminous intensity. Another factor may be the ionic radius of Gd closer to that of luminescent Tb due to lanthanide contraction. It can also favor intramolecular energy transfer. The closer the size of an ionic radius to that of luminescent ion, the greater is the enhancement of luminous intensity [28]. Another reason may be attributed to the efficient packing of different moieties of heteronuclear complex, thereby increasing the symmetry of coordination sphere. Two lanthanide ions (Gd and Tb) can bind the ligand fumarate

molecules more firmly, making the complex rigid, compact and regularly oriented. The efficient packing may facilitate intramolecular and intraionic energy transfer thereby increasing the luminous intensity of the complex.

3.5. Energy-transfer mechanism

The intramolecular energy transfer takes place from the triplet level of ligand to the emissive level of Tb^{3+} ion by the Dexter's resonant exchange interaction [29]. The triplet state energy level of the organic linkers, such as fumaric acid (24034 cm^{-1}), is higher than the resonance energy levels of Tb^{3+} (20430 cm^{-1}), therefore, the energy absorbed by the ligand can effectively transfer to Tb^{3+} , thus, the luminescence efficiency of Tb^{3+} ions is enhanced [30]. When the rare earth complexes composed of active rare-earth ions Tb^{3+} and inert rare-earth ions (La^{3+} , Y^{3+} and Gd^{3+}) were grown with some organic ligands, the characteristic emission bands of active rare-earth ions Tb^{3+} were enhanced greatly. The reason may be concerned with both the coordination structure of the complexes and the intramolecular energy transfer process. In this co-luminescence system the lowest excitation energy level of Gd (III) is 32200 cm^{-1} , which is higher than the lowest triplet level of the ligand. Therefore, the energy could not be transferred from the ligand to Gd (III) ions [31]. As reported in the literature [31], the excited states of other inert rare-earth ions La^{3+} and Y^{3+} are much greater than the triplet energy level of the ligands. Therefore, the absorbed energy of the ligand also could not be transferred to La^{3+} and Y^{3+} . However, the introduction of inert fluorescent rare-earth ions could reduce concentration quenching of Tb^{3+} ions, and more energy absorbed by the ligands could be transferred to Tb^{3+} ion in the mixed complex through the bridging ligands. Thus, the emission of the mixed complex is ascribed to direct excitation of the Tb^{3+} ion [32].

4. Conclusions

1. The photo luminescence spectra of the grown crystals indicate that the photo emission intensity was enhanced by Gd (III),

Fig. 6. PL of terbium fumarate heptahydrate complex.

Fig. 7. PL of GTFH crystals showing its enhanced luminescence intensity.

which might be due to the intra-molecular energy transfer between inert rare-earth ions and active rare-earth ions.

2. The introduction of inert fluorescent rare-earth ions could reduce concentration quenching of the Tb^{3+} ions, and more energy absorbed by the ligands could be transferred to Tb^{3+} ion through the bridging ligands. Hence, based on these factors, materials with higher luminescence could be obtained.
3. The study of UV-Vis spectra suggests the suitability of TFH and GTFH crystals for laser use.

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References

- [1] GENG D., LI G., SHANG M., PENG C., ZHANG Y., CHENG Z., LIN J., *Dalton T.*, 41 (2012), 3078.
- [2] BUONO-CORE G.E., LI H., MARCINIAK B., *Coordination Chem. Rev.*, 90 (1990), 55.
- [3] WU W.N., TANG N., YAN L., *J. Fluoresc.*, 18 (2008), 101.
- [4] WANG Q.M., YAN B., *J. Mater. Chem.*, 14 (2004), 2450.
- [5] EDWARD A., CHU T.Y., CLAUDE C., SOKOLIK I., OKAMOTO Y., DORSINVILLE R., *Synthetic Met.*, 84 (1997), 433.
- [6] KIDO K., NAGAI K., OKAMOTO Y., *J. Alloy. Compd.*, 192 (1993), 30.
- [7] YU J.B., ZHOU L., ZHANG H.J., ZHENG Y.X., LI H R., DENG R.P., PENG Z.P., LI Z.F., *Inorg. Chem.*, 44 (2005), 1611.
- [8] KUKHTA A., KOLESNIK E., GRABCHEV I., *J. Fluoresc.*, 16 (2006), 375.
- [9] MEARES C.F., WENSEL T.G., *Accounts Chem. Res.*, 17 (1984), 202.
- [10] WU F.B., ZHANG C., *Anal. Biochem.*, 311 (2002), 57.
- [11] NISHIOKA T., YUAN J.L., YAMAMOTO Y.J., SUMITOMO K., WANG Z., HASHINO K., HOSOYA C., IKAWA K., WANG G.L., MATSUMOTO K., *Inorg. Chem.*, 45 (2006), 4088.
- [12] SCOTT L.K., HORROCKS W.D., *J. Inorg. Biochem.*, 46 (1992), 193.
- [13] WEISSMAN S.I., *J. Chem. Phys.*, 10 (1942), 214.
- [14] CROSBY G.A., *Mol. Cryst. Liq. Cryst.*, 1 (1966), 37.
- [15] DE W., HORROCKS W., ALBIN M., *Prog. Inorg. Chem.*, 31 (1984), 9.
- [16] CHEN Y., CAI W.M., *Spectrochim. Acta A*, 62 (2005), 863.
- [17] WANG F.F., YAN B., *J. Photoch. Photobio. A*, 194 (2008), 238.
- [18] LEHN J.M., *Angew. Chem. Int. Edit.*, 29 (1990), 1304.
- [19] WANT B., SHAH M.D., *J. Cryst. Growth.*, 389 (2014), 39.
- [20] SHIRLEY R., *The CRYSFIRE System for Automatic Powder Indexing: User's Manual*, The Lattice Press, Guildford, 1999.
- [21] SHAH M.D., WANT B., *Current Appl. Phys.*, 15 (2015), 64.

- [22] MOORE E.G., SAMUEL A.P.S., RAYMOND K.N., *Accounts Chem. Res.*, 42 (2009), 542.
- [23] SABBATINI N., GUARDIGLI M., LEHN J.M., *Coordin. Chem. Rev.*, 123 (1993), 201.
- [24] ZHU W.H., WANG Z.M., GAO S., *Inorg. Chem.*, 46 (2007), 1337.
- [25] CHOPPIN G.R., PETERMAN D.R., *Coordin. Chem. Rev.*, 174 (1998), 283.
- [26] DE LI D.T., BETTENCOURT-DIAS DE A., CAHILL C.L., *Inorg. Chem.*, 46 (2007), 3960.
- [27] SOARES-SANTOS P.C.R., CUNHA-SILVA L., PAZ F.A.A., FERREIRA R.A.S., ROCHA J., TRINDADE T., CARLOS L.D., NOGUEIRA H.I.S., *Cryst. Growth Des.*, 8 (2008), 2505.
- [28] WHAN R.E., CROSBY G.A., *J. Mol. Spectrosc.*, 8 (1962), 315.
- [29] DEXTER D.L., *J. Chem. Phys.*, 21 (1953), 836.
- [30] CI Y.X., LAN Z.H., *Analyst*, 113 (1988), 1453.
- [31] KONG K., ZHANG H., MA R., CHEN Y., CHU H., ZHAO Y., *J. Rare Earth.*, 31 (2013), 32.
- [32] GUO L., WEN X., XIAO Y., XIAO J., XUE L., *J. Lumin.*, 129 (2009) 639.

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