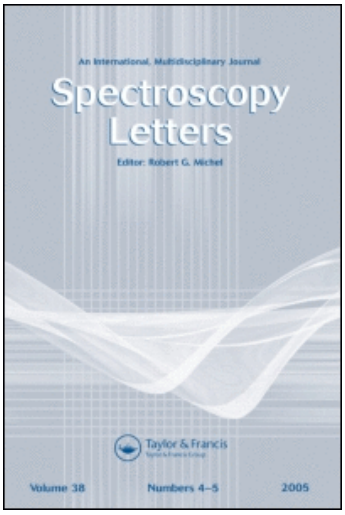

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ENHANCED FLUORIMETRIC DETERMINATION OF SAMARIUM WITH DIBENZOYLMETHANE AND DIPHENYLGUANIDINE BY GADOLINIUM

Keywords : Samarium Complex, Sensitized Luminescence, Energy Transfer

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ABSTRACT

The fluorescence of Sm-dibenzoylmethane (DBM)-diphenylguanidine (DPG) system was enhanced by about two to three orders of magnitude when it was excited in the presence of Gd in ethanol-water solution. The excitation and emission wavelegths were 390 nm and 652 nm, respectively. The fluorescence intensity was a linear function of the concentration of Sm in the range of 1.0×10^{-9}-2.0×10^{-6} M. The fluorescence mechanism of the system is discussed.

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INTRODUCTION

The technique of ligand-sensitized fluorescence has generally been employed to obtain luminescence enhancement of the lanthanides. In this process an organic ligand is first excited by absorption of light, followed by energy transfer to the excited energy levels of the lanthanide. It turned out that this process of indirect pumping of the excited energy levels of the lanthanide is more efficient than direct absorption of light by the lanthanide, owing to their poor absorptivities and low luminescence quantum yields. Several groups using a variety of organic ligands have shown enhancements of several orders of magnitudes in lanthanides such as Tb, Dy and Eu [1-6].

It has also been shown that the presence of certain ions in solution, such as La, Gd, Lu or Y, can lead to luminescence enhancement of the lanthanides Tb, Eu and Dy [7-11]. In this case an intermolecular energy transfer is believed to occur between the non-fluorescing donor complex (of La, Gd, Lu or Y) and the fluorescing acceptor complex (of Tb, Eu or Dy). As the concentration of the donor is generally much higher than that of the acceptor complex, each acceptor is surrounded by many donor chelates and the luminescence of the acceptor is greatly enhanced. In the present paper the luminescence of the Sm-DBM-DPG system enhanced by Gd is investigated. The sensitivity is increased by three orders of magnitude compared to the case in the absence of Gd. The method can be used for the determination of trace amounts of Sm in the different rare earth samples.

EXPERIMENTAL DETAILS

Apparatus.

All the luminescence measurements were made with a HITACHI 650-60 spectrofluorimeter. The excitation source was a 150 W Xe arc lamp. The excitation and emission slits were set at 5 nm. A 1 cm path length fluorescence free quartz cell was used for the measurements.

Reagents and Procedures.

Analytical reagent grade chemicals (Aldrich), distilled water and ethanol were used to prepare the solutions. Standard solution of SmCl (0.01 M) was prepared by dissolving the appropriate amount of Sm_2O_3 (99.9 % pure) in HCl and working solutions were prepared by dilution. Ethanol solution of $2.0x10^{-3}$ M DBM and $6.0x10^{-3}$ M DPG were used.

Solutions (1-1 ml) were added to a 10 ml test-tube in the following orders: Sm, Gd, DBM and DPG. The mixture was diluted to the mark with ethanol-water mixture of 7:3. The luminescence intensity of the system was measured after 20 min. The excitation and emission monochromators were set at 390 nm and 652 nm, respectively.

RESULTS AND DISCUSSION

Fig. 1. shows the excitation and emission spectra of the Sm-Gd-DBM-DPG system in ethanol-water solution.

At the Sm concentration of $1.0x10^{-7}$ M the solution containing Sm alone (without Gd) showed hardly perceptible luminescence under the experimental conditions described. From Fig. 1. it can be seen that the excitation maximum is at 390 nm and the emission maximum is at 652 nm. The fluorescence intensity of Sm in the Sm-Gd-DBM-DPG system is 2-3 orders of magnitude higher (about 600-fold) than that is in the system containing no Gd.

Effect of Concentration of Gd.

The effect of Gd concentration on the luminescence intensity was studied with fixed amounts of Sm in the range of $1.0x10^{-8}$ - $1.0x10^{-6}$ M. The results are shown in Fig. 2. When the concentration of Gd was increased the luminescence intensity of the system also increased, reaching a maximum at $1.5x10^{-5}$ M of Gd. At higher concentrations of Gd the luminescence intensity decreased gradually.

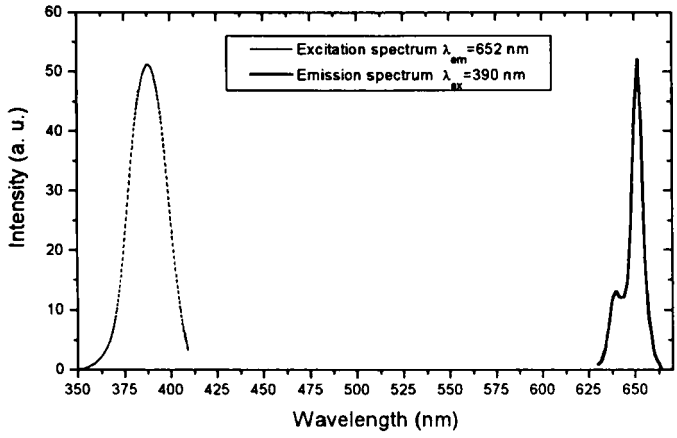

Fig. 1. Excitation and emission spectra of the Sm-Gd-DBM-DPG system in ethanol-water solution. Concentrations: Sm 1.0×10^{-7} M, Gd 1.5×10^{-5} M, DBM 2.0×10^{-4} M, DPG 6.0×10^{-4} M.

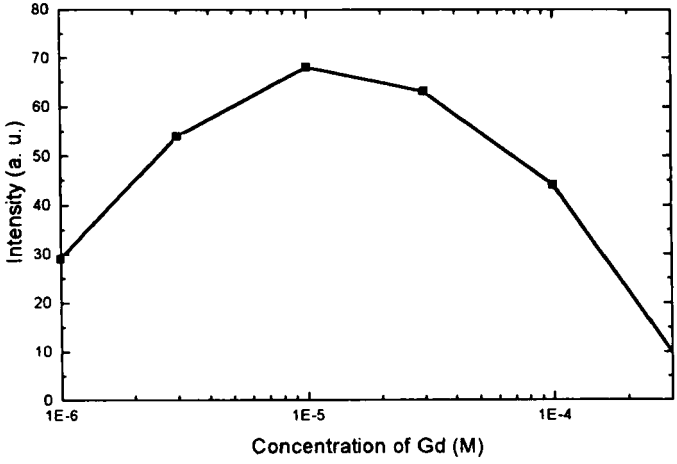

Fig. 2. Effect of concentration of Gd on the luminescence intensity. Concentrations: Sm 1.0×10^{-7} M, DBM 2.0×10^{-4} M, DPG 6.0×10^{-4} M.

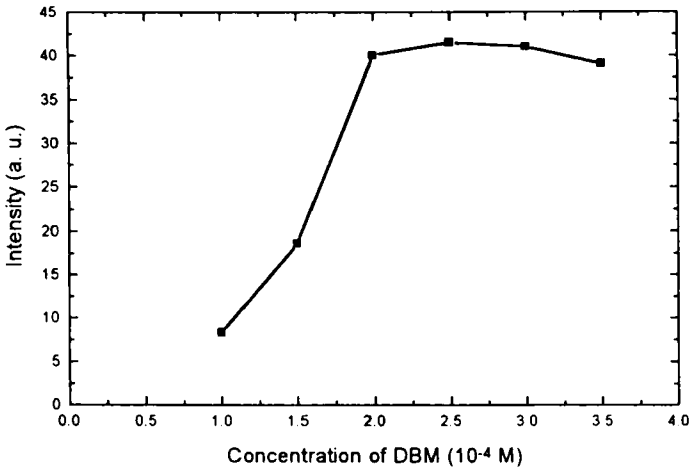

Fig. 3. Effect of concentration of DBM on luminescence intensity in ethanol solution. Concentrations: Sm $5.0x10^{-7}$ M, Gd $1.5x10^{-5}$ M, DPG $6.0x10^{-4}$ M.

Effect of Concentration of DBM and DPG on the Luminescence Intensity.

The effect of concentration of DBM on the luminescence intensity of the system was studied at fixed concentration of Sm ($5.0x10^{-7}$ M) and Gd ($1.5x10^{-5}$ M). The luminescence intensity was the highest when the concentration of DBM was between $1.8x10^{-4}$ M and $3.0x10^{-4}$ M. In the absence of DBM the intrinsic Sm emission was not observed. The effect of the concentration of DBM on the luminescence intensity of the system is shown in Fig. 3. This effect was studied under the above mentioned conditions. The highest and nearly constant luminescence intensity was obtained between $6.0x10^{-4}$ M and $7.0x10^{-4}$ M of DPG.

Effect of Concentration of Water on the Luminescence Intensity.

Fig. 4. shows the variation in the luminescence intensity with change in the percentage of water in the solution. When the concentration of water

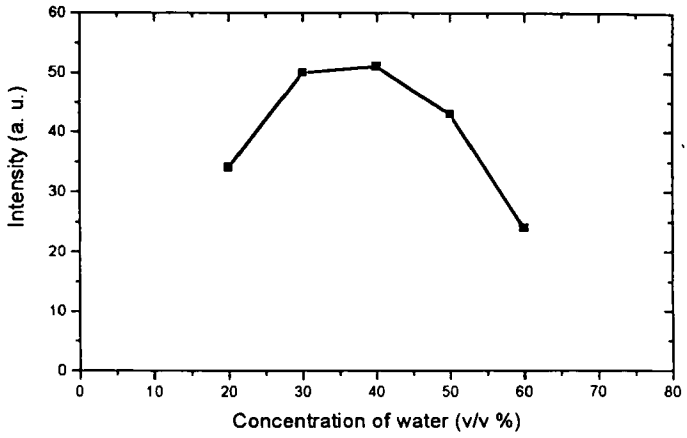

Fig. 4. Effect of concentration of water on luminescence intensity. Concentrations: Sm $5.0x10^{-7}$ M, Gd $1.5x10^{-5}$ M, DBM $2.0x10^{-4}$ M, DPG $6.0x10^{-4}$ M.

was increased the luminescence intensity also increased up to a 30-40 % contentration of water. At higher concentration of water the luminescence intensity decreased gradually.

Analytical Characteristics.

The luminescence intensity was measured in the $1.0x10^{-9}$ M - $1.0x10^{-5}$ M range of concentration of Sm under the optimal conditions (Fig. 5.). The intensity was a linear function of the concentration of Sm in the range of $1.0x10^{-9}$ M - $2.0x10^{-6}$ M.

The effect of other trivalent rare earth ions on the luminescence intensity of Sm-Gd-DBM-DPG system was studied for Er, Nd, La, Yb, Pr, Lu, Ho, Tm. The Sm-Gd-DBM-DPG system was applied to the determination of trace amounts of Sm in the rare earth oxides. The results obtained are given in Table 1.

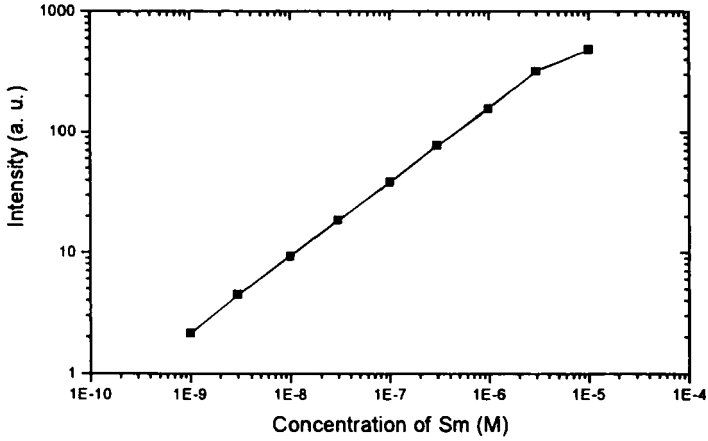

Fig. 5. Analytical curve of Sm in ethanol solution.

TABLE 1.
Determination of Sm in the Rare Earth Oxides.

Commercial rare earth oxides (weight %)	Sm_2O_3 found (weight %)
Er_2O_3 (99.9)	0.003
Nd_2O_3 (99.9)	0.012
La_2O_3 (99.9)	0.004
Yb_2O_3 (99.9)	0.021
Pr_2O_3 (99.9)	0.006
Lu_2O_3 (99.9)	0.015
Ho_2O_3 (99.9)	0.010
Tm_2O_3 (99.9)	0.009

Enhancement machanism.

It has been reported [12] that a $Sm(DBM)_3DPG_2$ complex was formed in the Sm-DBM-DPG system. In the complex the singlet states of DBM undergo a radiationless transition to the triplet states whose energy level is at 20300 cm^{-1}. This is close to the excited state energy level of Sm (17800 cm^{-1} for $^4F_{5/2}$ level) [13] and therefore an efficient intramolecular energy transfer can take place from DBM towards Sm. As Fig. 2. shows there is no constant mole ratio between Sm and Gd. It is considered that no new complex is formed, but $Gd(DBM)_3(DPG)_2$ is also formed. Thus Sm can be excited also by the energy from the triplet state of DBM being in the Gd complex, the concentration of which is much greater than that of the Sm complex in the solution. Thus the luminescence of Sm is considerably enhanced by an intermolecular energy transfer.

ACKNOWLEDGEMENT

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