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Non - Radiative Energy Transfer of $Tb^{3+} \rightarrow Eu^{3+}$ in sodium Fluoroborate Glass

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Abstract

This paper briefly reports the mechanism of non-radiative energy transfer process from $Tb^{3+} \rightarrow Eu^{3+}$ in Sodium fluoroborate glass by measuring the emission intensity of Tb^{3+} with varying Eu^{3+} concentration at room temperature. From the Fluorescence spectra, a decrease of terbium fluorescence intensity has been observed as a result of energy transfer from terbium ions to europium ions. Quantum efficiencies and energy transfer probabilities have been calculated.

Keywords: Energy transfer, Fluorescence, Fluoroborate glass

Introduction

Rare earths are suitable for energy transfer studies because of their well defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed. Several articles have appeared in literature on energy transfer process of rare-earth doped glasses, which is important for enhanced laser efficiency and optical devices [1-4]. Recently, fluorophosphates and fluoride glasses have been considered as suitable glass hosts for IR glass lasers due to their high transparency in IR range and low non radiative transition probability between the activated ions and the host glass on the basis of various spectroscopic investigations [5-8]. Based on the previous investigations on optical properties of rare-earth doped fluoroborate glasses[9-10], we have chosen Tb^{3+} and Eu^{3+} in sodium fluoroborate glass to analyse energy transfer mechanism at room temperature.

Experimental

The glasses were prepared by employing the quenching technique [11]. Pure chemicals from Analar grade (99.99%) of H_3BO_3, Na_2CO_3, NaF, TbF_3 and EuF_3 were properly weighted in mole %. Five Sodium Fluoroborate glasses have been prepared with the chemical composition as **(**79 – x) B_2O_3 +10 Na_2CO_3 + 10NaF + 1TbF_3 + x EuF_3 where x = 0, 0.25, 0.5 & 1.0 mole%**.** Each batch of the above chemicals with 8gm thoroughly mixed and melted in Silica crucible at 900-950^{o}C about 15min. The melts were quenched between two smooth surfaced plates to have the air bubble free glasses with good transparency. These glasses have been 2-4cm in diameter with a uniform thickness of 0.2cm. For the reference glass, the density and refractive index (d and n_d) were determined by using the conventional procedures [12]. The refractive index (n_d) of the reference glass is 1.423 and the density (d) is 1.657 g /cm^3. The emission spectra of the glasses have been recorded on an F-3010 Hitachi fluorescence spectrophotometer with a Xenon Arc lamp (150w) as the source of excitation at 365nm.

Results & Discussion

Emission spectra measured at room temperature for Tb^{3+} and (Tb^{3+},Eu^{3+}) sodium fluoro borate glasses are shown in Fig 1 [a-d]. The fluorescence spectrum of Tb^{3+} [Fig.1(a)] reveals four emission transitions arise due to the $^5D_4 \rightarrow {}^7F_6$, $^7F_5$, $^7F_4$, $^7F_3$ laying at 489nm, 544nm, 585nm & 621nm respectively. It is seen that on excitation at 365nm, the Tb^{3+} fluorescence decreases in the presence of Eu^{3+}. Fig. 2 shows the Tb^{3+} emission intensity of the more prominent transition ($^5D_4 \rightarrow {}^7F_5$) with varying Eu^{3+} concentration. It is observed that the intensities of $^5D_4 \rightarrow {}^7F_5$ level is drastically reduced with increasing dopant level. Another important parameter for evaluating the lasing potentiality of a given transition is the quantum efficiency (η). A method for calculating the probability and efficiency of energy transfer between inorganic ions from donor and acceptor luminescence intensities of given transition was proposed by Reisfeld etal [13]. In the case of rare-earths, the transfer is non-radiative one, i.e. no photon will appear in the system during the transfer.

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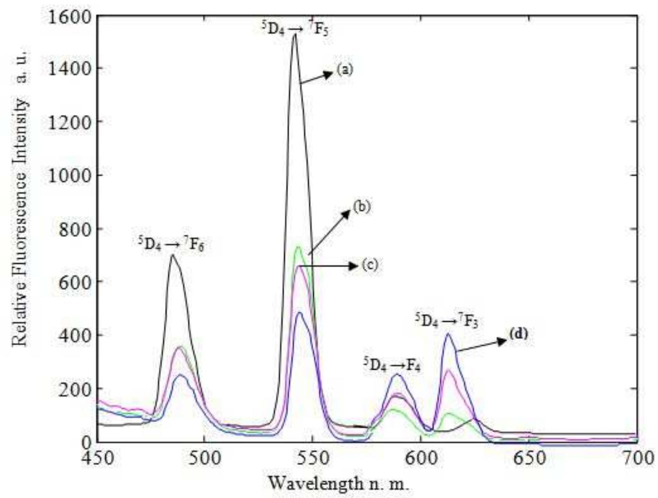

Fig. 1. Fluorescence Spectra of (a) Tb^{3+} (1.0 mole%) (b) Tb^{3+} + Eu^{3+} (0.25mole%) (c) Tb^{3+} + Eu^{3+} (0.5mole%) (d) Tb^{3+} + Eu^{3+} (1.0 mole%)

To determine the mechanism of energy transfer as electric dipole-dipole interaction the transfer probabilities are plotted as functions of square of the donor plus acceptor concentrations which gives a linear relation as described by Forster and Dexter [14-15]. Fig.4 confirms the above relation. It is found that the fluorescence life time (decay time) of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$) is about 2.7 ms and that of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) is 2.1ms. The energy level $^5D_0$ of europium lie at an energy lower than the $^5D_4$ of Tb^{3+}. When Tb^{3+} & Eu^{3+} ions are excited at 365 n.m., they have an electrostatic interaction with each other. An Excited Tb^{3+} ion relaxes from excited state to ground state non-radiatively and transfers the excitation energy to Eu^{3+} ion, promoting it from ground state to excited state. So the energy transfer from $Tb^{3+} \rightarrow Eu^{3+}$ is mainly non- radiative process as explained earlier in the literature [16]. Energy absorbed by sensitized ions can be transferred to fluorescence ions by means of energy transfer. Here, Eu^{3+} has strong effects on the sensitized fluorescence of Tb^{3+} and the overall emission of Tb^{3+} decreases. In Table#1, the energy transfer efficiencies (n_t) and transfer probabilities are presented by taking ($^5D_4 \rightarrow {}^7F_5$) transition fluorescence intensity.

Table -1

Donor concentration (mole %)	Acceptor concentration (mole%)	Donor intensity (η_o)	Donor Intensity in the presence of acceptor(η)	η/η_o	Quantum efficiency transferred $n_t=1-\eta/\eta_o$	Energy transfer probability $\left(\frac{1}{\tau_0}\right)\left(\frac{\eta_o}{\eta}-1\right)$ x10^3sec^{-1}.
1.0	0	1500 ($^5D_4 \rightarrow {}^7F_5$)	---	--	--	--
	0.25		732.4	0.49	0.51	0.39
	0.5		657.9	0.44	0.56	0.47
	1.0		514.6	0.34	0.66	0.71

$\tau_o \rightarrow$ Radiative life time of donor (Tb^{3+}) = 2.7ms.

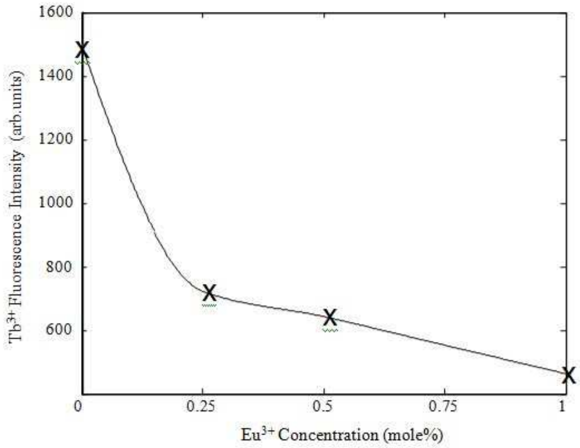

Fig. 2. Intensity of Tb^{3+} ($^5D_4 \rightarrow {}^7F_5$) transition co-doped with Eu^{3+}: sodium fluoroborate glass

Fig.(3) shows a plot of energy transfer efficiencies with varying Eu^{3+} concentration which shows the increase of efficiency due to energy transfer from $Tb^{3+} \rightarrow Eu^{3+}$.

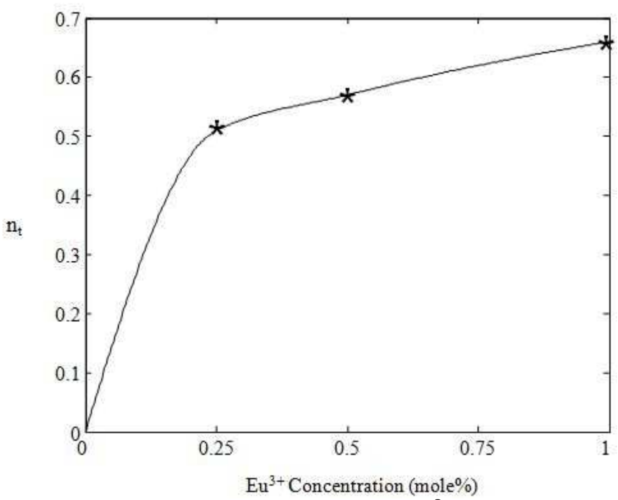

Fig. 3. Energy transfer efficiencies of Tb^{3+} co-doped with Eu^{3+} : sodium fluoroborate glass

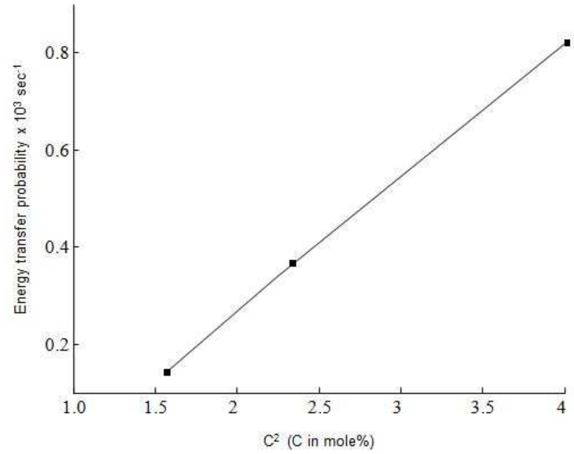

Fig. 4. Variation of Transfer probability with square of the donor plus acceptor concentration.

Conclusions

Based on the observed results in the table as well as the comparison of the profiles [Figs. (1),(2), (3) & (4)], it was observed that the effect of in nearing Eu^{3+} concentration in near the red emission via non radiative electric dipole-dipole interaction. The probability of transfer indicates that the phonons of the glasses are effective in assisting the energy transfer process and can be used as very important tool in studying the enhanced laser efficiency for optical devices.

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