Study of Non-radiative energy transfer from Tb(III) to Ho(III) ions in Borax Glasses

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ABSTRACT

In the present work, the study of emission of terbium Tb(III) with varying concentration of holmium Ho(III) in zinc Borax glass has been studied. Decrease in emission intensity of Tb(III) with increasing Ho(III) concentration indicates a non-radiative energy transfer from Tb(III) to Ho(III). The energy transfer mechanism, energy levels of Tb(III) and Ho(III) involved in energy transfer and other parameters necessary for the quantitative study e.g. energy transfer efficiencies, transfer probabilities, critical transfer distance etc. have been Calculated.
Keywords: Non-radiative energy transfer, Zinc Borax glass, Fluorescent spectra.

INTRODUCTION

Rare Earth ion doped glasses are often used as lasing materials for glass lasers, light emitting diode, memory device and fiber amplifiers for optical telecommunication. The luminescence of rare earth ions in glass has been a subject of renewed interest since the advent of laser. Due to small oscillator strength, RE ions cannot absorb a significant portion of excitation energy. In order to obtain high luminescent efficiency, the glasses doped with these ions (acceptor) can be coactivated with the help of some other ions (sensitizer) which absorbs an appropriate amount of excitation. Sensitizer transfers some of its excitation energy to the ion under study and consequently, the emission or efficiency of the later is enhanced. Many theories have been evolved out to understand the mechanism of energy transfer [1, 2, 3, 4, 8 and 10].

The terbium ion is well known for its relatively large absorption among rare earth ions and has bright green emission. Therefore, it is a suitable choice for sensitizing other RE ions. Much work has been done taking terbium as the energy donor in various hosts with an aim to transfer its excitation energy to other rare earth ions [9 and 11]. Joshi *et al.* [6] reported diffusion limited energy transfer at low Ho(III) concentration and electric dipole-dipole interaction at higher concentration. Yamashita and Ohisi observed energy transfer between Tb(III) to Yb(III) in borosilicate glass and found that co-operative energy transfer efficiency increases with increased doping concentration [7]. The present paper objects to find out the mechanism of energy transfer between Tb(III) and Ho(III) in zinc Borax glass and quantitative measurements for transfer probability and transfer efficiencies.

EXPERIMENTAL DETAILS

($Na_2B_4O_7.10H_2O$) (AnalR, India) and reagent grade zinc oxide (ZnO) were mixed in a proportion of 75:25 by weight % respectively to prepare the host glass matrix. The rare earths chosen for the work were terbium oxide (Tb_4O_7, 99.9% pure) and holmium oxide (Ho_2O_3, 99.9% pure) obtained from IRE LTD. Kerala, India. Pure as well as rare earth doped glass samples (Disc Shape of almost equal geometry and surface area) were prepared in an electric furnace at about 750^0C as described earlier paper [5 and 6].

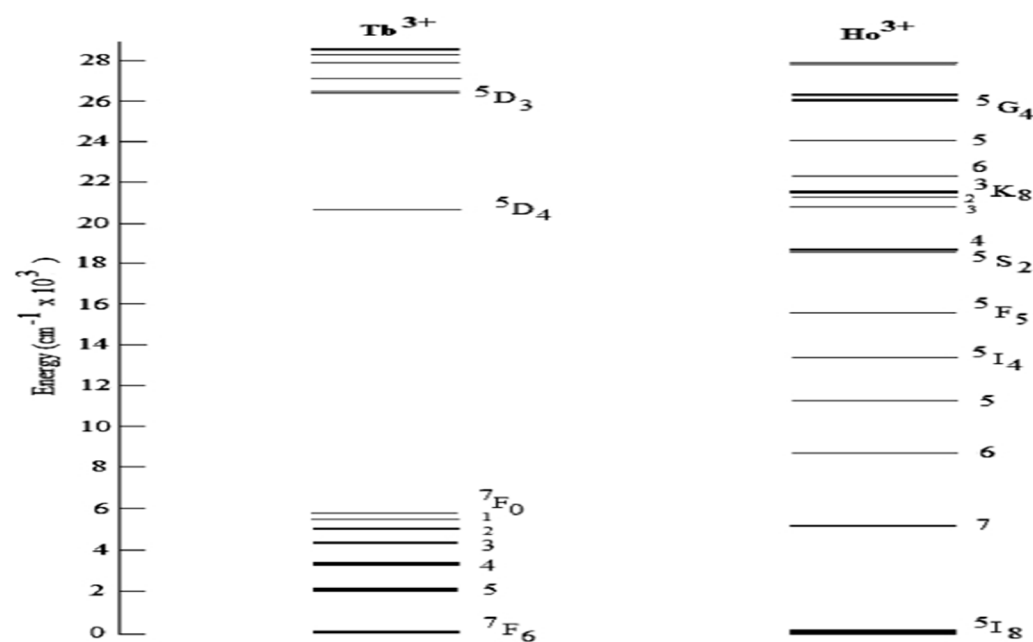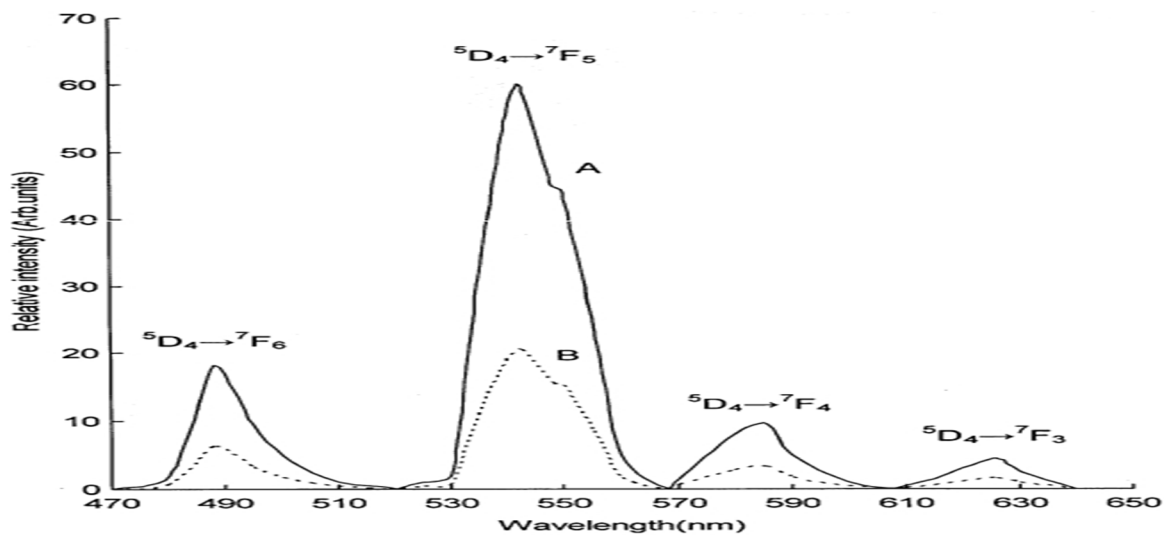**Fig. 1:** Energy level diagrams of Tb(III) and Ho(III)

Fig. 2: Emission spectra (Pure) of (A) Tb(III) (1.0 wt. % fixed) (B) Tb(III) (1.0 wt. %) +Ho(III) (1.0 wt%).

RESULTS AND DISCUSSION

The energy level diagrams of Tb(III) and Ho(III) are shown in Fig. 1. However It is shown in fig. 1, only terbium ion gives their characteristic emission in the visible region. Excited terbium ion in Borax glass decays rapidly to the metastable $^5D_4$ level. The emission spectra (pure) of terbium ion Fig (2) shows four peaks at about 485, 542, 586, 625 nm because of the following transition $^5D_4 {}^7F_6$, $^5D_4, {}^7F_5, {}^5D_4, {}^7F_4, {}^5D_4, {}^7F_3$, respectively. The emission from $^5D_3$ level of Tb (III) was not observed in our system (1 wt% Tb(III)). The reason of this may be the terbium ions make pairs (Tb-Tb) and because of this the excitation energy of the $^5D_3$ level relaxes to the $^5D_4$ level by cross-relaxation. Another

possible reason for this may be due to fast relaxation from $^5D_3$ level since its lifetime is very small. The pure spectra of Tb(III) (1 wt. % fixed) and the mixture of Tb(III) and Ho(III) (1 wt% each) are shown in Fig. 2 (A & B). A comparison of these two curves clearly shows that the intensity of emission of donor ion i.e. Tb(III) decreases when it is co-doped with acceptor ion in zinc Borax glass with varying concentration of acceptor Ho(III) and shows a decrease in Tb(III) emission. The decrease in donoremission intensity overall indicates that there is nonradiative energy transfer from $^5D_4$ level of Tb(III) to Ho(III) ions. Since the Ho(III) ion in zinc Borax glass does not have any observable emission when excited by the 360 nm mercury source therefore, back transfer of energy from Ho(III) to Tb(III)is extremely low. A close look to the energy level diagram indicates that the levels of Ho(III)close to the emitting $^5D_4$ level of Tb(III) is $^8K_3$. Therefore, the excitation energy of Tb(III) ion is transferred to $^8K_3$ level of Ho(III). The critical transfer distance (R_0), at which the energy transfer probability is equal to the radiative transition probability, in our system is 2.02 nm which can be compared with those obtained by Joshi *et al.*(8,9)for Tb-Er [1.59 nm] and Eu-Er [2.01 nm] in zinc Borax glass. In the present study, the energy transfer by exchange mechanism is not possible as it needs a donor-acceptor ion separation of about 0.3-0.4 nm with considerable overlap of wave functions. Level of terbium ion is quite large (τ=2.5 ms) and hence, this level have enough time to transfer its energy to$^8K_3$ level of Ho(III).

Table 1: Effect of acceptor concentration on energy transfer efficiencies, probabilities and average donor- acceptor distances for Tb(III)–Ho(III) system at donor concentration 1 (wt %)

C_{donor} (wt %)	$C_{acceptor}$ (wt %)	D_{D-A} (nm; ± 0.1)	I_{do} (± 1)	I_d (± 1)	η (± 0.05)	$P_{da}\times 10^3$ ($s^{-1}\pm 0.05$)
	0.2	2.23	73	50	0.34	0.21
	0.4	2.18	-	38	0.43	0.34
1.0	0.6	2.10	-	35	0.55	0.45
	0.8	1.95	-	30	0.63	0.55
	1.0	1.89	-	25	0.69	0.74

Where C_{donor} is the donor concentration; $C_{acceptor}$ the acceptor concentration; D_{D-A} the average donor-acceptor distance; I_{do} the donor intensity in the absence of acceptor; I_d the donor intensity in the presence of acceptor; η the energy transfer efficiency (=1−I_d/I_{do}); and P_{da} is the energy transfer probability [=(1/τ_0)(I_{do}/I_d - 1)]

CONCLUSION
Different concentrations of Tb(III) doped Zinc Borax glasses were prepared and their Fluorescence, spectra were studied. From these results, Non-radiative energy transfer from Tb(III) to Ho(III)occurs in zinc Borax glasses. Electric dipole-dipole interaction is mainly responsible for the energy transfer from Tb(III) to Ho(III).

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