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Buildup of the Acceptor Emission as a Result of Energy Transfer from Tb^{3+} to Sm^{3+} in Barium Borate Glass

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Intensity and lifetime data indicate that the self-quenching of Sm^{3+} fluorescence in barium borate glass matrix is by direct dipole–quadrupole interactions. The quenching of Tb^{3+} fluorescence by Sm^{3+} has been found due to direct dipole–dipole interactions. However, at relatively low Sm^{3+} concentrations, energy transfer through migration among Tb^{3+} ions also occurs. Further at low Sm^{3+} concentrations, there is an enhancement of Sm^{3+} emission due to energy transfer to an Sm^{3+} that is not coupled to a second Tb^{3+} or Sm^{3+} ion. At high Sm^{3+} concentrations, no enhancement of Sm^{3+} emission occurs and is attributed to transfer to Sm^{3+}–Sm^{3+} or Sm^{3+}–Tb^{3+} couples that take up the energy by simultaneous transitions that lie well below the $^4G_{5/2}$ manifold of Sm^{3+}.

Introduction

The study of interactions that enhance or decrease emission from fluorescing cations can be helpful in understanding luminescence. Early observations on energy transfer and energy transport or migration by resonance processes have been surveyed by Botden (*1*); more recent work has concentrated on rare earth ion interactions (*2–8*). The mechanisms involved in such interactions have been discussed by several workers (*9–12*). Energy transfer is generally associated with multipolar transitions and/or exchange (*10, 11*). Multipolar transitions are responsible for remote interactions (e.g., 20 Å), while exchange can be important for interactions involving near neighbors. The study of such interactions can be simplified considerably by employing trivalent rare earth ions as the interacting species. The absorption and emission linewidths for the *f–f* transitions of these ions are small. Hence, it is possible to obtain reasonable assessments of the proximities in energy of various states, or of the extents to which transitions between them overlap in energy.

The energy gained by one rare earth ion via transfer from a second ion may produce an enhancement of its emission. The present paper shows that it is possible to enhance the emission of Sm^{3+} by the transfer of energy absorbed through the agency of Tb^{3+} when the latter is present in relatively high concentration in barium borate glass matrix. This occurs under conditions where lattice processes which can enhance rare earth ion emission through the capture and transfer of energy by the formation and migration of excitons are absent or largely quenched.

Experimental

For preparation of the samples, Tb_2O_3

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and Sm_2O_3 (99.9%, Indian Rare Earths Ltd., Kerala) were first converted into their chlorides by repeatedly boiling their solutions in concentrated hydrochloric acid (A.R. Grade, Sarabhai Chemicals, India) and by recrystallizing the salts from the concentrated solutions. Triply distilled water was used as the solvent. The rare earth solution in the glassy media was obtained by mixing water solutions of rare earth chlorides containing a fixed concentration to a fixed mass of barium oxide (BDH Chemicals Ltd., Poole, England) and boric acid (A.R. Grade BDH, India) in a platinum crucible and the whole mass was heated slowly, so that it dried up. Now, this mass was melted in an electric furnace at about 1000°C for approximately 30 min. The molten mass was poured on a metal cast (made of brass) resting over a plane metallic surface at room temperature. The final base glass composition was obtained as $BaO : B_2O_3$ (52.4 : 47.6%, w/w). The excitation and emission spectra were recorded with Spex 1902 Fluorolog having two double Czerny–Turner scanning monochromators, each for excitation and emission. Detection was done with the help of a single photon amplifier discriminator (SPAD), S-20 (Ga–As) response photomultiplier, and a chart recorder. The decay times were measured by using a flash technique.

Results and Discussion

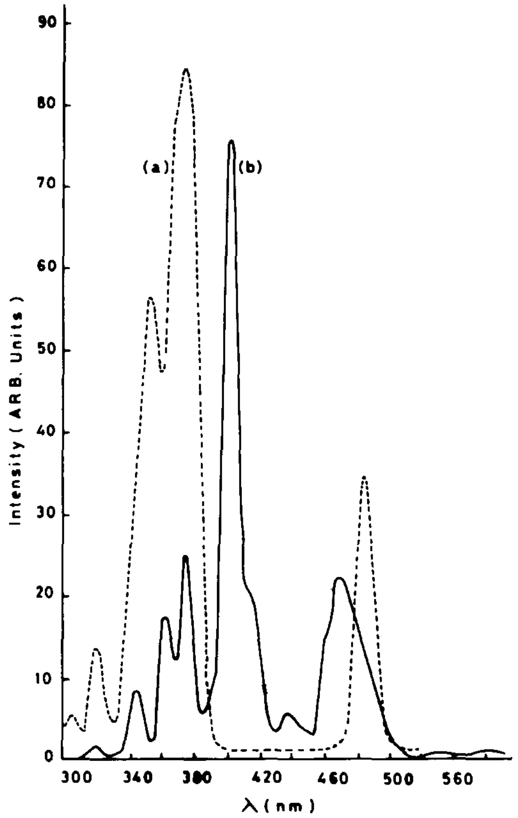

FIG. 1. Excitation spectra in barium borate glass at room temperature of (a) Tb^{3+} (1.0 wt%), and (b) Sm^{3+} (1.0 wt%).

Figure 1(a) shows the excitation spectrum of Tb^{3+} (1.0 wt%) $^5D_4 \rightarrow {}^7F_5$ fluorescence, while Fig. 1(b) shows the excitation spectrum of Sm^{3+} (1.0 wt%) $^4G_{5/2} \rightarrow {}^6H_{7/2}$ fluorescence. From these figures it is evident that Tb^{3+} strongly absorbs 352 nm of the exciting light, whereas the excitation of Sm^{3+} at this wavelength is relatively unimportant. So, 352 nm is the suitable wavelength for exciting Tb^{3+} ions to study energy transfer from Tb^{3+} to Sm^{3+} in barium borate glass matrix. The emission spectrum of Tb^{3+} (1.0 wt%), λ_{exc} at 352 nm is shown in Fig. 2(a). The emission peaks are at 544, 585, and 622 nm originating from the $^5D_4$ state of Tb^{3+}. Curves (b) and (c) in Fig. 2 depict the emission spectra of Tb^{3+} (1.0 wt%) + Sm^{3+} (0.2 wt%) and Tb^{3+} (1.0 wt%) + Sm^{3+} (0.5 wt%). The peaks at 565, 602, and 647 nm appearing in curves (b) and (c) are due to emission arising from the $^4G_{5/2}$ state of Sm^{3+}. Figure 2 presents an enhancement of Sm^{3+} emission accompanied by the quenching of Tb^{3+} emission, thereby suggesting that energy transfer from Tb^{3+} to Sm^{3+} in barium borate glass matrix is taking place. In the present study, the emission from the $^5D_3$ level of Tb^{3+} was not observed. This can be understood easily as

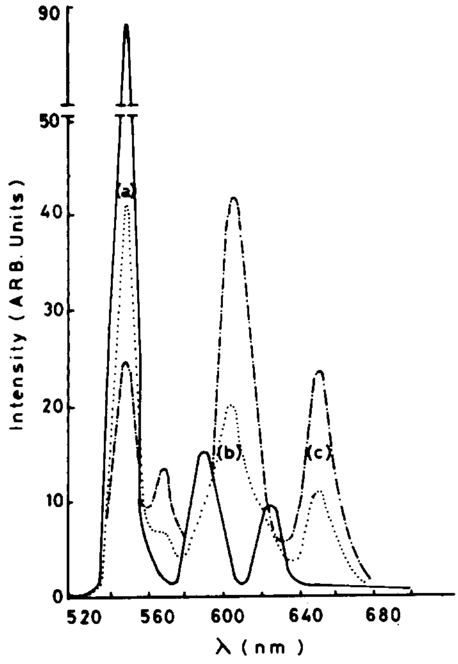

FIG. 2. Emission spectra at room temperature of (a) Tb^{3+} (1.0 wt%), (b) Tb^{3+} (1.0 wt%) + Sm^{3+} (0.2 wt%), and (c) Tb^{3+} (1.0 wt%) + Sm^{3+} (0.5 wt%).

the energy gap between $^5D_4$ and $^5D_3$ is matched by two phonons of the borate glass matrix, with phonon energy 1340–1480 cm^{-1}, multiphonon emission depopulates the ion quickly to its metastable $^5D_4$ level.

The decay plots for the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} emission were taken and it was found that the decay curve of pure terbium was a simple exponential with a decay time 2.7 msec. On incorporating Sm^{3+} ions in this matrix, the decay time decreases and the decay curve becomes nonexponential (in the present paper, however, the decay plots are not depicted). The exponential nature of Tb^{3+} (1.0 wt%) emission together with the observed fact that neither the intensity nor the decay time of Tb^{3+} emission in barium borate glass decrease up to 1.0 wt% concentration, show the absence of concentration quenching as reported by us earlier (*5*, *6*).

Figure 3 presents the variation of relative fluorescence yield (η_d) of Tb^{3+} as a function of acceptor (Sm^{3+}) concentration. The values of η_d have been obtained by measuring the total area under the emission profiles. An overall reduction in the relative emission yield points out the nonradiative nature of energy transfer.

A method for calculating the probability (P_{da}) and efficiency (η_T) of energy transfer between inorganic ions, using the experimental values of donor luminescence intensities and decay times at various activator concentrations was proposed by Reisfeld (*13*). When the absorption of donor ions is much higher than acceptor ions at the wavelength at which the system is excited (which is the practical case in optimum laser pumping), the transfer efficiency is given by a simple operational formula:

$$\eta_T = 1 - (\tau/\tau_0), \tag{1}$$

where τ_0 is the intrinsic donor lifetime and τ is the lifetime of donor when acceptors are present. The transfer probability is obtained as

$$P_{da} = (1/\tau) - (1/\tau_0). \tag{2}$$

The computed values of P_{da} and η_T are tabulated in Table I. It is evident from this table that both P_{da} and η_T increase with acceptor concentration.

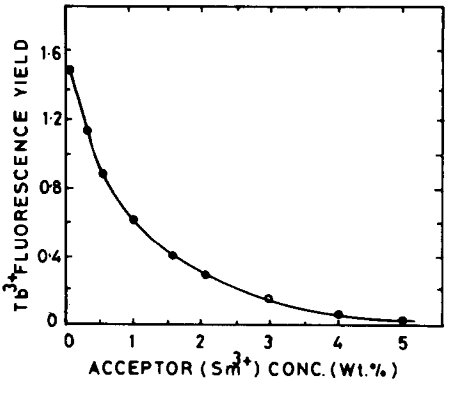

FIG 3. Variation of Tb^{3+} relative fluorescence yield (η_d) with Sm^{3+} concentration.

TABLE I

PROBABILITIES AND EFFICIENCIES OF ENERGY TRANSFER FOR Tb^{3+} TO Sm^{3+} SYSTEM IN BARIUM BORATE GLASS AT 300 K

Acceptor (Sm^{3+}) concentration C_a (wt%)	Relative Tb^{3+} fluorescence yield η_{d0}/η_d	Energy transfer probability $P_{da} \times 10^3$ (sec^{-1})	Energy transfer efficiency η_T	Donor–acceptor separation P (Å)
0.2	1.26	0.11	0.16	25.12
0.5	1.61	0.25	0.28	24.85
1.0	2.23	0.51	0.41	23.62
1.5	3.62	1.08	0.59	18.73
2.0	4.83	1.59	0.68	17.12
3.0	7.25	2.60	0.72	16.06
4.0	18.10	7.10	0.76	14.52

Note. Donor (Tb^{3+}) concentration = 1.0 w% (fixed). Intrinsic Tb^{3+} decay time (τ_0) = 2.7 msec.

The mechanism of nonradiative energy transfer is decoded by the concentration-dependent relations for energy transfer probability parameter (P_{da}). A graph between the experimentally observed values of P_{da} against C_a^2 gives a straight line, thus suggesting that the character of nonradiative energy transfer is electrostatic dipole–dipole. A similar plot based on Van Uitert's formula (*14*) for the fluorescence intensity measurements as

$$\log\left[\frac{I_0 - I}{I}\right] = \log \beta + \frac{\theta}{3} \log\left(\frac{C_a}{C_0}\right), \quad (3)$$

gives the slope of the straight line ($\theta/3$) = 1.9 which is very near to 2 (Fig. 4), a characteristic of dipole–dipole interaction. The value of the exponent θ which is somewhat lower than 6 may be due to the reasons suggested by Van Uitert and Johnson (*15*) who considered that the broadening of spectral lines in the absorption of rare earth ions corresponds to an increase in the intensity of excitation, which in turn lowers the value of θ to 5.7.

At concentrations above 1.0 wt% of Sm^{3+}, the emission as well as decay time of Sm^{3+} decrease. The variation of Sm^{3+} emission intensity with concentration is shown in Fig. 5. The decay curves of Sm^{3+} above 1.0 wt% show an initial nonexponential behavior which increases on increasing the Sm^{3+} concentration. This nonexponential decay behavior of Sm^{3+} emission at higher concentrations (above 1.0 wt%) indicates that the quenching is occurring by the cross-relaxation of energy among the excited and unexcited Sm^{3+} ions. The relaxation of $^4G_{5/2}$ level of Sm^{3+} by ion–ion energy transfer can be represented systematically

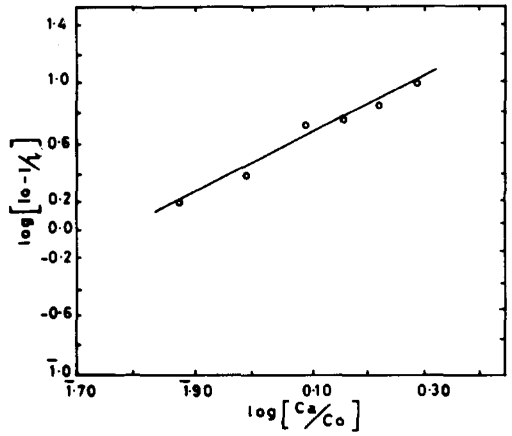

FIG. 4. Plot log[$(I_0 - I)/I$] versus log (C_a/C_0) for Tb^{3+} to Sm^{3+} energy transfer in barium borate glass. I_0 and I are the fluorescence intensities of Tb^{3+} alone and of Tb^{3+} in the presence of Sm^{3+}, respectively; C_a is Sm^{3+} concentration; C_0 is critical concentration of Sm^{3+} and corresponds to 50% quenching of Tb^{3+} fluorescence.

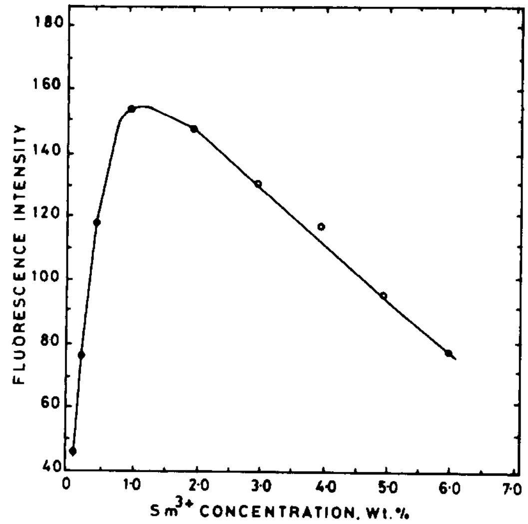

FIG. 5. Variation of Sm^{3+} emission intensity with varying Sm^{3+} concentration.

as (*16*)

$$^4G_{5/2}(17{,}730\ cm^{-1}) \rightarrow {}^6F_{11/2}(10{,}550\ cm^{-1}),$$
$$^6F_{5/2} \text{ or } {}^6H_{15/2}(7180\ cm^{-1}) \leftarrow$$
$$^6H_{5/2}(\approx 0\ cm^{-1}); \text{ and } {}^4G_{5/2}(17{,}730\ cm^{-1}) \rightarrow$$
$$^6F_{5/2} \text{ or } {}^6H_{15/2}(7180\ cm^{-1}),$$
$$^6F_{11/2}(10{,}550\ cm^{-1}) \leftarrow {}^6H_{5/2}(\approx 0\ cm^{-1}).$$

Absorption is strong at 7180 cm^{-1} and comparatively weak at 10,550 cm^{-1}. Strong emission at 947 nm, corresponding to the 10,550 cm^{-1} absorption transition, can be observed from dilute Sm samples.

In order to find out the multipolar term responsible for ion–ion energy transfer or the cross-relaxation of energy between Sm^{3+} ions, Inokuti–Hirayama's theory (*17*) has been applied. The transient decay of luminescence intensity after a time "t" is given by

$$\phi(t) = \phi(0) \exp[-(t/\tau_0) - \Gamma(1 - 3/S)(C_a/C_0)(t/\tau_0)^{3/S}], \quad (4)$$

where C_0 is a "critical concentration" and is defined as the concentration of acceptor at which the energy transfer probability is equal to the intrinsic decay rate of donor; C_a is the acceptor concentration; S is an interaction parameter and equal to 6, 8, or 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The maximum Sm^{3+} concentration without quenching effects is 1.0 wt%. Therefore the acceptor (Sm^{3+}) ions are assumed to interact after 1.0 wt%. The theoretical decay curves for $S = 6$ and $S = 8$ given by Eq. (4) for $C_a = 3.0$ wt% are plotted in Fig. 6 along with the experimental decay curve for the above sample. A look at Fig. 6 reveals that the experimental data fit best with the theoretical curve for $S = 8$ (within experimental error), thus predicting that a dipole–quadrupole interaction mechanism is mainly responsible for the cross-relaxation between Sm^{3+} ions. These results are in agreement with the observations made by Reisfeld *et al.* (*18*) but differ from the results reported by Van Uitert and Johnson (*15*). The observations also support the views advanced by Axe and Weller (*19*) that dipole–quadrupole mechanism has enhanced proportions in the internal quenching processes.

The numerical computations for transfer efficiencies, probabilities as a function of Sm^{3+} concentration have also been made

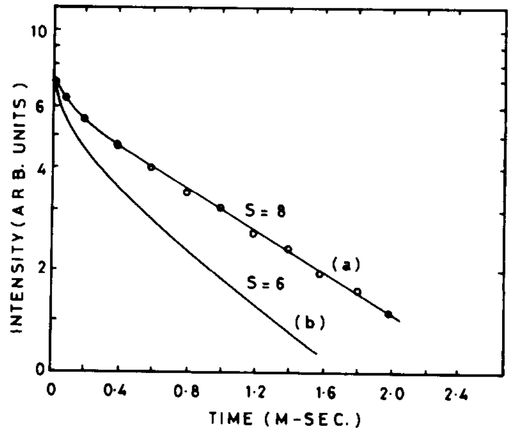

FIG. 6. The decay curves (a) and (b) are the theoretical curves for $S = 8$ and $S = 6$, respectively, and the points are experimentally obtained values for the decay curve of Sm^{3+}.

TABLE II

COMPUTED VALUES OF TRANSFER EFFICIENCIES (η_T) AND TRANSFER PROBABILITIES (P_{da}) FOR Sm^{3+} TO Sm^{3+} ION-PAIR ENERGY TRANSFER IN BARIUM BORATE GLASS AT 300 K

Sm^{3+} concentration (wt%)	Average distance between Sm^{3+} ions (Å)	Sm^{3+} decay time (μ sec)	Transfer efficiency (η_T)	Transfer probability $P_{da} \times 10^3$ (sec^{-1})
0.2	38.5	2300	—	—
0.5	28.3	2300	—	—
1.0	22.5	2300	—	—
1.5	17.8	2000	0.13	0.064
2.0	15.6	1540	0.33	0.210
3.0	14.2	1265	0.45	0.440
4.0	13.2	897	0.61	0.680

by using the equations given earlier (Table II).

At low Sm^{3+} concentrations, the transfer from Tb^{3+} is through migration among Tb^{3+} ions as revealed by exponential decay obtained at these Sm^{3+} concentrations. Such energy migration has been observed in glasses earlier for other rare earth ions (*3*–*5*). In both the direct and migrational transfer the final step is transfer to Sm^{3+} ions, coupled or isolated depending on Sm^{3+} concentration, most probably through a multipolar transfer. The present observed fact that Sm^{3+} emission enhancement due to energy transfer from Tb^{3+} ceases after Sm^{3+} concentration of about 1.0 wt% shows that above this concentration the transfer occurs to Sm^{3+}–Sm^{3+} or Sm^{3+}–Tb^{3+} coupled pairs. The self-quenching of Sm^{3+} emission due to cross-relaxation observed above 1.0 wt% supports this mode of transfer. However, when the terminal step is transfer from Tb^{3+} to an Sm^{3+} that is not coupled to other Sm^{3+} or Tb^{3+} ion, the energy gained by the single Sm^{3+} should be equal to that lost by excited Tb^{3+} plus or minus a small amount of energy exchanged with the phonon spectrum. Obviously Sm^{3+} emission is then expected to enhance as has actually been observed. Since at any Sm^{3+} concentration there is a probability that the transfer occurs to Sm^{3+}–Sm^{3+} or Sm^{3+}–Tb^{3+} couples, only a part of transferred energy builds up Sm^{3+} emission even at low Sm^{3+} concentration.

Acknowledgment

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