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Nonradiative Energy Transfer from $Tb^{3+} \rightarrow Er^{3+}$ in Calibo Glass

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Energy transfer studies have been made in a terbium–erbium coactivated calibo-glass system at room temperature and at liquid-air temperature. A study of the emission and decay of $^5D_4$ level of Tb^{3+} has been made by varying the acceptor (Er^{3+}) concentration. Probabilities and efficiencies of energy transfer as well as donor–acceptor distances have been calculated. At low acceptor concentration the decay of the donor (Tb^{3+}) emission has been found to be diffusion limited. At high acceptor concentration the mechanism governing the transfer is found to be dipole–dipole.

1. Introduction

The theory of nonradiative energy transfer from one ion (donor) to another ion (acceptor) has been discussed in detail by several authors. The preliminary approach has been made by Forster (*1*) and later on by Dexter (*2*). Inokuti and Hirayama (*3*) have analyzed the problem by studying the nature of the decay of the donor luminescence. More recently Yokota and Tanimoto (*4*) have treated this problem by taking into account the diffusion of the excitation.

When a system containing randomly distributed donors and acceptors, where migration of the excitation energy among the donors is absent, is optically excited, the decay of the donor emission as a function of time t is given by (*3*)

$$\phi(t) = \exp\left\{-\frac{t}{\tau_0} - \Gamma\left(1-\frac{3}{s}\right)\cdot \frac{C}{C_0}\left(\frac{t}{\tau_0}\right)^{3/s}\right\} \qquad (1)$$

where τ_0 is the donor decay time, S is the interaction parameter and is equal to 6 for dipole–dipole, 8 for dipole–quadrupole, and 10 for quadrupole–quadrupole interactions, respectively. C is the acceptor concentration and C_0 is the critical transfer concentration of acceptor which corresponds to critical separation (R_0) for which the probability of transfer from, and emission by, the excited ion are equal. In order to find out the interaction mechanism the experimental data are tallied with those obtained from Eq. (1). This is also corroborated by plotting P_{da} (transfer rate) vs C^2 (where C is the sum of the donor and acceptor concentrations) (*5*).

Much work has already been done taking Tb^{3+} as the energy donor in various hosts with an aim to transfer its excitation energy to several other rare-earth ions (*6*, *7*). Nakazawa and Shionoya (*8*) have studied energy transfer between Tb^{3+} and Er^{3+} in $Ca(PO_3)_2$ glass and observed a dipole–quadrupole mechanism of energy transfer. The present paper aims to find out the mechanism of energy transfer between Tb^{3+} and Er^{3+} in calibo glass and to make quantitative measurements for transfer probabilities and transfer efficiencies.

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Transfer probabilities (P_{da}) and transfer efficiencies (η_T) were calculated using the formulas expressed as:

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

where τ_0 is the decay time of the donor alone and τ is the decay time of the donor in the presence of the acceptor.

2. Experimental Details

Boric acid (Analar, BDH), calcium oxide (Analar, Riedel Germany), and lithium carbonate (Analar, Lab Chemie Industry, Bombay) were used for the host glass matrix. The composition of the host glass was CaO (20%):Li_2O (5%):B_2O_3 (75%) w/w. The density of the host glass was found to be 2.2 g cm^{-3}. Tb_2O_3 (99.9%, Indian Rare Earths Ltd., Kerala) and Er_2O_3 (99.9%, Koch Light Laboratories, England) were used as activators. Fixed quantities of host materials were thoroughly mixed with appropriate quantities of rare earths. The mixture was then placed inside an electric furnace in a platinum crucible for about 35 min at a temperature about 800°C. The hot melt was then poured into a metallic ring resting on a hot aluminum plate, and tablets of almost equal geometry were prepared.

The emission spectra were taken by exciting the samples in a fixed geometry on frontal illumination by a high-pressure mercury lamp with Wood's filter giving out 3650-Å groups of Hg lines. A prism-monochromator (SPM-2, Carl Zeiss Jena) was used to analyze the spectrum. A photomultiplier tube (EMI 9558 Q/B) was attached to it. The output of the photomultiplier was delivered either to a multiflex galvanometer or to a Honeywell chart recorder fed by an electrometer amplifier.

The fluorescence decay was studied by exciting the sample with a mercury flash lamp (BH-6 Hg) with a filter by 3650-Å units of radiation. The flash half-width was about 10 μsec. The selected output was fed to a photomultiplier tube (RCA-931 A) and was displaced on the screen of a cathode-ray oscilloscope (dual beam, Tektronix, Type 502 A). The decay curves were traced and analyzed both at room temperature and liquid-air temperature.

3. Results and Discussion

In Fig. 1 A is the emission spectrum of Tb^{3+} (2 wt%) in calibo glass showing four peaks at about 4880, 5425, 5850, and 6260 Å arising from the transitions: $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, and $^5D_4 \rightarrow {}^7F_3$, respectively. Concentration quenching of the $^5D_4$ emission was not found at this Tb^{3+} concentration. Emission from the $^5D_3$ level of Tb^{3+} was not observed in our system (2 wt% Tb^{3+}), the reason being that (*9*) the Tb^{3+} ions make pairs (Tb–Tb) and due to this the excitation energy of the $^5D_3$ level relaxes to the $^5D_4$ level by cross relaxation. In Fig. 1 B shows the emission of Tb^{3+} coactivated with Er^{3+} (2 wt%) in calibo glass. This clearly indicates the transfer of excitation energy from Tb^{3+} to Er^{3+}.

The decay of the $^5D_4$ level of Tb^{3+} when plotted on a semilogarithmic scale gives a straight line suggesting its exponential behavior (Fig. 2, A). This curve gives a lifetime about 2.5 msec for Tb^{3+}. When Er^{3+} ions are also incorporated in the glass, the initial portion of decay becomes nonexponential (*10, 11*) because those Tb^{3+} ions which are close to Er^{3+} ions will relax directly by multipolar interactions. At very small acceptor concentrations the final portion of the decay curve is again a straight line because the excitation energy of the Tb^{3+} ions will diffuse among the nonexcited Tb^{3+} ions by resonance and finally will go over to sink (Er^{3+}) by direct interaction. On increasing the acceptor-ion concentration slowly more Er^{3+} ions will be close to Tb^{3+} ions and the decay will show more nonexponentiality, the tail of the curve will again be a straight line (Fig. 2; B, C, D, E). This behavior of excitation decay, where both the diffusion among the donor system and the donor–acceptor interaction via dipole–dipole

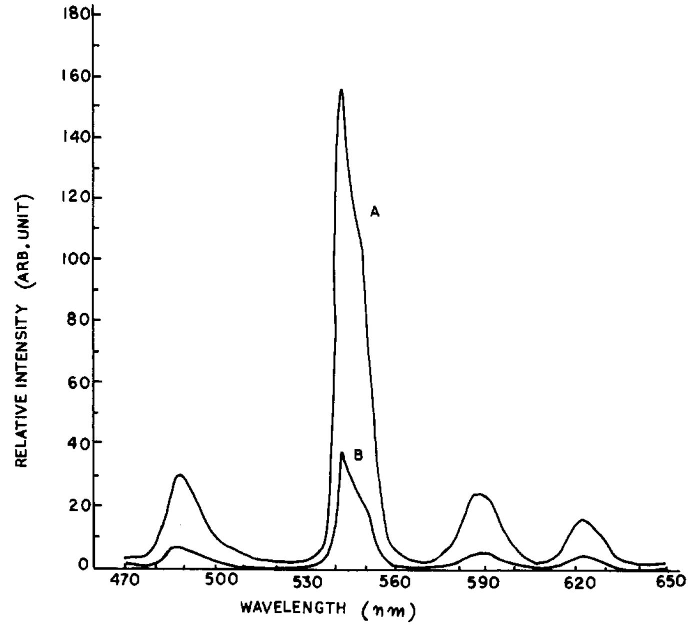

FIG. 1. Fluorescence spectra of (A) Tb^{3+} (2 wt%) and (B) Tb^{3+} (2 wt%) + Er^{3+} (2 wt%) in calibo glass at room temperature (300°K).

interaction occurs, has been treated by Yokota and Tanimoto (*4*). Their expression for the transient intensity is:

$$\phi(t) = \phi_0 \exp\left[-\frac{t}{\tau_0} - \frac{4}{3}\pi^{3/2} Na(Ct)^{1/2} \times \left(\frac{1 + 10{\cdot}87x + 15{\cdot}50x^2}{1 + 8{\cdot}743x}\right)^{3/4}\right],$$

where $x = DC^{-1/3}\, t^{2/3}$, D is the diffusion constant, C is the dipole–dipole coupling parameter. For early times of decay, i.e., when $t \ll C^{1/2} D^{-3/2}$ diffusion is insignificant and the above equation reduces to the Inokuti and Hirayama equation for $S = 6$, so that the head portion of the decay curve becomes non-exponential. For larger times, $T \rightarrow \infty$, the above equation reduces to an exponential function of time (the tail portion of decay becomes exponential). This time-dependent behavior is a characteristic of diffusion-limited decay (*10*).

At high acceptor concentrations diffusion is unimportant since the acceptors are more abandoned and the energy will relax directly. To find the mechanism of interaction in this case we tallied our experimental data with the theoretically obtained ones from Eq. (1) for $S = 6$ and $S = 8$. The critical distance of the donor–acceptor obtained from the critical

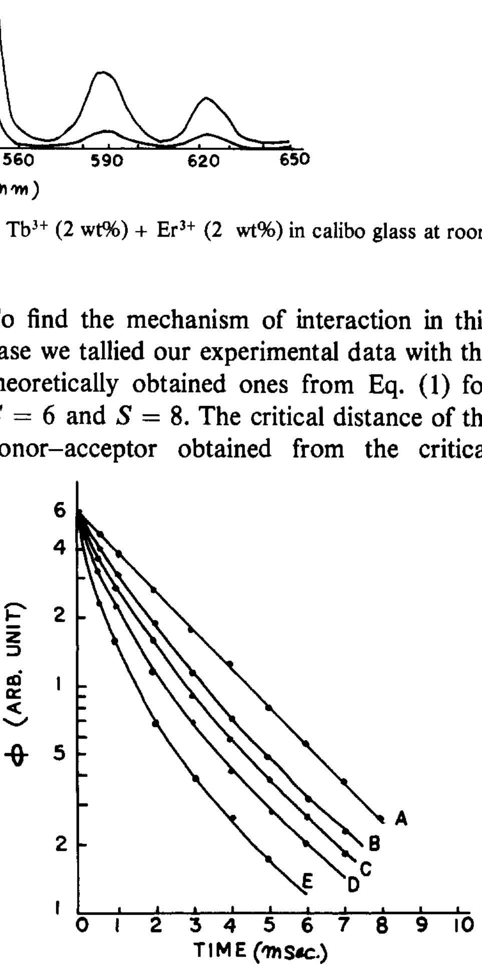

FIG. 2. Decay curves of Tb^{3+} with varying concentrations of Er^{3+}. (A) Tb^{3+} (2 wt%) alone; (B) Tb^{3+} (2 wt%) + Er^{3+} (0.5 wt%); (C) Tb^{3+} (2 wt%) + Er^{3+} (1 wt%); (D) Tb^{3+} (2 wt%) + Er^{3+} (2 wt%); (E) Tb^{3+} (2 wt%) + Er^{3+} (3 wt%).

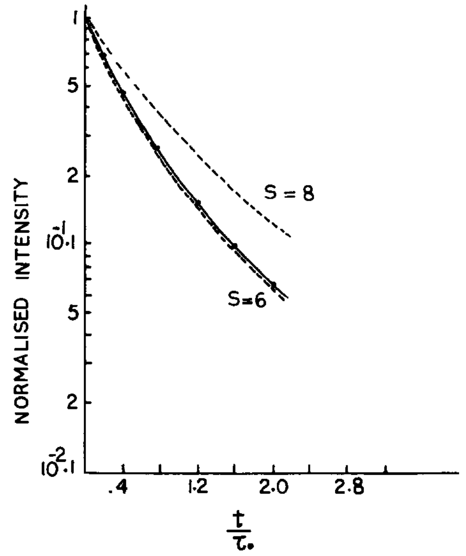

FIG. 3. Experimental curve (solid line) and theoretical curves (dotted lines) calculated from Eq. (1) for $S = 6$ and $S = 8$.

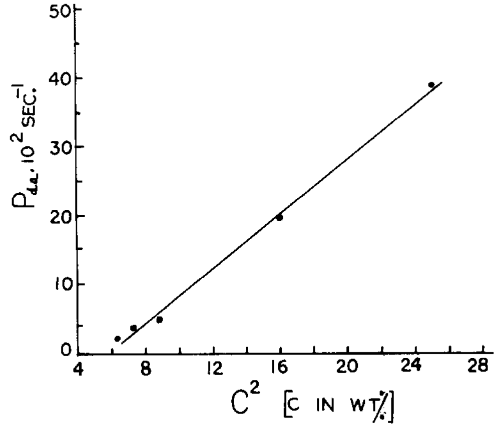

FIG. 4. Variation of P_{da} with the square of the sum of donor and acceptor concentrations.

concentration (*12*) in our system is ~15.0 Å. A look at the curve (Fig. 3) shows that our data fit best with the $S = 6$ curve, thereby suggesting a dipole–dipole interaction mechanism of energy transfer. Further, a plot of P_{da} vs C^2 which gives a straight line suggests the dipolar mechanism of energy transfer (Fig. 4). This is, however, different from the mechanism proposed for $Tb^{3+} \rightarrow Er^{3+}$ energy transfer in calcium metaphosphate glass by Nakazawa and Shionoya (*8*).

The calculated values of P_{da}, η_T, and R at room temperature are presented in Table I.

At liquid-air temperature (80°K) the Tb^{3+} fluorescence lifetime becomes 2.8 msec. Energy transfer from $Tb^{3+} \rightarrow Er^{3+}$ also decreases at this temperature. This is evidenced by comparing the calculated values of $P_{da} = 0.243 \times 10^3\ \text{sec}^{-1}$ and $\eta_T = 0.35$ at liquid-air temperature with the calculated values of $P_{da} = 0.490 \times 10^3\ \text{sec}^{1-}$ and $\eta_T = 0.55$ at room temperature. It seems that in glassy matrices, due to randomness in their structure, the energy levels of doped rare-earth ions broaden inhomogeneously. Thus the blurred-out energy levels of rare-earth ions in glasses at room temperature due to thermal vibrations make a broad path for energy transfer. When the temperature is lowered, the thermal vibrations decrease thereby causing relatively sharp energy levels and lessening the transfer. The

TABLE I

CALCULATED VALUES OF TRANSFER EFFICIENCIES, TRANSFER PROBABILITIES AND DONOR–ACCEPTOR DISTANCE PARAMETERS AT ROOM TEMPERATURE (300°K)

Donor concentration (fixed)	Acceptor concentration (wt%)	Energy transfer efficiency (η_T)	Energy transfer probability ($P_{da} \times 10^3\ \text{sec}^{-1}$)	Donor–Acceptor distance R (angstrom units)
	0.1	0.02	0.012	17.9
	0.3	0.18	0.088	17.3
	0.5	0.42	0.280	16.9
2 wt%	0.7	0.50	0.400	16.5
	1.0	0.55	0.490	15.6
	2.0	0.82	1.932	14.5
	3.0	0.90	3.764	13.6

increased lifetime of Tb^{3+} at low temperature indicates that some energy is being dissipated from the Tb^{3+} ion to the lattice at room temperature. This mechanism for increase in the Tb^{3+} lifetime at low temperatures was also reported by Pearson *et al.* (*13*).

Energy transfer by exchange is ruled out in our case since this process requires a separation of rare-earth ions not more than 3–4 Å with considerable overlap, while in our case the donor–acceptor distance even for the highest acceptor concentration is as high as 13.6 Å.

In conclusion, the energy transfer from Tb^{3+} to Er^{3+} at low Er^{3+} concentration in calibo glass is diffusion limited. At high acceptor concentration the transfer occurs by a dipole–dipole mechanism. At low temperature the energy transfer becomes less.

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