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Transfer of Optical Excitation Energy from $Dy^{3+} \rightarrow Nd^{3+}$ in Calibo Glass

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A study of energy transfer from trivalent dysprosium to trivalent neodymium in calibo glass has been done. The emission intensity of the $^4F_{9/2}$ level of Dy^{3+} and the time behavior of its decay with varying acceptor (Nd^{3+}) concentrations have been studied. The study at low acceptor concentrations has been done in some detail. The dipole–dipole coupling constant (C) and the diffusion constant (D) have been calculated. The observed mechanism of energy transfer is electric dipole–dipole. A radiative energy transfer from the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) emission transition of Dy^{3+} to $^4I_{9/2} \rightarrow {}^4G_{5/2}$ absorption transition of Nd^{3+} was also observed. The study was also carried out at high (493°K) and low (80°K) temperatures. The data at room temperature (290°K) were analyzed to obtain transfer efficiencies and transfer probabilities.

1. Introduction

Energy transfer from one ion (donor) to another ion (acceptor) occurs via both radiative and nonradiative processes (*1*). The radiative process is related simply to the emission of photons by the donor and its subsequent absorption by the acceptors. In the nonradiative process the two types of ions (donors and acceptors) should be coupled by electric or magnetic forces (*2*). The nonradiative transfer may be due to multipolar interactions and/or exchange interactions. The latter is of less importance in our case, since the donor–acceptor distance is too large. The transfer of energy by multipolar interactions is a one-step process. When the acceptor concentration is very low relative to the donor concentration, a multistep process becomes important. Owing to the perfect resonance between the ions of the same species, the excitation energy of one donor ion will make many hops among other donor ions before going finally to the sink (acceptor). This type of process is called ***diffusion*** or ***migration*** (*3*). When there is an increase in the acceptor ion concentration, two competitive processes take part; the first is the direct transfer of energy from donors to acceptors, and the second involves the migration of excitation among the donors. This type of process is called *diffusion-limited transfer.* Yokota and Tanimoto (*4*) have obtained an expression for the transient decay in which both the above processes play a role:

$$\phi(t) = \phi(0) \exp\left[-\frac{t}{t_0} - 7{\cdot}44(at)^{1/2}\left(\frac{1 + 10{\cdot}87x + 15{\cdot}50x^2}{1 + 8{\cdot}743x}\right)^{3/4}\right], \tag{1}$$

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where τ_0 is the donor decay time, $x = DC^{-1/3}t^{2/3}$, D is the diffusion constant, and C is the dipole–dipole coupling constant between donors and acceptors from $a = C \cdot N_a^2$. Here N_a is the acceptor ion concentration. The main feature of this equation is that for very small values of t ($t \ll C^{1/2}D^{-3/2}$), it reduces to the Inokuti and Hirayama equation for the dipole–dipole case and for large t ($t \to \infty$) it becomes an exponential function of time (*5, 6*).

We have applied the above equation in our case for diffusion-limited decay. Dy^{3+} is the donor and Nd^{3+} is the acceptor ion in our system. It is surprising that Antipenko *et al.* (*7*) found no energy transfer in the above pair of interacting ions, in $POCl_3:SnCl_4$ solutions. Cabezas and De Shazer (*8*) reported radiative transfer from $Dy^{3+} \to Nd^{3+}$ in borosilicate glass. Our purpose is to determine whether the excitation transfer is radiative or nonradiative, to investigate the nature of the transfer mechanism, and to calculate the transfer probabilities and other parameters.

2. Experimental

Boric acid (Analar, BDH), calcium oxide (Analar, Riedel, Germany) and lithium carbonate (Analar, Lab Chemie Industry, Bombay) were used for the host matrix. Their compositions and the method of preparation have been discussed elsewhere (*9*). Dy_2O_3 was obtained from GTE Sylvania, Towanda USA and Nd_2O_3 (99.9%) from Indian Rare Earths Ltd., Kerala.

The emission spectra were taken by exciting the samples with a 365-nm group of Hg lines, and a quartz prism monochromator was used to analyze the spectra. The decay time measurements were made by exciting the samples with a BH-6 Hg lamp (Half-width 10 μsec) by a single-flash technique. A Bellingham Stanley monochromator was used to select the desired wavelength. Other experimental details can be seen in our earlier papers (*9, 10*).

3. Results and Discussion

The optical behavior of Dy^{3+} in various inorganic glasses has been reported by several workers (*11–13*). It is observed that in glassy matrices with high phonon energies the emission occurs only from the $^4F_{9/2}$ level of Dy^{3+} to various ground levels. For calibo glass the emission spectrum of Dy^{3+} as observed is shown in Fig. 1A, in the visible region. The three peaks shown in the figure represent $^4F_{9/2} \to {}^6H_{15/2}$ (482 nm), $^4F_{9/2} \to {}^6H_{13/2}$ (575 nm), and $^4F_{9/2} \to {}^6H_{11/2}$ (670 nm) fluorescence transitions of Dy^{3+} (2.0 wt%) in calibo glass. The decay curve of Dy^{3+} (2.0 wt%) has been plotted in Fig. 2A on a semilogarithmic scale, which is purely exponential. The presence of Nd^{3+} ions disturbs the exponential behavior in the initial portion of the decay curve followed by an exponential tail (Figs. 2B–D). This case is different from that for fast diffusion, where the decay curves become exponential

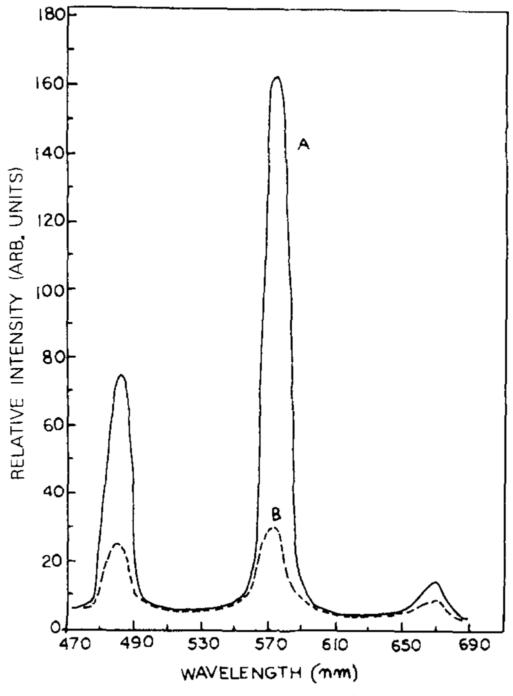

FIG. 1. Emission spectra of: (A) Dy^{3+} (2.0 wt%); (B) Dy^{3+} (2.0 wt%) + Nd^{3+} (1.0 wt%) in calibo glass at room temperature (290°K), at 365-nm excitation.

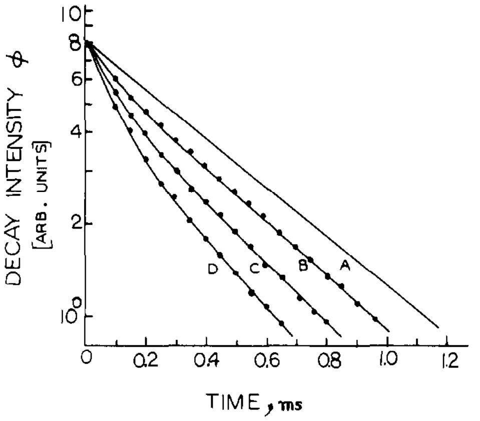

FIG. 2. Semilogarithmic plot of fluorescence decay of Dy^{3+} in calibo glass at room temperature: (A) Dy^{3+} (2.0 wt%); (B) Dy^{3+} (2.0 wt%) + Nd^{3+} (0.1 wt%); (C) Dy^{3+} (2.0 wt%) + Nd^{3+} (0.25 wt%); (D) Dy^{3+} (2.0 wt%) + Nd^{3+} (0.50 wt%).

throughout the time range (*14*). The increasing acceptor concentration graudally promotes the nonexponential region. The direct transfer of optical excitation energy from $Dy^{3+} \rightarrow Nd^{3+}$ is suggested by this nonexponential region. At low acceptor concentrations diffusion-limited relaxation is significant, since in this limit the donor ions are more numerous than the acceptors. Those donor ions which have acceptor ions nearby transfer their excitation directly, and the rest of the excited donor ions first diffuse among the ground-state donor ions, owing to perfect Dy–Dy resonance, and finally to the quenching center (Nd^{3+}). The diffusion-limited relaxation is confirmed by the fact that the experimental value of the function $[(1 + 10.87x + 15.50\,x^2)/(1 + 8.743)]^{3/4}$ given by Eq. (1) increases with time, as is also predicted by Eq. (1) itself.

The mechanism of $Dy^{3+} \rightarrow Nd^{3+}$ energy transfer is found to be dipole–dipole in character, as is evident from a plot between transfer probabilities (P_{da}) and the square of the sum of donor and acceptor concentrations (*15*) (Fig. 3).

The value of the constant C in Eq. (1) was found by fitting the equation in the decay curve (Fig. 2D) in the region where diffusion is absent. We computed the parameter a (Eq. (1)) from the fitting and then, using the relation $a = C \cdot N_a^2$, the value of C is calculated as $(5.1 \pm 0.1) \times 10^{-38}$ cm^6/sec. The experimental error in the computation of C is ≈2.8%. The critical transfer distance R_0 computed from the relation $R_0 = (C\tau_0)^{1/6}$ is 16.0 ± 0.1 Å, where the value of τ_0, the decay time of Dy^{3+} in neodymium-free sample, was taken as 560 ± 10μsec. The diffusion constant D is evaluated from the relations

$$1/\tau_D = 8{\cdot}5NaC^{1/4}D^{3/4},$$

$$1/\tau_D = 1/\tau_L - 1/\tau_0,$$

where $1/\tau_L$ is the decay rate of 2.0 wt% Dy^{3+} in the presence of 0.1 wt% Nd^{3+} at long times after excitation. The values of D obtained for this sample at room temperature, ~8.0×10^{-12} cm^2/sec, can be compared with the values obtained by Weber (*6*) 6×10^{-10} cm^2/sec in a Eu–Cr ion-pair in europium phosphate, and Watts and Richter (14), <(3×10^{-14}–2.2×10^{-11}) cm^2/sec in the system YF_3 : YB : Ho. The value of the diffusion length

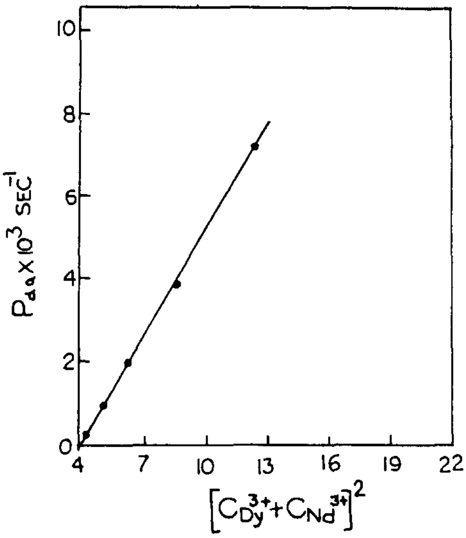

FIG. 3. The plot of transfer probability (P_{da}) against the square of the sum of donor and acceptor concentrations.

TABLE I

COMPUTED VALUES OF ENERGY TRANSFER EFFICIENCIES (η_T) AND TRANSFER PROBABILITIES (P_{da})

Donor (Dy^{3+}) concentration (wt%) fixed	Acceptor (Nd^{3+}) concentration (wt%)	Donor–acceptor distance (R) (Å)	Energy transfer efficiency η_T (at 290°K)	Energy transfer probability ($P_{da} \times 10^3$ sec^{-1})		
				At room temperature (290°K)	At low temperature (80°K)	At high temperature (493°K)
2.0	0.10	17.9	0.12	0.21	0.20	0.25
	0.25	17.5	0.38	0.98	0.88	1.07
	0.50	16.8	0.58	1.92	1.80	2.12
	1.00	15.7	0.68	3.78	3.50	3.80
	1.50	14.9	0.81	7.33	6.98	8.30
	2.00	14.2	0.84	9.32	9.20	10.50

$(D\tau_0)^{1/2}$ is about 10 Å, suggesting that the excitation energy migrates in a spherical volume of 10-Å radius within a 560-μsec duration, while the average distance between donor ions is 18.2 Å. The length parameter of diffusion $\rho = (0.68(C/D)^{1/4})$ is ~20 Å, which is less than the average acceptor distance 48 Å and greater than the distance between donors (18.2 Å). Hence the criterion $d \ll \rho \ll a$ of diffusion-limited relaxation is satisfied (*6*).

At high acceptor concentrations when almost all the Nd^{3+} ions are covered by the critical transfer distance R_0, the energy will relax directly to the acceptor ions and there will be no diffusion.

Varying the temperature does not affect the transfer appreciably, as is evident from Table I. The values of the transfer parameters agree with our experimental values within ±10%. A small variation of these parameters at temperatures 80 and 493°K is explained by the partial behavior of the host glass at different Dy^{3+} ion sites. The thermal broadening of energy levels at elevated temperatures results in a slight increase in the energy transfer, and the oppostie result is seen at low temperatures (*16*).

A radiative transfer from the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (575 nm) transition of Dy^{3+} to the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ absorption transition of Nd^{3+} also occurs, because the emission of Dy^{3+} corresponding to this transition covers the absorption of Nd^{3+} in this wavelength region completely. This is evident from Fig. 1B, which shows that the emission intensity of the yellow peak of Dy^{3+} decreases more rapidly than the other emission peaks, without affecting its shape. This point is further elucidated in Fig. 4, which shows the intensity ratios

$$\frac{^4F_{9/2} \rightarrow {}^6H_{13/2}}{^4F_{9/2} \rightarrow {}^6H_{15/2}} \quad \text{and} \quad \frac{^4F_{9/2} \rightarrow {}^6H_{11/2}}{^4F_{9/2} \rightarrow {}^6H_{15/2}}$$

plotted against the Nd^{3+} concentration, and it

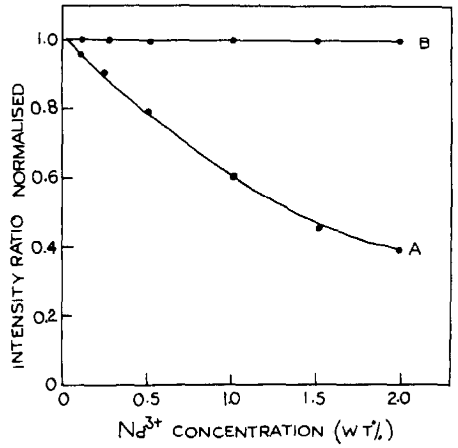

FIG. 4. Dy^{3+} fluorescence intensity ratios vs Nd^{3+} concentration plots: (A) corresponds to an intensity ratio of $(^4F_{9/2} \rightarrow {}^6H_{13/2})/(^4F_{9/2} \rightarrow {}^6H_{15/2})$; (B) corresponds to an intensity ratio of $(^4F_{9/2} \rightarrow {}^6H_{11/2})/(^4F_{9/2} \rightarrow {}^6H_{15/2})$.

was also observed by Cabezas and De Shazer (*8*) in borosilicate glass.

The transfer efficiencies (η_T) and transfer probabilities (P_{da}) were calculated using the following formulas (*17*, *18*) and are presented in Table I.

$$\eta_T = 1 - \frac{\tau}{\tau_0}; \qquad P_{da} = \frac{1}{\tau_0}\left(\frac{\tau_0}{\tau} - 1\right),$$

where τ_0 is the decay time of Dy^{3+} (2.0 wt%) in the absence of the acceptor (Nd^{3+}) and τ is the decay time in the presence of the acceptor (Nd^{3+}).

In conclusion, the mechanism governing the nonradiative energy transfer from Dy^{3+} to Nd^{3+} is electrostatic dipole–dipole in character. In addition, a radiative transfer from Dy^{3+} to Nd^{3+} takes place. At low acceptor concentrations diffusion-limited energy transfer is dominant, and the transfer is less sensitive to temperature.

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