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Quantum Efficiency of Diffusion-Limited Energy Transfer from $Eu^{3+} \rightarrow Nd^{3+}$ in Borate Glass

J. C. JOSHI,* N. C. PANDEY, B. C. JOSHI, R. BELWAL, AND JANARDAN JOSHI

Department of Physics, D.S.B. (University) College, Naini Tal, Nainital-263 002, India

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Radiative and nonradiative energy transfer from optically excited Eu^{3+} to Nd^{3+} has been studied in sodium borate glass. Probabilities and efficiencies of nonradiative $Eu^{3+} \rightarrow Nd^{3+}$ energy transfer were determined from Eu^{3+} fluorescence decay rates. The time course of Eu^{3+} fluorescence in the presence of Nd^{3+} is shown for the characteristic of diffusion-limited relaxation. At sufficiently high Nd^{3+} concentration, where energy migration along Eu^{3+} ions becomes less essential, the experimental data are analyzed for comparison with numerical calculations of the theory recently made by Inokuti and Hirayama. The observed approximate fitting between theory and experiment shows that energy transfer from $Eu^{3+} \rightarrow Nd^{3+}$ is carried out predominantly by dipole–dipole interactions.

1. Introduction

Considerable progress has been achieved in recent years toward improving the pumping efficiency of solid-state lasers containing trivalent rare earth ions as active agents. One approach which will be particularly fruitful is based on rare earth to rare earth energy transfer. The mechanism of energy transfer between Tb and Nd in sodium borate glass has been examined at 80, 300, and 500°K by Pant *et al.* (*1*), By the measurements of the concentration dependence of intensity and lifetime, they found that the transfer from the $^5D_4$ level of Tb^{3+} is predominantly by dipole–dipole interactions at high Nd concentrations. Another illustration of rare earth to rare earth energy transfer is the example of a Eu–Nd co-activated system where energy absorbed by Eu^{3+} ions is transferred to Nd^{3+}.

Radiative energy transfer in a Eu–Nd : borosilicate glass has been reported previously by Cabezas and De Shazer (*2*). They estimated that about a 10% increase in Nd^{3+} fluorescence resulted from $Eu^{3+} \rightarrow Nd^{3+}$ radiative transfer. Both radiative and nonradiative energy transfer and decay processes have been investigated in high silicate glasses codoped with Eu and Nd by Sharp *et al.* (*3*). The presence of nonradiative energy transfer from $Eu^{3+} \rightarrow Nd^{3+}$ was established from an examination of the excitation spectra and the increased decay rates in the presence of Nd. In calcium metaphosphate glass Nakazawa and Shionoya (*4*) discussed the results of transfer in terms of resonance theory of energy transfer using the numerical calculations of the theory made by Inokuti and Hirayama (*5*). Among the resonance mechanisms due to various electrostatic multipolar interactions, the dipole–quadrupole gave the best fit between theory and experiment. The mechanisms of energy transfer between Eu and Nd and the migration of excitation between Eu^{3+} ions in the $Na_{0.5}(YEuNd)_{0.5}WO_4$ and $(YEuNd)_2O_3$

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* Author to whom all correspondence should be addressed.

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were examined by Van Uitert *et al.* (*6*). Transfer from $Eu^{3+} \rightarrow Nd^{3+}$ appeared to be predominantly by dipole–dipole interactions. Excitation migration between $^5D_0$ states of Eu^{3+} ions in $Ca(PO_3)_2$ glass has been reported by Motegi and Shionoya (*7*). Their results indicate that the phonon-assisted process is more dominant than the resonant process for excitation migration in the system studied.

Looking to the various processes occurring in Eu and Eu–Nd systems, an elucidation of mechanism of energy transfer from $Eu^{3+} \rightarrow Nd^{3+}$ in sodium borate glass is also important in the understanding of sensitized luminescence.

2. Experimental

The Eu–Nd coactivated glass samples were prepared from Analar reagent grade disodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), Eu_2O_3 (99.9%, Koch Light Laboratories, England), and Nd_2O_3 (99.9% Indian Rare Earths Limited, Kerala). The base glass composition was Na_2O (30.8 wt%):B_2O_3 (69.2 wt%). The Eu^{3+} concentration was kept (0.5 wt%) fixed and the Nd^{3+} concentration was varied from 0.1 to 4 wt%. The mixed powder was melted in a platinum crucible at about 800°C for about 40 min. The hot melt was poured into a preheated metallic ring resting on an aluminum base so as to obtain transparent glass bullets of almost equal geometry. For obtaining the fluorescence spectra the samples were excited with a 125-W Phillips Hg lamp covered with a Wood's filter to transmit the 365.0-nm group of mercury lines. The emission was analyzed with a Carl–Zeiss Jena SPM-2 monochromator, a photomultiplier (EMI 9558 Q/B), and a multiflex galvonometer set. The lifetimes were measured by a single-flash technique as described in our previous paper (*8*). Most of the study was undertaken at room temperature. Some observations were also carried out at liquid air temperature (80°K).

3. Results and Discussion

The system studied was a Eu–Nd system in sodium borate glass. Experiments were conducted to study the fluorescence spectrum of 0.5 wt% Eu^{3+} glass alone and in the presence of 0.5 wt% Nd^{3+} as shown in Fig. 1. In recording these comparative spectra, the sample size and experimental conditions were maintained constant. Excited Eu^{3+} ions in borate glass (phonon energy 1340–1480 cm^{-1}) decay rapidly to the metastable $^5D_0$ level from which fluorescence is observed to the levels of ^7F_j multiplets. The observed fluorescence transitions are assigned as: $^5D_0 \rightarrow {}^7F_0$ (577.5 nm), $^5D_0 \rightarrow {}^7F_1$ (590 nm), $^5D_0 \rightarrow {}^7F_2$ (613 nm), and $^5D_0 \rightarrow {}^7F_3$ (657.5 nm), the $^5D_0 \rightarrow {}^7F_2$ emission being the most intense one.

The self-quenching of Eu^{3+} fluoresence via exchange interactions frequently occurs in crystals containing high concentrations of

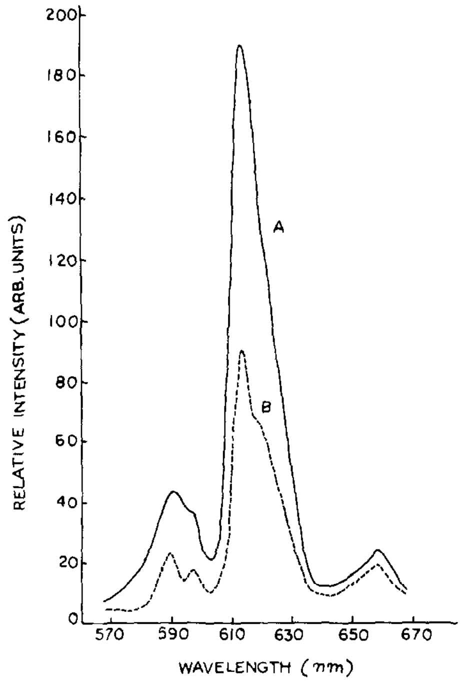

FIG. 1. (A) Fluorescence spectrum of 0.5 wt% Eu^{3+} in sodium borate glass at room temperature. (B) The dashed curve representing the emission spectrum of the same sample when 0.5 wt% Nd^{3+} is added.

Eu^{3+} ions. The absence of self-quenching in our glass activated with 0.5 wt% Eu^{3+} indicates that exchange coupling between Eu^{3+} ions is not occurring. To verify that Eu^{3+} decay in the absence of Nd^{3+} was purely radiative, the decay was measured both at room and liquid air temperature for the Nd^{3+}-free samples. The Eu^{3+} fluorescence from undoped glass decays exponentially following pulsed excitation. The lifetimes were the same (2.2 msec) thereby also indicating that nonradiative decay by the multophonon process (*9*) does not make a significant contribution to the Eu^{3+} decay rate in borate glass at room temperature.

The shortening of the Eu^{3+} fluorescence lifetime in the presence of Nd^{3+} is presented in Fig. 2. In cases where decay curves are markedly nonexponential, it is a matter of definition how one defines a decay time. In this paper the decay time will be taken as the time after which intensity is $1/e$ times the initial intensity. The presence of nonradiative energy transfer from $Eu^{3+} \rightarrow Nd^{3+}$ is experimentally established by observing the decrease in luminescence intensity of Eu^{3+} ions and increased fluorescence decay rates as shown in Fig. 1 and Fig. 2. This selective decrease at about 580 nm in fluorescence spectrum of 0.5 wt% Eu^{3+} in the presence of 0.5 wt% Nd^{3+} corresponds to main visible absorption transition $^4I_{9/2} \rightarrow (^4G_{5/2}, {}^2G_{7/2})$ of Nd^{3+} therefore suggests that radiative transfer is also taking part in addition to the nonradiative process. The observed radiative transfer fulfills the essential requirement (spectral overlap) for resonance radiationless energy transfer from the $^5D_0$ level of Eu^{3+} to Nd^{3+} in borate glass.

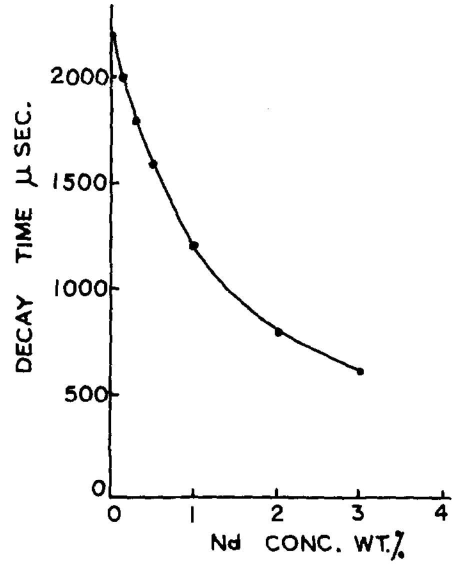

FIG. 2. Dependence of fluorescence decay times of Eu^{3+} upon Nd^{3+} concentration at room temperature.

Three processes (*10*) affect the donor lifetime in a sensitized rare earth system:

I. intrinsic donor radiative and nonradiative relaxation,
II. direct relaxation transfer to acceptors,
III. energy migration among the donors followed by transfer to acceptors (diffusion-limited relaxation).

Diffusion alone in a system of excited ions is generally a resonant process and is not observed in fluorescence decay measurements (*11*) as the decay rate is not changed by the diffusion of excitation among the ions. In our system Eu^{3+} fluorescence decay for Nd^{3+}-free samples (Fig. 3A) exhibits a single exponential and shows no direct evidence for diffusion of excitation among the donors but the presence and the effect of diffusion of excitation among Eu^{3+} ions become observable through the combination of quenching (energy transfer to Nd^{3+}) and diffusion (Figs. 3B, C, D). The time dependence of the fluorescence decay as a result of quenching is independent of geometry and in this way is less subject to error.

Yokota and Tanimoto (*12*) have worked out the expected fluorescence decay when both quenching and diffusion are active. The most important characteristic of decay curves is its behavior at long times, a regime that is more easily investigated experimentally. In Fig. 3 it is also important to note that at very long times the slopes of the decay curves on a semilogarithmic plot give approximately the same radiative rate indicating that all ions near quenching centers have already decayed. This long-time behavior is referred to as diffusion-

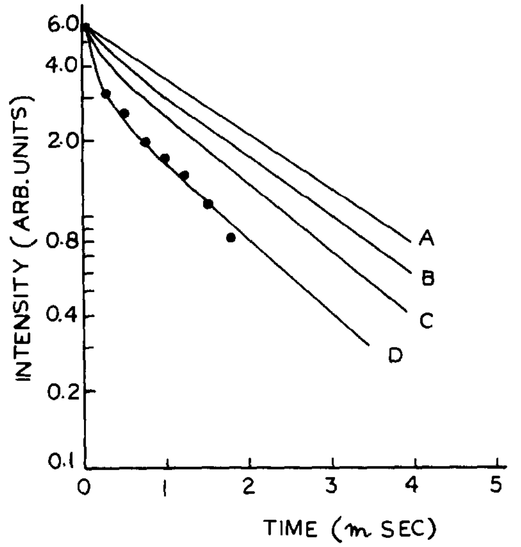

FIG. 3. Variation of the time dependence of Eu^{3+} fluorescence decay in sodium borate glass with increasing Nd content, excited with a BH-6 Hg flash lamp (10-μsec duration). $\lambda = 365.0$ nm. The neodymium concentration is x wt%, where: (A) $x = 0$, (B) $x = 0.5$, (C) $x = 1$, (D) $x = 2$. The balck spots represent the theoretical points calculated for dipole–dipole interaction ($S = 6$).

limited energy transfer (*13–15*) and is characterized by exponential decay at long times. Since the intrinsic Eu^{3+} lifetime τ_0 is 2.2 msec, an $Eu^{3+} \rightarrow Eu^{3+}$ energy diffusion process therefore must occur within this duration. As the Nd^{3+} concentration is increased a larger fraction of the excited donors (Eu^{3+}) are then within the critical interaction range of acceptors (Nd^{3+}) and may interact with them via multipolar or exchange forces with a direct transfer of energy. The initial nonexponential portion of the decay in Fig. 3 is attributed to relaxation by this direct energy transfer. For direct multipolar interactions, Inokuti and Hirayama (*5*) obtained the following expression for intensity decay of the emission of sensitizer surrounded by many acceptors:

$$I(t) = I(0) \cdot \exp\left[\frac{-t}{\tau_0} - \Gamma\left(1 - \frac{3}{S}\right) \cdot \frac{C}{C_0} \cdot \left(\frac{t}{\tau_0}\right)^{3/S}\right] \quad (1)$$

where $S = 6$ for dipole–dipole, $S = 8$ for dipole–quadrupole and $S = 10$ for quadrupole–quadrupole interactions. $\Gamma(x)$ is the Γ function, C is the activator concentration, C_0 is the critical concentration at which the probability for quenching is equal to the radiative probability. The value of Nd^{3+} at which $\tau = \tau_0/2$ corresponds to the critical concentration C_0.

The comparison between experimental decay and the theoretical expression was used to determine the index of multipolar interactions. The theoretical points thus obtained over experimental decay for 0.5 wt% Eu^{3+} : 2.0 wt% Nd^{3+} system are shown in Fig. 3D where Eq. (1) was used for dipole–dipole interaction ($S = 6$). The fitting between experimental decay and the theoretical expressions for higher multipolar interactions such as dipole–quadrupole and quadrupole–quadrupole interactions are worse than for the dipole–dipole case. Thus among the resonance mechanisms due to various electrostatic multipolar interactions, the dipole–dipole gave the best fit between theory and experiment suggesting therefore that the mechanism governing the transfer from $Eu^{3+} \rightarrow Nd^{3+}$ possesses predominantly dipole–dipole interactions between the donor and acceptor ions. Energy transfer by exchange is ruled out in our case since this mechanism requires a separation of *RE* ions not more than 3–4 Å with considerable overlap of wavefunctions.

The critical transfer distance R_0 for which excitation transfer and spontaneous deactivation of Eu^{3+} ions have equal probability is calculated from $C_0 = 3/4\ II\ R_0^3$. Putting the value of $C_0 = 1.2$ wt% (8.52×10^{19} ions/cm^3), R_0 comes about 14.1 Å.

Quantitative measurements for probabilities and efficiencies of nonradiative $Eu^{3+} \rightarrow Nd^{3+}$ energy transfer were made by analyzing Eu^{3+} fluorescence lifetime data in the presence of Nd^{3+} for the simple operational definitions of P_{da} and η_T. It is clear from Table I that nonradiative transfer efficiency for 0.5 wt% Eu^{3+} : 3 wt% Nd^{3+} is 72.7%; however, the radiative transfer will increase this figure for the total transfer efficiency.

TABLE I

CALCULATED VALUES OF PROBABILITIES AND EFFICIENCIES OF NONRADIATIVE ENERGY TRANSFER

Donor (Eu^{3+}) concentration	Acceptor (Nd^{3+}) concentration (wt%)	Eu^{3+} fluorescence decay time (in the absence of neodymium) τ_0	Eu^{3+} fluorescence decay time in the presence of Nd (msecs) τ	Probability of energy transfer $P_{da} \times 10^2\ \mathrm{sec}^{-1}$ $P_{da} = \tau^{-1} - \tau_0^{-1}$	Efficiency of energy transfer $\eta_T = 1 - (\tau/\tau_0)$
0.5 wt% (fixed)	0.1	2.2 msec	2.0	0.45	0.090
	0.125		1.9	0.72	0.136
	0.25		1.7	1.33	0.227
	0.5		1.5	2.12	0.318
	1.0		1.2	3.78	0.454
	2.0		0.8	7.93	0.636
	3.0		0.6	12.12	0.727

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