Quantum Yield of Ce^{3+} and Energy Transfer between Ce^{3+} and Tb^{3+} in Borax Glasses*

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Quantum yields of Ce^{3+} in borax glasses were obtained by the comparative method and by lifetime measurements. Energy transfer from Ce^{3+} to Tb^{3+} was detected in borax glasses from the excitation spectrum. The transfer probabilities were calculated from the increase in the Tb^{3+} fluorescence in the presence of Ce^{3+} and the decrease of the Ce^{3+} fluorescence in the presence of Tb^{3+}. A linear dependence of the transfer probabilities was found with the squared sum of the concentrations of the donor and acceptor ions. This is consistent with dipolar mechanism and interactions of one Ce^{3+} donor with two Tb^{3+} acceptors, in view of the Fong–Diestler theory.

Introduction

Energy transfer between Ce^{3+} and Tb^{3+} in a crystalline host has been thoroughly studied by Blasse and Bril (*1*), Loriers and Heindl (*2*), Bourcet et al. (*3, 4*), and Verstegen et al. (*5*). In $Ca[(PO_3)_2]$ glasses, the phenomenon of energy transfer between Ce^{3+} and Tb^{3+} was reported by Shionoya and Nakazawa (*6*); however, to our knowledge, no quantitative measurements have been made in the glassy state. It is the purpose of this work to calculate the transfer probabilities by the methods described earlier by one of the present authors (*7, 8*).

Experimental

The materials used were borax (A. R. Mallinckrodt 99.5% purity), cerium as $(NH_4)_2Ce(NO_3)_6$ (A.R. B.D.H. 97% purity), terbium as Tb_2O_3 (Molycorp. 99.9% purity) and mannitol (National Biochemical Co.).

The technique of glass preparation has been previously described (*9*). In glasses containing Ce^{3+}, 50 mg mannitol was added

to batches containing 6 gr of the initial mixture during the melting process in order to keep a reducing atmosphere. A series of glasses of the following final compositions were prepared.

1. Ce^{3+}—0.049, 0.972, 0.143, 0.286 wt%
2. Tb^{3+}—0.5, 1.0, 2.0, 3.0, 4.0, 5.0 wt%
3. 0.025 wt% Ce, Tb^{3+}—0.0, 1.0, 2.0, 2.5, 3.0 wt%
4. 0.5 wt% Tb, Ce^{3+}—0.025, 0.03, 0.036, 0.052, 0.075 wt%.

Emission and excitation spectra were obtained by use of a Xenon lamp and a spectrofluorimeter built in our laboratory (*9*). Decay times of Ce^{3+} were measured using a N_2 laser with emission line at 3371 Å. The duration of the laser is 10 nsec. All measurements were taken at room temperature.

Results

The absorption and emission of Tb^{3+} as well as its quantum efficiencies in borate glasses are given in Ref. (*10*). The absorption spectrum of Ce^{3+} in borax is given in Refs. (*8*) and (*11*). Its major peak is at 310 nm, at which the excitation was performed. The emission
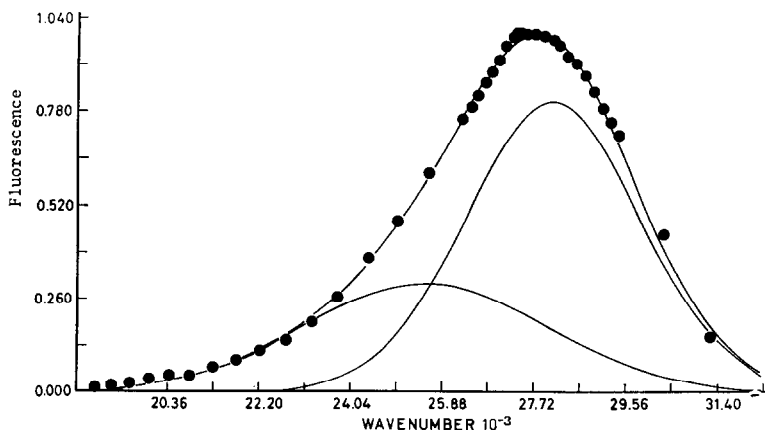
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FIG. 1. Gaussian Analysis curve of the emission spectrum of Ce^{3+} in borax concentration 0.025 wt%.

spectrum of 0.025 wt% Ce^{3+} in borax is presented in Fig. 1. The curve is resolved into two components arising from the emission from the lowest component of the ^2D state to the $^2F_{7/2}$ and $^2F_{5/2}$; the corresponding peaks are at 25.565 and 28.097 cm^{-1}. The ratio between the emission of $^2F_{7/2}$ and $^2F_{5/2}$ is 0.53.

Quantum Efficiency of Ce^{3+} in Borax

Quantum yield was calculated by (a) the comparative method and (b) measurement of the radiative transition probabilities.

a. The comparative method has been described in detail in Ref. (8). [For the determination of quantum efficiency of Ce^{3+} excited at 310 nm, Tl doped KCl disks of quantum efficiency of 0.5 (12) were used as a standard.] The η_u thus obtained is 0.44 ± 10%.

b. The quantum yield η was calculated by use of the expression

$$\eta = \tau_{meas}/\tau_{nat}, \qquad (1)$$

where τ_{meas} is the measured fluorescent lifetime, which in the present case, is 34.5 msec, and τ_{nat} is calculated by use of (13);

$$1/\tau_{nat} = K^r = 2.88 \times 10^{+9} n^2 <v_f^{-3}> \tfrac{-1}{av}gl/gu$$
$$\int \varepsilon(v)dv/v \qquad (2)$$

The quantity $<v_f^{-3}>\tfrac{-1}{av}$ is given by

$$<v^{-3}>\tfrac{-1}{av} = \int F(v)dv/F(v)^{-3}dv \qquad (3)$$

The symbols appearing in formulas 2 and 3 are explained in detail in Ref. (8). The radiative

transition probability K^r due to the transition $^2F_{5/2} \rightarrow\ ^2D$ was obtained from the absorption spectrum. The total transition probability $1/\Sigma\tau_{nat}$ was computed from this value and the ratio between the two equations, and is given by

$$1/\Sigma\tau_{nat} = 1.53 \text{ K } (^2D_{5/2} \rightarrow\ ^2F_{5/2}) \qquad (4)$$

In this way, $\Sigma\tau_{nat} = 71.22 \times 10^{-9}$ nsec and from (1) 0.48 ± 10%.

Energy Transfer

The evidence for energy transfer between Ce^{3+} and Tb^{3+} is seen in Fig. 2. In this figure, the excitation spectrum of Tb^{3+} fluorescence is shown. In presence of Ce^{3+} an additional band peaking at 315 nm is observed. This band is characteristic of the excitation of Ce^{3+}. Figure 3 presents the increase of fluorescence of Tb^{3+} (0.5 wt%) on excitation via Ce^{3+} at 310 nm. As can be seen from Fig. 3, the increase of fluorescence is dependent linearly on donor concentration. Figure 4 presents the decrease of Ce fluorescence at 365 nm. The decrease is monotonous and nonlinear.

The energy transfer probability was computed by use of formulas (5) and (6) (see Ref. (14)):

$$P_d = 1/\tau_d(\eta^0{}_d/\eta_d - 1), \qquad (5)$$

in which τ_d is the measured decay time of the fluorescence of the donor, $\eta^0{}_d$ the donor emission intensity with no acceptor present,
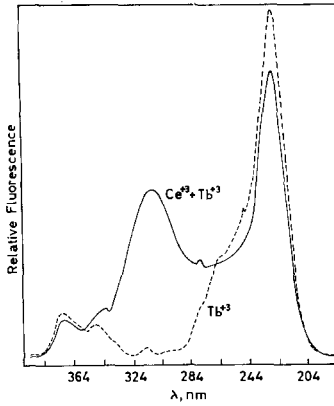
FIG. 2. Excitation spectrum of Tb^{3+} alone (monitored at 540 nm) and of Tb^{3+} in the presence of Ce^{3+}.

and η_d the emission of the donor in the presence of the acceptor.

Alternatively, energy transfer probability P_a can be derived from the increase of acceptor according to

$$P_a = \eta^0_d \Delta\eta_a / \eta^c_B \tau_d \eta_d \qquad (6)$$

where η^0_d, η_d, and $1/\tau_d$ have the same values as in (5), $\Delta\eta_a$ is the increase in fluorescence of
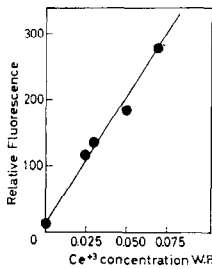

FIG. 3. Relative fluorescence of 0.5 wt% Tb^{3+} at 540 nm (excited at 310 nm) as a function of Ce^{3+} concentration.
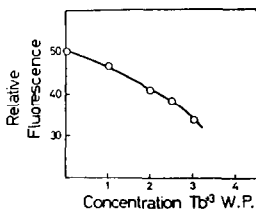

FIG. 4. Decrease of 0.025 wt% Ce^{3+} fluorescence (excited at 310 nm) as a function of Tb^{3+} concentration.

TABLE I

Concentration	(wt%)	$P_d \times 10^{-6}$	η_t
Ce^{3+}	Tb^{3+}		
0.025	1.0	2.0	0.07
0.025	2.0	6.7	0.19
0.025	2.5	8.7	0.23
0.025	3.0	13.9	0.32

TABLE II

Concentration	(wt%)	$P_a \times 10^{-5}$	η_t
Ce^{3+}	Tb^{3+}		
0.025	0.5	5.21	0.0176
0.030	0.5	5.31	0.0179
0.036	0.5	5.61	0.0189
0.052	0.5	5.67	0.0192
0.075	0.5	6.88	0.0231

the acceptor in the presence of the donor, and η^c_B is the quantum efficiency of the acceptor from the emitting level excited to a higher level (for a detailed description see Ref. (14)).

The efficiency of energy transfer η_t is given by

$$\eta_t = 1 - (\eta_d/\eta^0_d) \qquad (7)$$

Moreover, η_t can also be expressed by

$$\eta_t = Pa\tau_d/1 + Pa\tau_d$$

From these formulas, transfer probabilities and efficiencies were computed and are given in Tables I and II.

Discussion

The quantum efficiency of Ce^{3+} in borax glasses, which is about 0.46, is slightly higher than that obtained by Blasse and Bril (1) in lanthanum borate activated crystals with quantum efficiencies of 0.3–0.4.

The classical approach for energy transfer mechanism is that of exchange which is active for very short distances, or that of multipolar interaction, which is active when the interionic distances are about 10 Å and more (15). Since in this work the interionic distances were

higher than 10 Å, the experimental results were interpreted by Dexter formulae for multi-polar transfer. The corresponding formulae for a probability of dipole–dipole transfer may be written as: $P_{da} = CR^{-6}$ and for dipole – quadrupole interaction, as: $P_{da} = C'R^{-8}$. The exact expressions for C and C' can be found in (7 and 10).

In order to decide whether the energy transfer from Ce^{3+} to Tb^{3+} is of the dipole–dipole or dipole–quadrupole nature, we have plotted our experimentally obtained values of P_{da} vs $C^{6/3} \sim 1/R^6$ and vs $C^{8/3} \sim 1/R^8$ (C being the acceptor concentrations). The linear dependence of P_{da} on the square of concentration, as presented in Figs. 5 and 6, may be evidence for a dipole–dipole mechanism of energy transfer. It should be noted that Fong and Diestler in their recent work (17) using a statistical approach to the nonradiative energy transfer between ions in crystals,
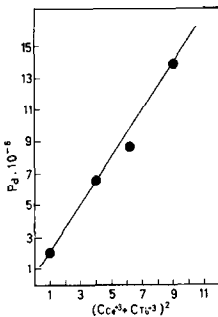

FIG. 5. Energy transfer probability P_d as a function of the squared sum of the concentrations of the donor and acceptor ions.

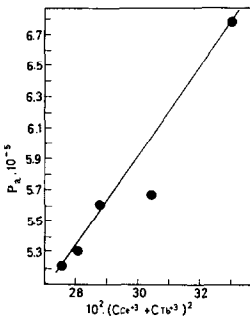FIG. 6. Energy transfer probability P_a as a function of squared sum of the concentrations of the donor and acceptor ions.

connected the transfer probability dependence on concentration with the number of inter-acting particles. Specifically, the dependence of P_{da} on the square of concentration will be interpreted by the Fong–Diestler theory as a statistical probability that two acceptor ions will be found near a donor ion. This is feasible in our case, since the concentration of the acceptor Tb^{3+} is much higher than that of the donor Ce^{3+}.

The values of energy transfer efficiency and probabilities between Ce^{3+} and Tb^{3+} in borax glasses presented in Table I, are comparable in magnitude to those obtained very recently by Bourcet and Fong (18) in $La_{1-x-}Ce_xTb_yPO_4$ crystals. In their paper (18) a detailed study of energy transfer efficiency dependence on donor concentration and temperature was performed. It was found that energy transfer between Ce^{3+} and Tb^{3+} is enhanced at elevated temperature, the enhancement being larger in samples with high concentration of Ce^{3+} ($La_{0.35}Ce_{0.6}Tb_{0.05}$) and only slight with low concentration of Ce^{3+} ($La_{0.9}Ce_{0.05}Tb_{0.05}$). These observations are consistent with our results given in Table II where a slight increase of η_t with Ce^{3+} concentration at room temperature was observed. The increase of energy transfer efficiency with donor concentration may be explained by energy diffusion within the donor system. In consequence of such diffusion, the effective distance between the excited donor ions and the acceptor ions is decreased, thus resulting in increase of energy transfer efficiency. A detailed theory of diffusion dependent energy transfer was presented by Weber (19) and applied by Bourcet and Fong (18). The diffusion constant of resonant energy migration may be given in the form:

$$D \alpha N_d \sum_f \frac{g_f \exp(-E_f/KT)}{\Delta \Sigma_f g_f \exp(-E_f/kT)} \left(\frac{g_f}{g_i}\right) \frac{f_{if}^2}{v_{if}^2 \Delta v_{if}}$$

where, i and f denote initial and final states involved in the resonant transfer process occuring between two donors, g_f and g_i denote the degeneracies of the fth and ith states, E_f is the energy of the fth state, f_{if}, v_{if} and Δv_{if} are the oscillator strengths, frequency and linewidth of the transition between the initial and final states, respectively. Since the

f_{if} of Ce^{3+} is of the order of 10^{-1}, the diffusion should be noticeable even at low concentrations of Ce^{3+}.

From our experimental results, it can be seen that in glasses having a concentration of 0.025 wt% Ce^{3+} and 3 wt% of Tb^{3+}, the transfer efficiency is 32%. In crystals of $LaPO_4$ which contain a similar concentration of Tb^{3+} and a concentration of Ce^{3+} which is about two orders of magnitude higher, the value of transfer efficiency (4) when excited at 250 nm, was only 23%. Our experimental results indicate the practical use of glasses as fluorescence devices.

Acknowledgment

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