

## Energy Transfer from $\text{UO}_2^{2+}$ to $\text{Sm}^{3+}$ in Phosphate Glass\*

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Energy transfer from  $\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$  is described. The transfer efficiencies are calculated from the decrease of donor luminescence and lifetimes and from the increase of the acceptor fluorescence. It is shown that the transfer is nonradiative. The energy transfer efficiencies are greater when the donor is excited at higher energy levels due to stronger overlap between electronic levels of donor  $\text{UO}_2^{2+}$  and acceptor  $\text{Sm}^{3+}$ . From the comparison of energy transfer efficiencies from  $\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  it is deduced that the overlap between excitation levels of donor and acceptor is a sufficient condition for the transfer.

### Introduction

The visible emission of  $\text{Sm}^{3+}$  is of practical value as it may be utilized in various fluorescence devices.  $\text{Sm}^{3+}$  as a single dopant in borate (1), phosphate (1), germanate (2), and tellurite (3) glasses has been studied. The radiative transition probabilities along with the transition matrix elements have been calculated recently in these glasses (4). The intensity of fluorescence is ruled by the product of radiative transition probabilities and the population of the excited levels. Since radiative transition probabilities of  $\text{Sm}^{3+}$  from  $^4G_{5/2}$  are  $3.57 \times 10^{-2}$  per second, the way to increase  $\text{Sm}^{3+}$  fluorescence is to increase the population of its levels via energy transfer (5). It has been shown previously (6) that the best way to achieve high population of excited states of rare earth ions is to use donors with high absorption coefficients. In this paper we report the phenomenon of energy transfer (E.T.) from

$\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$  in phosphate glass and compare the results to E.T. from the same donor to  $\text{Eu}^{3+}$ .

Energy transfer from  $\text{UO}_2^{2+}$  to other rare earth ions in solutions (7, 8), crystals (9, 10), and glasses (11-16) was studied. To the best of our knowledge there is no quantitative study of transfer from  $\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$ . The fluorescence characteristics of glasses doped with  $\text{UO}_2^{2+}$  only which are needed for such a study are reported in Ref. (17).

### Experimental

Reagents  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (Mallinckrodt), 99.5% purity,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (BDH Chemicals),  $\text{Eu}_2\text{O}_3$ , and  $\text{Sm}_2\text{O}_3$  (Molycorp), 99% purity, were used.

A mixture of phosphate with the appropriate weight of rare earth (R.E.) was homogenized in an electric vibrator and melted in a platinum crucible at  $900^\circ\text{C}$ . Drops of hot melt were poured on a glazed ceramic plate into a ring of 1-cm diameter and pressed with another glazed ceramic.

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Fluorescence spectra were recorded by a spectrofluorimeter built in our laboratory (18).

Lifetime measurements were performed using an EGG-FX-6AU flash lamp, having an average pulse duration of 3  $\mu$ sec. The pulsed fluorescence was transmitted into a 162 PAR boxcar integrator and recorded on an XY recorder.

## Results

The appearance of the  $\text{UO}_2^{2+}$  excitation bands in the excitation spectrum of  $\text{Sm}^{3+}$  (Fig. 1) is the proof for the energy transfer from  $\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$ . The excitation bands of  $\text{UO}_2^{2+}$  in phosphate glass are at 330, 430, and 470 nm when monitored at one of the five fluorescence peaks between 500 and 600 nm, as can be seen from Fig. 2.

The emission of  $\text{UO}_2^{2+}$  was quenched in the presence of  $\text{Sm}^{3+}$  as a result of the E.T. The decrease was observed in all five peaks and in the same amount, indicating the nonradiative character of the transfer. The transfer efficiencies were calculated according to Ref. (19) by

$$\eta_t = 1 - \frac{\tau_d}{\tau_d^0}, \quad (1)$$

where  $\eta_t$  is energy transfer efficiency,  $\eta_d^0$  the fluorescence efficiency of the pure donor, and  $\eta_d$  the fluorescence efficiency of the donor with acceptor present. The values of  $\eta_t$  are given in Table I. In this table we also give the results of E.T. efficiencies from  $\text{UO}_2^{2+}$  to  $\text{Eu}^{3+}$  in phosphate glass.

The decay time of  $\text{UO}_2^{2+}$  was measured alone and with the presence of  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$ . The decay was not a simple exponential in all cases. Examples of the decay curves of  $\text{UO}_2^{2+}$  in the presence of  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  are presented in Figs. 3 and 4, where the shortening of the  $\text{UO}_2^{2+}$  lifetime is demonstrated.  $\tau$  was taken where the intensity fell to  $1/e$  of its initial value.

Transfer efficiencies were calculated according to the equation

$$\eta_t = 1 - \frac{\tau_d}{\tau_d^0}, \quad (2)$$

where  $\tau_d^0$  is the lifetime of the pure donor and  $\tau_d$  is the lifetime of the donor in the presence of the acceptor. The efficiencies thus calculated are given in Table II.

The enhancement of  $\text{Sm}^{3+}$  fluorescence in the presence of  $\text{UO}_2^{2+}$  obtained by measuring the relative fluorescence of the 645-nm

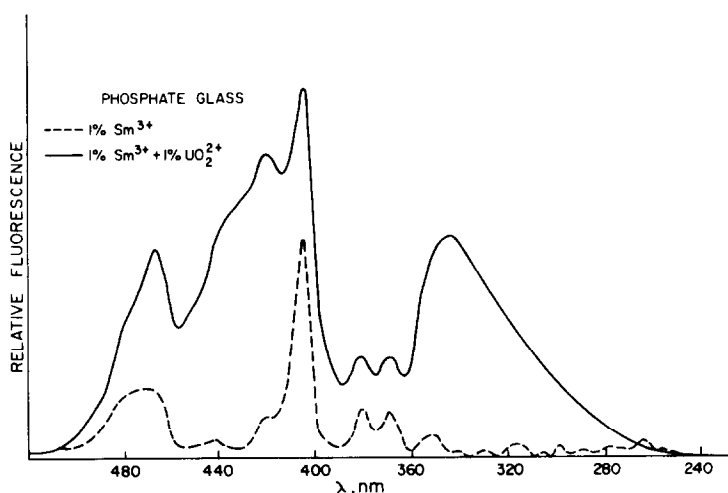


FIG. 1. Excitation spectrum of  $\text{Sm}^{3+}$  (---) and  $\text{Sm}^{3+}$  in presence of  $\text{UO}_2^{2+}$  (—) monitored at 645 nm.

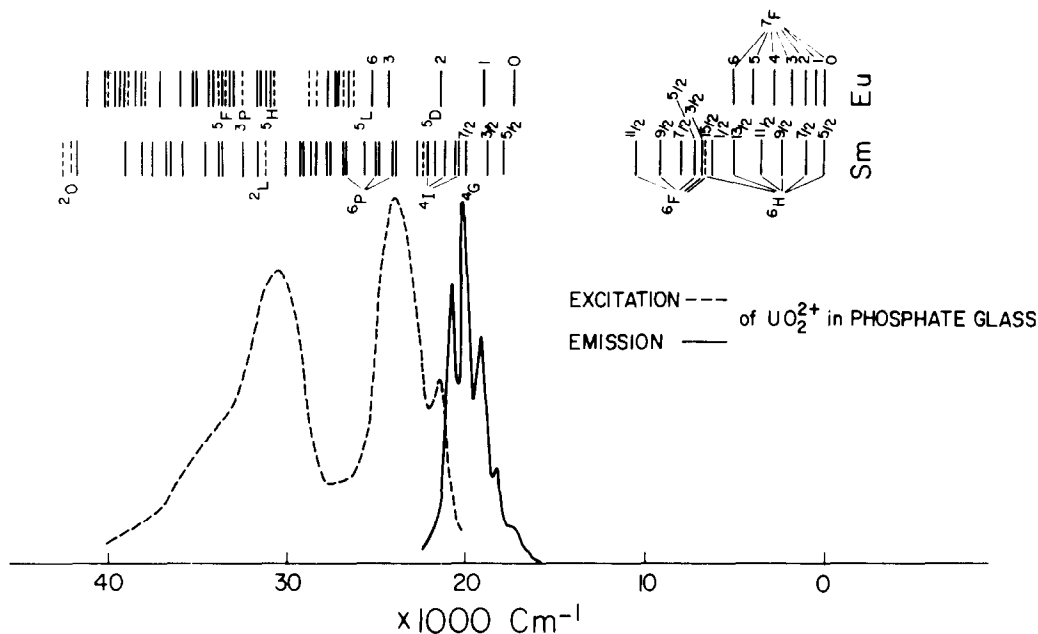


FIG. 2. Excitation and emission of  $\text{UO}_2^{2+}$  in phosphate glass compared to the electronic energy levels of  $\text{Sm}^{3+}$  and  $\text{Eu}^{3+}$  according to Ref. (5, p. 93).

peak when excited at 330, 405, 430, and 470 nm given in Table III.

The relation between the increase of  $\text{Sm}^{3+}$  fluorescence  $\Delta\eta_a$  to the transfer efficiency  $\eta_t$  is shown in Eq. (3):

$$\Delta\eta_a = kAd_\lambda\phi d_\lambda S_\lambda\eta_{t\lambda}, \quad (3)$$

where  $Ad_\lambda$  is the absorption of the donor at the excitation wavelength  $\lambda$ ,  $\phi d_\lambda$  the quantum efficiency of the donor fluorescence where excited at wavelength  $\lambda$ ,  $S_\lambda$  the spectral sensitivity of the spectrofluorimeter (including light source and monochromator), and  $k$  the proportionality constant, obtained by equating  $\eta_{t\lambda}$  ( $\lambda = 330$  nm) from

Eq. (1) to  $\eta_{t\lambda}$  obtained by Eq. (3). The three factors  $Ad_\lambda$ ,  $\phi d_\lambda$ ,  $S_\lambda$  are intrinsically included in the excitation curve of  $\text{UO}_2^{2+}$  and are eliminated by dividing  $\Delta\eta_a$  by the intensity of  $\text{UO}_2^{2+}$  peaks at wavelength  $\lambda$  in the excitation spectrum. The values thus obtained are given in Table IV.

TABLE I  
EFFICIENCIES OF E.T. BETWEEN  $\text{UO}_2^{2+} \rightarrow \text{Sm}^{3+}$   
AND  $\text{UO}_2^{2+} \rightarrow \text{Eu}^{3+}$  OBTAINED FROM STEADY  
STATE FLUORESCENCE CALCULATED BY EQ. (1)

1% wt $\text{UO}_2^{2+}$ +	$\eta_t$	1% wt $\text{UO}_2^{2+}$ +	$\eta_t$
0.5% $\text{Sm}^{3+}$	0.18	0.5% $\text{Eu}^{3+}$	0.27
1% $\text{Sm}^{3+}$	0.25	1% $\text{Eu}^{3+}$	0.36

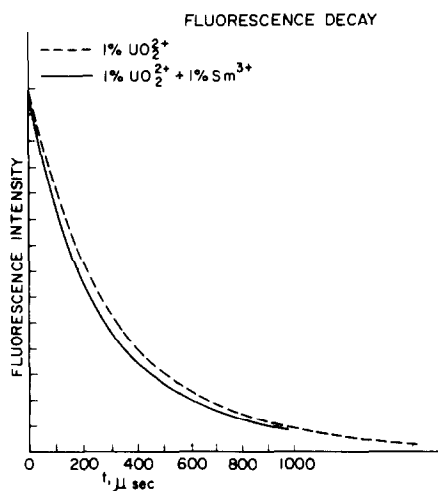


FIG. 3. Fluorescence decay curves of  $\text{UO}_2^{2+}$  and with presence of 1 wt%  $\text{Sm}^{3+}$ .

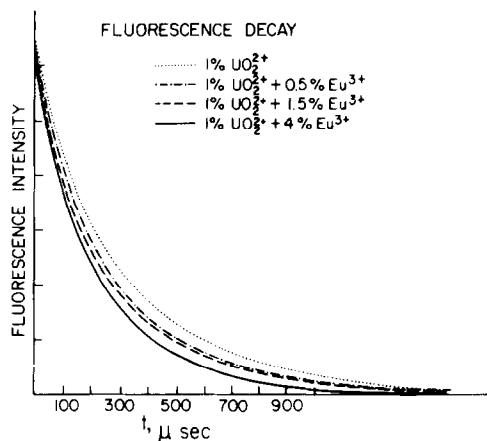


FIG. 4. Fluorescence decay curves of  $\text{UO}_2^{2+}$  and with presence of various concentrations of  $\text{Eu}^{3+}$ .

From Table IV it can be seen that the transfer efficiencies are greater when the excitation level is at higher energy. This can be connected with the stronger overlap between electronic levels of  $\text{Sm}^{3+}$  and  $\text{UO}_2^{2+}$  at higher energies as presented in Fig. 2. In this figure we also see that for  $\text{Sm}^{3+}$  electronic levels there is a good overlap between both excitation and emission bands of  $\text{UO}_2^{2+}$ , while in case of  $\text{Eu}^{3+}$  there exists a good overlap only between the excitation of  $\text{UO}_2^{2+}$  and the electronic levels of  $\text{Eu}^{3+}$ . Since transfer efficiencies are somewhat higher for  $\text{Eu}^{3+}$  (Table I) we can deduce that overlap of the excitation spectrum of the donor with the acceptor electronic levels satisfies the condition that energy transfer will occur.

It is worthwhile to note the highest increase of  $\text{Sm}^{3+}$  fluorescence in the presence of  $\text{UO}_2^{2+}$  at excitation 405 nm (Table III),

TABLE II

EFFICIENCIES OF E.T. BETWEEN  $\text{UO}_2^{2+} \rightarrow \text{Sm}^{3+}$ ,  $\text{UO}_2^{2+} \rightarrow \text{Eu}^{3+}$  CALCULATED FROM LIFETIME MEASUREMENTS BY USING EQ. (2)

1% wt $\text{UO}_2^{2+}$ +	$\eta_i$	1% wt $\text{UO}_2^{2+}$ +	$\eta_i$
—	—	0.5% $\text{Eu}^{3+}$	0.14
1% $\text{Sm}^{3+}$	0.22	1% $\text{Eu}^{3+}$	0.17

TABLE III

$\text{Sm}^{3+}$  FLUORESCENCE INTENSITY AT 645 nm EXCITED AT VARIOUS WAVELENGTHS

$\lambda$ Excitation (nm)	R.f. <sup>a</sup> 0.5% $\text{Sm}^{3+}$ + 1% $\text{UO}_2^{2+}$	R.f. 0.5% $\text{Sm}^{3+}$	R.f. 1% $\text{Sm}^{3+}$ + 1% $\text{UO}_2^{2+}$	R.f. 1% $\text{Sm}^{3+}$
330	93	480	96	630
405	300	600	430	760
430	32	500	36	590
470	167	330	196	403

<sup>a</sup> R.f. = Relative fluorescence, arbitrary unit.

where the excitation of  $\text{UO}_2^{2+}$  is relatively low. This can arise from a linear combination of the electronic state of  $\text{Sm}^{3+}$  with the wavefunction of  $\text{UO}_2^{2+}$  thus increasing the transition probability of this state origination from the  $^6P_7$  multiplet of  $\text{Sm}^{3+}$ . This can be seen in the excitation spectrum of  $\text{Sm}^{3+}$  codoped with  $\text{UO}_2^{2+}$  (Fig. 1).

The energy transfer from  $\text{UO}_2^{2+}$  to  $\text{Sm}^{3+}$  mainly occurs in a nonradiative way. This can be seen from the decrease of the  $\text{UO}_2^{2+}$  decay time in the presence of  $\text{Sm}^{3+}$  and from the equivalent decrease in the five fluorescent peaks of  $\text{UO}_2^{2+}$  in the presence of  $\text{Sm}^{3+}$ .

The detailed nonradiative mechanism of the energy transfer cannot be calculated. The various sites of ions present in the glass host create many distances for pairs of  $\text{UO}_2^{2+}$ – $\text{Sm}^{3+}$ , and thus they interact in a different fashion (6). For instance, at very small dis-

TABLE IV

EFFICIENCIES OF E.T. OBTAINED FROM THE INCREASE OF  $\text{Sm}^{3+}$  FLUORESCENCE CALCULATED BY EQ. (3)

$\lambda$ Excitation (nm)	$\eta_{ia}$ 0.5% $\text{Sm}^{3+}$ + 1% $\text{UO}_2^{2+}$	$\eta_{ia}$ 1% $\text{Sm}^{3+}$ + 1% $\text{UO}_2^{2+}$
330	0.18	0.25
430	0.17	0.21
470	0.12	0.15

tances quadrupole–quadrupole or exchange interactions may be effective, whereas at larger distances a dipole–dipole interaction would predominate. In addition diffusion of energy between equivalent sites of  $\text{UO}_2^{2+}$  and  $\text{Sm}^{3+}$  may be important at the concentration measured. In order to elucidate this problem it is advisable to perform energy transfer measurements under laser excitation using time-resolved spectroscopy.

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