Optical Transitions of Sm^{3+} in Oxide Glasses*

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Eigenvectors of the $4f^5$ electronic configuration of Sm^{3+} were calculated in intermediate coupling, and used to obtain the reduced matrix elements $U^{(\lambda)}$. Absorption spectra of Sm^{3+} were recorded in phosphate, borate, germanate and tellurite glasses. The Judd–Ofelt Ω_λ's intensity parameters were then deduced from the measured oscillator strengths by least-squares fitting. Radiative transition probabilities and integrated cross-sections of stimulated emissions are obtained. Calculated branching ratios and decay lifetimes are compared with the experimental values.

1. Introduction

Samarium ion has valuable fluorescence properties, that make it useful as laser material and phosphor. At room temperature the absorption and fluorescence study of Sm^{3+} in phosphate (1), borate (1) and germanate (2) oxide glasses was performed at this laboratory. The effect of temperature on the fluorescence properties of Sm^{3+} in tellurite glass is now in progress (3).

The fluorescence of samarium is quenched at higher concentration because of ion–ion cross relaxation (1). However, this difficulty can be circumvented by utilizing the increase of Sm^{3+} population via energy transfer (4).

Therefore, it is of interest to obtain predictions of the radiative transition probabilities and branching ratios of Sm^{3+} emission, and verify them with experimental results.

II. Matrix Element Calculations

As a first step of this calculation the $4f^5$ "free ion" eigenvectors were obtained, in the intermediate coupling scheme, by diagonalizing[1] the energy matrices for each J using radial parameters obtained by linear interpolation between Nd^{3+} (5) and Tm^{3+} (6) ions. Justification of such procedure will be discussed in connection with experimental results. The values of these parameters are given in Table 1. The resulting eigenvectors were then introduced into a code by A. Caird and resulted in the reduced matrix elements $U^{(\lambda)}$ presented in Table II. Recently, matrix elements of Sm^{3+} in LaF$_3$ were computed by Carnall *et al.* (7), using different radial parameters for calculation of the eigenvectors. Maximum deviation between the reduced matrix elements obtained in this work and the reference cited, do not exceed 10%.

It should be remarked that the lowest fluorescent level of $J = \frac{5}{2}$ is sometimes

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[1] The diagonalization was performed using a code kindly provided to us by Dr. Frey.

Parameter	Diag. (cm^{-1})
A	79643
F_2	370
F_4	56
F_6	6.2
α	30
β	-900
ζ	1200

referred to as ^4F and sometimes as ^4G (8). According to our calculation the percentage composition of this level is ^4_3F 27% and ^4_4G 25%. Therefore the assignment of this level is a matter of taste.

III. Intensity Parameters

The intensity parameters Ω_λ's were obtained by least-squares fit to the experimental oscillator strengths f in the spectral region 0.5 μ–2.2 μ using Eq. (1)

$$f_{JJ'} = \frac{8\pi^2 mc\sigma}{3h(2J+1)}\left[\frac{(n^2+2)^2}{9n}\right] \sum_{\lambda=2,4,6} \Omega_\lambda$$

$$|\langle f^N \psi J \| U^{(\lambda)} \| f^N \psi' J'\rangle|^2 \qquad (1)$$

TABLE II

$(SLJ\|U^{(\lambda)}\|S'L'J')^2$ FOR SOME TRANSITIONS OF THE f^5 CONFIGURATION

Designation	$U(2)^2$	$U(4)^2$	$U(6)^2$
$^6H_{5/2} \to {}^6F_{1/2}$	0.1947	0.0	0.0
$^6F_{3/2}$	0.1389	0.1329	0.0
$^6F_{5/2}$	0.0346	0.2594	0.0
$^6F_{7/2}$	0.0042	0.1099	0.3939
$^6F_{9/2}$	0.0001	0.0183	0.3526
$^6F_{11/2}$	0.0	0.0006	0.0527
$^4G_{5/2} \to {}^6H_{5/2}$	0.0002	0.0006	0.0
$^6H_{7/2}$	0.0	0.0067	0.0081
$^6H_{9/2}$	0.0112	0.0066	0.0021
$^6H_{11/2}$	0.0	0.0056	0.0030
$^6H_{13/2}$	0.0	0.0	0.0022
$^6F_{1/2}$	0.0008	0.0	0.0
$^6F_{3/2}$	0.0013	0.0001	0.0

where σ (in cm^{-1}) is the baricenter of the absorption band, n is the index of refraction of the glass taken as constant over the range of observation and $2J+1$ are the degeneracies of the J manifold.

Experimentally, f is obtained from the absorption spectrum by

$$f = 4.318 \times 10^{-9} \int \varepsilon(\sigma)\, d\sigma \qquad (2)$$

where ε is the molar extinction coefficient.

In our previous work (9, 10) we have found that for calculation of the Ω_λ parameters of Sm^{3+} the levels of this ion must be divided into a low set of energies ($<10\ 000$ cm^{-1}) and a high lying set of levels ($>17\ 000$ cm^{-1}), and only the low set is compatible with Judd–Ofelt theory. Recalculation has shown that three additional upper levels, namely $^4G_{5/2}$, $^4F_{3/2}$ and $^4G_{7/2}$ can still be fitted into the low lying set of levels, without affecting the values of the low set of Ω_λ parameters.

The slight difference between the intensity parameters obtained in this work, as presented in Table III, and those reported in Ref. 2, arises from the reidentification of the Sm^{3+} transition in the infrared part of the spectrum.

IV. Radiative Spectral Characteristics

The radiative transition probability $A_{JJ'}$, is obtained from the oscillator strength $f_{JJ'}$

TABLE III

INTENSITY PARAMETERS Ω_λ OF Sm^{3+} IN OXIDE GLASSES

Glass Matrix	$\Omega_2 \times 10^{20}$ cm^2	$\Omega_4 \times 10^{20}$ cm^2	$\Omega_6 \times 10^{20}$ cm^2	n
Borate	6.36	6.02	3.51	1.46
Phosphate	4.31	4.28	5.78	1.48
Germanate	6.48	4.98	3.18	1.64
Tellurite	3.17	3.65	1.61	2.04

TABLE IV

RADIATIVE TRANSITION PROBABILITIES A, AND STIMULATED CROSS-SECTIONS OF SOME SELECTED TRANSITIONS OF Sm^{3+}

Transition	Wavelength μ	Borate		Phosphate		Germanate		Tellurite	
		$A(\text{s}^{-1})$ $\int \sigma(\nu)d\nu$ $\times 10^{18}$ cm		$A(\text{s}^{-1})$ $\int \sigma(\nu)d\nu$ $\times 10^{18}$ cm		$A(\text{s}^{-1})$ $\int \sigma(\nu)d\nu$ $\times 10^{18}$ cm		$A(\text{s}^{-1})$ $\int \sigma(\nu)d\nu$ $\times 10^{18}$ cm	
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	0.560	20.2	0.039	17.7	0.034	26.8	0.041	45.1	0.045
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	0.596	119.0	0.263	133.0	0.286	147.0	0.258	206.0	0.233
$^4G_{5/2} \rightarrow {}^6H_{9/2}$	0.642	152.0	0.390	117.0	0.292	205.0	0.417	247.0	0.325
$^4G_{5/2} \rightarrow {}^6H_{11/2}$	0.702	43.8	0.134	41.6	0.124	52.5	0.128	76.2	0.120

using Eq. (3)

$$A_{JJ'} = \frac{8\pi^2 e^2 n^2}{mc\bar\lambda^{-2}} \times f_{JJ'} \quad (3)$$

where $\bar\lambda$ is the mean wavelength of the relevant transition. The integrated emission cross-section is related to the radiative transition probability by (11):

$$\int_{J \rightarrow J'} \sigma(\nu) \, d\nu = \frac{\bar\lambda^2}{8\pi cn^2} A_{JJ'} \quad (4)$$

The values of these two quantities in four oxide glasses are given in Table IV. It should be remarked that the four transitions in the Table account for 85% of the total fluorescence.

The branching ratio β_{ij} for a transition $i \rightarrow j$ is given by

$$\beta_{ij} = \frac{A_{ij}}{\sum_j A_{ij}} \quad (5)$$

The values of the calculated decay lifetimes from the $^4G_{5/2}$ at 17 700 cm^{-1} of Sm^{3+} are given in Table V and compare with the measured ones, taken at concentrations at which quenching does not occur yet. In Table VI we compare the calculated and experimental values of the branching ratio of the three strongest emission bands of Sm^{3+} in phosphate glass. The contributions of these

three transitions to the total branching ratio is more than 75%. The reasonable agreement between both values justifies the method of calculation of the eigenvectors.

V. Conclusions

In the present work we predict the radiative transition probabilities and other spectroscopic characteristics of Sm^{3+} ion in the four oxide glasses, based on the intensity parameters which are the average values for the inhomogeneously broadened bands. It is shown that these values predict correctly the experimental data. Similar results may be expected if the Sm^{3+} were excited by a laser instead of a broad band xenon source, because of the fast diffusion of energy among the different sites in the Sm system.

Another feature of the present treatment is the possibility to control the red ($^4G_{5/2}-{}^6H_{9/2}$ at 642 nm) to orange ($^4G_{5/2}-{}^6H_{7/2}$ at 596 nm) intensity ratio by varying the glass host. The phosphate glass is

TABLE V

DECAY LIFETIMES OF THE $^4G_{5/2}$ LEVEL OF Sm^{3+} IN OXIDE GLASS

Matrix	τ_{exp} (msec)	τ_{cal} (msec)
Borate	2.63	3.54
Phosphate	2.34	2.80
Germanante	2.15	1.97

TABLE VI

BRANCHING RATIOS FROM THE $^4G_{5/2}$ LEVEL TO
THE ^6H MANIFOLD OF Sm^{3+} IN PHOSPHATE
GLASS

Transition	β_{exp}	β_{cal}
$^4G_{5/2} \rightarrow {}^6H_{5/2}$	0.07	0.05
$\rightarrow {}^6H_{7/2}$	0.35	0.37
$\rightarrow {}^6H_{9/2}$	0.33	0.33

characterized by having the orange emission
stronger than the red emission while in the
other glasses the opposite holds. This fact
may be of practical value in phosphors and
related devices.

The stimulated emission cross-section at
650 nm is $\sigma_p \sim 5 \times 10^{-21}$ cm^2, assuming a $\Delta\nu$
value of 200 cm^{-1}. This σ_p is lower by almost
one order of magnitude than stimulated
emission cross-section of the $^4F_{3/2}-^4I_{11/2}$
transition of Nd^{3+} in silicate glass (11). Thus,
larger excited state population densities will
be required for efficient laser operation. For
this purpose energy transfer from ions having
large absorption cross-section such as $Bi^{3+}-$
Sm^{3+} (12) or $UO_2^{2+}-Sm^{3+}$ (4) can be utilized.

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