

# Optical Characteristics and Intensity Parameters of $\text{Sm}^{3+}$ in $\text{GeO}_2$ , Ternary Germanate, and Borate Glasses\*

R. REISFELD, A. BORNSTEIN, AND L. BOEHM

*Department of Inorganic and Analytical Chemistry,  
The Hebrew University of Jerusalem, Israel*

Received April 25, 1974

Absorption and fluorescence spectra of  $\text{Sm}^{3+}$  were measured in  $\text{GeO}_2$ , ternary germanate, and borate glasses. From these the intensity parameters were calculated by use of the Judd-Ofelt formula.

Visible emission and decay times from the  ${}^4G_{5/2}$  level and its relative quantum efficiencies were measured. The quantum efficiencies (QE) of the fluorescence in ternary germanate was higher by a factor of 20 than in  $\text{GeO}_2$ . The small QE in  $\text{GeO}_2$  is explained by cross-relaxation between neighboring  $\text{Sm}^{3+}$  ions. The later process is hindered by the change in glass structure in the presence of modifier ions. A similar effect is observed in other glasses such as borate, where the addition of modifiers increases the QE of fluorescence.

## 1. Introduction

As a result of the application of rare earth (RE)-doped glasses as lasers, a considerable literature has accumulated on the optical and fluorescent properties of RE-doped glasses. Most of the work has dealt with silicate, borate, and phosphate glasses. Less information is available on the germanates, which can be used as laser host material.

One of the more important criteria in the evaluation of laser hosts is the fluorescence quantum efficiency (QE). It is known that in the quenching of fluorescence by radiationless transitions, high-frequency phonons play a major role (1, 2). It has been shown (3-5) that the fluorescence QE of RE ions may be increased by dissolving the activator ion in a medium wherein perturbations due to high-frequency modes are minimized. Such a case exists in the germanate glasses. In this paper an additional effect of increase of fluorescent quantum efficiency by the existence of modifier ions is studied. The paper reports the oscillator strengths of  $\text{Sm}^{3+}$  in  $\text{GeO}_2$  and

ternary germanate glasses (TGG), the QE's and fluorescent decay times in the above matrices, and compares these values with those obtained for borate glass of final composition  $35\text{Na}_2\text{O} \cdot 65\text{B}_2\text{O}_3$  and  $22\text{Na}_2\text{O} \cdot 78\text{B}_2\text{O}_3$ . The last matrix doped by  $\text{Sm}^{3+}$  was investigated recently by Reisfeld et al. (6, 7).

## 2. Experimental

The materials from which the germanate glasses of final composition  $17\text{K}_2\text{O} \cdot 17\text{BaO} \cdot 66\text{GeO}_2$  (mole %) were prepared were  $\text{GeO}_2$  (Fluka Buchs 99.999%),  $\text{K}_2\text{CO}_3$  (Mallinckrodt), and  $\text{BaCO}_3$  (Baker Analyzed). The  $\text{Sm}^{3+}$  added to the glass was  $\text{Sm}_2\text{O}_3$  (Molycorp 99.9%). Batches containing 0.1-1.2 wt % of  $\text{Sm}^{3+}$  in the base glass materials were mixed in an electric vibrator and were melted at  $1250^\circ\text{C}$  for 10 hr in a Pt crucible. Glass disks 1 mm thick and 12 mm in diameter were prepared by molding the melt on a tile. In case of pure  $\text{GeO}_2$ <sup>1</sup> and  $\text{GeO}_2$ <sup>1</sup>-doped  $\text{Sm}^{3+}$  glass, the temperature of

<sup>1</sup> The authors are grateful to M. Ish-Shalom, Israel Ceramic and Silicate Institute, Haifa, Israel for preparing these glasses.

\* Partially supported by U.S. Army Contract DAJA 37-74-C-1628.

the melt was increased up to  $1450^\circ\text{C}$ , and the glass was annealed at  $500^\circ\text{C}$  overnight.

Two types of borate glasses were prepared. (a) From borax as a starting material: The final composition of these glasses after dehydration and slight loss of  $\text{B}_2\text{O}_3$  at melting temperature was  $35\text{Na}_2\text{O}\cdot 65\text{B}_2\text{O}_3$ . (b) From a mixture of borax and boric acid 2:1 (wt %): The final composition of this glass is  $22\text{Na}_2\text{O}\cdot 78\text{B}_2\text{O}_3$ .

The absorption spectra of the glasses were recorded on Cary 14 and Cary 17 spectrophotometers using undoped  $\text{GeO}_2$  and germanate glasses as blanks. Excitation and emission spectra were obtained on a spectrofluorimeter described earlier (8); the spectra were corrected with respect to the distribution of excitation sources and detection unit by use of a Turner 210 spectrofluorimeter. The decay times of the doped glasses were measured using a spectrofluorimeter built in this laboratory, in which the light source was replaced by a flash unit with an EGG-FX-6AU flash lamp, having an average pulse duration of  $3 \mu\text{sec}$ . All measurements were taken at room temperature.

### 3. Results

#### 3.1. Absorption and Intensity Parameters of $\text{Sm}^{3+}$

The spectra of the  $\text{Sm}^{3+}$  arise from intra-configuration transitions within the  $4f$  shell. These transitions, which are responsible for the crystal spectra, are forbidden in free ions by the parity rule for electric dipole transitions. In a glass, they become allowed by vibronic interaction and by admixture of electronic wave functions of opposite parity due to the odd terms in the crystal field. In the calculations by Judd (9) and Ofelt (10) such contributions were taken into account. The theoretical expression derived by Judd is

$$P = T_\lambda \sigma(f^N \psi J \| U^{(\lambda)} \| f^N \psi' J')^2, \quad \lambda = 2, 4, 6 \quad (1)$$

where  $P$  is the oscillator strength corresponding to the induced electric-dipole transition between the levels,  $\psi J \rightarrow \psi' J'$  at

energy  $\sigma$  ( $\text{cm}^{-1}$ ), and  $U^{(\lambda)}$  is a tensor operator of rank  $\lambda$ . The symbol  $\psi$  stands for additional quantum numbers that may be necessary to define the level uniquely. The three quantities  $T_\lambda$  are related to the radial parts of the  $4f^N$  wave functions, the wave functions of perturbing configurations, of which the nearest is the  $5d$  or charge transfer, the refractive index of the medium, and the ligand field terms which characterize the environment of the ion.

The oscillator strength for the induced electric dipole transitions were obtained experimentally from the absorption spectra by use of the following equation from Carnall et al. (11):

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

where  $\varepsilon$  is the molar absorptivity of energy  $\sigma$  ( $\text{cm}^{-1}$ ). (In this calculation only induced electric dipole transitions were taken.)

From our experimentally obtained oscillator strengths and theoretically calculated reduced matrix elements of Carnall et al. (11), we have obtained  $T_\lambda$  coefficients by the rms method (12), calculating the minimum deviation between the observed oscillator strengths and those calculated by means of Eq. (1). The matrix elements do not depend on the environment as shown in (12).

As can be seen from Table I, the oscillator strengths of  $\text{Sm}^{3+}$  may be arranged in two groups, one referring to transitions up to  $10\,700 \text{ cm}^{-1}$  (low energy region) and the second to transitions between  $17\,600$  and  $32\,800 \text{ cm}^{-1}$  (high energy region). For calculation of  $\tau_\lambda$ , only the low energy region was taken into account, since Judd's equation (a) applies only to this region (7, 12).

The  $\tau_\lambda$  parameters ( $\tau_\lambda = T_\lambda / (2J + 1)$ ) of  $\text{Sm}^{3+}$  in TGG are compared to previously obtained parameters of  $\text{Sm}^{3+}$  in borate and phosphate glasses and are given in Table II.

As seen from Table I, the values of oscillator strengths are higher in  $\text{GeO}_2$  glass than in TGG and those obtained for  $\text{Sm}^{3+}$ -doped borate glass of composition b are higher than in borate glass of composition a.

The splitting of the absorption bands is higher in TGG than in  $\text{GeO}_2$  glass as shown in Fig. 1, which presents the main band of

TABLE I  
OSCILLATION STRENGTH OF  $\text{Sm}^{3+}$  IN VARIOUS GLASSES

Transition	Borate b $22\text{Na}_2\text{O} \cdot 78\text{B}_2\text{O}_3$		Borate a $35\text{Na}_2\text{O} \cdot 65\text{B}_2\text{O}_3$		TGG $17\text{K}_2\text{O}17\text{BaO}66\text{GeO}_2$	
	$\nu \text{ cm}^{-1} f \times 10^6$		$\nu \text{ cm}^{-1} f \times 10^6$		$\nu \text{ cm}^{-1} f \times 10^6$	
${}^6F_{1/2}$	6154	0.86	6144	0.08		6114 1.25
${}^6F_{3/2}$	6593	1.68	6541	1.68		6559 1.19
${}^6H_{5/2}$	6826	2.85	6828	1.86		6826 2.85
${}^6F_{5/2}$	7326	2.3	7329	1.97		7326 2.3
${}^6F_{7/2}$	8163	4.36	8191	3.43		8163 4.36
${}^6F_{9/2}$	9303	2.74	9314	2.25		9303 2.74
${}^4I_{13/2}$	21 645	0.4				21 645 0.4
$({}^6P, {}^4P)_{5/2}$						
${}^4F_{7/2}, {}^6P_{3/2}, {}^4K_{11/2}$	24 814	5.93	24 780	5.83	24 723 6.90	24 814 5.69
${}^4L_{15/2}, {}^4G_{11/2}$	25 641	0.13	25 536	0.16		25 641 0.3
${}^4D_{1/2}, {}^6P_{7/2}$						
${}^4L_{17/2}, {}^4K_{13/2}, {}^4F_{9/2}$	26 631	1.98			26 648 2.77	26 631 1.98
${}^4D_{3/2}, ({}^4D, {}^6P)_{5/2}$	27 360	1.75			27 654 2.62	27 700 1.09
${}^4K_{15/2}, {}^4H_{9/2}, {}^4D_{7/2}$	27 984	1.4			28 898 2.51	28 230 0.32
$({}^4K, {}^4L)_{17/2}, {}^4L_{19/2}$						
${}^4H_{11/2}$						

TABLE II  
PARAMETERS FOR  $\text{Sm}^{3+}$  IN VARIOUS MATRICES

Matrix	Energy range ( $\text{cm}^{-1}$ )	Number of data points	$\tau_2$ (cm)	$\tau_4$ (cm)	$\tau_6$ (cm)
Phosphate low	4525–10 600	7	$6.06 \times 10^{-9}$	$4.17 \times 10^{-9}$	$8.04 \times 10^{-9}$
Borate b low	4520–10 700	8	$3.14 \times 10^{-9}$	$6.0 \times 10^{-9}$	$0.54 \times 10^{-9}$
Borate a low	6000–1000	6	$7.23 \times 10^{-9}$	$5.42 \times 10^{-9}$	$2.0 \times 10^{-9}$
Germanate low	6000–1000	6	$5.92 \times 10^{-9}$	$4.96 \times 10^{-9}$	$4.24 \times 10^{-9}$

absorption of  $\text{Sm}^{3+}$  peaking at 402 nm. Similar situations occur also with other absorption and emission bands.

### 3.2. Emission Spectra and Decay Times of $\text{Sm}^{3+}$

The emission of  $\text{Sm}^{3+}$  consists of three bands due to the transition from the  ${}^4G_{5/2}$  level to the  ${}^6H$  ground manifold. Figure 2 presents the emission of  $\text{Sm}^{3+}$  in  $\text{GeO}_2$ , ternary germanate, and borate glasses. The relative areas are corrected for the appropriate absorption, and the values are pro-

portional to the quantum efficiencies. These values and the values of half-bandwidths of the various transitions are given in Table III. An increase of intensity is observed in TGG as compared to  $\text{GeO}_2$ . The same phenomenon is true when comparing borate glass of composition a to that of composition b. It is also evident that the half-bandwidths of emission decrease in the order borate a > borate b > ternary germanate >  $\text{GeO}_2$ .

The fluorescence exhibited by the  $\text{Sm}^{3+}$  ion in TGG is linear with concentrations up to  $\sim 0.4 \text{ wt} \%$ , up to  $\sim 0.25 \text{ wt} \%$  in borate glass b,

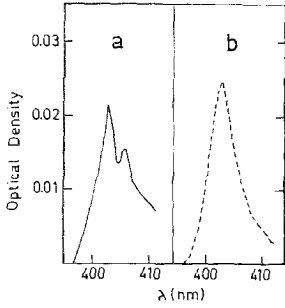


FIG. 1. Absorption band of  $\text{Sm}^{3+}$  at 402 nm in (a) ternary germanate and (b)  $\text{GeO}_2$  glasses.

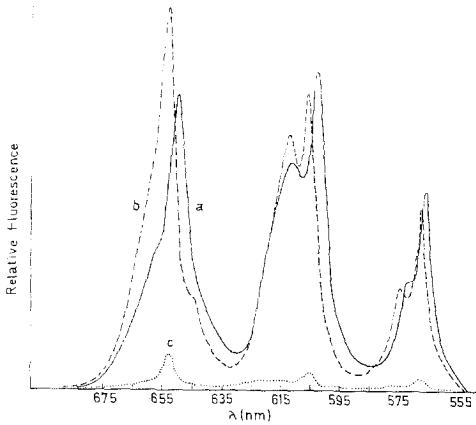


FIG. 2. Emission spectra of  $\text{Sm}^{3+}$  in (a) borate, (b) ternary germanate, and (c)  $\text{GeO}_2$  glasses.

and up to  $\sim 0.3$  wt% in borate glass a. The quenching at higher concentrations is the result of ion-ion energy transfer (6, 7). This will be explained below.

The lifetime  $\tau$  of  $\text{Sm}^{3+}$  in ternary germanate glasses was measured on glasses containing less than 0.3 wt%  $\text{Sm}^{3+}$ , at which concentration quenching of fluorescence does not occur and the decay of fluorescence is exponential. The measured lifetimes of the  ${}^4G_{5/2}$  level in various glasses are given in Table IV. It is seen that  $\tau$  in pure  $\text{GeO}_2$  is shorter than it is in mixed germanate glass. The same phenomenon was observed for the decay time of  $\text{Tb}^{3+}$ -doped fused silica glass (1.7 msec) (13) as compared to  $\text{Tb}^{3+}$  in sodium silicate glass (3.9 msec) (14). Hirayama et al. (5) also observed an increase in the decay time of  $\text{Nd}^{3+}$  in germanate glass upon addition of heavier glass modifiers.

TABLE III

RELATIVE AREAS AND HALF-BANDWIDTHS OF THE  ${}^4G_{5/2}$  EMISSION OF  $\text{Sm}^{3+}$  EXCITED AT 402 NM

Transition assignment	Wavelength (nm)	Half-bandwidth ( $\text{cm}^{-1}$ )			Relative area			Relative area <sup>a</sup>			
		Borate b glass	Borate a glass	$\text{GeO}_2$ glass	Borate b glass	Borate a glass	$\text{GeO}_2$ glass	Borate b glass	Borate a glass	$\text{GeO}_2$ glass	TGG
${}^6G_{5/2} \rightarrow {}^6H_{5/2}$	$\sim 565$	388	402	248	1	1	1	25.0	27.3	1	30
${}^4G_{5/2} \rightarrow {}^6H_{7/2}$	$\sim 602$	502	542	205	2.76	2.70	3	72.3	74.5	3	69.7
${}^4G_{5/2} \rightarrow {}^6H_{9/2}$	$\sim 649$	214	230	107	2.1	2.0	3.5	56.0	58.3	3.5	77.6

<sup>a</sup> Relative to  ${}^6G_{5/2} \rightarrow {}^6H_{5/2}$  in  $\text{GeO}_2$ .

TABLE IV

DECAY TIMES AND PERCENT QUANTUM EFFICIENCIES OF  $\text{Sm}^{3+}$  WHEN EXCITED AT 402 NM

Matrix	$\tau$ ( $\times 10^3$ sec)	QE (%)
Borate b glass	2.30	19.0
Borate a glass	2.63	22.8
$\text{GeO}_2$ glass	1.62	1.2
TGG	2.15	27.4

### 3.3. Quantum Efficiency of $\text{Sm}^{3+}$ in Various Glasses

The quantum efficiency (QE) of the  ${}^4G_{5/2}$  fluorescence upon excitation to a higher level (at 402 nm, which is the most intense band), was calculated by use of the formula

$$\text{QE}_u = \text{QE}_s \frac{F_u A_s (\lambda_{\text{ex}})_s}{F_s A_u (\lambda_{\text{ex}})_u}, \quad (3)$$

where  $F$  is the total area under the emission peaks,  $A$  the absorbance,  $\lambda_{\text{ex}}$  the excitation wavelength, and the subscripts  $u$  and  $s$  denote unknown and standard, respectively. In our calculation, the standard used was  $\text{Sm}^{3+}$ -doped phosphate glass. The values obtained for  $\text{Sm}^{3+}$  in  $\text{GeO}_2$  and ternary germanate glasses are presented in Table IV. As can be seen from this table, the QE of  $\text{Sm}^{3+}$  in TGG is about 20 times higher than in pure  $\text{GeO}_2$  glass.

## 4. Discussion

In general, the spectral behavior of  $\text{Sm}^{3+}$  in germanate glasses is very similar to that found in phosphate and borate glasses. The band shapes of the ion are similar, with small differences in half-bandwidths and peak positions. These results suggest that the RE ions reside in essentially similar sites in ternary germanate, phosphate, and borate glasses.

In a previous paper on  $\text{Sm}^{3+}$  in borate and phosphate glasses (6), we concluded that  $C_s$  is the predominant symmetry site of this ion in glasses. It has been proposed (15) that in an oxide glass a RE ion is surrounded by eight nonbridging oxygens belonging to the

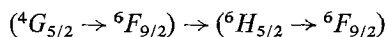
corners of  $\text{BO}_4$  and  $\text{PO}_4$  glass, forming tetrahedra, with each tetrahedron donating two oxygens. From the similarity of spectral features in ternary germanate and  $\text{GeO}_2$  glasses, the  $\text{Sm}^{3+}$  ion is situated in a distorted cube formed by four tetrahedra of  $\text{GeO}_4$  linked at the corners.

Higher free volume and lower density of mixed germanate glass, compared to pure  $\text{GeO}_2$  upon the addition of more than 10% alkali oxide, was based on viscosity measurements and described by Riebling (16). Since the  $\text{GeO}_2$  structure is more dense, the cavity in which the  $\text{Sm}^{3+}$  ion is embedded is smaller. Because of the smaller distance between  $\text{Sm}^{3+}$  and the surrounding oxygens in  $\text{GeO}_2$  glass, the vibrational coupling between the  $\text{Sm}^{3+}$  ion and its medium is stronger, and hence the oscillator strengths are higher in this matrix (see Table I). This was predicted by Judd (9) and by Ofelt (10).

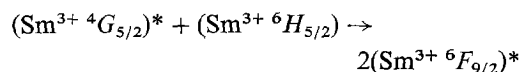
The higher free volume of TGG results in a higher degree of asymmetry in this glass as compared to  $\text{GeO}_2$ . This assumption is verified in the higher splitting of the spectral bands in the TGG (see Fig. 2). Also, because of higher free volume, more  $\text{Sm}^{3+}$  ion sites are present. The number of sites in the glass can be estimated by comparing the half-bandwidth of the spectrum of  $\text{Sm}^{3+}$  in the various glasses. As can be seen from Table III, the half-bandwidth increases in the case of TGG as compared to the  $\text{GeO}_2$  glass. The same phenomenon is true for borate glass of composition a, which contains more  $\text{Na}_2\text{O}$  as modifiers than does borate glass of composition b and, hence, has a more open structure (17).

The high QE of  $\text{Sm}^{3+}$  in TGG as compared to  $\text{GeO}_2$  can be explained by the stronger cross-relaxation (resulting in nonradiative losses) between neighboring  $\text{Sm}^{3+}$  ions in the later matrix.

The mechanism of such a cross-relaxation process is as follows (18):



or



This process is responsible for a nonradiative depopulation of the  $^4G_{5/2}$  level from which the fluorescence occurs. The transfer, which is of dipole-quadrupole type (6), begins to be important when the mean  $\text{Sm}^{3+}$ - $\text{Sm}^{3+}$  distance,  $r$ , approaches 12–15 Å and increases with  $r^8$ .

The higher efficiency of cross-relaxation in  $\text{GeO}_2$  is due to (a) the smaller  $\text{Sm}^{3+}$ - $\text{Sm}^{3+}$  distance in this matrix because of lower solubility and the existence of aggregates of  $\text{Sm}^{3+}$  ions and (b) phonon assisted cross-relaxation in  $\text{GeO}_2$ . In this medium only Ge-O phonons exist with higher frequencies, while in ternary germanate glass other less energetic phonons such as K-O and Ba-O are responsible for the dispersion of energy of  $\text{Sm}^{3+}$  in the matrix and do not contribute to the cross-relaxation process.

A similar situation was observed in the case of borate a glass, in which case the addition of modifier ( $\text{Na}_2\text{O}$ ) increases the quantum efficiency, as can be seen from Table IV.

To summarize, the efficiency of visible fluorescence is higher in TGG than in  $\text{GeO}_2$  or borate glasses. This fact is explained by the higher probability of cross-relaxation in  $\text{GeO}_2$  causing nonradiative losses. The stability and transparency of TGG are much better than those of pure  $\text{GeO}_2$  glass.

Since the germanate glasses have lower phonon energies than the conventional phosphate, silicate, and borate glasses and since the nonradiative losses are proportional to the phonon energies, we can expect that these glasses may be suitable for laser host mat-

erials for various RE ions which have small energy gaps between the lasing and the next lower level.

## References

1. M. J. WEBER, *Phys. Rev. B* **8**, 54 (1973).
2. R. REISFELD, Y. ECKSTEIN, N. LIEBLICH, AND L. BOEHM, *Int. Conf. Photochem.* **3**, 43 (1973).
3. R. REISFELD AND N. LIEBLICH, *J. Phys. Chem. Solids* **34**, 1467 (1973).
4. R. REISFELD AND Y. ECKSTEIN, *J. Non-Cryst. Solids* **12**, 357 (1973).
5. C. HIRAYAMA, F. E. CAMP, N. T. MELAMED, AND K. B. STEINBRUEGGE, *J. Non-Cryst. Solids* **6**, 342 (1971).
6. R. REISFELD, L. BOEHM, AND E. GREENBERG, *10th Rare Earth Conf.* **2**, 1149 (1973).
7. R. REISFELD, E. GREENBERG, AND E. BIRON, *Solid State Chem.* **9**(3) 224–233 (1974).
8. R. REISFELD, A. HONIGBAUM, G. MICHAELI, C. HAREL, AND M. ISH-SHALOM, *Isr. J. Chem.* **7**, 613 (1969).
9. B. R. JUDD, *Phys. Rev.* **127**, 750 (1962).
10. G. S. OFELT, *J. Chem. Phys.* **37**, 511 (1962).
11. W. T. CARNALL, P. R. FIELDS, AND K. RAJNAK, *J. Chem. Phys.* **49**, 4412 (1968).
12. R. REISFELD, L. BOEHM, N. LIEBLICH, AND B. BARNETT, *10th Rare Earth Conf.* **2** 1142–1148 (1973.)
13. N. F. NELSON, F. T. KING, AND S. W. BARKER, *3rd Conf. Rare Earth Res.* **1**, 573 (1963).
14. R. REISFELD, E. GREENBERG, L. KIRSHENBAUM-BOEHM, AND G. MICHAELI, *8th Rare Earth Conf.* **2**, 743 (1970).
15. R. REISFELD AND Y. ECKSTEIN, *J. Solid State Chem.* **5**, 174 (1972).
16. E. F. RIEBLING, *J. Chem. Phys.* **39**, 3022 (1963).
17. K. PATEK, in "Glass Lasers," (J. G. Edwards, Ed.) Butterworths, London (1970).
18. L. G. CLITERT AND L. F. JOHNSON, *J. Chem. Phys.* **44**, 3514 (1966).