

Absorption and Emission Spectra of Thulium and Erbium in Borate and Phosphate Glasses*

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Absorption and emission spectra of Tm^{3+} and Er^{3+} were measured in phosphate and borate glasses.

The oscillator strengths of the transitions were calculated from the experimental data and compared with those of aqueous solutions. It was found that the oscillator strengths in the glasses are higher than in the solutions. The measured bands were attributed to forced electric transitions which occur when the ion is situated in glass at C_2 symmetry. A model of the average site is proposed. From the spectral shift of the hypersensitive transitions conclusions were drawn as to the influence of the crystal field in glass. From the width of the inhomogeneous broadening it was concluded that the number of rare earth sites is higher in phosphate than in borate glass. The relation between the nonradiative transitions and the phonon energy of the glasses is discussed. The high luminescence efficiency arising from transitions to levels which are higher than the ground state of thulium indicate a possibility of population inversion.

Introduction

The objective of this work was:

1. To study the influence of two different glass hosts on the transition probabilities of trivalent Er and Tm ions (henceforth R.E.).
2. To compare the intensities of the spectra of these R.E. in glasses with those of liquid solutions and doped oxide lattices.
3. To compare the broadening of the R.E. fluorescence bands in glasses with those in aqueous solutions and doped crystals.

The characteristics of glasses containing rare earths as the active ions are of particular interest because these media are used as laser amplifiers and oscillators. There is at present considerable interest in extending laser operating wavelengths into the blue and ultraviolet regions of the spectrum. To our knowledge, Tm^{3+} is the only rare earth ion whose transitions from higher levels to levels above the ground multiplet (e.g., 3P_0 , $^1I_6 \rightarrow ^3H_4$, and $^1D_2 \rightarrow ^3H_4$ transitions) are much stronger and sharper than the transitions to the 3H_6 ground level. It is highly possible that these transitions can be effective in lasers (1).

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The present study is based on the systematic investigation of the luminescent characteristics of glasses containing rare earth ions which has been carried out in this laboratory (2-11).

Absorption spectra have been interpreted for erbium in solutions (12), and in crystals (1, 14, 15); and for thulium in solutions (12) and in crystals (1, 15-17). The fluorescence spectra of erbium in crystals (1, 14, 19) and of thulium in crystals (1, 20, 21) have also been studied. The most complete investigations have been made on thulium ethylsulfate, thulium chloride hydrate crystals and Y_2O_3 and LaF_3 crystals doped with thulium and erbium. To our knowledge, no information on the absorption and fluorescence properties of the two trivalent R.E. has yet been obtained quantitatively in glasses. Qualitative information on these ions can be found in a review paper by Karapetyan (22). It was therefore of interest to make a systematic study of the absorption and emission characteristics of thulium and erbium in glasses. It is expected that in a glass a rare earth ion will occupy a symmetry site similar to that occupied in sesquioxides. This was shown by Rice and De Shazer (23) to be the case in europium incorporated into a borosilicate glass. Later it was shown by us (11)

that the sesquioxide structure of Eu_2O_3 will be preserved in a glass, and the inhomogeneous broadening is observed because of a slight change in the crystal field parameters of a rare earth site and the presence of a variety of sites of the same symmetry.

According to Roth and Schneider (24), thulium and erbium sesquioxides have only one stable polymorph, which belongs to the cubic type. Each unit cell of cubic form has one site of eight R.E. on C_{3i} sites, one set of 24 R.E. on C_2 sites and 48 oxygen ions on C_1 sites. By analogy to europium we can expect that these symmetries of erbium and thulium will be found in glasses. It will be possible to distinguish between the C_2 and C_{3i} from the optical transitions in the spectrum of the rare earth, as it is known (25) that the first one can give rise to a forced electric dipole while the latter can be effective only for a magnetic dipole transition due to the presence of a center of inversion. The type of the absorption spectrum can thus be used to define the site symmetry of the rare earth in glasses.

From the emission spectrum we can obtain information on the radiative transition probabili-

ties to various electronic levels and on the interaction of the electronic levels of the R.E. with the glass "lattice." The results which follow allow us to derive conclusions about the crystal field in different glasses, and to compare glasses and aqueous solutions with respect to the following parameters:

- (1) change in line intensity;
- (2) shift of the spectral lines;
- (3) splitting and broadening of the spectral lines.

From the experimentally determined oscillator strengths given in Tables I and II, it is possible to obtain the crystal field parameters using Judd's theory (25) by a method similar to that used by Carnall (26). This will be done in our next paper. A knowledge of these parameters would give insight into the crystal field strength of glasses.

Spectral Intensities: Theory

The ground level electronic configuration of trivalent Tm^{3+} and Er^{3+} are f^{12} and f^{11} , respectively. Transitions within the f shell are respon-

TABLE I

OSCILLATOR STRENGTHS OF Tm^{3+} IN PHOSPHATE AND BORATE GLASSES COMPARED TO EXPERIMENTAL RESULTS OBTAINED IN DIFFERENT AQUEOUS AND SOLID MEDIA

Energy level	Borate			Phosphate			LiNO ₃ -KNO ₃ (molten)		Tm ₂ O ₃				
	Wave no. (cm ⁻¹)	Wavelength (nm)	$f \times (10^6)$	Wave no. (cm ⁻¹)	Wavelength (nm)	$f \times (10^6)$	HClO ₄ -DClO ₄ $f \times (10^6)$	$f \times (10^6)$ (12)					
³ H ₄	5847-6134	1630.0-1710.0	3.94	5714	1750.0	—	1.06	4.70	2.77				
³ H ₅	8257	1211.0	2.09	8250	1212.0	1.82	1.24	2.10	2.66				
³ F ₄	12626	792.0	4.39	12626	792.0	3.00	2.10	5.41	2.96				
	12903	775.0											
³ F ₃	14619	684.0	4.02	14550	687.2	2.53	3.93	3.97	2.08				
³ F ₂	15100	662.0	0.70	15060	664.0	0.22				0.39			
¹ G ₄	21231	471.0	2.19	21052	475.0	1.58	0.74	2.05	1.13				
	21505	465.0		21505	465.0								
¹ D ₂	27855	356.5	3.75	27855	359.0	3.06	2.31	3.49	2.82				
	28050	355.0											
¹ I ₆ / ³ P ₀	34246	292.0	4.14	33057	302.5	31.87	0.84 (26)	—	3.32				
	34662	288.5		34364	291.0								
	35082	285.0		35057	286.0								
³ P ₁	36363	275.0		36166	276.5		0.56 (26)	—	1.95				
³ P ₂	37950	262.5	6.13	38095	262.5	14.46	3.28 (26)	—	4.72				
	38387	260.5											

TABLE II

OSCILLATOR STRENGTHS OF Er^{3+} IN PHOSPHATE AND BORATE GLASSES COMPARED TO EXPERIMENTAL RESULTS OBTAINED IN DIFFERENT AQUEOUS AND SOLID MEDIA

Energy level	Borate glass			Phosphate glass			HClO ₄ -	LiNO ₃ -	Y ₂ O ₃
	Wave no. (cm ⁻¹)	Wavelength (nm)	$f \times (10^6)$	Wave no. (cm ⁻¹)	Wavelength (nm)	$f \times (10^6)$	DClO ₄ $f \times (10^6)$ (12)	KNO ₃ $f \times (10^6)$ (12)	$f \times (10^6)$ (15)
⁴ I _{13/2}	6544	1528.0	3.19	6527	1532	2.31	1.76	1.74	1.25
	6697	1493.0		6688	1495				
	7235	1382.0		10256	975.0				
⁴ I _{11/2}	10256	975.0	1.2	10256	975.0	1.09	0.54	0.95	0.34
⁴ I _{9/2}	12547	797.0	1.2	12500	800.0	0.5	0.30	0.28	0.31
⁴ F _{9/2}	15349	651.5	3.2	15209	657.5	2.8	2.24	2.0	1.73
				15325	652.5				
⁴ S _{3/2}	18390	543.7	1.07	18331	544.5	0.73	0.74	18.4	0.34
² H _{11/2}	19175	521.5	4.94	18921	528.5	4.76	2.57		2.46
				19230	520.0				
⁴ F _{7/2}	20470	488.5	2.76	20470	488.5	2.55	2.03	2.46	1.13
⁴ F _{5/2}	22172	451.0	1.19	21857	457.5	1.05	1.34	1.33	0.40
				⁴ F _{3/2}	22573				
² H _{9/2}	24539	407.5	1.5	24539	407.5	2.94	0.74	0.98	0.61
⁴ G _{11/2}	26176	382.0	30.61	26246	381.0	26.24	4.87	36.3	20.55
	26420	378.5		26420	378.5				
² K _{15/2}	27322	366	4.7	27322	366.0	4.0	0.91 (26)	—	—
² G _{9/2}	28011	357	1.2	28030	356.7	1.44	1.75 (26)	—	—
² P _{3/2}	31595	310.5	1.72	31207	320.5	3.24	0.091 (26)	—	0.03
	32200	316.5		31527	317.2				
	32679	306.0		31986	312.7				
				32597	306.7				
	33147	301.7		33682	296.7				
	33361	299.7		34071	293.5				
² D _{5/2}	34050	293.5	1.45	34752	287.7	3.03	0.14 (26)	—	0.09
	34722	288.0		35345	283.0				
⁴ G _{9/2}	35590	281	2.27	36403	274.7	5.22	0.44 (26)	—	0.57
⁴ D _{5/2}	38834	257.5	15.24	38989	256.5	15.55	10.2 (26)	—	8.89
	⁴ D _{7/2}	39138							

sible for the crystal spectra. They are forbidden in a free ion by the parity rule for electric dipole transitions. In a crystal or a glass, forced electric transitions became allowed as a consequence of the coupling of odd electronic wave functions due to the odd parity terms in the crystal field expansion. In the theory developed by Ofelt (27) and Judd (25), in the static field approximation, the contribution of the odd parity part of the crystal field is calculated by mixing states of different parity.

Judd's result, for the oscillator strength f

corresponding to the induced electric dipole transition $\Psi J \rightarrow \Psi' J'$ at energy σ (cm⁻¹), may be written:

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

where $U^{(\lambda)}$ is a tensor operator of rank λ . The three quantities T_λ are related to the radial parts of $4f^N$ wave functions of perturbing configurations, the refractive index of the medium, and the ligand field parameters which characterize the environment of the ion.

The measured intensity of an absorption band is related to f by the following expression (26):

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

where ϵ is the molar absorptivity at the energy σ (cm^{-1}).

In cases where the transitions occur partially by a magnetic dipole mechanism following the selection rules $\Delta J = 0, \pm 1$, $\Delta L = 0$, $\Delta S = 0$ and $\Delta I = 0$

$$f_{\text{exp}} = f_{\text{md}} + f_{\text{ed}}$$

where f_{exp} is the experimentally observed oscillator strength, f_{ed} is the induced electric dipole transition, and f_{md} is the magnetic dipole transition.

The intensities of the absorption of Er^{3+} and Tm^{3+} in aqueous solution have been calculated using the above consideration.

In the present work the oscillator strengths of Er^{3+} and Tm^{3+} in glasses were measured and compared to results obtained in aqueous solution (12, 15) and in Tm_2O_3 and Y_2O_3 crystals (1).

Experimental

Reagents. For borate glasses: Riedel sodium tetraborate and Frutarom boric acid (123 g:62 g), 99.5% purity. For phosphate glasses: Mallinckrodt sodium dihydrogen monohydrate, 99.5% purity; Molycorp Tm_2O_3 and Er_2O_3 , 99.9% purity.

Preparation of Glasses. Glass containing 3 wt% erbium or thulium was prepared from a mixture which was homogenized in an electric vibrator.

The glass was melted in a platinum crucible at 1100°C . Drops of the hot melt were allowed to fall directly onto a clean white glazed ceramic surface. The drop was placed inside the circumference of a ring 1 mm thick and pressed with a second ceramic tile so as to obtain glasses of constant 1 mm thickness.

The absorption spectra of the glasses were recorded on a Cary 14 spectrophotometer in the spectral region from 2500 to 20 000 \AA , using undoped glass as a blank. All measurements were made at room temperature. The experimental absorption spectra were encoded and fitted to a computer program from which $\int \epsilon(\sigma) d\sigma$ was obtained. Oscillator strengths were computed using formula (2). The absorption and emission curves were assumed to be of a gaussian shape in the computation of areas. Figure 1 presents the energy levels of thulium

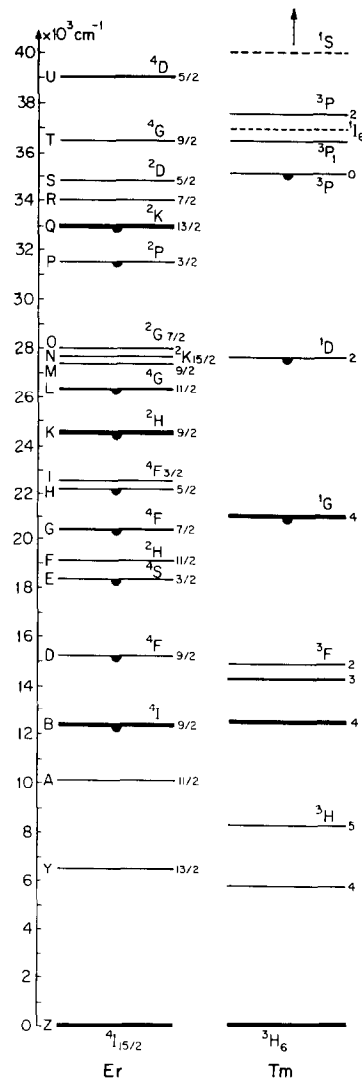


FIG. 1. Energy levels of Tm^{3+} and Er^{3+} taken after Dieke and Crosswhite (28).

and erbium taken from Dieke and Crosswhite (28).

The corrected fluorescence spectra were taken with a Turner "Spectro" Model 210 spectrofluorimeter. The uv and visible fluorescence of thulium results not only from the transitions to the 3H_6 ground state, but also from the transitions between excited levels. Therefore the proper transitions were identified from the difference of emission under selective excitation. For example, to estimate the intensity of the emission band corresponding to the $^1D_2 \rightarrow ^3F_4$ transition and to extract it from the $^1G_4 \rightarrow ^3H_4$ and $^3F_2 \rightarrow ^3H_6$ transitions we proceed as follows: First, the

relative area shape, the half-width, and the maximum intensity of two gaussian peaks around 652 and 660 are obtained by excitation to the 1G_4 (470 nm) level. The emissions correspond to the $^1G_4 \rightarrow ^3H_4$ and $^3F_2 \rightarrow ^3H_6$ transitions, respectively. Next, the total area of the three transitions, $^1D_2 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_4$ and $^3F_2 \rightarrow ^3H_6$ is obtained by excitation to the 1D_2 (358 nm) level. The $^1D_2 \rightarrow ^3F_4$ transition is then evaluated by taking the difference in relative area between the emission bands from the 358 nm and the 470 nm excitations. In this calculation we assumed that the short-wave range makes no contribution to the $^1G_4 \rightarrow ^3H_4$ transition. See also Fig. 2.

Results

Tables I and II give the oscillator strengths (expressed as the f numbers) and spectral assignments of Tm^{3+} and Er^{3+} , respectively, in borate and phosphate glasses, as compared to aqueous solutions, molten KNO_3 - $LiNO_3$, Tm_2O_3 and doped Y_2O_3 crystals. We were able to observe

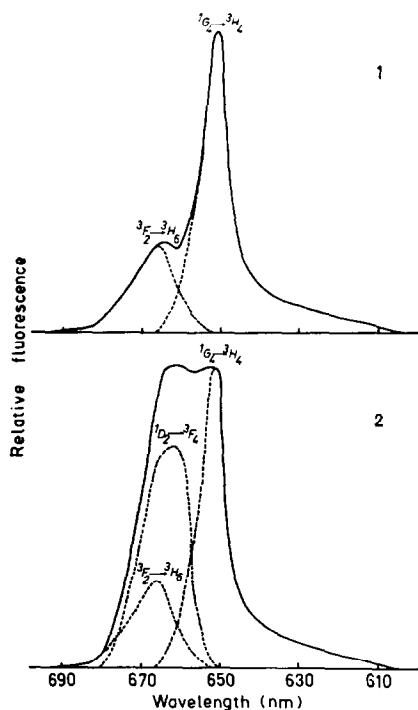


FIG. 2. Part of the corrected emission spectrum of Tm^{3+} in phosphate glass: (1) excitation at 470 nm; (2) excitation at 358 nm. --- Represent gaussian component of the transitions indicated.

transitions from the 3H_6 ground state of Tm^{3+} to all the remaining 3H , 3F , 1G , 1D , and 3P multiplets. We also observed almost all the absorption bands of Er^{3+} corresponding to transition from the ground state $^4I_{15/2}$ to higher multiplets. Comparison of the absorption spectra of the R.E. in the two different glass media shows that in the uv region the relative intensities of a given transition are higher in the phosphate than in the borate glass. In the latter case higher splitting occurs as well.

In the visible and the near infrared regions the results are opposite: higher intensities are observed in borate but the splittings are higher in phosphate.

The differences in the uv absorption spectra of Er^{3+} between the two kinds of glasses are smaller than those for Tm^{3+} in the same media. The reproducibility of the absorption spectra in all the spectral regions investigated excludes the possibility of contributions to the absorption from background absorption or from the tail of the large bands with maxima $> 50\,000\text{ cm}^{-1}$.

Comparison of the absorption intensities in the ultraviolet, visible and near infrared regions in glasses with those obtained in aqueous solutions ($HClO_4$ - $DClO_4$) shows that all absorption bands are more intense in the glass "lattices" and are comparable to the results obtained in a molten $LiNO_3$ - KNO_3 , Tm_2O_3 crystals and Er^{3+} -doped Y_2O_3 crystals.

It should be noted that the assignments of several absorption bands of Er^{3+} as given by Krupke (14) are not identical to the assignments given by Carnall et al. (26), although the regions of characteristic absorption are comparable. For comparison purposes we used the assignments of transitions given by Krupke.

Tables IIIa and IIIb present the emission spectrum of Tm^{3+} in borate and phosphate glass as obtained at various excitation wavelengths. For the excitation to the 3P_1 (275 nm), 3P_2 (263 nm) and the highly possible S levels (about 200 nm) of Tm^{3+} , only the possible transitions and relative fluorescence intensities are given. It was impossible to obtain the relative area of each of the transitions listed, since the spectra obtained are very complicated and cannot be resolved by our simple method of gaussian analysis. Table IV gives the wavelength maxima, relative intensities and half bandwidths for several fluorescence bands from the 1D_2 to the 3H multiplet for Tm^{3+} in borate and phosphate glasses as compared to Y_2O_3 -doped crystals (1).

TABLE IIIa
EMISSION SPECTRUM OF Tm³⁺ AT VARIOUS EXCITATION WAVELENGTHS

Excitation (nm)	Assigned transition	Emission			
		Borate		Phosphate	
		λ (nm)	R.A. ^a	λ (nm)	R.A. ^a
468.0(¹ G ₄)	¹ G ₄ → ³ H ₄			651.50	1.000
	¹ G ₄ → ³ H ₅			752.75	0.114
	³ F ₂ → ³ H ₆			665.50	0.083
	³ F ₂ → ³ H ₆			690.00	0.708
358.0(¹ D ₂)	¹ D ₂ → ³ H ₄	456.00	1.000	453.00	1.000
	¹ D ₂ → ³ H ₅	517.00	0.008	513.00	0.011
	¹ D ₂ → ³ F ₄	665.00	0.127	663.50	0.034
	¹ G ₄ → ³ H ₆	478.00	0.118	478.00	0.063
	¹ G ₄ → ³ H ₄	652.50	0.180	651.50	0.074
	³ F ₂ → ³ H ₆	665.50	0.014	665.50	0.009
288.0(³ P ₀)	¹ I ₆ → ³ H ₄	355.00	0.446	350.00	1.000
	¹ I ₆ → ³ H ₅	385.00	0.125	383.00	0.094
	³ P ₀ → ³ F ₄ }	465.00	0.155	463.00	0.200
	¹ I ₆ → ³ F ₄ }				
	¹ I ₆ → ³ F ₃	500.00	0.110	498.00	0.060
	³ P ₀ → ³ F ₃ }	530.00	0.061	521.50	0.094
	¹ I ₆ → ³ F ₂ }				
	³ P ₀ → ¹ G ₄ }	705.00	0.754	701.00	1.000
	¹ I ₆ → ¹ G ₄ }				
	¹ D ₂ → ³ H ₆	367.50	0.275	365.00	0.133
	¹ D ₂ → ³ H ₄	456.00	1.000	453.00	0.455
	¹ D ₂ → ³ H ₅	517.00	0.067	513.00	0.044
	¹ D ₂ → ³ F ₄	—	—	—	—
	¹ G ₄ → ³ H ₆	480.00	0.190	478.00	0.105
	¹ G ₄ → ³ H ₄	—	—	—	—
	³ F ₂ → ³ H ₆	—	—	—	—
³ F ₃ → ³ H ₆	—	—	—	—	

^a Relative areas; for each excitation the areas are given relatively to the strongest emission band which is taken as unity.

The uv and visible fluorescence of Er³⁺ in our glasses is much weaker than that of Tm³⁺ and only uncorrected spectra could be measured. The fluorescence was observable only in phosphate glasses, with 382 nm excitation (from a xenon source) and 255 nm excitation (from a mercury low pressure lamp). In Table V we present the wavelengths of fluorescence together with the transition assignments obtained under excitation at 382 and 255 nm.

Discussion

The causes of the differences in the absorption bands of the R.E. in two different glass lattices

will be discussed first. The influence of the medium on the intensities, shift of spectral bands and broadening of the absorption bands will then be compared for glass and other matrices. It should be noted that most of the absorption and emission bands of Tm³⁺ and Er³⁺ are caused by forced electric dipole transitions.

In glasses the R.E. is surrounded by nonbridging oxygens of the phosphate and the borate tetrahedra, and the relative positions of these tetrahedra in relation to the R.E. can be slightly distorted just by a change in the O-Tm or O-Er distance (*l*).

However, while in the phosphate glass the phosphorus is always four-coordinated, in the

TABLE IIIb
EMISSION SPECTRUM OF Tm^{3+} AT VARIOUS EXCITATION WAVELENGTHS

Excitation (nm)	Assigned transition	Emission			
		Borate		Phosphate	
		λ (nm)	R.I. ^a	λ (nm)	R.I. ^a
273.0(³ P ₁)	³ P ₀ → ³ H ₄	355.00	0.50	351.00	1.00
	¹ I ₆ → ³ H ₄				
	¹ D ₂ → ³ H ₆	367.50	—	365.00	0.20
	³ P ₀ → ³ H ₅	392.00	0.15	385.00	0.10
	¹ I ₆ → ³ H ₅				
	³ P ₀ → ³ F ₄	457.00	1.00	455.00	0.50
	¹ I ₆ → ³ F ₄				
	¹ D ₂ → ³ H ₄				
	³ P ₀ → ³ F ₃	473.00	0.25	478.00	0.10
	¹ I ₆ → ³ F ₃				
	¹ G ₄ → ³ H ₆				
	³ P ₁ → ³ F ₂	—	—	515.00	0.10
	³ P ₀ → ³ F ₂				
	¹ I ₆ → ³ F ₂				
	¹ D ₂ → ³ H ₅				
	?	587.00	0.07	585.00	0.05
	¹ D ₂ → ³ F ₄	650.00	0.10	662.25	0.05
	¹ G ₄ → ³ H ₄				
	³ F ₂ → ³ H ₆				
	³ P _{1,0} → ¹ G ₄	706.00	0.40	701.00	0.65
	¹ I ₆ → ¹ G ₄				
	³ F ₃ → ³ H ₆				
³ P ₁ → ³ F ₄	759.00	0.07	—	—	
¹ D ₂ → ³ F ₃					
¹ G ₄ → ³ H ₅					
262.0(³ P ₂)	³ P ₀ → ³ H ₆	294.00	0.07	292.00	0.12
	³ P → ³ H ₄	352.00	0.40	349.00	1.00
	¹ I ₆ → ³ H ₄				
	¹ D ₂ → ³ H ₆	366.00	0.33	363.00	0.10
	³ P → ³ H ₅	385.00	0.08	383.00	0.07
	¹ I ₆ → ³ H ₅				
	³ P → ³ F ₄	455.00	1.00	455.00	0.50
	¹ I ₆ → ³ F ₄				
	¹ D ₂ → ³ H ₄				
	³ P → ³ F ₃	475.00	0.20	478.00	0.10
	¹ I ₆ → ³ H ₄				
	¹ G ₄ → ³ H ₆				
	?	598.50	0.05	585.00	0.05
	¹ D ₂ → ³ F ₄	667.50	0.10	660.00	0.03
	¹ G ₄ → ³ H ₄				
	³ F ₂ → ³ H ₆				
	³ P → ¹ G ₄	705.00	0.40	700.00	0.78
	¹ I ₆ → ¹ G ₄				
³ F ₃ → ³ H ₆					
³ P → ³ F ₄	730.00	0.15	735.00	0.06	
¹ D ₂ → ³ F ₃					

^a Relative intensities; for each excitation the intensities are given relatively to the strongest emission band which is taken as unity.

TABLE IIIb—continued

Excitation (nm)	Assigned transition	Emission			
		Borate		Phosphate	
		λ (nm)	R.I. ^a	λ (nm)	R.I. ^a
200.0(S?)	$^3P_2 \rightarrow ^3H_6$	265.00	0.17	—	—
	$^3P_{1,0} \rightarrow ^3H_6$	298.00	0.30	300.00	0.10
	$^3P_2 \rightarrow ^3H_4$				
	$^3P \rightarrow ^3H_4$	—	—	355.00	0.35
	$^1I_6 \rightarrow ^3H_4$				
	$^3P_2 \rightarrow ^3H_5$	366.00	0.55	366.00	0.30
	$^1D_2 \rightarrow ^3H_6$				
	$^3P \rightarrow ^3H_5$	388.00	0.03	385.00	0.07
	$^1I_6 \rightarrow ^3H_5$				
	$^3P \rightarrow ^3F_4$	415.00	0.40	415.00	0.08
	$^1I_6 \rightarrow ^3F_4$				
	$^1D_2 \rightarrow ^3H_4$	457.00	1.00	455.00	1.00
	$^3P \rightarrow ^3F_3$				
	$^1I_6 \rightarrow ^3F_3$	475.00	0.40	478.00	0.27
	$^1G_4 \rightarrow ^3H_6$				
	$^3P \rightarrow ^3F_2$	525.00	0.25	525.00	0.20
	$^1I_6 \rightarrow ^3F_2$				
$^1D_2 \rightarrow ^3H_5$	560.00	0.10	—	—	
?	600.00	0.10	—	—	
?	625.00	0.03	—	—	
?	675.00	0.02	—	—	

^a Relative intensities; for each excitation the intensities are given relatively to the strongest emission band which is taken as unity.

borate glass part of the boron undergoes a change in coordination from three to four as the metal oxide (Me₂O) concentration increases. Bray et al. (29) and Krogh-Moe (30) found that above 40 Me₂O mole % almost all the boron atoms are four-coordinated and we can assume that in our borate glasses (see Experimental) only the four-coordinated boron exists.

As pointed out in the Introduction, the R.E. in the glass "lattice" will assume a site symmetry similar to that existing in oxide crystals, which is C₂ and C_{3i} for Tm³⁺ and Er³⁺. This assumption was confirmed by Rice and DeShazer (23) and our experimental studies on Eu³⁺ ions (11) in different glasses. We assume that the predominant point symmetry of Tm³⁺ and Er³⁺ in glasses is

TABLE IV
RELATIVE INTENSITIES AND HALF-BANDWIDTHS OF ¹D₂ AND ¹G₄ EMISSIONS OF Tm³⁺

Transition	Borate			Phosphate			Y ₂ O ₃ :Tm ³⁺ (I)	
	λ (Å)	R.I. ^a	$\Delta\lambda$ (Å)	λ (Å)	R.I.	$\Delta\lambda$ (Å)	λ (Å)	$\Delta\lambda$ (Å)
$^1D_2 \rightarrow ^3H_4$	4560	56.0	830.0	4530	68.0	670.0	4540	13.9
$^1G_4 \rightarrow ^3H_6$	4800	1.1	1410.0	4780	0.8	1080.0	4884	19.3
$^1D_2 \rightarrow ^3H_5$	5170	0.06	750.0	5130	0.07	750.0	5154	4.2
$^1G_4 \rightarrow ^3H_4$	6525	5.3	175.0	6515	5.6	170.0	—	—

^a R.I., Relative intensity; $\Delta\lambda$, half-bandwidth.

TABLE V
EMISSION SPECTRUM OF Er^{3+} AT VARIOUS EXCITATION WAVELENGTHS

Excitation (nm)	Assigned transition	Wavelength (nm)
255.0 ^a	${}^2P_{3/2} \rightarrow {}^4I_{15/2}$	310.0–320.0
	${}^2G_{7/2}, {}^2G_{9/2}, {}^2K_{15/2} \rightarrow {}^4I_{15/2}$	360.0–370.0
	${}^4G_{11/2} \rightarrow {}^4I_{15/2}$	388.0
	${}^2P_{3/2} \rightarrow {}^4I_{13/2}$	404.0
	${}^2P_{3/2} \rightarrow {}^4I_{11/2}$	473.0
	${}^2P_{3/2} \rightarrow {}^4I_{9/2}$	530.0
	${}^2H_{11/2} \rightarrow {}^4I_{15/2}$	
	${}^4S_{3/2} \rightarrow {}^4I_{15/2}$	540.0–550.0
382.0 ^b	${}^2H_{11/2} \rightarrow {}^4I_{15/2}$	524.0–530.0
	${}^4S_{3/2} \rightarrow {}^4I_{15/2}$	548.0–557.0

^a Excitation with mercury low pressure source.

^b Excitation with xenon source.

C_2 . The degeneracy of each electronic J level of Tm^{3+} (f^{12}) in the C_2 sites is completely lifted, giving rise to $2J + 1$ crystalline Stark levels. The degeneracy of each J level of Er^{3+} (f^{11}) in the C_2 sites is only partially removed giving rise to $J + \frac{1}{2}$ crystalline Stark levels, because of Kramer's rule. Electronic transitions are governed by different selection rules for the ions in two different sites. If Tm^{3+} or Er^{3+} are present in the C_{3i} symmetry then only magnetic dipole transitions are allowed. For ions on the C_2 sites magnetic as well as forced electric dipole transitions are allowed since there is no center of inversion. From our experimental results we see that mainly the transitions obeying the selection rule $1 < J \leq 6$ are observed, from which we conclude that these are forced electric dipole transitions. They can occur in the C_2 but not in the C_{3i} symmetries. We therefore conclude that C_2 is the predominant symmetry site of Tm^{3+} and Er^{3+} in the glasses. This conclusion is also consistent with Judd's prediction and the results of Gruber et al. (1) for splitting of Tm^{3+} and Er^{3+} levels in Y_2O_3 crystals.

Fournier and Bartram (31), in their paper on inhomogeneous broadening of the optical spectra of Yb^{3+} in glass, proposed a model in which the Yb^{3+} ion is surrounded by three phosphate tetrahedra which coordinate the rare earth through the nonbridging oxygens. The MO_4 tetrahedra are undistorted since covalent bonding strongly favors preservation of the MO_4 geo-

metry. On the other hand, the relative position of the tetrahedra in relation to the rare earth can be changed, thus producing differences in symmetry at the R.E. sites. In the case of Tm^{3+} and Er^{3+} in phosphate or borate glasses we propose that the R.E. is coordinated by four MO_4 tetrahedra so that two sets of two opposite tetrahedra (each set in a different position relative to the second one) are in a similar position relative to the R.E., so preserving the eight-coordination of the metal ion by nonbridging oxygens (two oxygens contributed by each tetrahedron) and thus producing the C_2 symmetry (Fig. 3). The phosphate glass forming tetrahedron has P–O and O–O distances of 1.57 and 2.56 Å, respectively (31). In the borate glass the B–O and O–O distances, forming the BO_4 tetrahedron, are 1.48 and 2.40 Å, respectively (32). By taking the radius of the nonbridging oxygen as around 1.2 Å and that of the rare earth as 0.9 Å, we obtain the distance O–R.E.³⁺ around 2.1 Å. Such structure maintains the eightfold coordination of the rare earth similarly to that existing in sesquioxide crystals.

A comparison of the transition intensities for Tm^{3+} and Er^{3+} in various media (Tables I and II) shows that the intensities in the uv region are smaller in borate than in phosphate glasses by a factor of 2–3, and in water they are smaller by a factor of 6–10.

Jorgensen and Judd (33) observed that certain

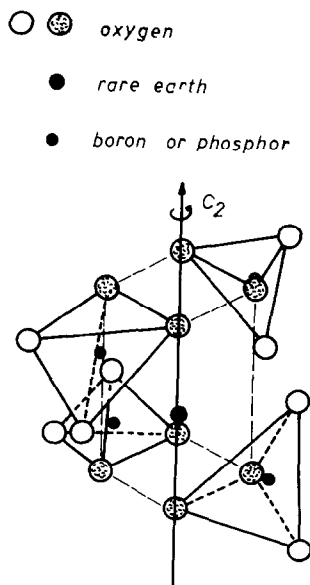


FIG. 3. Proposed rare earth site model. ⊗—Represent nearest oxygen neighbors surrounding the rare earth.

transitions which obeyed the $\Delta J = 2$ rule are "hypersensitive" to changes in the ion environment and they suggested an asymmetrical distribution of the dipoles induced in the host medium by an electromagnetic field. The gradient of the electric field across the rare earth is enhanced, thus resulting in a greatly enhanced electric quadrupole transition. But in a later reevaluation of the sources of the "hypersensitivity" in the rare earth spectra, Judd (34) suggested that only the following symmetry classes will give rise to "hypersensitive" transitions: C_s , C_1 , C_2 , C_{2v} , C_{3v} , C_{4v} , and C_6 . The assumed symmetry of Tm^{3+} and Er^{3+} in glasses is in accordance with Judd's prediction of symmetries giving rise to hypersensitive transitions. In addition, we think that the great difference in the absorption spectra of Tm^{3+} and Er^{3+} in uv as compared to small changes in the visible and ir regions in the two glasses can be explained only by the contribution of J mixing by the crystal field which should be stronger in the higher levels where the J levels are closer together in energy. We also observed that transitions for $\Delta J = 2$ are the strongest. This is always observed in the absorption spectrum (see Tables I and II) but in the fluorescence spectrum (see Tables IIIa, IIIb and V) this rule is not always obeyed because of the possibility of nonradiative transitions between levels, which are dominant when the energy gap is less than 3000 cm^{-1} . This energy corresponds to about three phonons in the glass lattices. A similar observation was made by Weber (19) for the fluorescence of Er^{3+} in LaF_3 crystals. In the case of Tm^{3+} doped glasses the fluorescence arising from the transition ${}^1G_4 \rightarrow {}^3H_4$, ${}^1D_2 \rightarrow {}^3H_4$ and ${}^1I_6 \rightarrow {}^3H_4$ are the strongest and just satisfy the selection rule $\Delta J = 2$. The high contribution to radiative transition here is caused by the great energy gap between the emitting level and the next lower one. The thulium fluorescence from 3P_2 , 3P_1 in addition to 3P_0 can be explained by the thermal population of the higher levels 3P_2 and 3P_1 from 3P_0 , 1I_6 . It should be noted that due to the inhomogeneous broadening of the levels in glasses—the difference in the tails of the relevant absorption band is lower than the difference in the maxima of the bands as they appear in Table I. A similar thermal equilibrium exists between 3F_2 and 3F_3 states.

The assumption that nonradiative decay between levels is dominant for energy gaps $< 3000\text{ cm}^{-1}$ still holds because of the very low quantum efficiencies of the 3P_2 and 3P_1 fluores-

cence compared to $({}^3P_0, {}^1I_6)$ and 3F_2 compared to 3F_3 .

In Er^{3+} the high probabilities arising from the transitions ${}^4I_{15/2} \rightarrow {}^4I_{11/2}$, ${}^4I_{15/2} \rightarrow {}^4H_{11/2}$, ${}^4I_{15/2} \rightarrow {}^4G_{11/2}$ are observed only in the absorption spectrum, while the emission from the ${}^4G_{11/2}$ and $H_{11/2}$ is very weak due to the small energy gap between the emitting level and the next-lower one, thus causing nonradiative losses. The observed erbium fluorescence from (${}^2G_{7/2}$, ${}^2G_{9/2}$, ${}^2K_{15/2}$) is possible because of thermal population from the ${}^4G_{11/2}$, but the efficiency is very low. The energy difference between the lower state of this multiplet and the ${}^4G_{11/2}$ is 607 cm^{-1} , while the difference between ${}^2H_{11/2}$ and ${}^4S_{3/2}$, where such an equilibrium is well known to exist, is 590 cm^{-1} . Weber (19) has also observed fluorescence from the ${}^4G_{11/2}$ in LaF_3 . Here also our assumption that nonradiative decay between levels is predominant for energy differences of $< 3000\text{ cm}^{-1}$ still holds because we see that the yield of ${}^4G_{11/2}$ fluorescence is very low.

According to the ligand field theory an increase in the separation of the crystal field split degenerated levels indicates an increase in the strength of the ligand field shown by the R.E. In cases of transition between two non-degenerated energy levels an increase in the ligand field causes the two levels' displacement towards lower energy levels. Stronger outer perturbation will induce energy level shifts towards longer wavelengths; this is reflected in the longer wavelength emissions in borate glasses than in phosphate glasses.

In order to approximate the glass host crystal fields, we used a simple expression for an "effective" ionic field strength $F = z/r^2$, where z is the valence of the network forming ions and r their ionic radius (in Å). The "effective" field strengths for the network forming ions B^{3+} and P^{5+} are 75.0 and 43.2, respectively. It can be seen, therefore, that the sodium borate glass host has a stronger "effective" ionic field than the phosphate glass (9).

In comparing the bandwidth of the ${}^1D_2 \rightarrow {}^3H_4$ transition of Tm^{3+} in borate glass with phosphate glass and doped yttrium oxide crystals (830, 670 and 13.9 Å (1), respectively (see Table IV)), we came to the conclusion that there are about 40–60 different sites of C_2 symmetry in a glass host. This result is consistent with results obtained for Eu^{3+} in phosphate glass. As previously explained above, the slight differences in environment are caused by small

variations in the crystal field parameters. The energy level shifts for ions in different environments lead to slight changes in the transition wavelength from one ion to another one, thus producing the broadening of the spectra. We believe that a similar situation exists in aqueous solutions, as can be seen from the example of Eu^{3+} (II), where the broadening of the ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ bands resulted in a variety of sites for the same symmetry due to a slight change in the distances between the ligands and the R.E.

The half-bandwidths in the absorption and fluorescence spectra are larger in phosphate than in borate (see Table IV). This can be attributed to the fact that the cavity in which the R.E. can be situated is larger in phosphate glasses, permitting a larger variety of sites with slightly different crystal field parameters, producing inhomogeneous broadening. From this we can conclude that the large half-width in the emission spectrum of R.E. in a glass is produced by inhomogeneous broadening rather than by crystal field splitting. A similar effect was observed in Eu^{3+} (II) where the emission half-widths in silicate glass are slightly higher than those in the phosphate glasses. The crystal field strength expressed as z/r^2 is 43.2 in phosphate and 23.8 in silicate, while the respective ionic radii are 0.34 and 0.41 Å.

The fact that the change in the relative absorption intensities (Table II) between phosphate and borate glasses is smaller for Er^{3+} doped glasses than for Tm^{3+} doped glasses can be explained by a somewhat weaker interaction of Er^{3+} with the glass network. The cation radius of Tm^{3+} (0.87 Å) is smaller than that of Er^{3+} (0.89 Å) and as a consequence the cation–oxygen nuclear distance becomes also smaller. Both the increase in the effective charge and the smaller cation–oxygen distance cause an increase in the electrostatic attraction of cation for oxygen. The increased attractive force must be balanced by an increased oxygen–oxygen repulsion, and this increase should be reflected in a shortening of the B–O or P–O bond and an increase in the frequency of vibration of the borate and phosphate ions. Thus, as the cation changes from Er^{3+} to the smaller Tm^{3+} , we shall get a slightly more dense structure which thus gives eventually a different arrangement of the structural unit (35). Even small differences in arrangement of the structural unit can cause the intensities of absorption bands of the two R.E. to differ.

Conclusions

(1) The “average” point symmetry of Tm^{3+} and Er^{3+} in glasses is C_2 .

(2) The inhomogeneous broadening due to the large number of sites is larger than the broadening due to crystal field splitting.

(3) The absorption bands corresponding to the transitions with $\Delta J = 2$ are the strongest, in agreement with Judd’s theory, while in the fluorescence spectrum the measured intensities of transition are dependent on the nonradiative losses which are phonon assisted, and therefore are influenced differently in different glass hosts.

(4) The high luminescence efficiency arising from the transitions to terminating levels which are higher than the ground state 3H_6 is more significant in Tm^{3+} than in any other R.E., because of the fact that the ΔJ between these levels and the emitting levels equals 2 and the energy gap between the emitting level and the next lower level is more than 3000 cm^{-1} .

(5) From the last paragraph it follows that the population inversion in Tm^{3+} can be achieved, and therefore a glass can serve as a possible laser.

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