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Spectral Broadening of Europium Ions in Glass*†

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The fluorescence and absorption spectra of trivalent europium ions in glass were measured and compared with the spectra of single crystals of Gd_2O_3:Eu. It was determined that there is a great similarity between the optical properties of the rare-earth glasses and rare-earth sesquioxide crystals. The spectral studies showed that the europium ions locate in two, and possibly three, average environment sites in glass, mirroring the three sites in which the ion locates in the monoclinic form of the sesquioxide. The primary broadening mechanism was found to be inhomogeneous as determined by the temperature independence of the spectral half width and peak wavelength in the range from 4 to 300°K. This inhomogeneous broadening arises from the heterogeneity of the ion environment in glass.

INTRODUCTION

THE objective of this investigation was to obtain a better understanding of the optical properties of the rare-earth ion in glass. The characteristics of glasses with the rare-earth ion as the active ion are of particular interest because these media are used as laser amplifiers and oscillators. In particular a knowledge of the site symmetry or local ion environment will allow a better interpretation of many laser experiments. Previous studies have been done in determining energy levels, linewidths, and cross sections for the Nd^{3+} ion in glass; more information can be obtained for an even-electron system and thus the motivation for the study of the Eu^{3+} ion in glass. Particular attention was given to the broadening mechanisms and additional observations were made on single crystals of Gd_2O_3:Eu for comparison to the glass studies.

It was recognized early that glasses containing rare earths were useful as light filters for many optical applications, but it remained until 1939 for Tomaschek[1] to report the absorption and fluorescence spectra of europium ions in several glasses. Only a very limited amount of research on rare-earth glasses was conducted until the advent of rare-earth glass lasers in 1961.[2] Although europium glass is not a laser medium, several investigators[3] noted that the europium spectrum contained many simple features which greatly assisted in the analysis of rare-earth ions in glass. In particular, absorption and fluorescence from the singlet ($J=0$) levels of the europium ion make it possible to study linewidths and positions without the complications of overlapping lines.

THEORETICAL BACKGROUND

A detailed theoretical analysis of the optical properties of rare-earth ions in a noncrystalline solid, like glass, has never been achieved, although the analysis of rare-earth ions in crystals has been extensive and at present it is rather complete.[4,5] The understanding of rare-earth ions in crystals will be the foundation of any analysis of rare-earth ions in noncrystalline solids. A crystallographic definition of a noncrystalline solid is a solid having short-range order without the long-range order of crystals.[6] Thus, the short-range environment of each rare-earth ion approximates a crystal environment, but the environment is different for various ions. This heterogeneity of ionic environment can usually be described as a distribution of differing environments about an "average" environment. Of course, the form of this distribution will depend on the particular noncrystalline solid: A common description is random distortions of the structure of the "average" environment. Here, the approach will be to analyze the trivalent europium ion in its oxide crystal-lattice site, and then to investigate the modifications introduced by the heterogeneity of ionic environment in glass.

The theory of europium ions in a crystal has been carried out in the past, and only the evaluation of the influence of the crystal environment on this free ion will be considered. A spherical symmetry exists for the free ion, and each level is $(2J+1)$-fold degenerate. The spherical symmetry is destroyed by placing the ion in a crystal, and each level splits under the influence of the electric field produced by the environment. The Hamiltonian for a rare-earth ion in a crystal is the sum of the free-ion Hamiltonian and the potential V provided by the crystal environment about the ion. V can be regarded as perturbation. The assumption that this perturbation is an electrostatic potential with

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the symmetry of the crystal site has been very successful for many crystals, giving reasonable agreement between calculated and observed level splittings. This electrostatic model of the crystal field is a good approximation for rare-earth sesquioxide crystals.[7] For calculations, the crystal potential is expanded in a spherical-harmonic series whose expansion coefficients depend on the specific structure of the crystal environment. In principle these coefficients can be calculated by summations over the lattice, and one feature of this summation has importance for this study: Summation over nearest neighbors is a reasonable approximation to the complete sum for the coefficients.[8,9] Therefore, the short-range environment dominates in the weak-field approximation that we are following. Covalent bonding effects might modify this viewpoint.[10] Once the point symmetry and the appropriate form of the crystal potential have been determined, the crystal-field splitting of the free-ion levels can be calculated, i.e., the number of sublevels split from a level of known J can readily be determined.

In order to know the point symmetry at the rare-earth ion site, the detailed crystal structure must be known. The rare-earth sesquioxides have three different forms: trigonal, monoclinic, and cubic. Each sesquioxide may crystallize into two or three of the chemically identical, but crystallographic distinct forms: i.e., they are polymorphic. The stability of these phases depends on the atomic number of the rare-earth, temperature, time held at a particular temperature, pressure, and original low-temperature phase.[11,12] Each sesquioxide has only one stable polymorph: La_2O_3, Ce_2O_3, Pr_2O_3, and Nd_2O_3 belong to the trigonal form; Sm_2O_3, Eu_2O_3, and Gd_2O_3 to the monoclinic type; Tb_2O_3, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3 to the cubic type.[13]

The trigonal form is of space group $D_{3d}{}^3$ with one molecule per unit cell. Each rare-earth ion is bonded to seven oxygen ions (four short bonds and three long bonds) and the two types of oxygen ions are bonded to five or four metal ions, respectively. In a unit cell there are two rare-earth ions on two identical C_{3v} sites, and two oxygen ions on two identical D_{3d} sites.[13,14]

The monoclinic form is of space group $C_{2h}{}^3$ with six molecules per unit cell; each rare-earth ion has sevenfold coordination. Each unit cell has three sets of four rare-earth ions on three different C_s point-symmetry sites, four sets of oxygen ions on four different C_s sites, and one set of two oxygen ions on C_{2h} sites.[15–17]

The cubic form of the rare-earth sesquioxides is of space group $T_h{}^7$ with 16 molecules per unit cell. Each unit cell has one set of eight rare-earth ions on C_{3i} sites, one set of 24 rare-earth ions on C_2 sites, and 48 oxygen ions on C_1 sites.[18]

The case of interest is that of Sm_2O_3, Eu_2O_3, and Gd_2O_3 which crystallize in the cubic form at low temperatures and invert directly and irreversibly to the monoclinic form if held at 1240, 1370, and 1530°K, respectively, for several days or at 1370, 1570, and 1670°K, respectively, for an hour.[11] Therefore, considering the process by which europium glass is prepared, the monoclinic structure is the crystallographic form of the rare-earth sesquioxides to be used in the analysis.

The principal modification of the crystalline theory due to the noncrystalline nature of glass is a distortion of the sesquioxide crystal environment which is different for each ion in glass. It will be assumed that the "average" environment is that of the oxide crystal, an assumption supported by the experimental studies reported here. A description of the environment symmetry in the europium glass is the point symmetry C_s, so the crystal potential is that corresponding to C_s symmetry. Now, each environment will be expressed as a monoclinic C_s symmetry, but the environments will differ in the magnitudes of the crystal-field parameters. Then the differences in environment for the rare-earth ions are expressed in terms of small variations of these crystal parameters. The energy-level shifts for ions in different environments lead to changes in the transition wavelength from ion to ion. This situation produces a broadening of the single spectral line found in the sesquioxide crystal. The half-width of a spectral line in the sesquioxide crystal is about 2 cm^{-1}, and about 100 cm^{-1} in an oxide glass.

This broadening of spectral lines due to heterogeneity of the environment is a special instance of inhomogeneous broadening. Inhomogeneous broadening arises from perturbation differences between individual ions, with these slight differences leading to a distribution of center wavelengths. Then an inhomogeneous line can be thought of as composed of a superposition of many homogeneous lines from individual ions. An analog of the environmental broadening presented here is Doppler broadening, where the frequency is shifted by motion of the emitting atoms. Theoretical studies of environmental broadening in solids are difficult,[19] but experimental verification of inhomogeneous broadening

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in rare-earth glasses has been supplied by several laser experiments.[20–22]

EXPERIMENT

The experimental configuration was the usual system for observing fluorescence and absorption spectra of transparent samples. An added feature was a stainless-steel liquid-helium Dewar having temperature control capability (Andonian model 024/7M). The sample temperature was varied from 4 to 310°K, enabling a study of the variations of spectra with temperature. The Dewar utilized gaseous cooling of the sample thus avoiding many of the problems of liquid cooling, such as attenuation of the signal by scintillation of the bubbling coolant and destruction of the sample by immersion into the liquid coolant. By varying the gaseous cooling flow and utilizing electric heaters in the sample and vaporization blocks, the temperature of the sample could be stabilized within one-half degree for one-half hour, a period of time adequate to observe the fluorescence and absorption spectra.

Two scanning spectrometers were used in this study: a 0.5-m $f/8.6$ Ebert mounting (a modified Jarrell-Ash Model 82-000), and a 1.0-m $f/8.7$ Czerny-Turner mounting (Jarrell-Ash Model 78-466). A thermoelectric-cooled RCA 7102 photomultiplier tube (S-1 surface) was the detector with the 0.5-m spectrometer; an RCA 1P28 photomultiplier tube having an S-5 surface was used with the 1.0-m spectrometer. The detector signal was amplified by a balanced electrometer amplifier (Jarrell-Ash Model 26-780) and recorded by a strip chart recorder (Moseley Model HP7127A).

The light source used for excitation of fluorescence was a water-cooled, high-pressure, kilowatt, mercury arc (GE Model AH-6). For absorption studies the source was a 650-W type DWY quartz iodide lamp.

Two types of glasses were investigated. The principal study was done on europium borosilicate glass which was made at Hughes Aircraft Co. in the Ceramics and Materials Department by D. K. Auda and one of the authors (LGD); the composition was 40.2% SiO_2, 30.2% B_2O_3, 13.4% ZnO, 7.9% Na_2O, 5.4% Li_2O, and 2.9% Eu_2O_3 (sample dimensions: length was 2.174 cm and diameter was 0.630 cm). To back up the results on this material another glass was studied; it was 1% Eu_2O_3 in a dense, phosphate crown glass supplied by Bausch & Lomb (sample dimensions: length was 2.273 cm and diameter was 0.632 cm). A single crystal of Gd_2O_3:Eu provided by Korad Department of Union Carbide Corp.[23] was investigated (sample dimensions: length was 0.048 cm, height was 0.610 cm, and width was 0.325 cm).

All fluorescence and absorption data taken from the recorder traces were corrected for the spectral response of the detection system. The spectral response was calculated using a standard tungsten ribbon lamp (Phillips Research Laboratory No. 1926), whose brightness temperature was measured with a micro-optical pyrometer (Pyrometer Instrument Co., Model 95). The spectral distribution function was determined by taking the product of the emissivity of tungsten as a function of wavelength with the calculated spectral adiant intensity of a blackbody per unit area of emitter. rurface per second in a wavelength range between λ and s$\lambda+d\lambda$ into a solid angle of 2π sr using Planck's equation The correction was made using the comparison between

TABLE I. Energy levels of Eu^{3+} in glass and $LaCl_3$.

Classification $^{2S+1}L_J$	Energy (cm^{-1}) Glass	$LaCl_3$
$^7F_0$	0	0
$^7F_1$	424	372
$^7F_2$	1095	1037
$^7F_3$	1972	1887
$^7F_4$	2897	2846
$^7F_5$	4897	3896
$^7F_6$	5897	4942
$^5D_0$	17 297	17 267
$^5D_1$	19 017	19 029
$^5D_2$	21 540	21 506

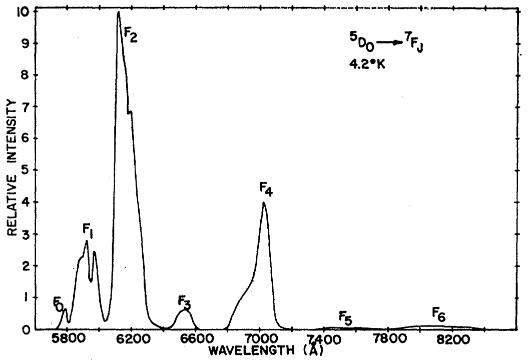

FIG. 1. Fluorescence spectra of 3% Eu: borosilicate glass at 4.2°K. Intensities relative to peak of $^5D_0 \rightarrow {}^7F_2$.

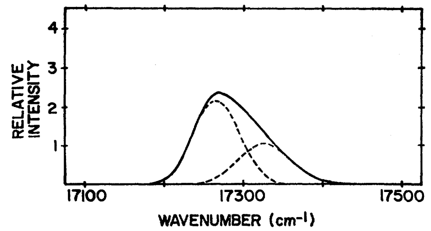

FIG. 2. $^5D_0 \rightarrow {}^7F_0$ fluorescence of 3% Eu: borosilicate glass at 4.2°K (5780 Å). Intensity relative to peak of $^5D_0 \rightarrow {}^7F_1$.

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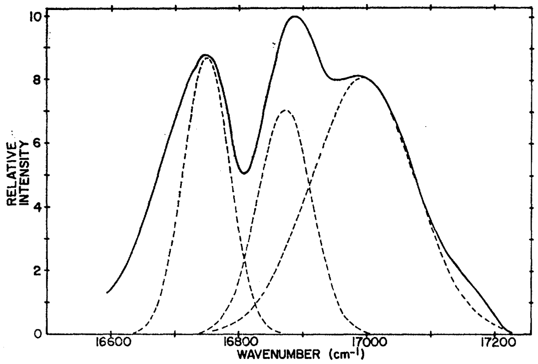

FIG. 3. ${}^5D_0 \rightarrow {}^7F_1$ fluorescence of 3% Eu: borosilicate glass at 4.2°K (5900 Å). Intensity normalized to peak.

this calculated spectral distribution and the measured distribution. Therefore, all spectral curves shown in this paper have been corrected for the spectral response of the system.

RESULTS

Fluorescence

The energy levels of the Eu^{3+} ion in glass are listed in Table I as compared with $LaCl_3$.[24] Above 25,000 cm^{-1} the energy levels are very dense, leading to a continuous band in glass. The only fluorescence level is the ${}^5D_0$, and there are seven fluorescence spectral groups corresponding to transitions from the ${}^5D_0$ to all the ${}^7F$ levels. All these groups were observed in this study. These fluorescence groups with the sample at 4.2°K are shown in Fig. 1. The ${}^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions were studied in detail.

Figure 2 shows the ${}^5D_0 \rightarrow {}^7F_0$ fluorescence at a glass sample temperature of 4.2°K; this transition is seen to consist of two inhomogeneous lines of unequal intensity giving an asymmetry to the over-all line shape on the short-wavelength side. For the ${}^5D_0 \rightarrow {}^7F_0$ transition there should be one line; the surprising presence of two inhomogeneous lines separated by approximately 45 cm^{-1} indicates that the active ion locates in two preferred average environments of low symmetry in glass. The line shape was identical in both glass samples.

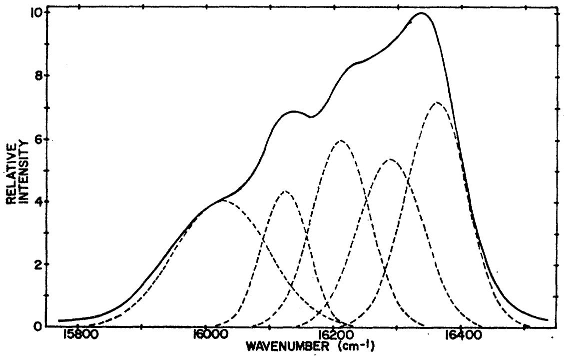

FIG. 4. ${}^5D_0 \rightarrow {}^7F_2$ fluorescence of 3% Eu: borosilicate glass at 4.2°K (6200 Å). Intensity normalized to peak.

Figure 3 shows the ${}^5D_0 \rightarrow {}^7F_1$ fluorescence of the glass at 4.2°K. A best fit of three inhomogeneous lines is shown, and is seen to be insufficient. The wings of the group do not fit, again showing evidence for multiple-site occupation. Excellent fitting could be done with six lines, but the three inhomogeneous lines give a better description because it is a minimum numbered fit. With six lines it would be impossible to tell which pair corresponded to the transition between the ${}^5D_0$ level and a particular ${}^7F_1$ sublevel, while the three Gaussian lines give the approximate locations and separations of the ${}^7F_1$ sublevels.

Similarly, the ${}^5D_0 \rightarrow {}^7F_2$ fluorescence is shown in Fig. 4 as fitted with five inhomogeneous lines. Again the wings of the group do not fit; a 10-line fit corresponding to the dual site occupation would undoubtedly be sufficient, but, as previously mentioned, would give no real information.

The fluorescence spectra for these two groups for the 1% europium phosphate crown glass was almost identical to the aforementioned data on the 3% europium borosilicate glass when normalized to the same peak intensities. This indicates that the ion has a similar local environment in the two different glasses. Although the glass host is heterogeneous and causes a broadening of the lines, the clue from the above is that the Eu_2O_3 is the principal factor in the symmetry consideration.

Absorption

To confirm multiple-site occupation, a study of the absorption and fluorescence spectra of single-crystal

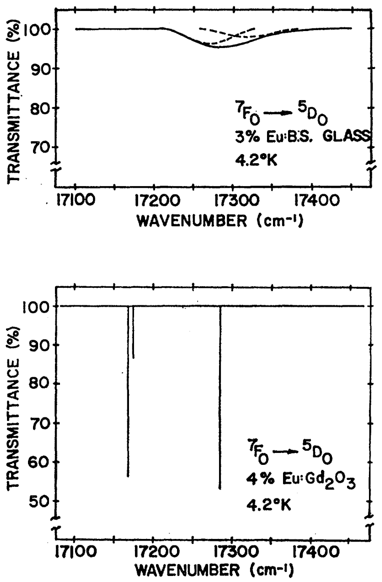

FIG. 5. ${}^7F_0 \rightarrow {}^5D_0$ absorption at 4.2°K for 3% Eu: borosilicate glass and 4% Eu in Gd_2O_3.

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4% Gd_2O_3:Eu was done. The gadolinium sesquioxide crystal was chosen over pure europium sesquioxide because Gd_2O_3 has the same crystal symmetry as Eu_2O_3 but does not obscure the properties of the Eu^{3+} ion with resonant effects. There is no absorption or fluorescence of the gadolinium ion in the region of study and so no complication arose for this reason. Since Gd_2O_3 is a biaxial crystal, the sample was polished and oriented such that polarization of the ${}^7F_0 \leftrightarrow {}^5D_0$ europium transition was completely linear.

Figure 5 shows a comparison of the ${}^7F_0 \rightarrow {}^5D_0$ absorption of the borosilicate glass and the gadolinium sesquioxide crystal at a temperature of 4.2°K. This weak-glass absorption was fitted with two inhomogeneous lines as was the comparable fluorescence. The absorption of the europium in the Gd_2O_3 crystal was seen to consist of three instrument-broadened lines. This indicates that there are three preferential sites for the Eu^{3+} ion in the Gd_2O_3 crystal. Noticing that two of the absorption lines are very close together with one much weaker than the other, it is easily seen why a third low-level line could not be detected in the ${}^7F_0 \rightarrow {}^5D_0$ glass absorption. The crystal absorption lines were completely polarized which is typical of $0 \leftrightarrow 0$ transitions. The ${}^7F_0 \rightarrow {}^5D_0$ absorption in the phosphate crown glass was identical to the borosilicate sample.

The ${}^7F_0 \rightarrow {}^5D_1$ absorption of the borosilicate glass and the gadolinium sesquioxide crystal are shown in Fig. 6. A best fit of three inhomogeneous lines was found to describe this group very well, and this is reasonable because the crystal absorption is seen to consist of seven lines which fall into three groups. There are evidently two other lines in this crystal absorption which were too weak to be detected or which are at the same energy location as two of the others.

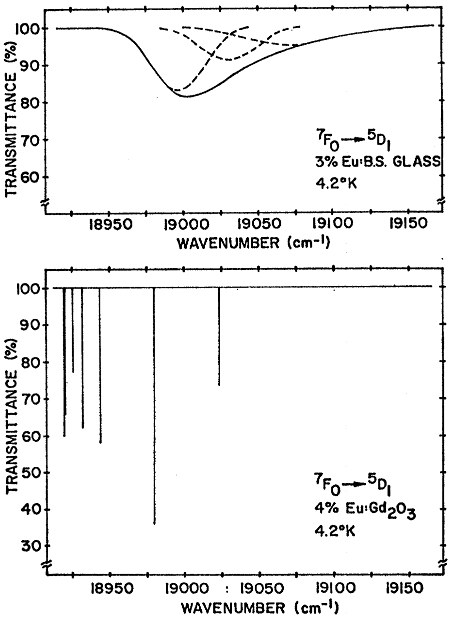

FIG. 6. ${}^7F_0 \rightarrow {}^5D_1$ absorption at 4.2°K for 3% Eu: borosilicate glass and 4% Eu in Gd_2O_3.

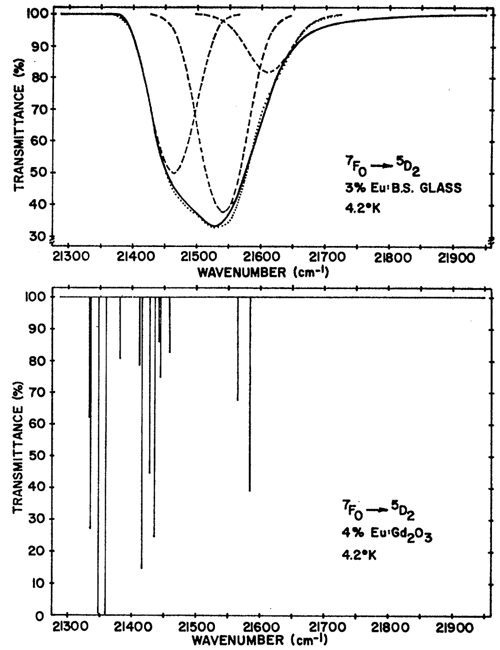

FIG. 7. ${}^7F_0 \rightarrow {}^5D_2$ absorption at 4.2°K for 3% Eu: borosilicate glass and 4% Eu in Gd_2O_3.

Figure 7 shows the comparison of the ${}^7F_0 \rightarrow {}^5D_2$ absorption in the borosilicate glass and the Gd_2O_3 crystal at 4.2°K. A best fit of three inhomogeneous lines corrected for overabsorption was done for the glass data; the solid line represents the experimental information and the dotted line represents the sum of the three overabsorbed Gaussian lines. The three-line fit is seen to agree well with the gadolinium sesquioxide absorption data since the Gd_2O_3 absorption consists of 14 lines which fall into three dominant groups. There is one missing line which is again too weak to observe or is overlapping with another line. Overabsorption was taken into consideration because the measured half-width of an absorption line will be greater than the true half-width and this must be considered for peak transmissions of less than approximately 70%.

The absorption spectra of the ${}^7F_0 \rightarrow {}^5D_{1,2}$ was identical for the phosphate crown glass as far as line shapes were concerned but naturally has less absorptiv-

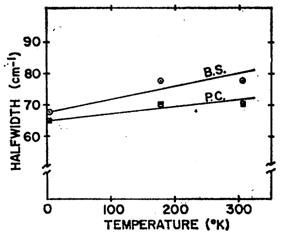

FIG. 8. Half-width versus temperature of site-1 line of ${}^5D_0 \rightarrow {}^7F_0$ fluorescence for 3% Eu: borosilicate glass and 1% Eu: phosphate crown glass.

TABLE II. Half-width and peak wave number versus temperature for two site fluorescence lines of $^5D_0 \rightarrow {}^7F_0$ transition of 3% Eu: borosilicate glass and 1% Eu: phosphate crown glass.

	Site 1				Site 2			
	B. S. glass		P. C. glass		B. S. glass		P. C. glass	
Temp. (°K)	Half-width (cm^{-1})	Peak (cm^{-1})	Half-width (cm^{-1})	Peak (cm^{-1})	Half-width (cm^{-1})	Peak (cm^{-1})	Half-width (cm^{-1})	Peak (cm^{-1})
4.2	67.5	17 266.0	65.0	17 267.5	77.5	17 327.0	75.0	17 320.0
177.5	77.5	17 273.5	70.0	17 270.0	87.5	17 328.5	77.5	17 320.0
306.5	77.5	17 273.0	70.0	17 276.0	87.5	17 330.0	80.0	17 321.5

ity because of the lesser concentration of Eu^{3+}. The $^7F_0 \rightarrow {}^5D_3$ absorption was too weak to be observed in the glasses and too much overlapped with the continuous band transitions in the Gd_2O_3 to be discernible.

Thermal Effects

Figure 8 shows a plot of half-width versus temperature for the site-1 $^5D_0 \rightarrow {}^7F_0$ fluorescence line for the two different glasses. The half-width difference is very slight from 4.2 to 300°K. Table II shows the half-widths and peak wave numbers of both of the lines for the two samples as a function of temperature. The variation is minor which is indicative of inhomogeneous broadening. The temperature dependence is probably even less than shown because of self-absorption effects. Since the $^5D_0 \rightarrow {}^7F_0$ is a resonant transition, the fluorescence will tend to be reabsorbed and thus slightly effect the line shape. In addition, a probable low-level third site line, as concluded from the Gd_2O_3 data, undoubtedly effects the shape and makes the temperature dependence appear more than it is.

CONCLUSION

There is a great similarity between the optical properties of the rare-earth glasses and rare-earth sesquioxide crystals. From the spectral studies on neodymium glass,[25] it was observed that the Nd^{3+} ion locates in only one average environment site in glass, mirroring the fact that there is only one kind of Nd^{3+} ion site in neodymium sesquioxide having a point-group symmetry of C_{3v}. These spectral studies on europium glass show that the Eu^{3+} ion locates in two, and possibly three, average environment sites in the glasses. As stated previously, in the monoclinic form of europium sesquioxide there are three kinds of Eu^{3+} ion sites with point-group symmetries of C_s. The rare-earth ion locates in an environment in glass much like the environment it has in its crystal form. Thus it is fallacious to try to draw conclusions on the rare-earth glasses without a detailed knowledge of the rare-earth sesquioxide crystal structure. For instance, the three components of the $^7F_0 \rightarrow {}^5D_2$ absorption in glass do not correspond to transitions to sublevels of the $^5D_2$ level, but are products of the large glass broadening of the 14 crystal lines which were divided into three groups.

Even though the Eu^{3+} ion maintains a crystallike local environment in the glass, the spectral lines are inhomogeneously broadened because of the slightly different surroundings of the ion due to the heterogeneity of the glass. The interaction of the active ion with the diverse electrostatic fields of the glass leads to a distribution of the center wavelengths of spectral ionic lines giving the inhomogeneous broadening. The minor temperature dependence of the half-widths and peak wavelengths of the spectral lines of the europium ion in the glass studies described in this paper, and of the neodymium ion in previous glass studies,[25] confirm that this broadening is inhomogeneous. Therefore, the primary broadening mechanism of the europium ion in a glass host is inhomogeneous, arising from the heterogeneity of the ion environment.

Preliminary results of studies with higher concentrations of Eu_2O_3 in glass show a concentration narrowing of the spectral lines which supports the conclusions of local crystallike environment of the rare-earth ion in glass. In addition, preliminary studies of high-temperature effects indicate thermal broadening of the spectral lines becomes significant at approximately 600°K, again confirming the inhomogeneous-broadening mechanism. The results of these investigations will be presented in future papers. Furthermore, the complete results of the 4% Gd_2O_3:Eu spectral studies will be given in a subsequent publication.

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