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A STUDY OF THE Eu^{3+} CHARGE-TRANSFER STATE IN LANTHANIDE–BORATE GLASSES

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The luminescence properties of the Eu^{3+} ion in lanthanide–borate glasses were investigated and compared with those of Eu^{3+} in crystalline GdB_3O_6. In these materials the emission observed is from the $^5D_0$ to the ^7F_J levels. The rate of nonradiative relaxation from the charge-transfer state to the ^7F_J levels depends strongly on the host material. In the glasses it is high, whereas it is low in the crystalline lattice. Improving the glass quality by increasing the amount of lattice modifiers increases the rate even further. This difference is discussed and explained in terms of a configurational coordinate diagram.

1. Introduction

The luminescence properties of the Eu^{3+} ion have attracted much attention over the last decades. As a consequence, a large amount of spectral data on this ion is available in the literature. In research on the structure of glasses the Eu^{3+} ion is often used because of its high luminescence efficiency and because there is detailed knowledge on changes in its emission spectrum caused by a variation of the crystal field, in symmetry as well as in strength [1–3].

However, not much research has been performed on the behaviour of the Eu^{3+} ion in glasses under UV (i.e. charge-transfer) excitation. The quantum efficiency under this condition is low which excludes practical application. Recently, a number of studies appeared which show a new interest in rare earth luminescence in glasses under UV excitation [4,5]. The quantum efficiency of the luminescence of Tb^{3+} and Ce^{3+} under UV excitation is as high as 80 and 65%, respectively. For Eu^{3+} this efficiency is low.

In the case of charge-transfer-state (CTS) excitation the local environment and surrounding ligands play an important role. It has been shown before that in the case of crystalline solids the position of the CTS has a large influence on the luminescent efficiency [6–8].

It is the purpose of this study to compare the Eu^{3+} luminescence under CTS excitation in glasses and crystalline solids of comparable chemical composition in order to obtain a better understanding of the CTS relaxation in the glassy state. It turns out that the expansion of the CTS in the glassy state is larger than in the crystalline state.

2. Experimental

2.1. Preparation of the glasses

Glass samples are prepared by mixing the raw materials intimately. The rare earths are Gd_2O_3, La_2O_3, and Eu_2O_3 (Highways 5N). Other raw materials are H_3BO_3, Na_2CO_3 and $CaCO_3$ (Merck extra pure). The mixture is dried in an oven at 180 °C for 2 to 3 h. An excess of H_3BO_3 (~ 2.5%) was added to the starting mixture to compensate for evaporation. Before the batch is added, the platinum crucible is heated to the melting temperature. After melting in air, the crucible is covered with a platinum lid to prevent the evaporation of boron oxide. The melt is fired for about 20 min at 1200 °C. The fining and casting temperature was 1100 °C for ~ 15 min. The glass was poured into a carbon mould at 650 °C and cooled slowly to room temperature. Glass compositions are given

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Table 1
Composition of the glasses under investigation (in mol%)

Glass No.	$2H_3BO_3$	$CaCO_3$	Na_2CO_3	Al_2O_3	Gd_2O_3	La_2O_3	Eu_2O_3
1	75	10	5		9		1
2	75	5	2.5		16.5		1
3	75	2.5	1.25		20.25		1
4	75	4	2		18		1
5	75			14	10		1
6	75	4	2			18	1
7	75	4	2			19	
8	75	4	2		18		1%Tb_2O_3

in table 1. Samples were ground with great care to obtain grains of similar sizes.

The crystalline powder was prepared as described in ref. (9). Its composition is $Gd_{0.99}Eu_{0.01}B_3O_6$.

2.2. Spectroscopic measurements

Luminescence spectra were measured on powdered samples. Measurements were carried out at various temperatures from 4.2 to 300 K. Emission and excitation spectra were recorded using a Perkin–Elmer MPF-3L spectrofluorometer equipped with an Oxford Instruments helium flow cryostat. The excitation spectra were corrected for the lamp intensity and the transmittance of the monochromator with the use of Lumogen T-rot GG as a standard. Since the excitation spectra measured with the spectrofluorometer are not very accurate for wavelengths shorter than 240 nm due to the Xe light source, another arrangement was used to measure the excitation spectra in the shorter wavelength region. This arrangement consists of a water-cooled Hamamatsu 200 W deuterium lamp as a light source, a Carl Zeiss grating monochromator (blazed at 200 nm) for excitation wavelength selection, a filter set (interference, cut-off and band pass filters) for emission wavelength selection and a cooled RCA C31034 photomultiplier tube for emission signal detection. The spectra were corrected for the intensity distribution of the excitation source and the transmittance of the excitation monochromator, using sodium salicylate as a standard. Diffuse reflection spectra of the powdered samples were recorded at room temperature with a Perkin–Elmer Lambda 7 UV/VIS spectrophotometer. The same apparatus was used to measure the absorption spectra of glass samples of 2 and 0.6 mm thickness. The absorption spectra were not corrected for reflectance losses.

3. Results and discussion

3.1. Emission spectra

Figures 1 and 2 show the emission spectra of Eu^{3+} in glassy and crystalline powders, at 300 and

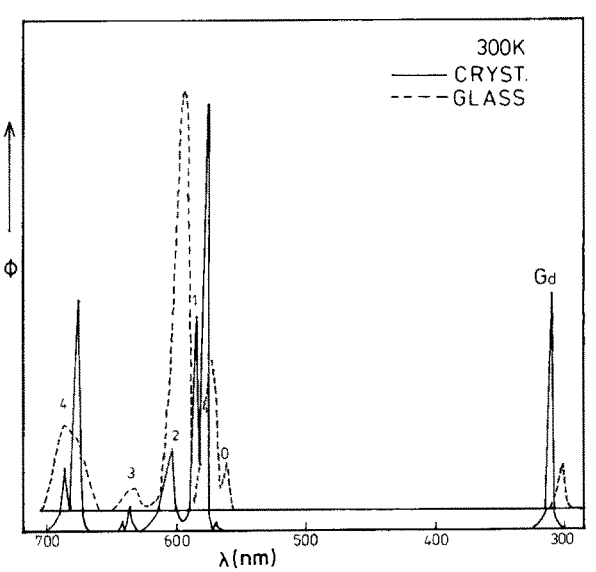

Fig. 1. Emission spectra of crystalline GdB_3O_6:Eu and glass No. 1 at 300 K. Excitation wavelength is 274 nm. The numbers 0,..., J denote the Eu^{3+} transitions $^5D_0-^7F_J$. Φ denotes the photon flux density. The spectra have been shifted relative to each other for reasons of clarity.

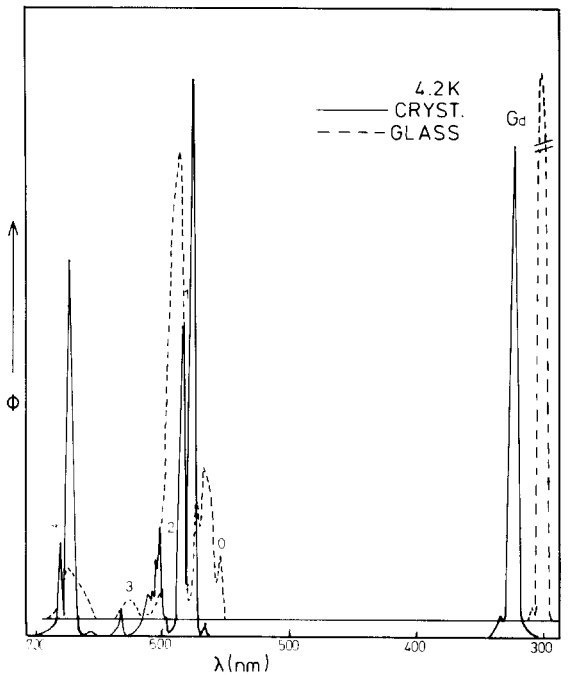

Fig. 2. Emission spectra of crystalline GdB_3O_6 and glass No. 1 at 4.2 K. Excitation wavelength is 274 nm. The Gd^{3+} emission intensity at 313 nm of the glass (dotted line) is 8× as high as shown in the figure. The numbers 0,..., J denote the Eu^{3+} transitions $5D_0-{}^7F_J$. Φ denotes the photon flux density. The spectra have been shifted relative to each other for reasons of clarity.

4.2 K, respectively. It is clear that the $^5D_0-{}^7F_2$ emission in glass is much stronger than in the crystalline phase, whereas the intensities of the other emission lines do not change much. As a matter of fact they all show considerable inhomogeneous broadening in the glassy phase. One of us has shown that the Eu^{3+} site symmetry in crystalline GdB_3O_6–Eu is not far from D_{4d}, a site symmetry which forbids the $^5D_0-{}^7F_2$ transition [10].

As a consequence the $^5D_0-{}^7F_2$ emission in the crystalline phase is relatively weak. The spectra for the glass phase show that the site symmetry deviates much more from D_{4d} symmetry than in the crystalline phase. Most probably the site symmetries in the glass are quite different. The emission spectra of the Eu^{3+} luminescence are independent of excitation wavelength.

However, upon specific Gd^{3+} excitation, we observe, next to a dominating Eu^{3+} emission, a weak Gd^{3+} emission at 313 nm. The excitation wavelength for these spectra was 274 nm, i.e. in the Gd^{3+} $^8S-{}^6I$ transition. Table 2 shows the ratio of the integrated intensity of the Gd^{3+} and Eu^{3+} emissions under several conditions. All the spectra show a strong Eu^{3+} emission upon Gd^{3+} excitation, which means that there occurs an efficient migration from the Gd^{3+} ions [9,11]. At 4.2 K the Gd^{3+} emission is much stronger than at 300 K. This increase is due to the fact that in a disordered solid the Gd^{3+} energy levels differ energetically. The energy mismatch is made up by phonons. As a consequence the energy migration over the Gd^{3+} ions is temperature-dependent.

At 4.2 K the Gd^{3+} ions with the lowest energy levels act as traps. They trap the excitation energy and emit subsequently [12,13]. The change is stronger in the case of the glasses. This is not unexpected, because glasses have 'structurally' more traps than crystalline solids. The emission spectra of the glassy and the crystalline samples are not comparable: the glass has a CTS absorption at 274 nm (see below), i.e. direct Eu^{3+} excitation occurs also. This direct excitation explains the weaker Gd^{3+} emission intensity in the glass at 300 K. This interpretation was checked by comparing the emission spectra of a Tb^{3+}-doped GdB_3O_6 glass and crystalline powder. At 274 nm the crystal and the glass show only Gd^{3+} absorption, the allowed Tb^{3+} f–d band being situated at shorter wavelengths. The ratio of the integrated Gd^{3+} and Tb^{3+} emissions at 300 K under Gd^{3+} excitation are almost equal.

3.2. Excitation spectra and efficiency

Figure 3 shows the excitation spectra of the Eu^{3+} emission of the crystalline and a representa-

Table 2
The ratio of the integrated intensities of the Gd^{3+} and Eu^{3+} emission at 290 and 4.2 K, in a glass and in the crystalline lattice (GdB_3O_6). Excitation wavelength is 274 nm

Temperature (K)	Gd^{3+}/Eu^{3+}	
	Glass No. 1	Crystalline $GdB_3O_6 \cdot Eu$
290	1/50	1/8
4.2	1/2.5	1/5

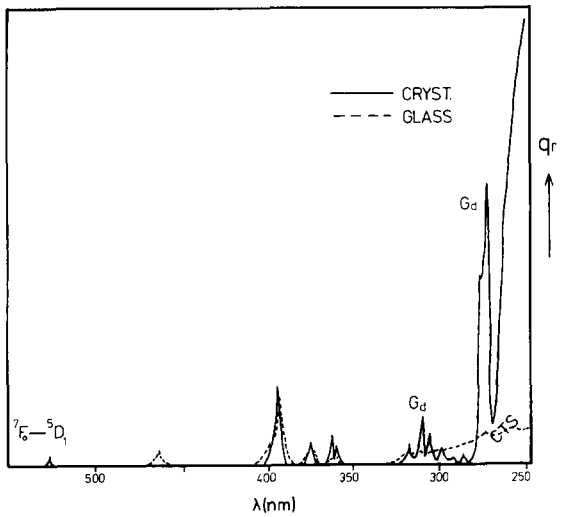

Fig. 3. Excitation spectra of the Eu^{3+} $^5D_0-^7F_4$ emission (700 nm) of crystalline GdB_3O_6: Eu and glass No. 4 at 4.2 K. q_r denotes the relative quantum output in arbitrary (linear) units. The $^7F_0-^5D_1$ emission intensity is used as a standard to compare the spectra.

tive glass sample at 4.2 K, from 250 to 600 nm. The $^7F_0-^5D_1$ magnetic-dipole transition is used as a standard in order to compare the spectra. It is well known that the intensity of this transition does not depend strongly on the nature of the Eu^{3+} surroundings [7]. No spectacular changes were found for higher temperatures up to 300 K. There was no decrease, with in experimental error, in efficiency with increasing temperature.

The quantum efficiency (q) of the crystalline phase is high, independent of excitation wavelength. Its value approaches 100% [9,14]. Using the excitation spectra, and taking the $^7F_0-^5D_1$ intensity as an internal standard and correcting for absorption strength, q for the glassy samples is found to be 10–15% for CTS excitation and > 70% for $4f^6$ excitation. We arrive, therefore, at the surprising result that CTS excitation of Eu^{3+} in a glass results in a much lower emission efficiency than CTS excitation of Eu^{3+} in a crystalline host of nearly the same composition. Oversluizen [4] came to the same conclusion for different glass compositions.

Only a small improvement is seen for the glasses with less Na_2CO_3 and $CaCO_3$. When lanthanum is used instead of gadolinium, a further small improvement is seen. It is not clear whether this improvement is the result of the La^{3+} ion being a better network modifier than the Gd^{3+} ion, or because it is a bigger ion. These effects are negligible in comparison with the change in q going from the crystalline to the glassy phase.

Figure 4 shows the excitation spectra in the charge-transfer region at room temperature. The charge-transfer band ranges from 205 to 275 nm for the crystalline sample, while for the glasses it ranges from 205 to around 330 nm. Here it should be noted that 205 nm is a limit set by the instrumental setup and host structure absorption, which makes the result inaccurate (see below). The maximum of the excitation band tends to be situated at a higher energy for glasses than for the crystalline sample. Figure 5 shows diffuse reflection spectra of glass No. 1, the crystalline powder and of a lanthanum borate glass without the Eu^{3+} dopant. It shows that the absorption by the host material

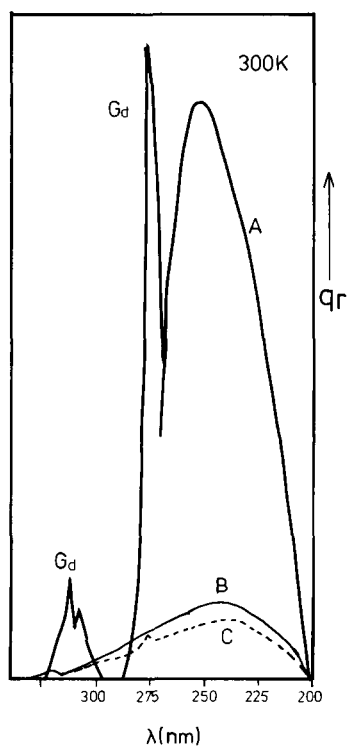

Fig. 4. Room temperature excitation spectra of the Eu^{3+} emission in the CTS region for (A) the crystalline host (GdB_3O_6); (B) glass No. 6; and (C) glass No. 4. q_r denotes the quantum output in arbitrary (linear) units.

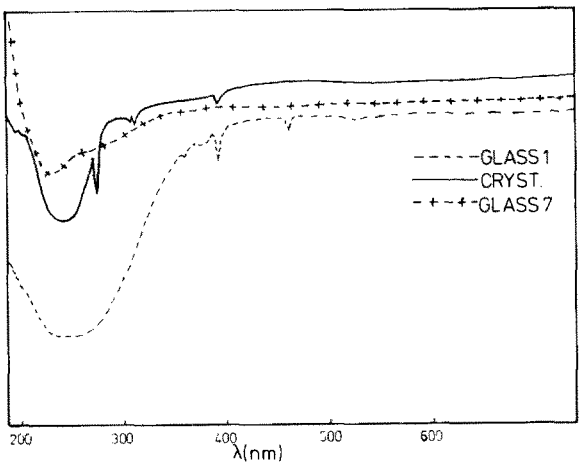

Fig. 5. Diffuse reflection spectra of powdered glass No. 1, glass No. 7 and crystalline $GdB_3O_6:Eu^{3+}$.

is very weak in the spectral region of interest. This result is in accordance with earlier studies on borate glasses [15].

3.3. Absorption spectra

The diffuse reflection spectra show strong absorption in the charge transfer region. Because of this absorption, we recorded also some absorption spectra of glass samples of 2 and 0.6 mm thickness. These are given in fig. 6. The spectra are in accordance with the diffuse reflection and the excitation spectra. The absorption spectrum of the lanthanum borate glass without the Eu^{3+} dopant shows that, though the host material does not show much optical absorption for the larger part of the UV region, strong optical absorption occurs for wavelengths shorter than 210 nm.

3.4. The CTS in the glassy and the crystalline state

One of us has proposed earlier a qualitative model based on the configuration coordinate model to explain charge-transfer quenching [16]. Essential to this model is that the CTS parabola in the configuration coordinate model is situated at the same equilibrium position in different (crystalline) solids. When the CTS parabola moves to lower energy, q is expected to decrease, as is observed experimentally [14]. This model, however successful it may be for crystalline lattices, fails to explain the present results: although the CTS in the glassy phase tends to be at higher energy than in the comparable crystalline phase, q is clearly much lower for Eu^{3+} in the glass.

This smaller q shows that the CTS parabola in case of the glassy phase must be placed in such a way that a non-radiative transition from CTS to the ^7F_J parabola is possible. Because q is temperature-independent, this process may not require thermal activation of any importance. Consequently the CTS parabola minimum must be situated near the ^7F_J parabolae.

The configuration coordinate diagram in fig. 7 is able to explain our experimental results. The maximum of the charge-transfer absorption band is at a higher energy in the glass than in the crystal, while at the same time excitation into this band in the glass is possible at lower energy, and the efficiency is low. For a crystalline structure such a combination of low q and high CTS has never been observed and is not possible within the model [16] sketched above. For a glass the situation is clearly different, as shown by the present results and those of Oversluizen [4].

The only way to obtain a model in which thermal activation in the CTS-to-^7F_J relaxation is absent as required by the experimental results, is to decrease the force constant of the CTS parabola

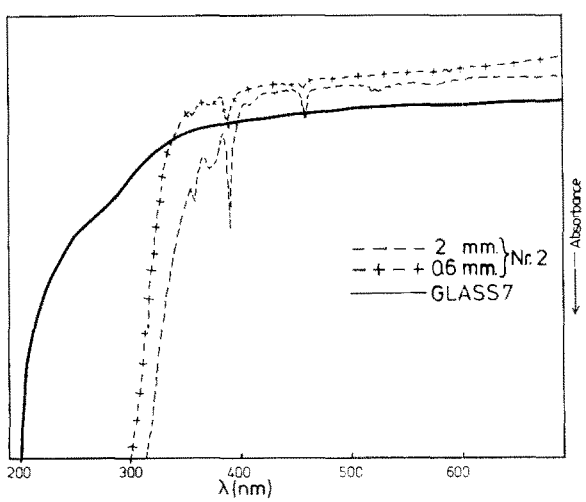

Fig. 6. Room temperature absorption spectra of glass No. 2 (Eu^{3+}-doped) and glass No. 7 (Eu^{3+}-free).

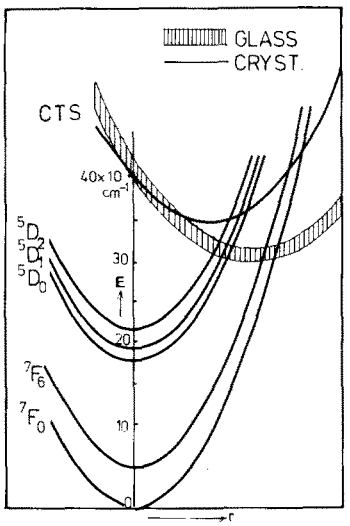

Fig. 7. Schematic configuration coordinate diagram model. Only a few of the $4f^6$ parabolae have been drawn. The CTS (glass) has been shifted relative to the CTS (crystal) according to the experimental results (see text).

in the glass relative to that in the crystal. Further the CTS parabola in the glass is drawn as a band to account for the variation in the Eu^{3+} surroundings. The weaker force constant and the higher value of the equilibrium distance shows that the Eu^{3+} CTS in the glass is more weakly bonded and more expanded than in a crystalline phase. In view of Oversluizen's results [4], this weaker bonding and expansion seems to be a general result. Because of the lower density of the glassy phase in comparison with the crystalline phase of the same composition, this condition is not unexpected [17,18].

Our results suggest also that the efficiency of broad-band emission from ions in glasses cannot be expected to have a high quantum efficiency, because the off-set of the excited state parabola in a glass is relatively large. In fact, this low quantum efficiency is what has been observed for Cr^{3+} [19] and UO_2^{2+} [20] in glasses.

Van Die et al. [21] have shown that the inhomogeneous broadening in borate glasses is relatively large. From the present data we find for the Eu^{3+} CTs a halfwidth of about 14500 cm^{-1} in the borate glass. This value is much larger than the width of the CTS in the corresponding crystalline phase (6500 cm^{-1}). The difference between the two values is due to inhomogenous broadening.

In conclusion, the Eu^{3+} CTS in glasses, even if it is at high energies, relaxes preferably to the ^7F_J parabolae in a non-radiative way. This is due to its large expansion and its low bonding strength.

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