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Ultraviolet Luminescence of Pr^{3+} in a Glass

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The luminescence of Pr^{3+} in a borate glass is investigated. The results are compared to those for Pr^{3+} in crystalline LaB_3O_6. For the glass as well as for the crystalline material the emission after $f \rightarrow d$ excitation is mainly in the ultraviolet spectral region. The Stokes shift is small, and the quantum efficiency high. © 1989 Academic Press, Inc.

1. Introduction

Recently the luminescence of $LnBO_3$: Pr^{3+} (Ln = Sc, Y, La) has been reported (*1*). In this series the Stokes shift increases from Sc to La, because the relaxation of the excited state becomes less restricted. An extrapolation to borate glass was made. It could not be excluded that Pr^{3+} ($4f^2$) shows efficient $5d \rightarrow 4f$ emission in such a glass.

We have also investigated the efficiency of the Eu^{3+} luminescence after charge transfer excitation in the crystalline and glass modifications of LnB_3O_6 (Ln = La, Gd) (*2*). The quantum efficiency of the glass was found to be one order of magnitude smaller than that of the crystalline material. Since the excitation of the Eu^{3+} ion under UV corresponds to a charge transfer transition, the offset of the excited parabola is large and, in a glass, too large to yield efficient luminescence. Also according to Oversluizen (*3*) the Eu^{3+} ion in a glass does not shown efficient luminescence upon charge transfer excitation. However, it has been shown that Ce^{3+} and Tb^{3+} in glasses emit efficiently upon $f \rightarrow d$ excitation (*3, 4*) if this excited state is at high enough energy. This fits our recent results (*1*).

It seemed tempting to investigate the possible ultraviolet $d \rightarrow f$ emission of Pr^{3+} in a glass. In the course of our studies on LnB_3O_6 glasses we selected for this study LaB_3O_6:Pr^{3+} in the crystalline and glass modifications.

2. Experimental

Crystalline samples LaB_3O_6 and GdB_3O_6 were prepared as described in Ref. (*5*). The Pr^{3+} and Tb^{3+} concentrations were 0.5–1.0 at.%. Starting materials were La_2O_3, Gd_2O_3, Tb_4O_7, Pr_6O_{11} (Highways International, 5N), and H_3BO_3 (Merck extra pure). The firing atmosphere was a N_2/H_2 mixture (3 : 1). Care was taken to prevent the presence of the orthoborates $LnBO_3$. For the glass 2 mole% Na_2CO_3 and 4 mole% $CaCO_3$

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were added to the mixture. The melting temperature was 1160°C and a H_2 atmosphere was necessary to prevent oxidation of Pr^{3+} to Pr^{4+}. The samples were checked by X-ray powder diffraction. Optical measurements were performed as described in Ref. (*6*) using a Perkin–Elmer spectrofluorometer MPF 3 equipped with a helium flow cryostat. Diffuse reflection and absorption spectra were recorded at room temperature using a Perkin–Elmer Lambda 7 UV/Vis spectrophotometer. The absorption spectra were not corrected for reflectance losses. The setup to measure the X-ray-excited emission spectra has been described elsewhere (*7*). These measurements were also performed at room temperature.

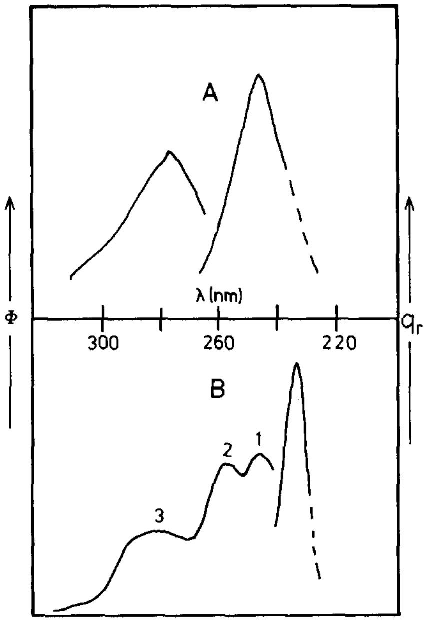

FIG. 2. (A) Emission and excitation spectra of Pr^{3+} in a lanthanum borate glass. Excitation wavelength 240 nm; monitored emission wavelength 290 nm. (B) Emission and excitation spectra of crystalline La B_3O_6:Pr^{3+}. Excitation wavelength 234 nm; monitored emission wavelength 280 nm. Φ denotes the radiant power per constant wavelength interval and q_r the relative quantum output (both are in arbitrary units).

3. Results and Discussion

3.1. Ultraviolet Excitation

Figure 1 shows the absorption spectrum of a lanthanum borate glass doped with 1% Pr^{3+} (A) and the diffuse reflectance spectrum of crystalline LaB_3O_6:Pr^{3+} (B). The usual $4f^2$ transitions are observed. The $4f$–$5d$ absorption in the glass starts at 260 nm, and in the crystal at 245 nm. For the crystalline material excitation into the $^3P_{0,1,2}$ and $^1I_6$ levels of the $4f^2$ configuration did not yield significant emission due to the high rate of multiphonon emission between levels of this configuration. This has been observed before for crystalline borates (*8*). Excitation in these levels results in the case of the glass in a weak luminescence from the $^1D_2$ level.

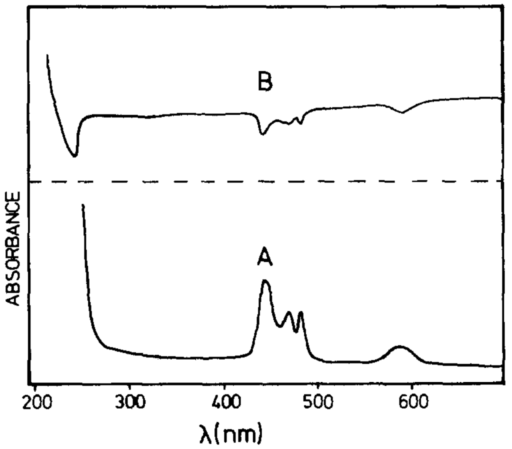

FIG. 1. Diffuse reflection spectrum of crystalline La B_3O_6:Pr^{3+} (A) and absorption spectrum of a lanthanum borate glass containing 1 mole% Pr^{3+} (B). Both were recorded at room temperature.

For the crystal excitation with short wavelength, ultraviolet radiation yielded an ultraviolet emission of high efficiency. The excitation spectrum (shown in Fig. 2) consists of a band with a maximum at 233 nm. This transition is ascribed to the lowest component of the $4f^2$–$4f5d$ transition. The emission spectrum consists of three bands numbered 1–3 in Fig. 2. These correspond to transitions from the lowest crystal-field component of the $4f5d$ configuration to the levels of the $4f^2$ configuration, viz., band 1 to $^3H_4$, band 2 to $^3H_5$, and band 3 to $^3H_6$, $^3F_2$, $^3F_3$, $^3F_4$.

The Stokes shift of the emission in the crystal is very small, viz., about 2000 cm^{-1}. This is a small value for an f–d transition. As a consequence thermal quenching is absent up to 300 K, as is interconfigurational quenching to the $4f^2$ configuration (*8*), so that a high quantum efficiency results. This emission has a strong overlap with the ^6I and ^6P levels of Gd^{3+}, so that in crystalline GdB_3O_6:Pr an efficient energy transfer from the Pr^{3+} ion to the Gd^{3+} sublattice is to be expected. Using Tb^{3+} as an activator, we observed an efficient green Tb^{3+} luminescence upon f–d excitation of Pr^{3+} in crystalline GdB_3O_6:Pr, Tb. This is in accordance with the work of Srivastava *et al.* on Gd BO_3:Pr (*9*).

The maximum of the excitation band in the glass is at 245 nm, which is considerably lower in energy than in the crystal. The maximum of the emission in the glass is at 277 nm. The Stokes shift is about 4800 cm^{-1}, which is larger than that in the crystal. There is, actually, some thermal quenching if the temperature is raised from 4.2 to 300 K: the UV-emission intensity at room temperature is ~60% of the UV-emission intensity at 4.2 K. This is at least partly due to interconfigurational decay at room temperature. This results in a $^1D_2$ emission intensity of ~2% of the total emission intensity. At 4.2 K this could not be observed. The UV-emission band of the Pr^{3+} in the glass could not be resolved as a result of the inhomogeneous broadening, which is pronounced for borate glasses (*10*).

If we compare the behavior of Pr^{3+} in the glass and in the crystalline modification of LaB_3O_6, it must be concluded that the main difference is the larger Stokes shift, pointing to a larger relaxation of the excited $4f5d$ configuration in the glass. This larger relaxation is not unexpected after previous work (*2, 3, 10, 11*). The consequences are that the ultraviolet emission in the glass has a lower efficiency at room temperature than that in the crystal, which holds most probably for many broadband emissions (*2, 3, 10, 11*).

3.2. *X-Ray-Excited Emission*

It seemed interesting to also study the X-ray-excited emission of our samples, because our ultraviolet instrumentation is not very sensitive in the region 200–250 nm. Unfortunately the X-ray-excited luminescence emission is not very strong and shows other emissions. The emission spectrum (Fig. 3) shows a broadband around 350 nm. This cannot be due to the Pr^{3+} ion, not only because there is no emission at all at this wavelength under UV excitation, but also because Pr^{3+} has no transition that matches radiation of this wavelength. The X-ray excitation also produces a deep-brown color in the crystal and a light-brown color in the glass. This has not been observed for the crystal and glass modification of LaB_3O_6:Gd^{3+} (*12*). Therefore we

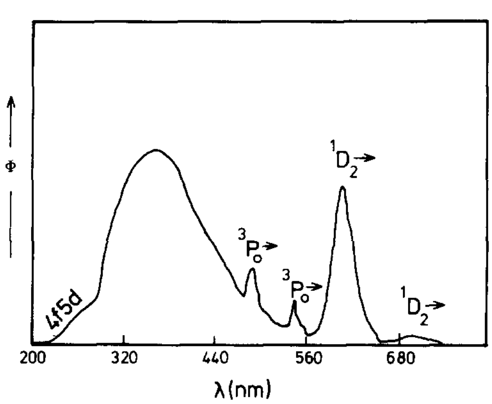

FIG. 3. X-ray-excited emission spectrum of lanthanum borate glass containing 1 mole% Pr^{3+} at room temperature. The initial levels have been indicated.

TABLE I

INTEGRATED EMISSION INTENSITIES OF Pr^{3+} IN LaB_3O_6 AT ROOM TEMPERATURE

Initial level	$4f5d$	^3P	$^1D_2$
X-ray excitation			
Crystal	10	2	88
Glass	20	15	65
Ultraviolet excitation			
Crystal	100	0	0
Glass	98	0	2

conclude that the X-ray excitation produces free-charge carriers, which recombine mainly at defect centers resulting in the 350-nm broadband emission, and only partly at Pr^{3+} resulting in $4f5d$ emission and $4f^2$ emission. The nature of the defect remains unknown. The brown color may be due to Pr^{4+}, i.e., a hole trapped by Pr^{3+}.

Let us now consider the part of the emission spectrum which is due to Pr^{3+}. Table I shows the integrated emission intensities of Pr^{3+} for X-ray and ultraviolet excitation. Upon X-ray excitation we observe a relatively strong $^1D_2$ emission and also some ^3P emission for the crystal and for the glass, and a weak $4f5d$ emission. Upon ultraviolet excitation, however, the emission from the f^2 levels is negligible, while the $4f5d$ emission is strong. This we ascribed to the absence of interconfigurational quenching. This leads us to the conclusion that under X-ray excitation the $4f^2$ levels of the Pr^{3+} ion are directly excited.

In conclusion we have shown that Pr^{3+} can show efficient ultraviolet emission in a glass, and that the excitation mechanisms under ultraviolet and X-ray excitation are different.

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