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LETTER TO THE EDITOR

Luminescence Quenching between Ce^{3+} and Eu^{3+} in LaB_3O_6

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The Ce^{3+} and Eu^{3+} ions in LaB_3O_6 quench each other's luminescence. However, Ce^{3+} quenches Eu^{3+} more effectively than Eu^{3+} quenches Ce^{3+}. The critical distances for this quenching are about 15 and 6 Å, respectively. © 1994 Academic Press, Inc.

1. INTRODUCTION

The ions Ce^{3+} and Eu^{3+}, which are both known as efficiently luminescent ions, quench each other's luminescence; this has been shown by qualitative observations (1). It is remarkable that rare earth ions can efficiently quench each other's luminescence. This phenomenon can also occur in commercial phosphors if the impurity levels are not sufficiently low (2). In this note we present a simple quantitative experiment on this quenching which shows simultaneously that the mechanism is more complicated than initially thought.

The luminescence of several rare earth ions in LaB_3O_6 has been reported before (3); the reader is referred to that paper for spectroscopical details. It was also shown that in GdB_3O_6 the Gd^{3+} sublattice acts as a sublattice which assists energy transfer between dopants by Gd^{3+} energy migration. Therefore we performed all experiments on LaB_3O_6 and GdB_3O_6. Their crystal structure has been described by Abdullaev *et al.* (4).

2. EXPERIMENTAL

Samples of general composition $Ln_{1-x-y}Ce_xEu_yB_3O_6$ (Ln = La or Gd) were prepared by standard methods as described in Ref. (3). The firing atmosphere was air or a N_2/H_2 mixture with composition 95%/5%. Since the results were the same within experimental error, this note discusses only samples fired in air. All samples were checked by X-ray powder diffraction using Cu$K\alpha$ radiation. They were found to be single phase.

The optical measurements were performed at room temperature using a Spex Fluorolog 2 spectrofluorometer.

3. RESULTS

All relevant spectra have been reported before (3). Excitation occurred at 265 nm. This wavelength excites the Ce^{3+} ions in the $4f \rightarrow 5d$ absorption transition and the Eu^{3+} ions in the charge-transfer absorption transition. These two optical transitions practically coincide in this metaborate host lattice (3).

Table 1 presents an overview of the experimental results. This table gives integrated emission intensities in arbitrary units, but in such a way that all data for one host lattice can be compared. Although the utmost care was taken to prepare and measure samples in an identical way, the accuracy of the data is probably not better than 20%.

Nevertheless, some interesting results can be deduced from this table. For this purpose we estimate the intensities for the hypothetic case in which the ions are isolated, i.e., they do not interact. This can easily be done, starting from the data for the singly doped samples, taking account of the concentrations, and neglecting possible absorption saturation in the sample with the highest concentration. Results of this estimation are also given in Table 1. In LaB_3O_6 the experimental total intensity is strongly quenched with increasing amount of europium relative to the hypothetical values. At 3% Eu the observed value is 10, the hypothetical value 91. In GdB_3O_6 this effect is considerably weaker (see Table 1).

Even more interesting is the fact that in LaB_3O_6 an amount of 1% Ce^{3+} seems to quench 75% of the Eu^{3+} emission, independent of the Eu^{3+} concentration. For 3% Eu this value is slightly higher, but the intensity value may be subject to saturation absorption in this high-concentration sample. The Ce^{3+} emission, however, is only

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TABLE 1
Integrated Emission Intensities I for $Ln_{1-x-y}Ce_xEu_yB_3O_6$ (Ln = La, Gd) at Room Temperature under 265-nm Excitation

Composition		I (experimental)			I (calculated)			% Eu^{3+} emission quenched
x	y	Ce	Eu	Total	Ce	Eu	Total	
				Ln = La				
0.01	0	16	—		16	—		
0	0.01	—	25		—	25		
0.01	0.003	19	2	21	16	8	24	75
0.01	0.01	20	6	26	16	25	41	76
0.01	0.03	4	6	10	16	75	91	92
				Ln = Gd				
0.01	0	0.6	—		0.6	—		
0	0.01	—	6		—	6		
0.01	0.003	0.7	4	4^7	0.6	2	2^6	—
0.01	0.01	0.5	6	6^5	0.6	6	6^6	—
0.01	0.03	0.3	7	7^3	0.6	18	18^6	61

quenched to about 75% by 3% Eu. In GdB_3O_6 these values are completely different.

Finally we note that by studying $La_{1-y}Eu_yB_3O_6$ up to $y = 0.1$, we observed that concentration quenching of the Eu^{3+} emission occurs far above $y = 0.03$, so that this effect cannot influence our measurements.

4. DISCUSSION

4.1. Ce^{3+}, Eu^{3+}-Codoped LaB_3O_6

As remarked already above, the Ce^{3+} and Eu^{3+} ions have a quenching action on each other, since dramatic quenching occurs already in the relatively low concentration region applied. This agrees with earlier observations and has been ascribed to electron-transfer quenching (1). This implies that the excited configuration Ce^{4+}–Eu^{2+} plays a role in the quenching process. In ion pairs in solution this phenomenon is called electron-transfer quenching; in solids it has become known in recent years as photoionization. Both terms indicate essentially the same phenomenon (5).

Up till now this Ce^{3+}–Eu^{3+} quenching was investigated by selective FF excitation in the Ce^{3+} ion. However, in LaB_3O_6 the $4f \rightarrow 5d$ transition of Ce^3 and the charge-transfer transition of Eu^{3+} practically coincide, so that in our experiments the ions are excited simultaneously. Although this complicates the interpretation, it yields also new results. In LaB_3O_6 an amount of 1% Ce^{3+} quenches the Eu^{3+} emission by about 75%. This means that one of the excited states of Eu^{3+} is quenched by Ce^{3+} in the ground state. It is obvious to assume that this is the charge-transfer state of Eu^{3+}, since the $4f^6$ levels lie at energies below the excited $5d$ configuration of Ce^{3+} and cannot be expected to undergo such strong quenching.

A critical distance R for this quenching can be estimated as follows: if a sphere of radius R containing n lanthanide sites is considered around an excited Eu^{3+} ion, the Eu^{3+} ion will only show emission if none of the n sites contains Ce^{3+}. For a 1% Ce^{3+} concentration, the amount of Eu^{3+} emission will be $(1–0.01)^n$. Since 75% of the Eu^{3+} emission is quenched, this expression equals 0.25. From this we find $n = 140$, and, using the crystallographic data (4), $R = 15$ Å. This is a large distance. Therefore we have to assume that the charge-transfer state of Eu^{3+} dissociates and that Eu^{2+} remains where it is, whereas the hole travels over (a maximum of) 15 Å before it is trapped by Ce^{3+}.

Dissociation of charge-transfer states is a known phenomenon and has been reported, for example, for $La_2O_2S : Eu^{3+}$ (6) and $Ba_5SiO_4Br_6 : Nb^{5+}$ (7). In LaB_3O_6 the hole is probably transported through the borate sublattice, which consists of coupled borate tetrahedra and triangles.

The excited state of Ce^{3+} is less strongly quenched by Eu^{3+} than in the reverse situation. In order to obtain the same amount of Ce^{3+} quenching as found for Eu^{3+}, i.e., 75%, we need 3% Eu^{3+}. Although the values for this higher concentrated sample are inaccurate, we used the same analysis as described above for the data in Table 1. This yields $n = 10$ and $R = 6$ Å. Although these values should be considered with care, they show that the quenching of the Ce^{3+} excited state occurs mainly by the effect of Eu^{3+} ions on nearest neighbor lanthanide sites in LaB_3O_6, i.e., there is a direct electron transfer from Ce^{3+} to Eu^{3+}.

The mutual quenching of the Ce^{3+} and Eu^{3+} luminescence in $LaB_3O_6 : Ce^{3+}$, Eu^{3+} occurs, therefore, by two different mechanisms: $(Ce^{3+})^*$ transfers an electron to

Eu^{3+}, a process with R ~ 6 Å, and $(Eu^{3+})^*$ transfers a hole to Ce^{3+}, a process with R ~ 15 Å. Here the asterisk indicates the excited state. Further experiments are needed to obtain more accurate results.

4.2. Ce^{3+}, Eu^{3+}-*Codoped* GdB_3O_6

The data in Table 1 show that the situation in GdB_3O_6 is very different from that in LaB_3O_6. Since both host lattices are isomorphous, this may seem surprising at first sight, but it is not. The data on the singly doped samples reveal what is happening. The Ce^{3+} emission intensity is much lower than that of Eu^{3+}. This is due to the fact that a considerable amount of Ce^{3+} excited-state energy is transferred to Gd^{3+}, from which efficient energy migration to other centers or quenching sites occurs (3). Actually, the sample with 1% Ce^{3+} and 0.3% Eu^{3+} shows more Eu^{3+} emission than predicted by the hypothetical model sketched above, whereas that with 1% Ce^{3+} and 1% Eu^{3+} shows the predicted values. The Ce^{3+} ion transfers its excitation energy to Gd^{3+}, which transports it to Eu^{3+}. The presence of Gd^{3+} makes possible $Ce^{3+} \rightarrow Eu^{3+}$ transfer; this process competes with the quenching process encountered in LaB_3O_6.

A clear quenching is only observed for GdB_3O_6 with 1% Ce^{3+} and 3% Eu^{3+}, indicating that the energy transfer via Gd^{3+} cannot dominate the quenching process completely. In view of the inaccuracy of the experimental data and the appearance of competing processes, a further analysis seems to be impossible.

In conclusion, the Ce^{3+} and Eu^{3+} ions quench each others luminescence, but Ce^{3+} quenches Eu^{3+} more effectively than Eu^{3+} quenches Ce^{3+}. This conclusion is valid for LaB_3O_6, but is not necessarily true for other host lattices.

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