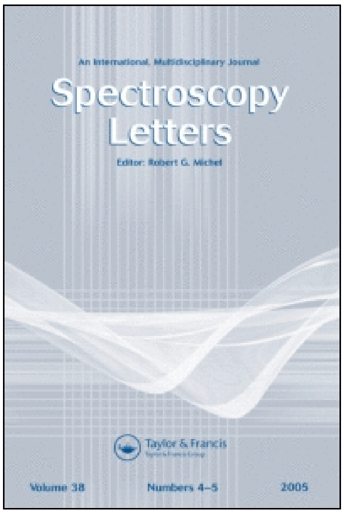

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FLUORESCENCE SPECTRA OF Eu^{3+} AND Tb^{3+} DOPED $Na_6Ln(BO_3)_3$ (Ln = La, Gd, Y) PHOSPHORS

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ABSTRACT

The fluorescence properties of Eu^{3+} and Tb^{3+} doped $Na_6La(BO_3)_3$, $Na_6Gd(BO_3)_3$, $Na_6Y(BO_3)_3$, $Na_6(Gd,Y)(BO_3)_3$ powder phosphors are reported. These phosphors display fluorescent RED and GREEN colours when droped with Eu^{3+} and Tb^{3+} ions, respectively. The best fluorescence performance was consistantly observed from the Na-Gd based hosts. The photoluminescence spectra were analysed by evaluating colour coordinates, relative intensity ratios, and stimulated emission cross-sections.

INTRODUCTION

Over the past four years, we have been extensively involved in the production and characterization of several rare earth ion doped oxyhalide powder phosphors.[1-6] In 1991, Leskela and Holsa[7] reported the luminescence properties of Eu^{3+} in $Li_6Ln(BO_3)_3$ and described the importance of these host materials and the details of their lattice structure. Here we report studies on the luminescence spectra of Eu^{3+} and Tb^{3+} ions in $Na_6Ln(BO_3)_3$ powder phosphors.

EXPERIMENTAL

The procedures employed in the preparation of the following powder phosphors were similar to that described earlier by Holsa.[8] For convenience, the Europium Phosphors are designated

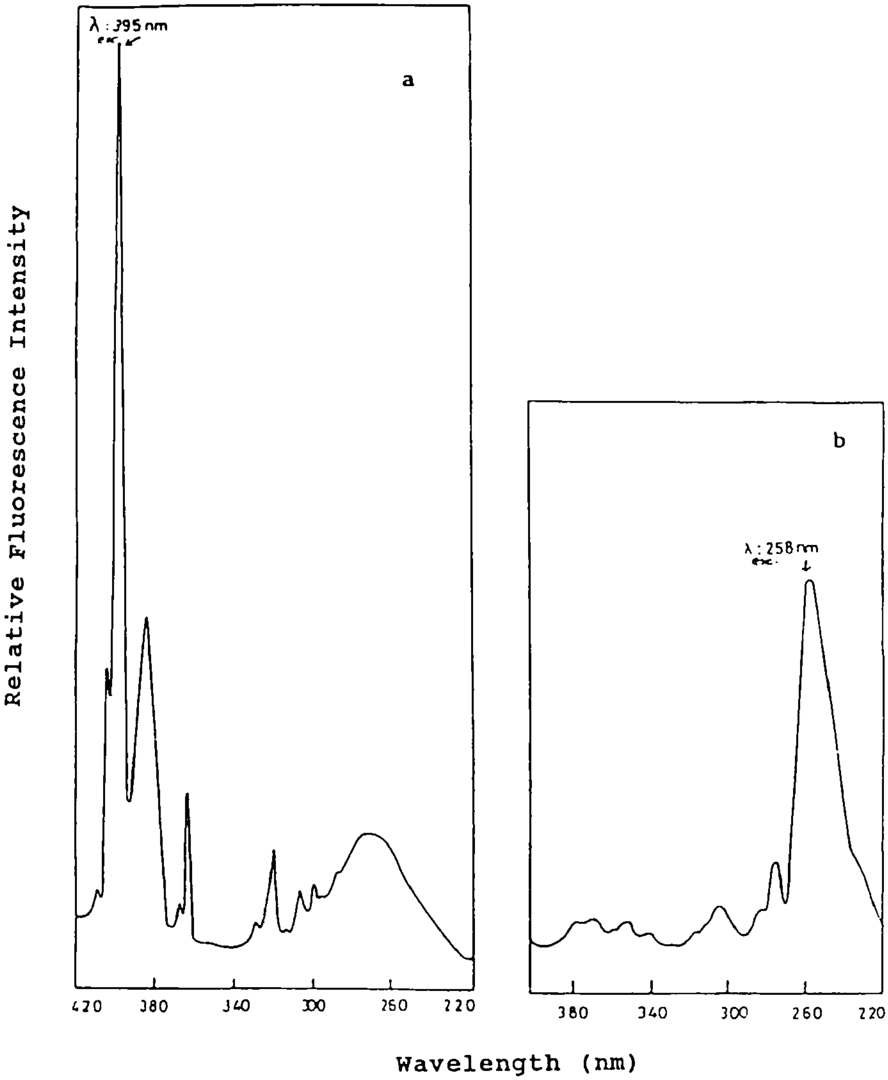

Fig.1: Excitation Spectra of (a) Eu^{3+} $Na_6Gd(BO_3)_3$ (b) Tb^{3+}: $Na_6Gd(BO_3)_3$ Phosphors

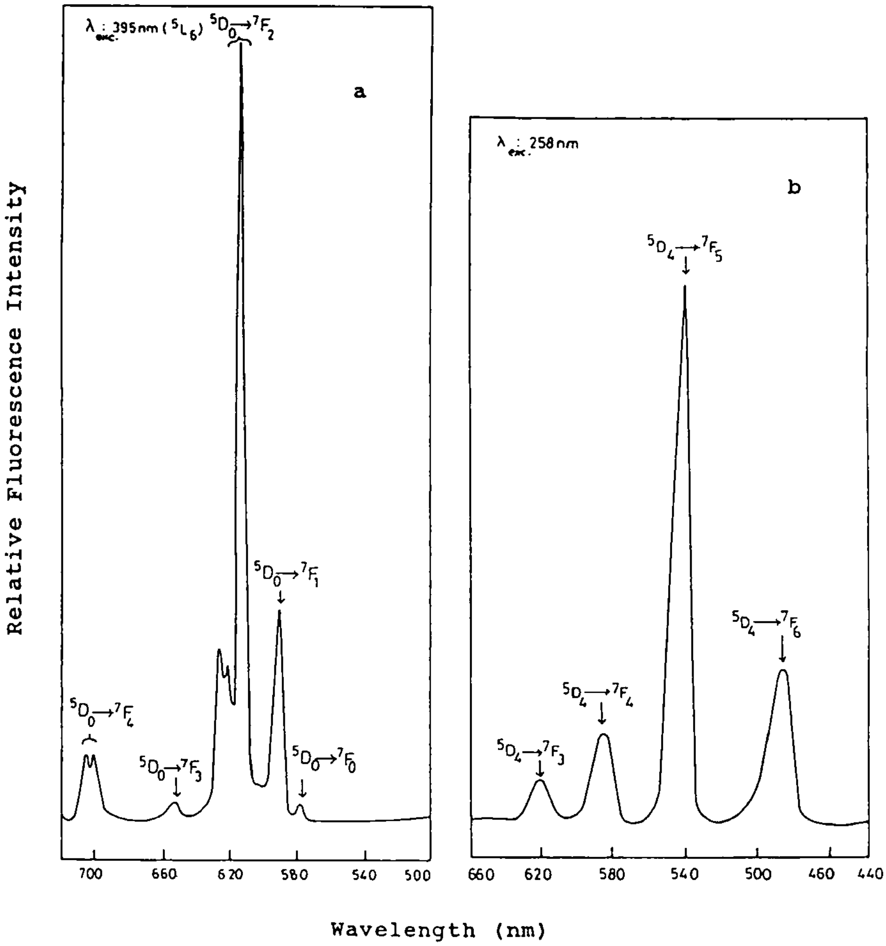

Fig.2: Photoluminescence Spectra of (a) Eu^{3+} $Na_6Gd(BO_3)_3$ (b) Tb^{3+}: $Na_6Gd(BO_3)_3$ Phosphors

as Red Phosphors (RP) and the Terbium Phosphors as Green Phosphors (GP).

RP-1. Eu^{3+}: $Na_6La(BO_3)_3$	GP-1. Tb^{3+}: $Na_6La(BO_3)_3$
RP-2. Eu^{3+}: $Na_6Gd(BO_3)_3$	GP-2. Tb^{3+}: $Na_6Gd(BO_3)_3$
RP-3. Eu^{3+}: $Na_6Y(BO_3)_3$	GP-3. Tb^{3+}: $Na_6Y(BO_3)_3$
RP-4. Eu^{3+}: $Na_6Gd_{0.3}Y_{0.1}(BO_3)_3$	GP-4. Tb^{3+}: $Na_6Gd_{0.3}Y_{0.1}(BO_3)_3$
RP-5. Eu^{3+}: $Na_6Gd_{0.2}Y_{0.2}(BO_3)_3$	GP-5. Tb^{3+}: $Na_6Gd_{0.2}Y_{0.2}(BO_3)_3$
RP-6. Eu^{3+}: $Na_6Gd_{0.1}Y_{0.3}(BO_3)_3$	GP-6. Tb^{3+}: $Na_6Gd_{0.1}Y_{0.3}(BO_3)_3$

Table 1: Colour coordinates $(\bar{X},\bar{Y})$, emission level peak wavelength (λ_p nm), and stimulated emission cross-sections ($\sigma_p^{\epsilon} \times 10^{22}$ cm^2) for transitions $^5D_0 \rightarrow {}^7F_2$ in RED for the Eu^{3+} and $^5D_4 \rightarrow {}^7F_5$ in GREEN for the Tb^{3+} doped $Na_6Ln(BO_3)_3$ Phosphors.

Eu^{3+}					Tb^{3+}				
Phosphor	$\bar{X}$	$\bar{Y}$	λ_p	σ_p^{ϵ}	Phosphor	$\bar{X}$	$\bar{Y}$	λ_p	σ_p^{ϵ}
RP-1	0.680	0.318	614	5.69	GP-1	0.287	0.554	543	19.37
			623	7.55					
			627	3.87					
RP-2	0.678	0.321	613	7.07	GP-2	0.274	0.568	542	19.22
			621	7.45					
			626	3.84					
RP-3	0.680	0.391	613	7.07	GP-3	0.279	0.550	542	19.23
			623	7.55					
			625	3.82					
RP-4	0.674	0.325	612	7.03	GP-4	0.298	0.545	542	19.23
			622	7.50					
			625	5.09					
RP-5	0.665	0.334	612	7.03	GP-5	0.279	0.552	542	21.97
			618	7.31					
			624	3.79					
RP-6	0.659	0.339	612	7.03	GP-6	0.285	0.554	543	15.49
			620	7.40					
			624	5.06					

The starting materials were in the form of rare-earth oxides [La_2O_3, Gd_2O_3, Y_2O_3, Eu_2O_3, Tb_4O_7]. Other salts, namely Na_2CO_3 and H_3BO_3, were of research grade. The fluorescence spectral measure-ments were carried out on a Hitachi 650-10S spectro-fluorimeter fitted with a 150W xenon arc lamp and a Hamamatsu Model R-928F photomultiplier tube. The recorded excitation spectra of Eu^{3+} and Tb^{3+} doped powder phosphors are shown in Figs. 1 (a,b). Using excitation lines 365 nm (for Eu^{3+}) and 268 nm (for Tb^{3+}), the photoluminescence spectra were recorded in the range 500-720 nm (Eu^{3+}) and 440-640 nm (Tb^{3+}), respectively. One typical profile of PL spectrum concerning Eu^{3+} and Tb^{3+}: phosphors has been shown in Figs 2 (a&b).

RESULTS AND DISCUSSION

The photoluminescence spectra of the powder phosphors contain the following transitions

Table 2 : Relative Fluorescence Intensity Ratios (R) of Eu^{3+}: Na_6 $Ln(BO_3)_3$ (RP) and Tb^{3+} Na_6 $Ln(BO_3)_3$ (GP) phosphors.

Dopant Ion	Emission transition ratio	RP-1	RP-2	RP-3	RP-4	RP-5	RP-6
	$\frac{^5D_0 \rightarrow {}^7F_0}{^5D_0 \rightarrow {}^7F_1}$	0.057	0.076	0.040	0.065	0.056	0.050
	$\frac{^5D_0 \rightarrow {}^7F_1}{^5D_0 \rightarrow {}^7F_1}$	1	1	1	1	1	1
Eu^{3+}	$\frac{^5D_0 \rightarrow {}^7F_2}{^5D_0 \rightarrow {}^7F_1}$	0.769 0.076 3.884	0.961 0.230 4.173	0.673 0.040 3.265	0.786 0.098 3.721	0.760 0.098 3.380	0.711 0.101 3.694
	$\frac{^5D_0 \rightarrow {}^7F_3}{^5D_0 \rightarrow {}^7F_1}$	0.096	0.076	0.081	0.081	0.084	0.084
	$\frac{^5D_0 \rightarrow {}^7F_4}{^5D_0 \rightarrow {}^7F_1}$	0.346 0.192	0.365 0.288	0.285 0.183	0.278 0.229	0.295 0.225	0.271 0.220

Dopant Ion	Emission transition ratio	GP-1	GP-2	GP-3	GP-4	GP-5	GP-6
	$\frac{^5D_4 \rightarrow {}^7F_6}{^5D_4 \rightarrow {}^7F_5}$	0.36	0.36	0.32	0.35	0.38	0.36
	$\frac{^5D_5 \rightarrow {}^7F_5}{^5D_4 \rightarrow {}^7F_5}$	1	1	1	1	1	1
Tb^{3+}	$\frac{^5D_4 \rightarrow {}^7F_4}{^5D_4 \rightarrow {}^7F_5}$	0.26	0.26	0.22	0.24	0.28	0.25
	$\frac{^5D_4 \rightarrow {}^7F_3}{^5D_4 \rightarrow {}^7F_5}$	0.18	0.17	0.13	0.16	0.20	0.17

$Eu^{3+}:Na_6Ln(BO_3)_3$	$Tb^{3+}:Na_6Ln(BO_3)_3$
$^5D_0 \rightarrow {}^7F_0$	$^5D_4 \rightarrow {}^7F_6$
$\rightarrow {}^7F_1$	$\rightarrow {}^7F_5$
$\rightarrow {}^7F_2$	$\rightarrow {}^7F_4$
$\rightarrow {}^7F_3$	$\rightarrow {}^7F_3$
$\rightarrow {}^7F_4$	

(where Ln = La, Gd, Y)

Five emission transitions occur in all Eu^{3+}:phosphors and four in all Tb^{3+}:phosphors. From the spectral features (Figs. 2 a,b), it is clear that changes of chemical composition of the powder phosphors exert a significant influence on the fluorescence colours. The common factor in the two phosphors sets is that the fluorescence intensity for the Gd-Na based phosphor is much higher than the La-Na or Y-Na for both Eu^{3+} and Tb^{3+} phosphors. Similar reports of the superior performance of Gd-based phosphors exists in literature.[9-11] A bright RED emission was observed from all Eu^{3+}: phosphors because of the existence of the ($^5D_0 \rightarrow {}^7F_2$) emission in at 614 nm. Similarly a GREEN emission occurs for Tb^{3+}:phosphors because of the ($^5D_4 \rightarrow {}^7F_5$) emission at 542 nm. Following standard procedures made available by CIE (France) we have computed the colour coordinates ($\bar{X},\bar{Y}$) given in Table 1. The same table reports computed values of stimulated emission cross sections (σ_P^E) for the emissions $^5D_0 \rightarrow {}^7F_2$ and $^5D_4 \rightarrow {}^7F_5$ of Eu^{3+} and Tb^{3+} doped powder phosphors. In order to compare the fluorescence efficiencies, we have also estimated the relative intensity ratios (R) for emissions of Eu^{3+} and Tb^{3+} phosphors (Table 2). It is concluded, based on the recorded photoluminescence spectral features, calculated colour coordinates ($\bar{X},\bar{Y}$), the relative intensity ratios (R), and the stimulated emission cross-sections (σ_P^E) that the $Eu^{3+}:Na_6Gd_{0.2}Y_{0.2}(BO_3)_3$ and the $Tb^{3+}:Na_6Gd(BO_3)_3$ are the best generators of bright fluorescent Red and Green respectively.

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