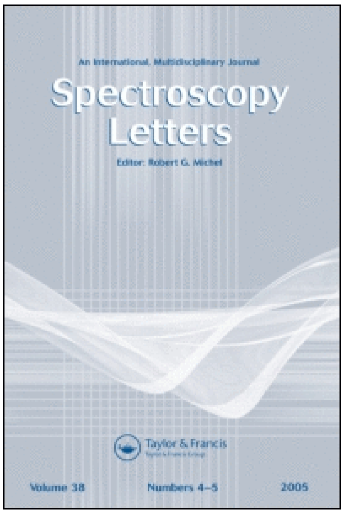

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THE EFFECT OF ZINC IONS ON THE FLUORESCENCE SPECTRA OF (Ln, Zn)OF:Eu^{3+}(Ln=Y, La and Gd) POWDER PHOSPHORS

Key words: Phosphors, oxyfluorides, fluorescence properties of Eu^{3+}

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ABSTRACT

This research note reports the fluorescence properties of Eu^{3+}*-doped in three sets* of (Y-Zn, La-Zn and Gd-Zn) oxyfluoride powder phosphors. On excitation with a UV-source, these phosphors have displayed orangish-red color and for which the chromaticity coordinates $(\overline{X}, \overline{Y})$ have been computed. The relative fluorescence intensity ratios (R) for the different measured emission transitions have been evaluated in order to examine the effect of substitution of zinc ions in the host matrix on the fluorescence behavior. Scanning electron microscopy studies have also been performed to investigate the average grain size of the synthesized phosphor material.

INTRODUCTION

Ever since the rapid development in the research of rare earth based phosphors in the last three decades, the rare earth oxyhalides have been identified for certain industrial applications. For example Y_2O_2S: Eu^{3+} phosphor has been used for color TVs and LaOBr:RE^{3+} (RE = Tm & Tb)[1] phosphors have been used in X-ray intensifying screens. The REOX (RE = Y, La, Gd; X = F, Cl & Br) compounds are widely isomorphos but they show considerable changes in the coordination of the RE^{3+}-ions[2]. This property allows one to observe the variation of crystal field effects on these materials. Over the past few years, we have produced and characterized certain rare earth doped lanthanide powder phosphors for their different applications.[3-6] In alkaline earths, zinc has been known for a long time as an excellent and a versatile, inexpensive host material for the preparation of luminescent phosphors for its use in ac thin film electroluminescent devices and TV monitors.[7-11] Rare earth ions (Eu^{3+}, Sm^{3+}, Tb^{3+}, Ce^{3+}, etc) have widely been used as the luminescent centers in phosphor materials due to their sharp 4f- intra shell transitions.[12] Earlier, we have studied the fluorescence spectra of individual lanthanide and alkaline earth based powder phosphors. Recently, we have reported a paper "The effect of zinc ions on the fluorescence spectra of (La, Zn)OF: Sm^{3+} powder phosphors, where fluorescence quenching has been observed due to the substitution of zinc ions in the host matrix.[13] Keeping in view the commercial importance of red emitting phosphors, we have prepared and characterized the Eu^{3+}-doped lanthanide–oxychloride, oxybromide, phosphate, and vanadate powder phosphors.[14,15] In order to reduce the cost of such useful materials, we now have made an attempt to understand the effect of the substitution of alkaline earth (Zn) ions in the lanthanide (Y, La & Gd) oxyfluoride host matrices on fluorescence of dopant ions.

EXPERIMENTAL

Generally, lanthanide oxyhalide phosphors are synthesized by solid state reactions at the temperatures higher than 800^{0}C by employing a flux method.[15] The synthesis of

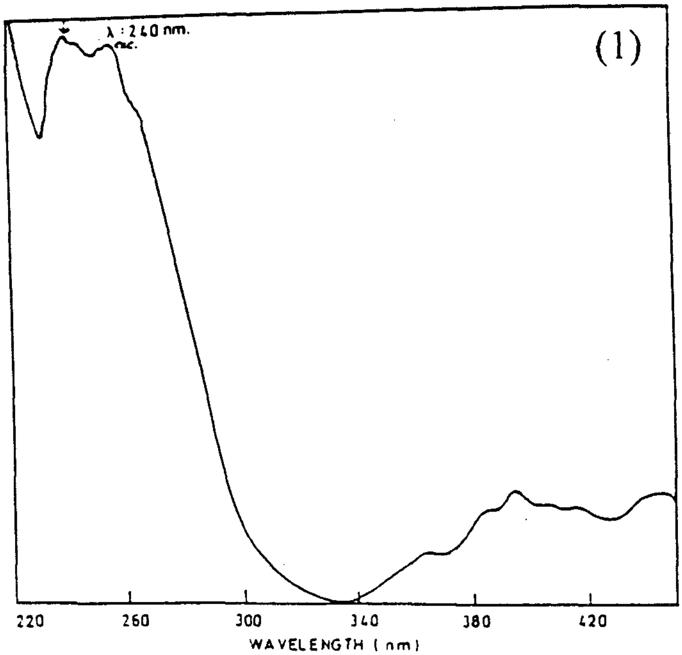

FIG. 1. Excitation spectrum of GdOF: Eu^{3+} powder phosphor.

these phosphors has been considered to be a little difficult, one due to the sensitivity of fluoride with the moisture and also due to the chemical instability. Ultra pure Y_2O_3, La_2O_3, Gd_2O_3, Eu_2O_3, zinc acetate ($(CH_3COO)_2Zn.H_2O$) and NH_4F were taken as the starting materials. In the present work a fixed dopant (Eu_2O_3) concentration (0.05 mol %) has been chosen to synthesize the following three sets of powder phosphors.

Set 1	**Set 2**	**Set 3**
$YOF:Eu^{3+}$	$LaOF:Eu^{3+}$	$GdOF:Eu^{3+}$
$(Y_{0.75},Zn_{0.25})OF:Eu^{3+}$	$(La_{0.75}, Zn_{0.25})OF:Eu^{3+}$	$(Gd_{0.75}, Zn_{0.25})OF:Eu^{3+}$
$(Y_{0.5}, Zn_{0.5})OF:Eu^{3+}$	$(La_{0.5}, Zn_{0.5})OF:Eu^{3+}$	$(Gd_{0.5}, Zn_{0.5})OF:Eu^{3+}$

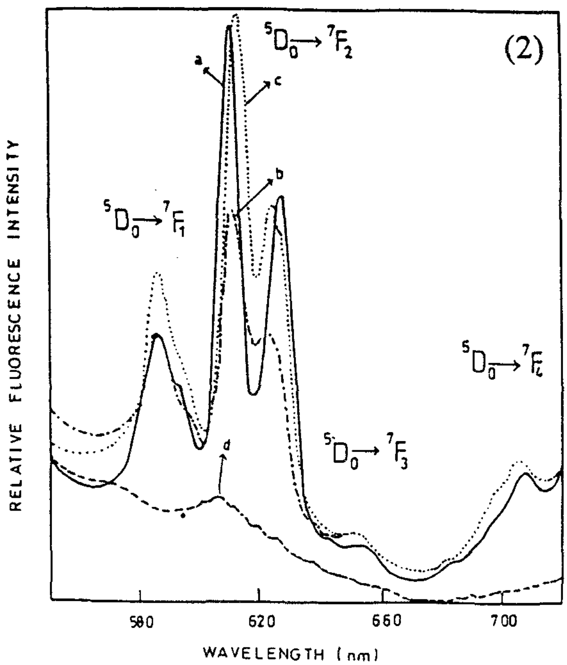

FIG. 2. Fluorescence spectra of Eu^{3+}- doped (a) GdOF, (b) LaOF, (c) YOF, and (d) ZnOF powder phosphors.

$(Y_{0.25}, Zn_{0.75})OF{:}Eu^{3+}$ $(La_{0.25}, Zn_{0.75})OF{:}Eu^{3+}$ $(Gd_{0.25}, Zn_{0.75})OF{:}Eu^{3+}$ $ZnOF{:}Eu^{3+}$

Each of the above batches has thoroughly been powdered by using acetone as a fluid medium. The dried mixture was transferred into an alumina boat and fired in a silica reactor in the central zone of a high temperature furnace for about an hour at 800^0C with N_2 atmosphere. Thus, powder obtained was put inside a dessicator and pulverized again with an additional amount of ammonium fluoride. Similarly, the second time firing has been performed at 1000^0C with N_2 atmosphere.[16] Here, ammonium fluoride serves as a fluorinating agent. These powder phosphors show a

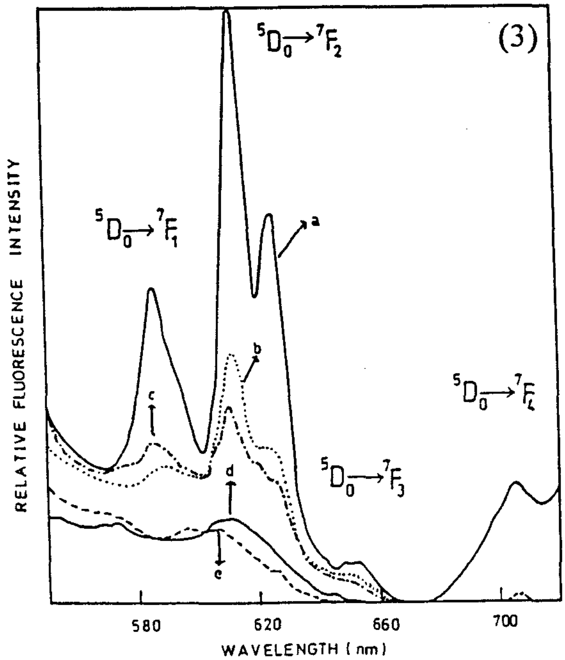

FIG. 3. Fluorescence spectra of Eu^{3+}- doped (a) YOF, (b) ($Y_{0.75}$, $Zn_{0.25}$)OF, (c) ($Y_{0.5}$, $Zn_{0.5}$)OF, (d) ($Y_{0.25}$, $Zn_{0.75}$)OF, and (e) ZnOF powder phosphors.

bright orangish-red color under a UV-source. Both excitation and fluorescence spectra of all these phosphors have been recorded at room temperature on a Perkin Elmer LS 50 luminescence spectrophotometer by using a xenon arc lamp as the excitation source. The recorded excitation and fluorescence spectra of these phosphors are shown in Figs. (1-5), respectively. The excitation spectra of these phosphors have been recorded with a UV-35 filter, the spectra for each phosphor was recorded in the wavelength region 550-720 nm. The average particle size of the synthesized (Y, Zn)OF set of powder phosphors and GdOF: Eu^{3+} was investigated by using Leica Stereoscan 440 model, scanning electron microscope. The samples were coated with a thin layer of gold in a polaran E5000 coating unit to prevent the

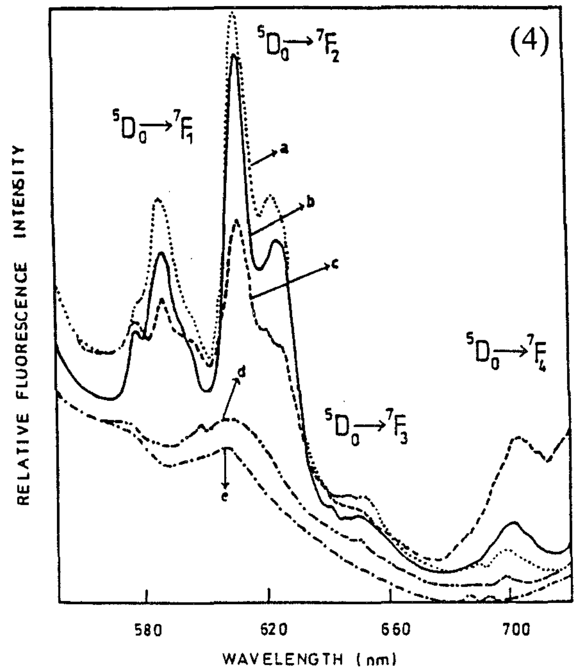

FIG. 4. Fluorescence spectra of Eu^{3+}- doped (a) GdOF, (b) ($Gd_{0.75}$, $Zn_{0.25}$)OF, (c) ($Gd_{0.5}$, $Zn_{0.5}$)OF, (d) ($Gd_{0.25}$, $Zn_{0.75}$)OF, and (e) ZnOF powder phosphors.

charging of the specimen. For a comparative study the electron beam parameters were kept fixed while analyzing samples. The SEM images of the samples were obtained with a 10 KV EHT and 25 PA beam current on a 35 mm camera on a high resolution recording unit. The SEM images for the set of (Y, Zn)OF and GdOF: Eu^{3+} phosphors are shown in Figs. 7 (a - f).

RESULTS AND DISCUSSION

From the excitation spectra it is clearly observed that the excitation peak has a weaker intensity with an increase in the Zn content of the samples. In addition, peak

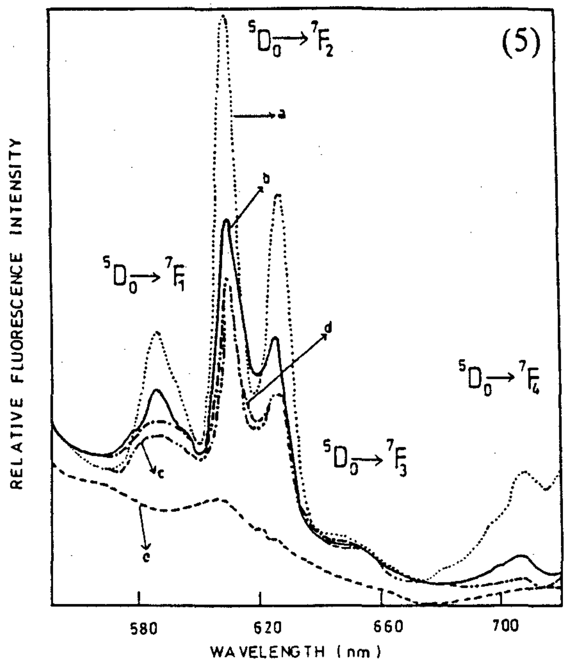

FIG. 5. Fluorescence spectra of Eu^{3+}- doped (a) LaOF, (b) ($La_{0.75}$, $Zn_{0.25}$)OF, (c) ($La_{0.5}$, $Zn_{0.5}$)OF, (d) ($La_{0.25}$, $Zn_{0.75}$)OF, and (e) ZnOF powder phosphors.

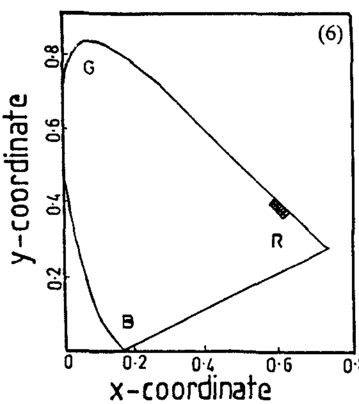

FIG. 6. CIE chromaticity diagram.

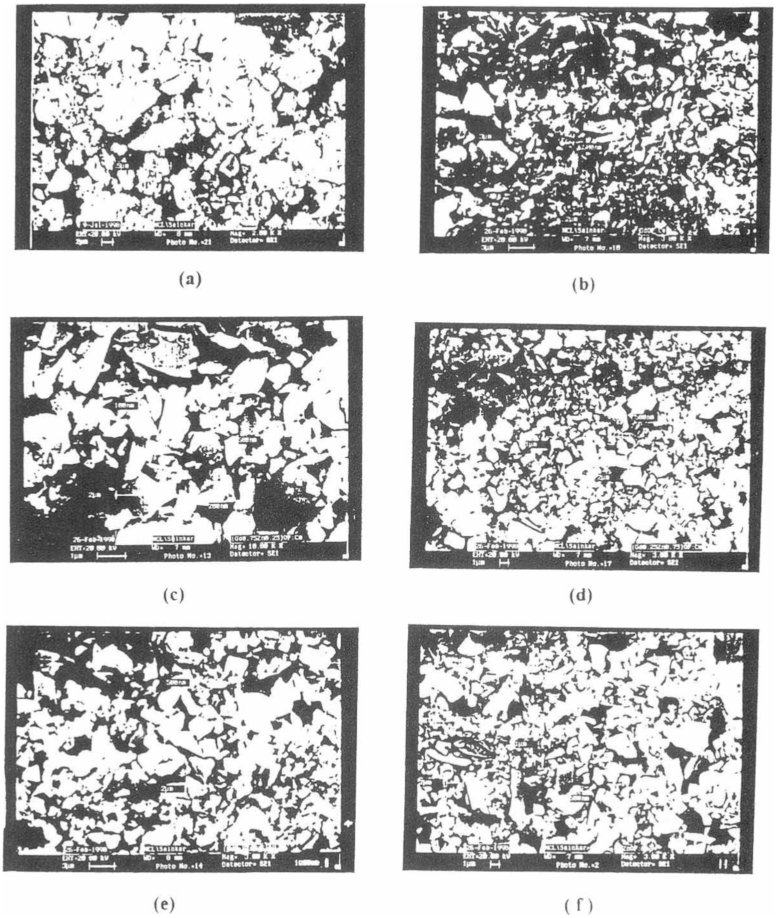

FIG. 7. SEM images of Eu^{3+}- doped (a) GdOF, (b)YOF, (c) $(Y_{0.75}, Zn_{0.25})OF$, (d) $(Y_{0.5}, Zn_{0.5})OF$, (e) $(Y_{0.25}, Zn_{0.75})OF$, and (f) ZnOF powder phosphors.

position shifted towards the lower wavelength side (blue-shifted). Following the reports in refs. [17-19], the profiles of the fluorescence spectra of all the thirteen Eu^{3+}: phosphors have been assigned in Figs. (2 - 5), the following are the emission transitions:

TABLE 1.

Color coordinates ($\bar{X},\bar{Y}$) and average particle size (μm) of Eu^{3+} -doped different (Ln, Zn)OF (Ln = Y, La & Gd) powder phosphors

Phosphor	Average particle size (μm)	$\bar{X}$	$\bar{Y}$
YOF:Eu^{3+}	0.73	0.6329	0.3666
($Y_{0.75}$, $Zn_{0.25}$)OF:Eu^{3+}	0.88	0.6016	0.3977
($Y_{0.5}$, $Zn_{0.5}$)OF:Eu^{3+}	3.70	0.6117	0.3874
($Y_{0.25}$, $Zn_{0.75}$)OF:Eu^{3+}	2.80	0.5912	0.4081
LaOF:Eu^{3+}	*	0.6230	0.3764
($La_{0.75}$, $Zn_{0.25}$)OF:Eu^{3+}	*	0.6164	0.3830
($La_{0.5}$, $Zn_{0.5}$)OF:Eu^{3+}	*	0.5936	0.3987
($La_{0.25}$, $Zn_{0.75}$)OF:Eu^{3+}	*	0.6015	0.3977
GdOF:Eu^{3+}	4.91	0.6390	0.3605
($Gd_{0.75}$, $Zn_{0.25}$)OF:Eu^{3+}	*	0.6149	0.3844
($Gd_{0.5}$, $Zn_{0.5}$)OF:Eu^{3+}	*	0.6113	0.3880
($Gd_{0.25}$, $Zn_{0.75}$)OF:Eu^{3+}	*	0.6064	0.3929
ZnOF:Eu^{3+}	1.26	0.5911	0.4081

$^5D_0 \rightarrow {}^7F_4, {}^7F_3, {}^7F_2, {}^7F_1$ & $^7F_0$. From these, the transition ($^5D_0 \rightarrow {}^7F_2$) has been split into two components in all phosphors studied. From the recorded fluorescence spectra, depending upon the host composition Y-Zn, La-Zn and Gd-Zn, the intensity of the each of the peaks has been found to change significantly. It is observed that for the phosphors YOF→ LaOF→ GdOF the transition $^5D_0 \rightarrow {}^7F_2$ has shown a shift of 2 nm towards the lower wavelength side. From each set of these Eu^{3+}: phosphors it has been noticed that the intensity of the transition $^5D_0 \rightarrow {}^7F_2$ was decreasing with the substitution of Zinc ions in the host matrix owing to the concentration quenching phenomena. It is obvious from the measured fluorescence spectra that the substitution

TABLE 2

The relative fluorescence intensity ratios (R) of Eu^{3+}-doped different (Ln, Zn)OF (Ln = Y, La & Gd) phosphors.

Phosphor	$\frac{^5D_0 \rightarrow {^7F_4}}{^5D_0 \rightarrow {^7F_1}}$	$\frac{^5D_0 \rightarrow {^7F_3}}{^5D_0 \rightarrow {^7F_1}}$	$\frac{^5D_0 \rightarrow {^7F_2}}{^5D_0 \rightarrow {^7F_1}}$	$\frac{^5D_0 \rightarrow {^7F_1}}{^5D_0 \rightarrow {^7F_1}}$	$\frac{^5D_0 \rightarrow {^7F_0}}{^5D_0 \rightarrow {^7F_1}}$
$YOF:Eu^{3+}$	0.514	0.324	1.77	1.00	0.613
	-	-	1.675	-	-
$(Y_{0.75}, Zn_{0.25})OF:Eu^{3+}$	0.388	0.375	0.986	1.00	0.942
	-	-	1.364	-	-
$(Y_{0.5}, Zn_{0.5})OF:Eu^{3+}$	0.401	0.516	1.00	1.00	0.957
	-	-	1.248	-	-
$(Y_{0.25}, Zn_{0.75})OF:Eu^{3+}$	0.421	0.543	1.066	1.00	1.036
$LaOF:Eu^{3+}$	0.505	0.387	1.010	1.00	0.711
	-	-	1.382	-	-
$(La_{0.75}, Zn_{0.25})OF:Eu^{3+}$	0.369	0.407	1.032	1.00	0.695
	-	-	1.451		-
$(La_{0.5}, Zn_{0.5})OF:Eu^{3+}$	0.347	0.443	1.203	1.00	0.940
$(La_{0.25}, Zn_{0.75})OF:Eu^{3+}$	0.442	0.592	1.096	1.00	1.117
$GdOF:Eu^{3+}$	0.576	0.341	1.422	1.00	1.608
	-	-	1.970	-	-
$(Gd_{0.75}, Zn_{0.25})OF:Eu^{3+}$	0.384	0.420	1.195	1.00	0.780
	-	-	1.628	-	-
$(Gd_{0.5}, Zn_{0.5})OF:Eu^{3+}$	0.359	0.518	1.171	1.00	0.908
	-	-	1.658	-	-
$(Gd_{0.25}, Zn_{0.75})OF:Eu^{3+}$	0.332	0.514	1.146	1.00	0.998
	-	-	1.595	-	
$ZnOF:Eu^{3+}$	0.061	0.434	0.853	1.00	-
	-		0.909	-	

of zinc ions in the host matrix played a tremendous role on fluorescence quenching. Usually, Eu^{3+}-doped powder phosphors show bright red emission with the lanthanides (Y, La and Gd) based hosts.[14,15,20] Presently, the synthesized powder phosphors show orangish-red emission due to the mixture of lanthanides and zinc ions. Following the standard formulations made by commission International de '1' Eclairage, France, we have computed the color coordinates $(\overline{X}, \overline{Y})$ for all Eu^{3+}-doped phosphors based on the features of the recorded fluorescence spectra (Table 1). The computed color coordinates $(\overline{X}, \overline{Y})$ are fitted in the CIE chromaticity diagram (Fig. 6) to check the validity of the results. From this diagram it is noticed that all these Eu^{3+}: phosphors were fitted in the orangish-red color region.[9] In order to compare the fluorescence efficiencies of all Eu^{3+}: phosphors, the relative fluorescence intensity ratios (R) were evaluated and are presented in Table 2. From the recorded SEM images of (Y, Zn)OF, GdOF: Eu^{3+} phosphors (Fig. 7) it has been noticed that, the average particle size varied depending upon the choice of the host matrix (Table 1). Based on the computed color coordinates and relative fluorescence intensity ratios (R), the phosphor GdOF: Eu^{3+} could be suggested as a potential material for its orangish-red color emission in certain electronics systems.

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