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Luminescence Studies of Eu doped CaO Phosphor without and with NH_4F flux

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Abstract
The present paper reports the photoluminescence studies of the rare-earth Eu^{3+} doped and CaO red phosphor without and with NH_4F flux is synthesized by solid state reaction method with varying Eu molar concentration as Eu(0.5,1.0,1.5,2.0 mol %). Powder samples were prepared by firing stoichiometric mixtures of $CaCO_3$ as raw material and Eu_2O_3 as activator at 1200 ºC for 2 hours. The photoluminescence spectra were obtained by using a spectrofluorophotometer with an 80-W Xe lamp and 0.25-m monochromators. Slit widths were 0.05 mm for emission and 1.56 mm for excitation. The excitation spectra of synthesized phosphor at 613 nm monitoring were composed of a broadband and a series of sharp peaks, the strongest excitation peak at 272 nm. The main emission spectra of samples under 272nm excitation is Eu^{3+} ions $^5D_0 \rightarrow {}^7F_2$ electric dipole transition with a strong red light, so that the phosphors may be a better candidate for red component for white light generation in display and lamps. The emission spectrum of Eu^{3+} site in CaO shows maximum intensity at 613 nm and 617nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition, and the transition of $^5D_0 \rightarrow {}^7F_1$ around 595nm is observed with low intensity in this phosphor. When the excitation spectrum monitored at 613 nm a broad band around 254-300nm of CaOwith low good intensity is observed. Both excitation bands correspond to the $[Eu^{3+} - O^{2-}]$ charge-transfer transitions. It is known that the position of the $[Eu^{3+} - O^{2-}]$ charge transfer transition is more or less fixed in octahedral VI coordination but moves to lower energy with increasing Eu-O distance.

Keywords—*Photoluminescence,wavelength,phosphor,doping,hostlattice*

1. INTRODUCTION

Recently various phosphors has been in market for red emitting phosphor component in the white light generating materials. Many researchers have been actively investigated to improve their luminescent properties and to meet the development of different display and luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators. As a new red luminescent material, Eu doped CaO phosphor has been widely studied since it was found by different preparation methods. The rare-earth Eu^{3+} doped and CaO red phosphor is synthesized by solid state reaction method. The excitation spectra of synthesized phosphor at 613 nm monitoring were composed of a broadband and a series of sharp peaks, the strongest excitation peak at 272 nm. The main emission spectra of samples under 272nm excitation is Eu^{3+} ions $^5D_0 \rightarrow {}^7F_2$ electric dipole transition with a strong red light, so that the phosphors may be a better candidate for red component for white light generation in display and lamps.

2. EXPERIMENTAL

Powder samples were prepared by solid state reaction method firing stoichiometric mixtures of $CaCO_3$ as raw material and Eu_2O_3 as activator of purity(99.9%) wereused asstarting materialsforthehost CaOphosphor.Allthecompoundswas weighed,addedinappropriate proportions synthesizedin order toanalyze thedopant naturei.e.theeffect of concentration anditsemissionlinesinthehostphosphor. EuropiumoxideEu2O3isusedas activatorionatdifferent concentration (0.5,1.0, 1.5,and2.0mol%).Andgrounded intoafinepowder using agatemortarandpestleabout Anhour and added NH_4F again grounded for 10 min. Thegrounded phosphors wereplacedinanalumina crucible andheatedinairatmosphereat1200°C for2 hoursinamufflefurnacethephosphorswerecharacterized bythe photoluminescence spectra were obtained by using a spectrofluorophotometer with an 80-W Xe lamp and 0.25-m mono chromators. Slit widths were 0.05 mm for emission and 1.56 mm for excitation. The emission spectrum of Eu^{3+} site in CaO shows maximum intensity at 613 nm and 617nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition, and the transition of $^5D_0 \rightarrow {}^7F_1$ around 595nm is observed with low intensity in this phosphor. The excitation spectrum monitored at 613 nm radiation has a broad band at about 254-300nm of CaOwith low good intensity. Both excitation bands correspond to the [Eu^{3+} - O^{2-}] charge-transfer transitions. It is known that the position of the [Eu^{3+} - O^{2-}] charge transfer transition is more or less fixed in octahedral VI coordination but moves to lower energy with increasing Eu-O distance.

3. RESULTS AND DISCUSSIONS

3.1 PhotoluminescenceStudy

The emission spectrum of Eu^{3+} site in CaO shows maximum intensity at 613 nm and 617nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition, and the transition of $^5D_0 \rightarrow {}^7F_1$ around 595nm is observed with low intensity in this phosphor. The excitation spectrum monitored at 613 nm is a broad band at about 254-300nm of CaOwith good intensity. Both excitation bands correspond to the [Eu^{3+} - O^{2-}] charge-transfer transitions. It is known that the position of the [Eu^{3+} - O^{2-}] charge transfer transition is more or less fixed in octahedral VI coordination but moves to lower energy with increasing Eu-O distance.

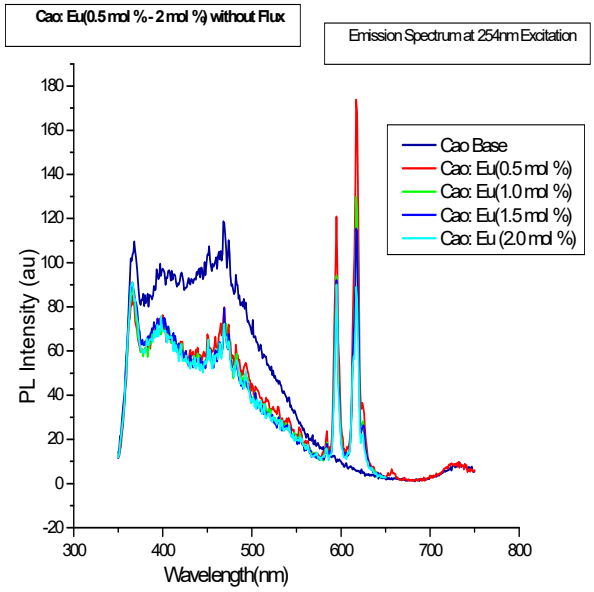

Fig. 1: Emission Spectrum at 272nm Excitation

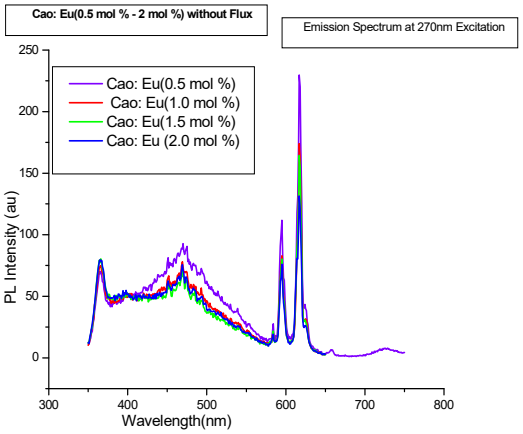

Fig. 2: Emission Spectrum at 272nm Excitation

EU%	λ_{ex} 254nm			
Base	λ	I		
	367	108		
	397	98		
	451	106		
	467	118		
EU%	λ_{ex} 254nm		λ_{ex}=270nm	
0.5	λ	I	Λ	I
	366	83	365	69
	398	75	451	78
	468	78	471	91
	594	119	594	111
	617	173	616	228
EU%	λ_{ex} 254nm		λ_{ex}=270nm	
1	Λ	I	Λ	I
	365	88	365	73
	401	71	450	65
	469	73	468	77
	594	93	594	81
	617	129	617	173
EU%	λ_{ex} 254nm		λ_{ex}=270nm	
1.5	λ	I	Λ	I
	365	898	364	79
	468	78	453	59
	594	90	468	71
	617	116	594	80
			617	163
EU%	λ_{ex} 254nm		λ_{ex}=270nm	
2	365	90	365	79
	397	75	396	53
	468	71	468	75
	594	90	594	76
	616	89	617	130

Table1: EU DOPED CaO (Eu mol% 0.5% TO 2%)

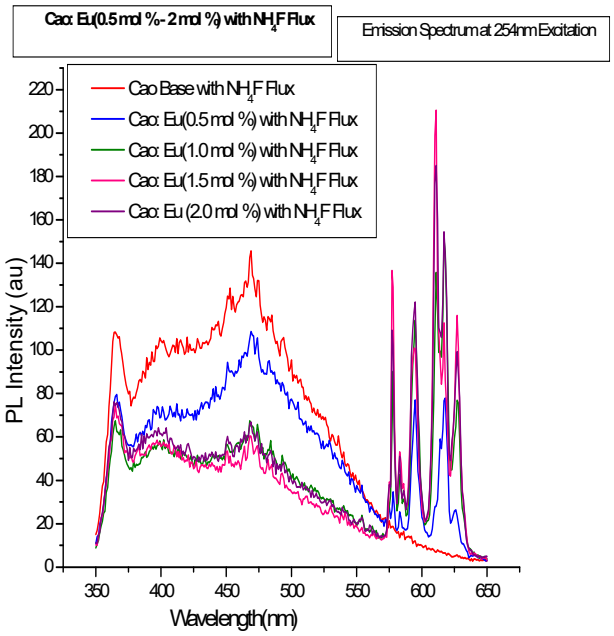

Fig. 3: Emission Spectrum at 272nm Excitation

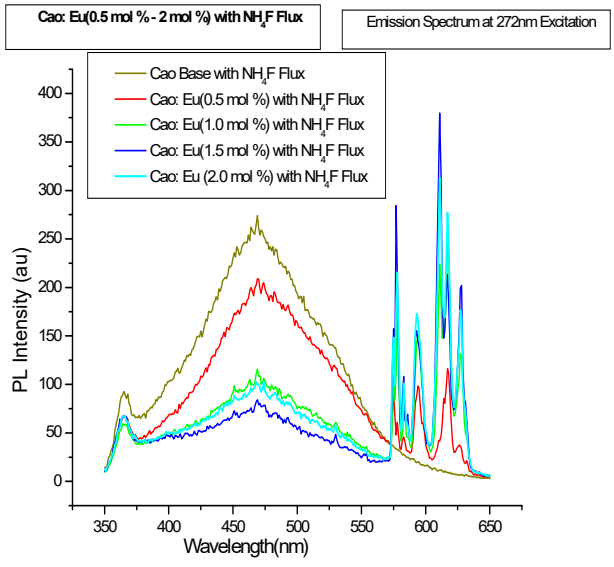

Fig. 4: Emission Spectrum at 272nm Excitation

Base CaO with NH_4F Flux	**λ_{ex} =254nm**		**λ_{ex}=272nm**	
	λ	**I**	**λ**	**I**
	364	106	365	89
	399	107	468	272
	453	126	483	237
	468	142		
CaO: Eu(0.5%) with NH_4F Flux	**λ_{ex} =254nm**		**λ_{ex}=272nm**	
	λ	**I**	**λ**	**I**
	367	76	363	66
	395	73	469	208
	439	82	481	193
	451	94	575	93
	468	107	592	98
	474	105	616	115
	507	76	626	37
CaO: Eu(1%) with NH_4F Flux	**λ_{ex} =254nm**		**λ_{ex}=272nm**	
	λ	**I**	**λ**	**I**
	367	68	368	59
	469	67	469	115
	579	91	579	177
	595	114	594	151
	610	136	610	224
	618	151	616	244
	627	77	626	131
CaO: Eu(1.5%) with NH_4F Flux	**λ_{ex} =254nm**		**λ_{ex}=272nm**	
	λ	I	λ	I
	365	72	364	72
	578	120	468	83
	594	102	578	285
	612	209	612	379
	628	115	616	217
	λ_{ex} =493nm		**λ_{ex}=393nm**	
	493	1024	393	1022
	504	189	610	12
CaO: Eu(2%) with NH_4F Flux	**λ_{ex} =254nm**		**λ_{ex}=272nm**	
	λ	I	λ	I
	364	72	366	66
	578	112	468	106
	593	126	579	209
	609	189	588	163
	618	160	610	313
	628	100	614	270
	λ_{ex} =395nm			
	392		1016	
	470		18	
	578		12	

Table2: EU DOPED CaO (Eu mol% 0.5% TO 2%) NH_4F flux

Figure1 shows the PL excitation and emission of Eu (0.1, 1.0, 1.5 and 2.0 mol %) doped Cao phosphor under 254nm excitation 616nm with good intensity.fig.2 shows the PL excitation and emission of Eu (0.1, 1.0, 1.5 and 2.0 mol %) doped Cao phosphor under 272nm excitation 616nm with good intensity.fig.3 shows the PL excitation and emission of Eu (0.1, 1.0, 1.5 and 2.0 mol %) doped Cao phosphor under 254nm excitation 616nm with good intensity.fig.4 shows the PL excitation and emission of Eu (0.1, 1.0, 1.5 and 2.0 mol %) doped Cao phosphor under 272nm excitation 616nm with good intensity. These different intensities because of Eu doped in Cao when Eu concentration is increased the intensity is also increased the observed peaks at 468,537,587 and 616nm are from transitions $^5D_2 \rightarrow {}^7F_0$, $^5D_1 \rightarrow {}^7F_1$ and also from $^5D_1 \rightarrow {}^7F_{1,2}$respectively. It is also observed that the intensity of peak at 616nm is increasing as the Eu concentration increases while the intensity of peaks at 460,530 and 582nm decreases. The peak around 610-620nm is due to the electrical dipole transition of $^5D_0 \rightarrow {}^7F_2$ which is induced by the lack of inversion symmetry at the Eu^{3+} sites. It is well know that the $^5D_0 \rightarrow {}^7F_2$ / $^5D_0 \rightarrow {}^7F_1$ intensity ratio is a good measure of the site symmetry of rare –earth ions in a doped material

Conclusions: The emission spectrum of Eu^{3+} site in CaO shows maximum intensity at 613 nm and 633nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition. However when the Ca is replaced with Ba the intensity of 613nm is doubled apart from other emissions in CaY_2O_4 and BaY_2O_4. This may bedue the presence of Eu ion whose atomic radius is nearly same as Eu ion in the crystal matrix.

Conclusion: The Eu doped CaO phosphor is successfully prepared. further work in progress.

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