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Investigations of Optical Properties and Characterization of $YAlO_3:Eu^{3+}$ Doped Phosphors

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Abstract—*The novel phosphor of $YAlO_3$ activated with the trivalent rare-earth Eu^{3+} ions were synthesized by solid-state method, and their characterization and luminescent properties were investigated. The Photoluminescence, thermoluminescence, XRD and FTIR were employed to study the luminescence properties. In the photoluminescence investigations, there is a single and highly symmetric site for activator ions in the $YAlO_3$ host lattice. The sharp emission properties show that the $YAlO_3$ is a suitable host for rare-earth doped laser crystal and phosphor material. The results of the XRD show that obtained $YAlO_3:Eu^{3+}$ phosphor has a orthorhombic structure. Thermoluminescence(TL) studies of $YAlO_3 : Eu^{3+}$ have been carried out by irradiating with UV – radiation, at a heating rate of 6.7 $^0Cs^{-1}$ showing two peaks at 118^0C and 261^0C for undoped phosphors and two peaks at 131^0C and 274^0C. The Kinetic parameters such as activation energy, frequency facter, trap depth were estimated using Chen's glow peak method and results are discussed in details.*

Keywords— *Luminescence, Prevoskite, Solid state method, $YAlO_3$, Thermoluminescence, XRD, FTIR,CIE & Photoluminescence.*

1. INTRODUCTION

Rare-earth ions have been extensively used as the active ions in phosphors for several decades. More recently, however,the development of flat panel displays, such as field emission displays (FEDs), plasma display panels (PDPs) and thin film electro-luminescent devices (TFEL), or white light emitting diode (LED), have emerged as the principal motivation for research into rare-earth luminescence, and the present article therefore concentrates on the variety of different ways in which rare-earth luminescence has been exploited in this field[1–3].The rare-earth ions are characterized by a partially filled 4f shell that is well shielded by $^5s_2$ and $^5p_6$ orbitals. The emission transitions, therefore, yield sharp lines in the optical spectra[4]..

2. EXPERIMENTAL

Samples of compounds of Eu^{3+}-doped $YAlO_3$ was synthesized via high temperature solid-state reaction method. The starting materials are as follows: Y_2O_3,Al_2O_3,Eu_2O_3 and H_3BO_3(purity≥99.99%) all of Hi. Media(Analytical grade) was used. The mixture of reagents was ground together to obtain a homogenous mixture. After being ground thoroughly in stoichiometric ratios(1:1) by using an agate mortar by dry grinding for nearly 45 minutes, to ensure the best homogeneity and reactivity, powder was transferred to alumina crucible, and then the homogeneous powder was heated for 1250^0c for 3 hours& cooled in the same furnace for about 15 h.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis Results

Fig.1 shows the XRD pattern of Eu^{3+} doped $YAlO_3$ phosphor. All the diffraction peaks are in agreement with those of the ICCD card number(98-000-4115)with space group P_{nma}/62 for Eu^{3+} doped confirm that the sample has a orthorhombic structure. Particle size of the prepared sample is found to be 57 nm.The lattice parameter for $YAlO_3:Eu^{3+}$ phosphors are a=5.33A^0,b=7.375A^0, c=5.180A^0. So all diffraction peaks in these XRD patterns could be attributed to the orthomrhombic perovskite crystal structure of $YAlO_3$ which confirm that the doping concentration does not influence the crystalline phase formation.The particle size of $YAlO_3 : Eu^{3+}$ calculated from the Scherrer 's formula is 57nm. The particle size of $YAlO_3$ (undoped) phosphors calculated from the Scherrer's formula is 9-16nm.

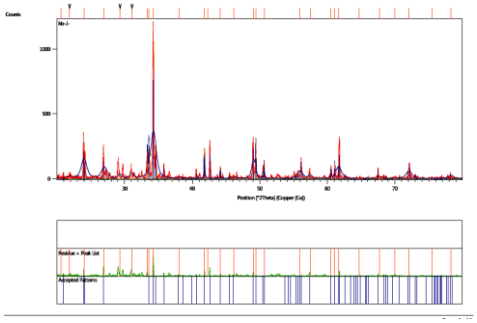


Fig. 1

3.2 FTIR Spectroscopy Analysis

Fig. 2 shows Fourier transform infrared (FTIR) spectra of undoped Eu^{3+} :$YAlO_3$ phosphors. Fig.3 shows FTIR of $YAlO_3$: Eu^{3+} mixed (3% and undoped) phosphors. All the observed peaks confirm the formation of Eu^{3+} : $YAlO_3$ phosphors.

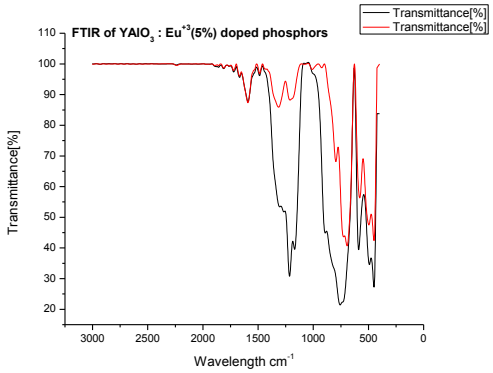


Fig. 2

3.3 Thermoluminescence Glow Curve of $YAlO_3$: Eu^{3+} Phosphor

TL glow curve for $YAlO_3$: Eu^{3+} phosphor was recorded with a UV exposure of 5 min at a heating rate 6.7°Cs−1. The order of kinetics and the activation energy with frequency factor are calculated using Chen's empirical 5,10,15,20,25 min. UV exposure time after CGCD. In the TL glow curve, two peaks were observed in Fig. 4-5. It is observed that TL glow peak intensity were found to be high in Eu^{3+} doped phosphors when compared to pure. The TLof undoped $YAlO_3$ phosphors shows two peak at 118 and 261^{0}C. The TL $YAlO_3$:Eu^{3+} shows two peaks at 131 and 274^{0}C.

From the Table 2 it can be easily seen that the variation with UV exposure performed at heating rate 6.7^{0}Cs^{-1}. The value of activation energy for first peak belongs to 0.04307 eV - 0.05684 eV and for second peak belongs to 0.13048eV – 0.14944 eV, frequency factor for first peak belongs to 0.1038 x 10^2 - 0.2124 x 10^4 s^{-1} and for second peak belongs to 0.4202 x 10^2- 0.8831 x 10^4 s^{-1}. The trap depth were evaluated using chen's formula using peak shape method & it was found for first peak in between 0.0242 - 0.0786eV and for second peak in between 0.1005 -0.19207 eV for different UV exposure time evaluated from second order Kinetics using Table 1.. Fig.6 shows intensity vs different time of $YAlO_3$: Eu^{3+}(3 mol%) doped phosphors at 6.7hr. Fig.7 shows intensity vs conc. at different heating rate.

Table 1

Shape factors(μ), Activation Energy E and Order of Kinetics b of Eu^{3+} doped $YAlO_3$ irradiated by UV exposure 254 nm source

UV Min	Peak	T_1	T_m	T_2	T	δ	Ω	Order of Kinetics b(μ=δ/ω)	Activation Energy	Frequency factor
5	1	97.968	123.556	158.141	25.588	34.585	60.173	2(0.57)	0.0555	0.382 x 10^2
	2	224.711	279.887	347.656	55.176	67.769	122.945	2(0.55)	0.1447	0.441 x 10^2
10	1	92.770	124.756	152.943	31.986	28.987	60.173	2(0.48)	0.0568	0.413 x 10^2
	2	215.715	265.693	329.865	49.978	64.172	114.15	2(0.56)	0.1415	0.577 x 10^2
15	1	92.770	127.355	161.940	34.585	34.585	69.17	2(0.50)	0.04908	0.144 x 10^2
	2	211.917	265.693	329.865	53.776	64.172	117.948	2(0.54)	0.13548	0.420 x10^2
20	1	92.770	127.355	168.336	34.585	40.981	75.566	2(0.54)	0.04307	0.891 x 10^3
	2	214.516	264.494	334.862	49.978	70.368	120.346	2(0.58)	0.13048	0.883 x10^4
25	1	95.802	135.051	171.558	39.249	36.507	75.756	2(0.48)	0.04965	0.104 x 10^2
	2	221.568	278.543	340.582	56.975	62.039	1190.14	2(0.52)	0.14944	0.582 x10^2
30	1	92.770	127.355	160.740	34.585	33.385	67.97	2(0.49)	0.05033	0.212 x10^2
	2	208.119	264.494	328.465	56.375	63.971	120.346	2(0.53)	0.13048	0.883 x 10^2

Table 2

The trap depth for the prominent glow peaks of the studied $YAlO_3$: Eu^{3+}, evaluated from second order kinetics

	Peaks	Activation energy, E(eV)					
		5 min UV	10 min UV	15 min UV	20 min UV	25 min UV	30min UV
$E_\omega = c_\omega\left(\frac{kT_m^2}{\alpha}\right) - b_\omega(2kT_m)$	1	0.0671	0.0482	0.04537	0.0472	0.04162	0.04446
	2	0.1626	0.1643	0.14701	0.19207	0.1506	0.1366
$E_\tau = c_\tau\left(\frac{kT_m^2}{\alpha}\right) - b_\tau(2kT_m)$	1	0.0517	0.0343	0.03064	0.0282	0.02416	0.02740
	2	0.1260	0.1126	0.1315	0.1327	0.11328	0.1006
$E_\delta = c_\delta\left(\frac{kT_m^2}{\alpha}\right) - b_\delta(2kT_m)$	1	0.0786	0.0653	0.06292	0.06304	0.06075	0.06213
	2	0.19137	0.18902	0.17521	0.18331	0.18348	0.16731

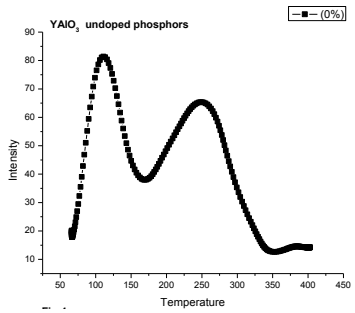


Fig. 4

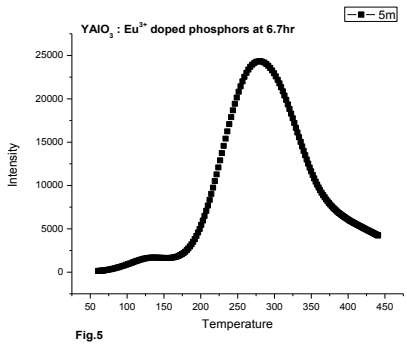


Fig. 5

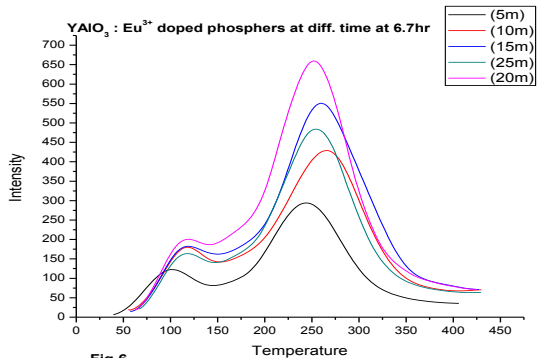


Fig. 6

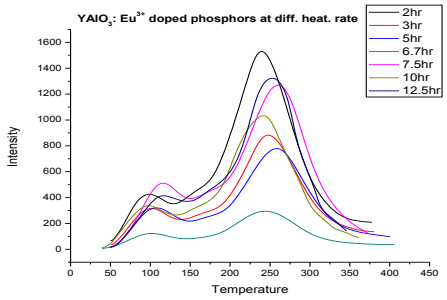


Fig. 7

3.4 Photoluminescence Studies

The excitation and emission spectra of $YAlO_3$: Eu^{3+} phosphor were recorded at room temperature.

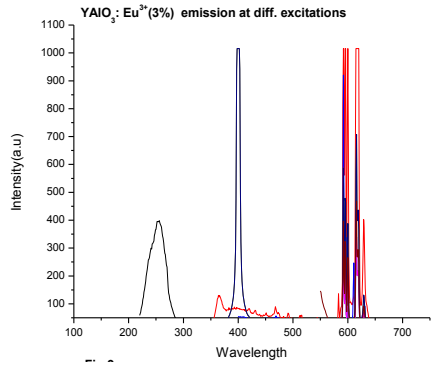
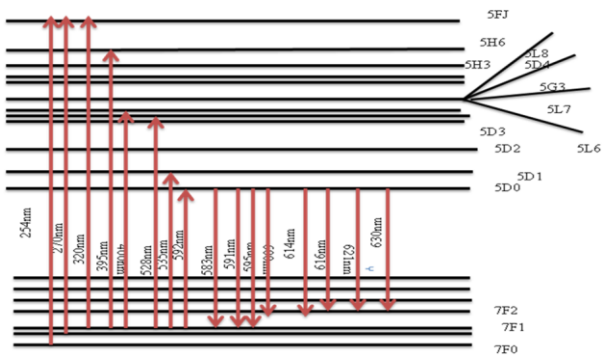


Fig. 8



$YAIO_3$: Eu^{3+} doped phosphors

Fig. 9

The excitation spectra of $YAlO_3$:Eu^{3+} phosphor mainly consist of the charge transfer and (CTB) of Eu^{3+} located in 240–592nm.The CTB of crystalline phosphor shows blue shift. The energy position of Eu^{3+} CTB is closely related to the covalency of Eu–O bond and the nearest cation M^{3+}(M = Y^{3+},Al^{3+})[6,7]. Stronger chemical bond between Eu–O bond and M^{3+}ions forms for the crystalline phosphor,compared with amorphous one. Therefore, the CTB of crys-talline $YAlO_3$:Eu^{3+} is located at shorter wavelength[5].

The emission spectrum is shown in Fig.8 which shows sharp emission lines.

Table 3

S.No	λ_{emi}	*Transitions*
1.	400nm	$^5D_0 - ^7F_1$
2.	528nm	$^5D_0 - ^7F_1$
3.	535nm	$^5D_0 - ^7F_1$
4.	583nm	$^5D_0 - ^7F_1$
5.	592nm	$^5D_0 - ^7F_1$
6.	595nm	$^5D_0 - ^7F_2$
7.	600nm	$^5D_0 - ^7F_2$
8.	614nm	$^5D_0 - ^7F_2$
9.	616nm	$^5D_0 - ^7F_2$
10.	621nm	$^5D_0 - ^7F_2$
11.	630nm	$^5D_0 - ^7F_2$

3.5 CIE Coordinate

The color co-ordinates for the Eu^{3+} doped sample are x=0.628123 and y=0.37145(these coordinates are very near to the orange light emission)and x=.628372 and y =. 340372 (these coordinates are very near to the red light emission). Hence this phosphor having excellent color tunability from orange-red light emission.

4. CONCLUSION

The orthorhombic face Eu^{3+} doped $YAlO_3$ phosphor was successfully synthesized by the solid state reaction method, which is confirmed by the XRD result well matched with ICCD card(98-000-4115). Crystallite size of Eu^{3+} : $YAlO_3$ using scherrer's formula is 57nm. PL excitation spectrum was found at 240- 592nm. In TL glow curve, only a two peak was observed. The value of activation energy belongs to 0.04307-.05684eV for first peak and 0.13048-0.1494eV for second peak and frequency factor for first peak is 0.1038×10^2 – 0.2124×10^4 s^{-1} and for second peak it's 0.4202×10^2 – 0.8831×10^4 s^{-1} and trap depth for first peak is 0.02416-0.07862eV and for second peak it's 0.10046-0.19137eV. $YAlO_3$:Eu^{3+}(3%) phosphor shows an orange-red emission under 254nm excitation. The photoluminescence study shows that the emission intensity of electric dipole transition (595,600,616,621 and 629 nm) ($^5D_0 \rightarrow ^7F_2$) dominates over that of magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) (400,528,535,582,592nm).The optimum concentration of Eu^{3+} in $YAlO_3$:Eu^{3+}(3mol%). In thermoluminescence study, maximum peaks show second order kinetics which means that more than one luminescent center is present in the phosphor sample.

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