Development of phosphors for optoelectronics Photoluminescent Liquid Crystal Display Devices

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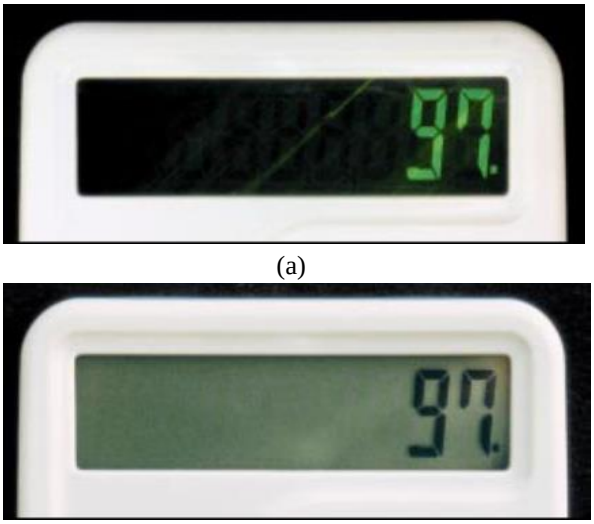
Abstract **- The main ingredient in Photoluminescent Liquid Crystal Display (PLLCD) is near UV excited phosphor for illumination. It is the need of PLLCD device to develop a phosphors that can absorbs excitation energy in the near UV region. To meet these requirement of PLLCD device, synthesis and photoluminescence characteristics of $CaSO_4:Eu^{2+}$, $Sr_5(PO_4)_3Cl:Eu^{2+}$, (Ba, Sr) $SiO_4:Eu^{2+}$, $(Y,Bi)_2O_3:Eu^{3+}$ is reported here. $CaSO_4:Eu^{2+}$ emits radiation in the near UV region at 388nm. This near UV energy is absorbed by (1) $Sr_5(PO_4)_3Cl:Eu^{2+}$ to emit blue radiation at 446 nm .(2) (Ba, Sr) $SiO_4:Eu^{2+}$ to emit green light at 537nm and (3) $(Y,Bi)_2O_3:Eu^{3+}$ to give red light emission at 611 nm. It found that these phosphors are promising RGB (Red, Green, Blue) emitters for fabrication of PLLCD device.**

Index Terms **- PLLCD, Photoluminescence, near UV.**

1.INTRODUCTION

Liquid crystal displays (LCD) are most widely used as flat panel screens. LCD require very small current. However, these are passive type of displays; they are not emissive. Optical transmission is modified by voltage applied to the display elements. A light source is needed to convert these modifications into visible display. Full colour LCD display can be obtained by using colour filter in addition to the back light source in its architecture. The main drawback of LCD display is its restricted viewing angle. All-important characteristics of LCD display such as contrast, brightness and colour are considerably vary with viewing angle [1-3]. On other hand a photoluminescent liquid crystal display (PLLCD) device gives rise a display with the same contrast, brightness and colour at all angles has been described by Crossland et al (1997) [4] and Vecht et al (1998)[5]. In PLLCD architecture, display consist of a narrow band, collimated, near UV back light, liquid crystal modulator and photoluminescent phosphor for illumination purpose. To achieve the optimum performance from the PLLCD device, specially engineered phosphors are required. These can be classified into two categories. First a narrow band, near UV emitting source is required with a peak emission wavelength close but not extending into the visible region. Second, for a full colour display, photoluminescent phosphors which can be excited by 390 nm and emit in three primary colours are required. For generating full colours the RGB phosphors should be narrow band emitters around 610, 550 and 450 nm, respectively. In all four phosphors are required, One for near UV emission and other three are Red, Green, and blue emitting phosphors excited by near UV - emitting phosphor. PLLCD device get rid of the need for full colour filter which is main component of LCD. Therefore, probability of efficiency of output light intensity increases to large extends. The comparison for appearance of PLLCD and LCD devise is shown below.



(a)

(b)

Fig 1. (a) PLLCD Device (b) LCD Device

This paper is focused on synthesis and characterization of low-cost phosphors required for PLLCD.

1. Near UV Emitting phosphor for back light

To fabricate Hg – free PLLCD then, in the place of Hg-lamp, a Near UV emitting GaN diode which requires less power to emit 390 nm near UV light can be used [6-9]. Calcium Sulphate Europium phosphor, $CaSO_4$: Eu, was synthesis for this purpose.

1.1 Synthesis of $CaSO_4$: Eu

Ca0.993Eu0.007SO4 was obtained by co-precipitation. CaCO3 was dissolved in nitric acid to which an appropriate quantity of Eu2O3 dissolved in nitric acid was added. Precipitation was carried out using an aqueous solution of ammonium sulphate. The precipitate was thoroughly washed and dried. It was then heated at 900 °C for 1 h followed by quenching to room temperature.

1.2 Optical characteristics of $CaSO_4$: Eu

Photoluminescence measurements of the obtained phosphor were performed using Hitachi-4000 spectro-fluorometer. Fig. (2) Shows the excitation and emission spectra of obtained $CaSO_4:Eu^{2+}$ phosphor. Near UV emission of $CaSO_4$: Eu^{2+} peaking at 388 nm is obtained after exciting the phosphor by 254 nm UV light. The obtained emission is having HWFM (Full-Width Half-Maximum) 16 nm, ideally suited for this purpose. The simple preparation procedure described here produces the phosphor with the desired characteristics. Eu^{2+} fluorescence centered at 388 nm is due to configuration transition from $_4f^6{}_5d^1$ state to $_4f^7$ ground state.

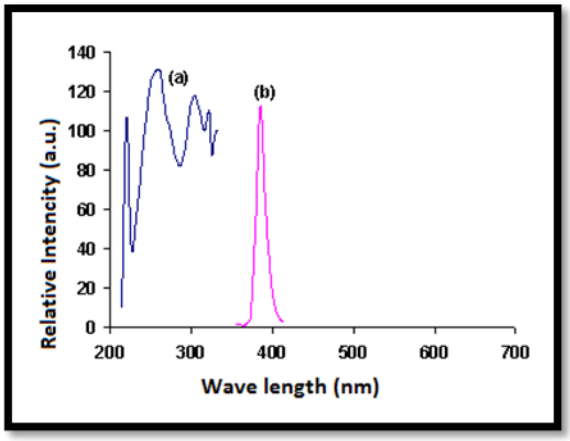


Fig 2 PL spectra of Near UV emitting PLLCD Phosphor

(a)$CaSO_4:Eu^{2+}$ excitation for 388 nm emission

(b)$CaSO_4:Eu^{2+}$ emission spectra for 254 nm excitation

2. BLUE EMITTING PHOSPHOR

$Sr_5(PO_4)_3Cl:Eu^{2+}$ is a well-known phosphor, emitting blue light by the excitation of longer UV wavelength [10-11].

2.1 Synthesis of $Sr_5(PO_4)_3Cl:Eu^{2+}$

The above phosphate was prepared by precipitation method followed by solid state diffusion.

$SrHPO_4$ was first prepared. By adding aqueous solution of $(NH_4)_2HPO_4$ drop by drop into the aqueous solution of $Sr(NO_3)_2$, a precipitate of $SrHPO_4$ was obtained. This precipitate was kept at 70^0C in an oven for drying.

$Sr(NO_3)_2+(NH_4)_2HPO_4 \rightarrow SrHPO_4+NO_2 + H_2O$

Next, we prepared $SrCl_2$:Eu. Aqueous solution of SrCl2 and $EuCl_2$ were made and Mixed. The mixture was then kept for evaporation to dryness.

$0.9SrCl_2 + 0.1EuCl_2 \rightarrow Sr_{0.9}Cl_2:Eu_{0.1}$

Stoichiometric amounts of $Sr(CO_3)_2$, $SrCl_2$:Eu, $SrHPO_4$ were taken and ground for 1-2hrs. The Mixture was processed through solid state reaction in a furnace at 700^0C for 12hrs.

$6SrHPO_4 + Sr_{0.9}Cl_2:Eu_{0.1} + 3Sr(CO_3)_2 \rightarrow 2Sr_{4.95}(PO_4)_3Cl:Eu_{0.05} +5H_2O +3CO_2$

The sample so obtained was then reduced at 700^0C for 1Hr.

2.2 Optical characteristics of $Sr_5(PO_4)_3Cl:Eu^{2+}$

It is well known that the emission peak at 450 nm for $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor results from the transition of electrons in the excited state of Eu^{2+}, $4f^65d^1$ to its ground state $4f^7$.

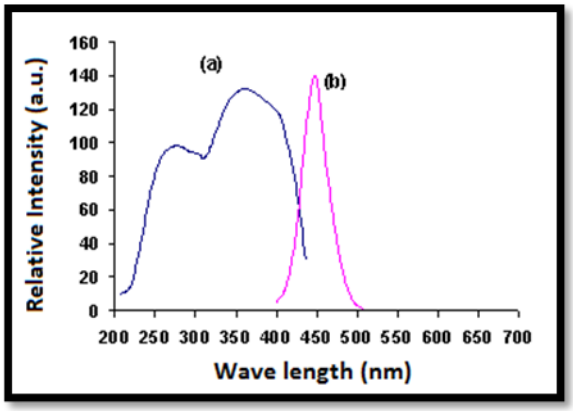


Fig. 3 *PL spectra of* $Sr_5(PO_4)_3Cl$: 5 mole % $Eu2^+$

(a) Excitation spectra $Sr_5(PO_4)_3Cl$: 5 mole % $Eu2^+$ *for 446 nm emission.*

(b) Emission spectra of $Sr_5(PO_4)_3Cl$: 5 mole % $Eu2^+$ *for 370 nm excitation*

PL measurements of the synthesized $Sr_5(PO_4)_3Cl:Eu^{2+}$ phosphor was performed using Hitachi-4000 spectro-fluorometer. The Fig.3 shows the excitation and emission spectrum of $Sr_{4.95}(PO_4)_3Cl$: $Eu_{0.05}$ phosphor. The excitation spectrum is characterized by peaks around 275 nm and 370 nm attributable to effective absorption by Eu^{2+}. Excitation spectrum consists of a broad band indicating appreciable response throughout the UV region. Consequently the utility of the material in PLLCD application is established

Table1 .PL- Results of synthesized Blue emitting phosphors for PLLCD

Complex/ compound	Excitation Wavelength (nm)	Emission wavelength (nm)	HWFH (nm)	Stock Shift (nm)	Relative Intensity (a.u.)
$Sr_5(PO_4)_3Cl:Eu^{2+}$	385	450	36	70	1118

3. GREEN EMITTING PHOSPHOR

Synthesis and photoluminescence characteristics of (Ba, Sr) SiO_4:Eu as green emitting phosphor were studied for PLLCD application.[12-15]

3.1 Synthesis of $(Ba,Sr)SiO_4:Eu^{2+}$

For preparing (Ba, $Sr_{0.96}$) $SiO_4:Eu^{2+}{}_{0.04,}$ $SrSiO_3$ was first prepared by precipitation method. By adding aqueous solution of Na_2SiO_3 drop by drop into the aqueous solution of strontium nitrate, precipitate of $SrSiO_3$ was obtained. This precipitate then kept at 70^0C in an oven for drying. An appropriate amount of Eu_2O_3 dissolved in dil. Nitric acid was then sprinkled on the mixture of stiochometric amount of dried precipitate of $SrSiO_3$ and Barium carbonate. The entire mixture was then crushed for couple of hrs. and subjected to the solid state diffusion process at 700^0C for 12 hrs . The obtained powder was then heated in the reducing atmosphere provided by burning charcoal at 900^0C for 1hr. PL measurements of the obtained $(BaSr)SiO_4:Eu^{2+}$ were preformed using Hitachi -4000 spectro-fluorometer.

3.2 Optical characteristics of $(Ba,Sr)SiO_4:Eu^{2+}$

Fig 4 shows that excitation can be achieved by long wavelength UV bordering onto visible region and the emission is in green region of the spectrum at 537 nm for $(Ba,Sr)SiO_4:Eu^{2+}$. Such phosphors can be useful for photoluminescent liquid crystal display (PLLCD) applications.

The as-prepared phosphors did not show intense emission, probably the activator Eu is not incorporated in divalent form. The phosphors were needed to reheated, in the reducing atmosphere provided by heating in a closed box with charcoal, at 900 C for 1 hour.

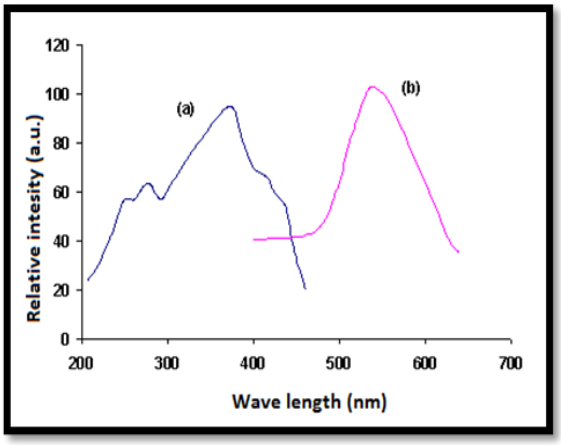


Fig 4 (a) Excitation spectra of $BaSrSiO_4$:4 mole%Eu^{2+} for 537 nm emission. (b) Emission spectra of $BaSrSiO_4$:4 mole%Eu^{2+} peaking at 537nm for 380nm excitation

4. RED EMITTING PHOSPHOR

$(Y,Bi)_2O_3:Eu^{3+}$ as a red emitting phosphor were synthesized and its photoluminescent behavior is studied.

4.1 Synthesis of $(Y,Bi)_2O_3:Eu^{3+}$

Y_2O_3: 5 mole % Eu, 15 mole% Bi; {($Y_{0.8,}$ $Bi_{0.15,}$ $Eu_{0.05})_2O_3$ OR $Y_{1.6}Bi_{0.3}Eu_{0.1}O_3$} phosphors were synthesized by using Co-precipitation method and obtained dried powder was calcinated at 1000^0C in air for 12 hrs. (Explained in chapter 2). Su Qiang Synthesized this phosphor by solid state reaction at 1200^0C under N_2 atmosphere [33]. Stiochometric amount of starting materials Bi $(NO_3)_2$. $5H_2O$ (s.d.fine chem. LTD. AR grade), Y_2O_3(IR), Eu_2O_3(IR) were taken.

4.2 Optical characteristics of $(Y,Bi)_2O_3:Eu^{3+}$

$(Y,Bi)_2O_3:Eu^{3+}$ is derived form original phosphor $Y_2O_3:Eu^{3+}$**[31,32].** It is well known that $Y_2O_3:Eu^{3+}$ is a

good phosphor for PDP, FED etc. Even it can be a good lamp phosphor, as it produces red emission on 254nm excitation. By introducing Bi ion in Y_2O_3:Eu^{3+}, it is observed that excitation spectrum extends to longer wavelength side (Red shift), whereas emission spectrum remains same as it was for Y_2O_3:Eu^{3+}. Thus in (Y, Bi) $_2O_3$:Eu^{3+} red emission is prominently produced by Eu^{3+}ion. In the host lattice Y_2O_3, the Bi^{3+} and Eu^{3+} ion occupy two inequivalent lattice sites, which possess the point symmetries C2 and S6. The Bi^{3+} reflection spectrum exhibits two broad bands peaking at 254 nm and 330 nm arising from $^1S_0 \rightarrow {}^1P_1$ and $^1S_1 \rightarrow {}^3P_1$ transitions. Under 337 nm excitation, two broad band emissions were observed around 410 nm and 520 nm. These emission bands overlap the absorption spectra of Eu^{3+}; Therefore, we observe an efficient energy transfer from the Bi^{3+} ions to Eu^{3+}, which emits red light at 611nm corresponding to its predominating transition $^5D_0 \rightarrow {}^7F_2$**. [16-20].**

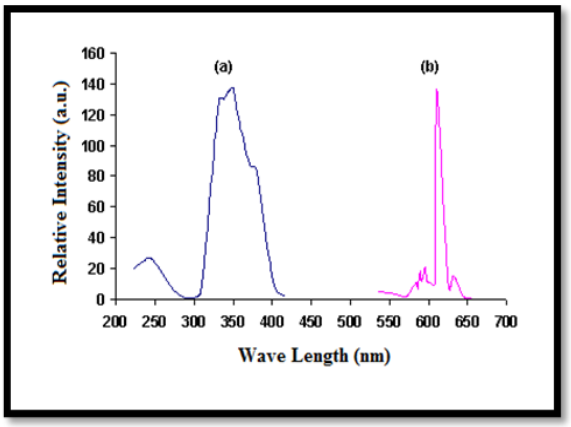


Fig 5 PL spectra of ($Y_{0.8}$, $Bi_{0.15}$, $Eu_{0.05}$)$_2O_3$ *(a) Excitation spectra of* ($Y_{0.8}$, $Bi_{0.15}$, $Eu_{0.05}$)$_2O_3$ *for 611 nm emission. (b) Emission spectra of* ($Y_{0.8}$, $Bi_{0.15}$, $Eu_{0.05}$)$_2O_3$ *for 380 nm excitation*

Emission intensity was found to be 311(arbitrary unit) for 380 nm excitation whereas intensity increases to 516 (arbitrary unit) for 350 nm excitation (Fig.4.17). In both cases emission wavelength remains same i.e.611 nm which is attributed to Eu^{3+} ion. As mentioned earlier excellent energy transfer takes place from Bi^{3+} to Eu^{3+}. We conclude that conventional phosphorY_2O_3:Eu^{3+} is not suitable for 380 nm excitation. But after introducing Bi^{3+} ion in Y_2O_3:Eu^{3+}, the phosphor produces red light for 385 nm excitation. If 385 nm back light is used, then (Y,Bi)$_2O_3$:Eu^{3+} can be useful for PLLCD application as a red light emitter.

5. CONCLUSION

Near UV emission of $CaSO_4$: Eu^{2+} peaking at 388 nm is obtained after exciting the phosphor by 254 nm UV light. This near UV further used for excitation purpose in PLLCD application. The emission peak at 450 nm blue radiation for $Sr_5(PO_4)_3Cl$:Eu^{2+} phosphor results from broad spectrum of excitation. At NUV excitation, emission is in green region of the spectrum at 537 nm for (Ba,Sr)SiO_4:Eu^{2+}.We conclude that conventional phosphorY_2O_3:Eu^{3+} is not suitable for 380 nm excitation. But after introducing Bi^{3+} ion in Y_2O_3:Eu^{3+}, the phosphor produces red light for 385 nm excitation. Hence $CaSO_4$: Eu^{2+}, $Sr_5(PO_4)_3Cl$:Eu^{2+}, (Ba,Sr)SiO_4:Eu^{2+} and (Y,Bi)$_2O_3$:Eu^{3+} are the promising phosphor candidates for PLLCD illumination.

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