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One step synthesis and X-ray induced luminescence in RGB PDP phosphors

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ABSTRACT

One step combustion synthesis of preparation of plasma display panel (PDP) phosphors for X-ray induced luminescence is reported. The prepared phosphors were characterized by XRD, PL and X-ray excited luminescence (XEL) techniques. Phosphors emitting three primary colors have been be prepared by using the combustion synthesis. These may be used for X-ray imaging phosphors.

Keywords: Phosphors; combustion synthesis; X-ray imaging phosphors; photoluminescence; XRD.

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Introduction

The plasma display panels (PDP) are gaining attention due to their high performance and scalability as a media for large format television (TV), particularly high definition TV (HDTV). Color plasma display panels (PDPs) have attracted considerable interest in recent years as components of wall-mounted television sets that are large, flat and thin [**1-4**] **.**The luminescence efficiency of a PDP depends upon various components such as phosphors, gas mixture, dielectric layer, reflective layer, black matrix, etc. The phosphor particles for PDP applications should have good luminescent characteristics under vacuum ultraviolet (VUV) light consisting of the resonance radiation of Xe atoms (147 nm) and the excited state of molecular Xe (172 nm). Phosphors for PDP must maintain their light output for thousands of hours. Often the maintenance is the restricting factor in using phosphors. In the initial devices the conventional phosphors, such as Y_2O_3: Eu and (Y, Gd) BO_3: Eu for red, $BaMgAl_{10}O_{17}$: Eu for blue and Zn_2SiO_4: Mn for green, which were already established as lamp/CTV phosphors, were used as PDP materials. However, several problems have arised. Y_2O_3: Eu phosphor has low luminescence efficiency. (Y,Gd)BO_3: Eu has poor color purity because of the orange-red emission instead of red [**5**]**.**Zn_2SiO_4: Mn is known to have a long decay time and a high discharging voltage [**6**]**.**$BaMgAl_{10}O_{17}$: Eu degrades fast. Precipitation of Eu as $EuMgAl_{11}O_{19}$ is one of the factors affecting the stability of compound [7].

Combustion synthesis is a convenient method for rapid synthesis of phosphors. The method makes use of the heat produced in exothermic reactions between metal nitrates and urea [**8, 9**].Recently, interesting and low cost synthesis reported in the literature for development of phosphors for different applications [**10-18**]. In order to improve the performance of PDP devices, novel phosphors with high luminescent efficiency and stability have been searched [**19**]. Under the investigation of red, green and blue phosphors for X-ray storage screen is the requirement of recent research work, due to product of every one phosphor industry has some drawback in term of full characterization of phosphors. Therefore, under investigation, development of new phosphors for X-ray storage screen by low cost synthesis technique. In this paper, we report combustion synthesis of some phosphors for PDP. The phosphors so prepared were characterized by XRD, PL and X-ray excited luminescence (XEL) techniques.

Experimental

Metal nitrates in stoichiometric ratios were mixed thoroughly with urea. Due to presence of large water of crystallization of aluminium nitrate, a thick paste was formed. Nitrate to urea ratio was calculated as desribed in the original paper [**8, 9**]. A porcelain dish containing the paste was inserted in the furnace heated to 500^{o}C. Within minutes the paste foamed and the flame was produced which lasted for several seconds. The porcelain dish was immediately removed from the furnace. X-ray diffraction patterns were recorded on Philips PANalytical x'pert Pro diffractometer. PL characteristics were studied using a Hitachi F-4000 spectroflourometer, at room temperature, using 1.5 nm spectral slit width in the range 200-700 nm. For studying XEL, X-rays use in the experiment it's from 20 kV, 10 mA source was allowed to fall on the samples. The emitted light was analysed using a fibre based spectro-fluorimeter (Ocean Optics USB-2000).

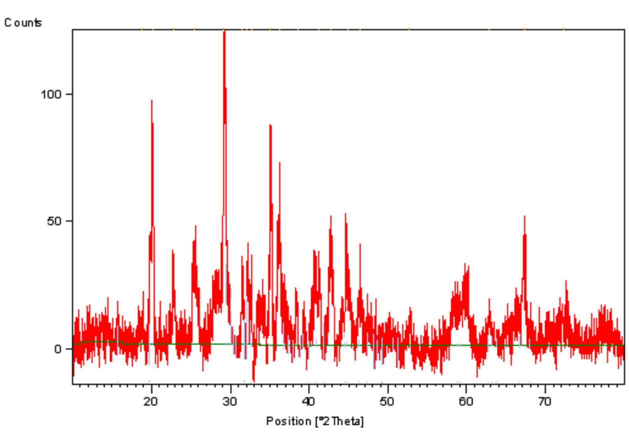

Fig. 1. XRD pattern of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor

Results and discussion

XEL measurements

In this paper, we report X-ray excited luminescence (XEL) of phosphors for all three primary colors i.e. blue, green and red using well known reported experimental setup[**20**]. All these phosphors were synthesized in our laboratory using combustion technique. Combustion synthesis furnishes a one step method for preparing this material. Formation of Blue phosphor- $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor, Green phosphor- $Ba_{0.975}Al_{12}O_{19}:Mn^{2+}{}_{0.025}$ phosphor, Red phosphor - ($Y_{0.65}$, Gd0.30) BO_3 :$Eu^{3+}{}_{0.05}$ phosphor was confirmed by XRD technique.

$Sr_3Al_{10}SiO_{20}:Eu^{2+}$ blue phosphor

Earlier, $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor was reported as a PDP phosphor with emission at 466nm by VUV excitation [**21**].In the present work $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor is synthesized by combustion method and annealed at 1100^{0}C. The XRD showed that the prepared compound was mixed phase (**Fig. 1**). Apart from $Sr_3Al_{10}SiO_{20}$, $Sr_3Al_9SiO_{18.5}$ was also present. In previous work the compound was prepared by the solid state reaction at temperatures between 1500-1700^{o}C [**21**]. It is likely that such temperatures were not attained during the combustion synthesis. Further studies with different Si source and/or fuel are necessary.

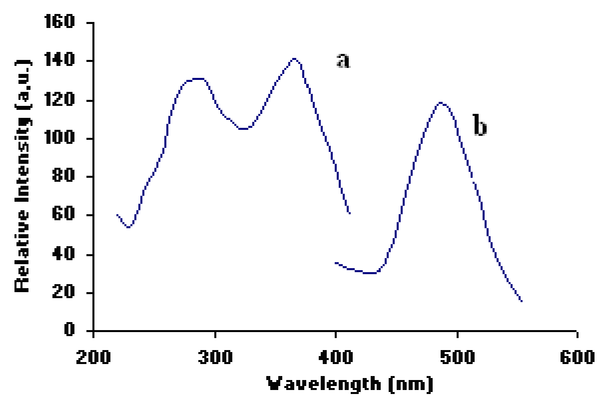

Fig 2. Photoluminescence spectra of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor (**a**) excitation curve monitor at 486nm and (**b**) emission curve at λex=365 nm.

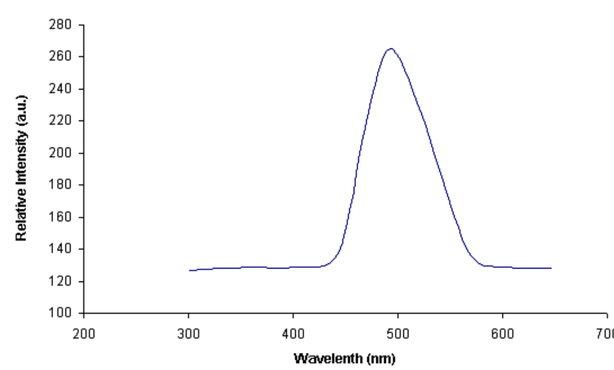

Fig. 3. X-ray excited luminescence of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$.

The PL results of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor are shown in **Fig. 2**.The PL emission observed at 486 nm (λex = 365 nm) is due to Eu^{2+} ion in the blue region of the spectrum. **Fig. 3** shows the XEL spectra of $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor. The XEL peak is observed at 492 nm in the blue region of spectrum .The PL results and XEL results matced very well (only 6nm difference). Therefore, the XEL peak at 492 nm much to be due to $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+} ion . The $Sr_3Al_{10}SiO_{20}:Eu^{2+}$ phosphor may be useful as blue XEL phosphor for X-ray imaging.

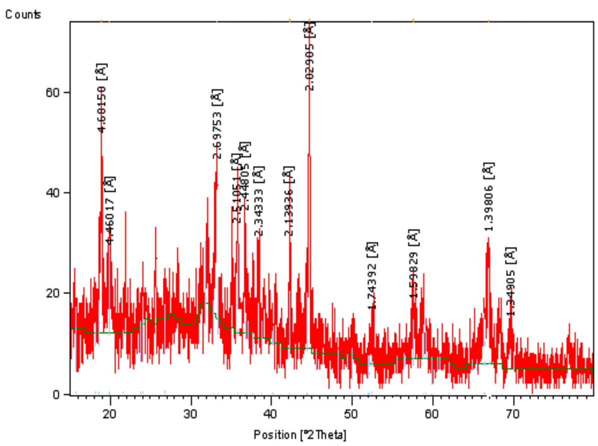

Fig. 4. XRD pattern of $BaAl_{12}O_{19}:Mn^{2+}$.

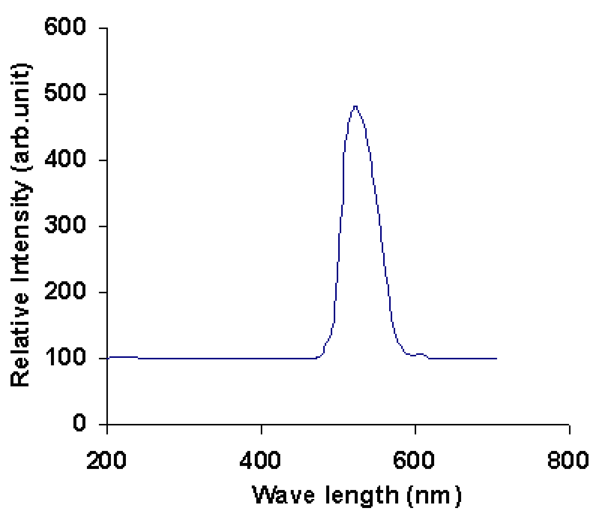

Fig. 5. X-ray excited luminescence of $BaAl_{12}O_{19}:Mn^{2+}$.

$Ba_{0.975}Al_{12}O_{19}$: $Mn^{2+}_{0.025}$ green phosphor

Lee *et.al* reported 516 nm emission by VUV excitation in the $Ba_{0.975}Al_{12}O_{19}$: $Mn^{2+}_{0.025}$ PDP phosphor [**22**].$Ba_{0.975}Al_{12}O_{19}$: $Mn^{2+}_{0.025}$ phosphor prepared by combustion synthesis and XEL characterization are reported here. The XRD pattern (**Fig. 4**) matched with the standard XRD JCPDs file. $Ba_{0.975}Al_{12}O_{19}:Mn^{2+}_{0.025}$ phosphor do not show any PL emission after UV excitation. Therefore, use of this material is very difficult in lamp industry. The XEL spectra of this phosphors is shown in **Fig. 5** .The XEL strong emission peak observed at 520 nm in the green region of the spectrum is due to $^4T_1 \rightarrow ^6A_1$ transition of Mn^{2+}ion.The green XEL emission of $Ba_{0.975}Al_{12}O_{19}:Mn^{2+}_{0.025}$ phosphor may be used as X-ray imaging phosphor.

$(Y_{0.65},Gd_{0.30})BO_3:Eu^{3+}_{0.05}$ red phosphor

The most widely used red emitting phosphor for PDP is $(Y_{0.65},Gd_{0.30})BO_3:Eu^{3+}_{0.05}$ for which the emission is observed at 595,617 and 702 nm by VUV excitation [**23,24**]. Here, $(Y_{0.65},Gd_{0.30})BO_3:Eu^{3+}_{0.05}$ phosphor prepared by combustion synthesis is calcinated at 850°c for 1hr. **Fig. 6** shows XRD pattern of $(Y_{0.65},Gd_{0.30})BO_3:Eu_{0.05}$ which matched excellently with the XRD pattern reported by Jong Rak Sohn et al. [**25**]. **Fig. 7** shows the PL excitation and emission spectra of $(Y_{0.65},Gd_{0.30})BO_3:Eu^{3+}_{0.05}$ phosphor. The excitation spectrum shows the prominent peak at 234nm. This band was assigned to the charge transfer (CT) transition within the Eu^{3+} - oxygen center. Another weak peak is observed at 275nm, due to the transition $^8S_{7/2} \rightarrow ^6I_{2/11}$ of Gd^{3+}, overlapping with the tail of the CT band. This implies that the energy transfer from Gd^{3+} to Eu^{3+} had taken place. Under the 234nm excitation, the emission peaks are observed at 595nm, 612nm, and 624nm due to $^5D_0 \rightarrow ^7F_1$,$^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ transitions of Eu^{3+} ion in the orange – red and red region of the spectrum (**Fig. 7**).

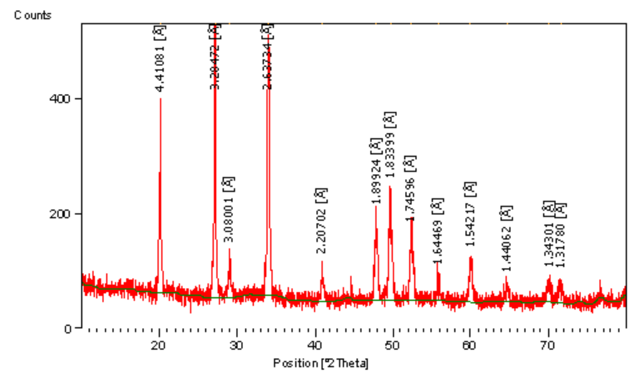

Fig. 6. XRD pattern of $(Y_{0.65},Gd_{0.30})BO_3:Eu_{0.05}$

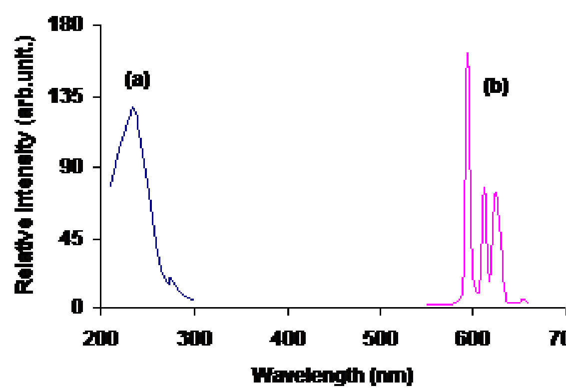

Fig. 7. (**a**)excitation spectra of $Y_{0.65}Gd_{0.30}(BO_3):Eu_{0.05}$ (**b**)emission spectra of $Y_{0.65}Gd_{0.30}(BO_3):Eu_{0.05}$.

XEL of $(Y_{0.65},Gd_{0.30})BO_3:Eu^{3+}_{0.05}$, is shown in **Fig. 8** The spectrum is bit noisy due to lesser sensitivity and poorer resolution of the fiber optic spectrometer. The maximum XEL peak observed at 596nm and 611nm in the red region of the spectrum due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ion .This is in good agreement with the literature value for the VUV excited luminescence. The observed XEL peaks are broad and slightly at longer wavelengths as compared to PL spectra. The broadness of the peak is due to overlapping of two peaks, in XEL spectra. The separation of peak is not observed in XEL spectra as compared to PL emission spectra.

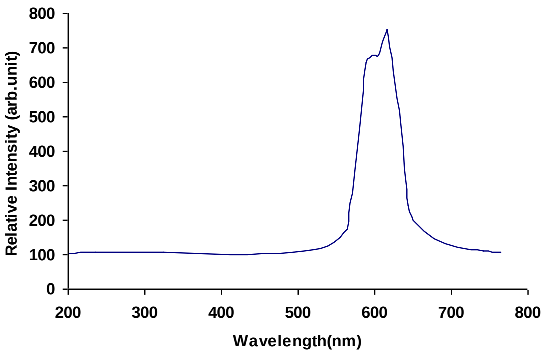

Fig. 8. X-ray excited luminescence of $Y_{0.65}Gd_{0.30}$ (BO_3):$Eu_{0.05}$.

XEL spectra of $(Y_{0.65}$, $Gd_{0.30})BO_3$:$Eu^{3+}{}_{0.05}$ shows that the Eu^{3+} emission is dominated by 611nm line corresponding to $^5D_0 \rightarrow {}^7F_2$ transition . Emission corresponding to $^5D_0 \rightarrow {}^7F_1$ is not properly resolved in XEL the strong XEL emission is thus observed at 596nm and 611nm in red region of the spectrum by X-ray excitation. This characteristic of $(Y_{0.65}$,$Gd_{0.30})BO_3$:$Eu^{3+}{}_{0.05}$ PDP phosphor is useful for X-ray imaging screen.

Conclusion

The well known PDP phosphors, $Sr_3Al_{10}SiO_{20}$:Eu^{2+} blue phosphor, $Ba_{0.975}Al_{12}O_{19}$:$Mn^{2+}{}_{0.025}$ green phosphor and $(Y_{0.65}$,$Gd_{0.30})$ BO_3 :Eu^{3+} $_{0.05}$ red phosphor are synthesized by one step combustion technique. XEL emission band observed at 492 nm, 520 nm and 611nm in the blue, green and red region of the spectrum respectively. Finally, from the obtained XEL emission spectra of above prepared phosphors may be applicable as blue, green and red phosphor in X-ray imaging screen.

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