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

J.G. Mahakhode¹, S.J. Dhoble², S.V. Moharil¹

¹Department of Electronics, D.B.Science College, Gondia, India
²Department of Physics, R.T.M Nagpur University, Nagpur 440033, India

Corresponding author. E-mail: jgmahakhode@yahoo.co.in, sjdhoble@rediffmail.com, svmoharil@yahoo.com

Received: 26 April 2011, Revised: 22 July 2011 and Accepted: 26 July 2011

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. Copyright © 2011 VBRI press.

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

J.G. Mahakhode obtained M.Sc. in Electronics from Amravati University, Amravati, India in 1987. He had been awarded with Ph.D. degree in optoelectronics display Materials by RTM Nagpur University, Nagpur, Maharashtra state, India, in the beginning of 2008. Dr. Jayant Gulabrao Mahakhode, is presently working as an Associate professor and Head Of the Department in Department of Electronics, Dhote Bandhu Science College, Gondia, Maharashtra state, India. There are some National and international research papers published in the refereed journal. He had work on display materials of OLED, Solid state lighting, X-ray imaging screen, PLLCD, FED, CRT and PDP phosphor.

S.J. Dhoble obtained M.Sc. degree in Physics from Rani Durgavati University, Jabalpur, India in 1988. He obtained his Ph.D. degree in 1992 on Solid State Physics from Nagpur University, Nagpur. Dr. S.J. Dhoble is presently working as an Associate Professor in Department of Physics, R.T.M. Nagpur University, Nagpur, India. During his research carrier, he is involved in the synthesis and characterization of solid state lighting nanomaterials as well as development of radiation dosimetry phosphors using thermoluminescence, mechano luminescence and lyoluminescence techniques. Dr. Dhoble published several research papers in International reviewed journals on solid-state lighting, LEDs, radiation dosimetry and laser materials. He is an executive member of Luminescence Society of India.

S.V. Moharil did his M.Sc. from Nagpur University, Nagpur, India. After having awarded Ph.D. degree in 1974 he joined Department of Physics, Nagpur University, Nagpur, India in 1983. He has also awarded D.Sc. degree in physics in 1984. Presently he is Head, Department of Physics, R.T.M. Nagpur University, Nagpur, India. He has number of research papers published in National and International journals. His field of interest is development and characterization phosphors for lamp industry and radiation dosimetry.

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 Y₂O₃: Eu and (Y, Gd) BO₃: Eu for red, BaMgAl₁₁O₁₇: Eu for blue and Zn₂SiO₄: Mn for green, which were already established as lamp/CTV phosphors, were used as PDP materials. However, several problems have arised. Y₂O₃: Eu phosphor has low luminescence efficiency. (Y,Gd)BO₃: Eu has poor color purity because of the orange-red emission instead of red [5],Zn₂SiO₄: Mn is known to have a long decay time and a high discharging voltage [6],BaMgAl₁₁O₁₇: 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 has been achieved 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 described in the original paper [8, 9]. A porcelain dish containing the paste was inserted in the furnace heated to 500°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 spectrofluorometer, 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 spectrofluorimeter (Ocean Optics USB-2000).

**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_{3}Al_{10}SiO_{20}:Eu^{2+} phosphor, Green phosphor B_{2}O_{3}Al_{2}O_{3}Mn^{2+} phosphor, Red phosphor - (Y_{0.65}, Gd0.30) BO_{3}:Eu^{3+} phosphor was confirmed by XRD technique.

**Sr_{3}Al_{10}SiO_{20}:Eu^{2+} blue phosphor**

Earlier, Sr_{3}Al_{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_{3}Al_{10}SiO_{20}:Eu^{2+} phosphor is synthesized by combustion method and annealed at 1100°C. The XRD showed that the prepared compound was mixed phase (Fig. 1). Apart from Sr_{3}Al_{10}SiO_{20}, Sr_{3}Al_{9}SiO_{18.5} was also present. In previous work the compound was prepared by the solid state reaction at temperatures between 1500-1700°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. 1. XRD pattern of Sr_{3}Al_{10}SiO_{20}:Eu^{2+} phosphor](image)

![Fig. 2. Photoluminescence spectra of Sr_{3}Al_{10}SiO_{20}:Eu^{2+} phosphor (a) excitation curve monitor at 486nm and (b) emission curve at λ_{ex}=365 nm.](image)

![Fig. 3. X-ray excited luminescence of Sr_{3}Al_{10}SiO_{20}:Eu^{2+}.](image)
The PL results of $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}:\text{Eu}^{2+}$ phosphor are shown in Fig. 2. The PL emission observed at 486 nm ($\lambda_{ex} = 365$ nm) is due to $\text{Eu}^{2+}$ ion in the blue region of the spectrum. Fig. 3 shows the XEL spectra of $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}:\text{Eu}^{2+}$ phosphor. The XEL peak is observed at 492 nm in the blue region of spectrum. The PL results and XEL results matched very well (only 6 nm difference). Therefore, the XEL peak at 492 nm much to be due to $4f^75d \rightarrow 4f^7$ transition of $\text{Eu}^{2+}$ ion. The $\text{Sr}_3\text{Al}_{10}\text{SiO}_{20}:\text{Eu}^{2+}$ phosphor may be useful as blue XEL phosphor for X-ray imaging.

$\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ green phosphor

Lee et al. reported 516 nm emission by VUV excitation in the $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ PDP phosphor [22]. $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ phosphor prepared by combustion synthesis and XEL characterization are reported here. The XRD pattern (Fig. 4) matched with the standard XRD JCPDs file. $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ 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 $^4\text{T}_{1} \rightarrow ^6\text{A}_1$ transition of $\text{Mn}^{2+}$ ion. The green XEL emission of $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ may be used as X-ray imaging phosphor.

$\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ red phosphor

The most widely used red emitting phosphor for PDP is $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ for which the emission is observed at 595, 617 and 702 nm by VUV excitation [23, 24]. Here, $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ phosphor prepared by combustion synthesis is calcinated at 850°C for 1 hr. Fig. 6 shows XRD pattern of $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ 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 $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ phosphor. The excitation spectrum shows the prominent peak at 234 nm. This band was assigned to the charge transfer (CT) transition within the $\text{Eu}^{3+}$-oxygen center. Another weak peak is observed at 275 nm, due to the transition $^8\text{S}_{7/2} \rightarrow ^8\text{I}_{21/2}$ of $\text{Gd}^{3+}$, overlapping with the tail of the CT band. This implies that the energy transfer from $\text{Gd}^{3+}$ to $\text{Eu}^{3+}$ had taken place. Under the 234 nm excitation, the emission peaks are observed at 595 nm, 612 nm, and 624 nm due to $^8\text{D}_0 \rightarrow ^8\text{F}_5$, $^8\text{D}_0 \rightarrow ^8\text{F}_2$ and $^8\text{D}_0 \rightarrow ^8\text{F}_3$ transitions of $\text{Eu}^{3+}$ ion in the orange-red and red region of the spectrum (Fig. 7).

$\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ green phosphor

Lee et al. reported 516 nm emission by VUV excitation in the $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ PDP phosphor [22]. $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ phosphor prepared by combustion synthesis and XEL characterization are reported here. The XRD pattern (Fig. 4) matched with the standard XRD JCPDs file. $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ 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 $^4\text{T}_{1} \rightarrow ^6\text{A}_1$ transition of $\text{Mn}^{2+}$ ion. The green XEL emission of $\text{Ba}_{0.975}\text{Al}_{12}\text{O}_{19}:\text{Mn}^{2+}$ may be used as X-ray imaging phosphor.

$\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ red phosphor

The most widely used red emitting phosphor for PDP is $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ for which the emission is observed at 595, 617 and 702 nm by VUV excitation [23, 24]. Here, $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ phosphor prepared by combustion synthesis is calcinated at 850°C for 1 hr. Fig. 6 shows XRD pattern of $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ 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 $\text{(Y}_{0.65}\text{Gd}_{0.30})\text{BO}_3: \text{Eu}^{3+}$ phosphor. The excitation spectrum shows the prominent peak at 234 nm. This band was assigned to the charge transfer (CT) transition within the $\text{Eu}^{3+}$-oxygen center. Another weak peak is observed at 275 nm, due to the transition $^8\text{S}_{7/2} \rightarrow ^8\text{I}_{21/2}$ of $\text{Gd}^{3+}$, overlapping with the tail of the CT band. This implies that the energy transfer from $\text{Gd}^{3+}$ to $\text{Eu}^{3+}$ had taken place. Under the 234 nm excitation, the emission peaks are observed at 595 nm, 612 nm, and 624 nm due to $^8\text{D}_0 \rightarrow ^8\text{F}_5$, $^8\text{D}_0 \rightarrow ^8\text{F}_2$ and $^8\text{D}_0 \rightarrow ^8\text{F}_3$ transitions of $\text{Eu}^{3+}$ ion in the orange-red and red region of the spectrum (Fig. 7).
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.

![Graph showing X-ray excited luminescence of \(Y_{0.65}Gd_{0.30}(BO_3)_3:Eu^{3+}_{0.05}\)](image)

**Fig. 8.** X-ray excited luminescence of \(Y_{0.65}Gd_{0.30}(BO_3)_3:Eu^{3+}_{0.05}\).

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 \( ^5D_0 \rightarrow ^7F_1 \) transition. Emission corresponding to \( ^5D_0 \rightarrow ^7F_2 \) 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, \(Sr_2Al_5O_{12}:Eu^{2+}\) blue phosphor, \(Ba_9O_{26}Al_{15}O_{26}:Mn^{2+}_{0.025}\) 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.

**Reference**

1. Bizarri G, Moine B., J. Lumin., 2005, 115, 53
   DOI: 10.1016/j.jlumin.2005.02.018
2. Pankratova V., Kirmb M., Von Seggern H., J. Lumin., 2005, 113, 143
   DOI: 10.1016/j.jlumin.2004.09.117
3. Zhang Y., Li Y., Yin Y., J. Alloys Compd., 2005, 400, 222
   DOI: 10.1016/j.jallcom.2005.04.001
4. Jung K.Y., Lee H.W., Kang Y.C., Park S.B., Yang Y.S., Chem. Mater., 2005, 17, 2729.
   DOI: 10.1021/cm050074f
5. Lin C.K., Pang M.L., Yu M., Lin J., J. Lumin., 2005, 114, 299.
   DOI: 10.1016/j.jlumin.2005.02.007
6. Lu S.W., Copeland T., Lee B.L., Tong W., Wagner B.K., Park W., Zhang F.J. Phys. Chem. Solids, 2001, 62, 777.
   DOI: 10.1016/S0032-3861(00)00252-3
7. Oshio S., Matsuoka T., Tanaka S., Kobayashi H., J. Electrochem. Soc., 1998, 145, 3903.
   DOI: org/10.1149/1.1838991
8. Kingsley J.J., Suresh K., H.K.C., J. Mater. Sci., 1990, 25, 1305.
   DOI: 10.1007/BF00585441
9. Kingsley J.J., Manickam N., Patil K.C., Bull. Mater. Sci., 1990, 13, 179.
   DOI: 10.1007/BF0249444.
10. Shinde K.N., Dhole S.J.; Micro & Nano Letters, 2010, 5, 340.
    DOI: 10.1049/mnl.2010.0129
11. Shinde K.N.; Dhole S.J.; Adv. Mat. Lett., 2010, 1(3), 254.
    DOI: 10.5185/amlett.2010.9164
12. Dhole S.J.; Pawade V.B.; Shinde K.N.; Eur. Phys. J. Appl. Phys., 2010, 52, 11104.
    DOI: 10.1051/epjap/2010.122.
13. Kalyani, N. Thejo ; Dhole S.J.; Pode, R.B.; Adv. Mat. Lett. 2011, 2(1), 65.
    DOI: 10.5185/amlett.2010.10169.
14. Deshmukh, Abhay D.; Dhole S. J.; Dhole, N.S.; Adv. Mat. Lett. 2011, 2(1), 38.
    DOI: 10.5185/amlett.2010.10171.
15. Chauhan, V.; Yunus M.; Sankarakarnakrishnan, N. Adv. Mat. Lett. 2010, 1, 225.
    DOI: 10.5185/amlett.2010.6135
16. Goyal, R. K.; Damkale, S. R.; Mulik, U. P.; Negi, Y. S.; Dadke, J. W.; Aiyer, R. C. Adv. Mat. Lett. 2010, 1, 264.
    DOI: 10.5185/amlett.2010.8150.
17. Shukla, S. K.; Bharadvaja, A.; Tiwari, A.; Parashar, G. K.; Dubey, G. C. Adv. Mat. Lett. 2010, 1, 129.
    DOI: 10.5185/amlett.2010.3105.
18. Singh, N.K.; Kumar, P.; Kumar, H.; Rai, R.; Adv. Mat. Lett., 2010, 1(1), 79.
    DOI: 10.5185/amlett.2010.3102.
19. Toda Kenji, J. Alloys and Compounds, 2006, 408–412, 665
    DOI: 10.1016/j.jallcom.2005.01.080.
20. Dhole S.J., Nagpure I.M., Mahakhode J.G., Godbole S.V., Bhide M.K., Moharil S.V., Nucl. Instrum. and Methods in Phys. Research B, 2008, 266, 3437
    DOI: 10.1016/j.nimb.2008.05.010.
21. Kubota S., Shimada M., Appl. Phys. Lett., 2002, 81, 2749
    DOI: 10.1063/1.1512306.
22. Lee D.Y., Kang Y.C.; Park H.D., Ryu S.K., J. Alloys Compd., 2003, 353, 252
    DOI: 10.1016/S0925-8388(02)01197-0.
23. Chadeyron G., Mahiou R., Arbus M.ELGhozzi A., Zambon D., Cousseins J.C.; J. Solid State Chem., 1997, 23, 72-74, 564
    DOI: 10.1016/S0022-4596(96)00191-3.
24. Chadeyron G., Mahiou R., Arbus M.ELGhozzi A., Zambon D., Cousseins J.C.; Solid State Chem., 1997, 128, 261
    DOI: 10.1016/S0038-1098(96)001696-7.
25. Sohn Jong Rak, Kang Yun Chan, Park Hee Dong and Yoon Soon Gil, Jpn. J. Appl. Phys., 2002, 41, 6007
    DOI: 10.1143/JAP.41.6007.
ADVANCED MATERIALS Letters

Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

Submit your manuscript: http://amlett.com/submitanarticle.php