www.vbripress.com, www.amlett.com, DOI: 10.5185/amlett.2011.3071am2011 Published online by the VBRI press in 2011

Eu^{3+} and Dy^{3+} activated $Sr_2V_2O_7$ phosphor for solid state lighting

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Received: 26 April 2011, Revised: 22 July 2011 and Accepted: 29 July 2011

ABSTRACT

Eu^{3+} and Dy^{3+} doped strontium vanadium oxide ($Sr_2V_2O_7$) phosphor has been successfully synthesized using solid state diffusion method and characterized by XRD as well as photoluminescence (PL) measurements. The PL emission of Eu^{3+} ion was observed in $Sr_2V_2O_7$ phosphor at 593 nm and 618 nm in orange and red region of the spectrum, which corresponds to $^5D_0 \rightarrow {}^7F_1, {}^5D_0 \rightarrow {}^7F_2$ transitions, at the excitation wavelength of 393 nm. The PL emission of Dy^{3+} ion was observed in $Sr_2V_2O_7$ phosphor at 484 nm and 575 nm in blue and yellow region of the spectrum, which corresponds to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, at the excitation wavelength of 349 nm. The 300 – 400 nm is Hg free excitation, which is characteristic of solid state lighting. Hence, $Sr_2V_2O_7$:RE [RE = Eu^{3+} and Dy^{3+}] phosphors may be efficient materials for solid state lighting.

Keywords: Phosphors; $Sr_2V_2O_7$; solid-state lighting; photoluminescence; XRD.

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Introduction

Rare earth luminescent materials have considerable practical applications in almost any device involving the artificial production of light, such as cathode ray tubes, lamps, and X-ray detectors, etc. [**1–7**].Recently Shinde et al [**8**] studied the influence of Li^+ doping on photoluminescence properties of $Sr_5(PO_4)_3:Eu^{3+}$. Deshmukh et al [**9**] studies the optical properties of $MAl_{12}O_{19}$:Eu (M = Ca,,Ba,Sr) nanophopshors. Europium ion is widely used as luminescent center in lots of phosphors for the exhibited characteristic red emission corresponding to its $^5D_0 \rightarrow {}^7F_2$ transition [**10,11**]. In the past years, the Eu^{3+}-activated YVO_4 has attracted considerable attention because of its broad application [**12**]. However, due to certain unperfected performance in luminescent intensity and color purity of the current commercial phosphors, much continuous work on the development of new high efficient phosphors still needs to be carried out. Recently, considerable efforts have been devoted to explore novel phosphors for white light-emitting diodes (W-LEDs) as they are replacing the traditional incandescent lamps and fluorescent lamps. Currently W-LEDs are preferred owing to low energy consumption and reduction of greenhouse gas emissions due to their high efficiency, long lifetime and environmentally friendly characteristics [**13-15**]. These W-LEDs can be generated by several different methods. The most promising techniques to obtain high quality phosphor converted white light-emitting diodes (PC-WLEDs) is to use red, green and blue light-emitting phosphor coated on a

near UV LED chip or the use of blue-emitting LEDs covered by green and a red phosphor, all encapsulated in epoxy resin[**16**].In order to fabricate excellent PC-WLEDs, the excitation wavelength of red phosphor should match the emission of the near UV LEDs (350-410nm) or blue LEDs (440-470nm),therefore the phosphor materials play an important role in PC-WLEDs. Ideally, white emission by an appropriate combination of near-UV LED suitable inorganic phosphors is desirable for signaling or illumination applications. It is thus necessary to develop efficient phosphor to convert the near-UV pump light with a range of 300-400nm into the visible wavelength [**17, 18**]. Recently rare earth doped vanadate phosphor have generated considerable attention owing to their long – wavelength excitation properties, which enable their use in LEDs, fluorescent lamps, and flat panel display(FPD) [**19-22**]. Eu $^{3+}$ ions, which have luminescence peaks at 593 nm and 618 nm due to the $^5D_0 \rightarrow {}^7F_1$,$^5D_0 \rightarrow {}^7F_2$ transitions have attracted much attention. Luminescent materials doped with Dy $^{3+}$ have drawn much interest for their white emission [**23, 24**]. Dy $^{3+}$ ions, which have luminescence in the 465-650 nm region due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions, have attracted much attention because of their light emission. In this paper we have reported $Sr_2V_2O_7$: RE [RE = Eu $^{3+}$ and Dy^{3+}] phosphor synthesis by solid state diffusion method and their luminescent properties were investigated. The prepared phosphors were also characterized by XRD technique.

Experimental

Eu^{3+} and Dy^{3+} doped strontium vanadium oxide ($Sr_2V_2O_7$) phosphor has been successfully synthesized using solid state diffusion method. The high purity (99.99%) starting materials were $SrCO_3$, V_2O_5, Eu_2O_3 and Dy_2O_3. The doping concentration of Eu^{3+} and Dy^{3+} were 0.1, 0.3, 0.5 and 1m%. Stiochiometric amounts of reagents were thoroughly mixed and ground using an agate mortar. The reaction mixture was taken in a high – purity silica crucible and slowly heated in an electrical furnace at 750^{0}C for 24 h and then cooled down to room temperature to obtain white powder. The reaction temperature was selected with reference to the work of Nikajima et al [**25**] they had prepared $M_2V_2O_7$(M=Ba,Sr,Ca) by solid state reaction . The reaction is as follows,

$$2\ SrCO_3 + V_2O_5 \rightarrow Sr_2V_2O_7 + 2CO_2\uparrow$$

The phase composition and phase structure were characterized by X-ray diffraction (XRD) pattern using a PAN – analytical diffractrometer. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample 2g was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. All the measurements were conducted at room temperature.

Results and discussion

Fig. 1 presents the XRD pattern of $Sr_2V_2O_7$:Eu $^{3+}$ phosphor prepared via solid state diffusion technique. The XRD pattern of prepared phosphor is shown by the stick pattern which matched well with the standard JCPDS file-00-030-1315.

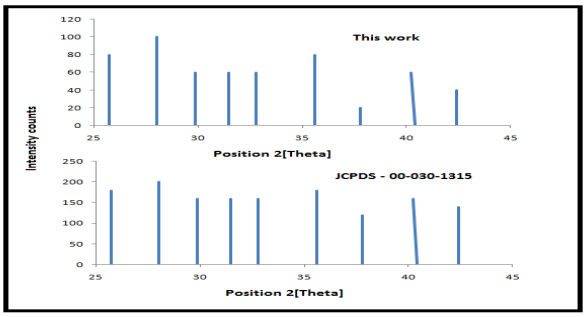

Fig. 1. XRD pattern of $Sr_2V_2O_7$: Eu^{3+} phosphor.

As presented in **Fig. 2** a broad band was observed in the wavelength region from 320 nm to 420 nm peaking at 392 nm. The broad band in the excitation spectrum originating from a charge transfer (CT) transition. This broad band took place by electron delocalization from an oxygen 2p orbital to an empty 4f orbital of europium ion. It was reported that the peak position of charge transfer band (CTB) is strongly depended on the Eu-O bond length [**26,27**].The excitation spectrum consist of an intense and broad excitation band centered at 392 nm, which is a CTB of Eu^{3+} - O^{2-} interaction and also due to V- O componants of the host matrices.The emission spectrum of all Eu^{3+} activated phosphors have been involved in the following emission lines of $^5D_0 \rightarrow {}^7F_1$and $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, which are determined by transitions between its f-electron energy levels.

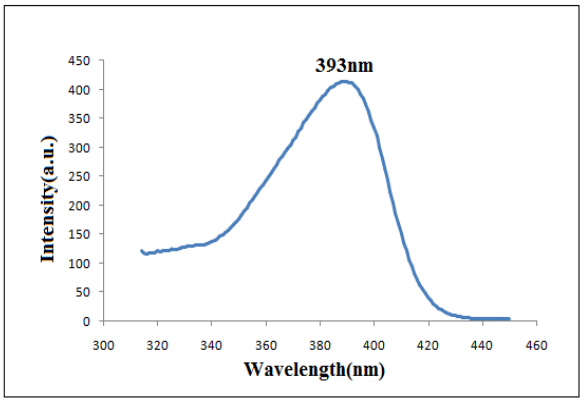

Fig. 2. Excitation spectra of $Sr_2V_2O_7$: Eu^{3+} phosphor.

Fig. 3 presents the emission spectrum of $Sr_2V_2O_7$:Eu^{3+} phosphor. We observed two emission peaks one at 595nm (orange region) and another at 618nm (red region).the orange line at around 593 nm originate from the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$, while the red line at around 618 nm originate from the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition by 393nm excitation i.e. solid state lighting excitation. From the emission spectrum of $Sr_2V_2O_7$:Eu^{3+} phosphor, we can find that peak position of the emission lines for all concentrations are almost same, but the intensity pattern of their luminescence spectrum shows maximum at 1mole% of Eu ion. According to the Judd–Ofelt theory, the magnetic dipole transition is permitted. However, the electric dipole

transition is allowed only when the europium ion occupies a site without an inversion center and the intensity is significantly affected by the symmetry in local environments around Eu^{3+} ions [**28**]. In this case the Eu^{3+} ion occupy an inversion symmetry site in the $Sr_2V_2O_7$ crystal lattice, the orange-red emission, magnetic transition $^5D_0 \rightarrow {}^7F_1$ (around 593 nm) is the dominant transition . On the contrary $^5D_0 \rightarrow {}^7F_1$ (around 610-620 nm). According to the emission spectra, it can be conclude that most Eu^{3+} ions have inversion centers and the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$(593nm) is dominant. All the PL characteristics indicate that prepared Eu activated $Sr_2V_2O_7$ phosphor may be good candidate for red emitting phosphor for lamp industry as a solid state lighting phosphor.

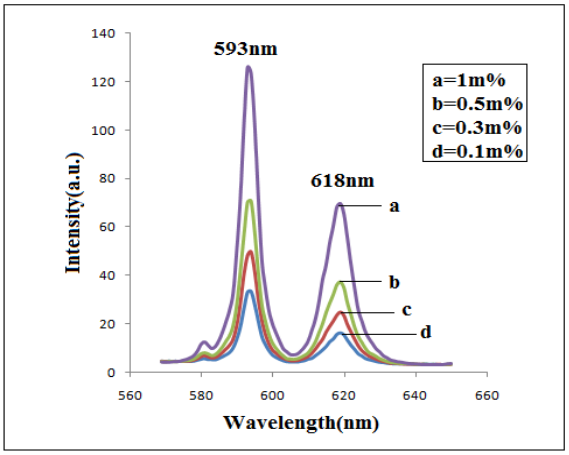

Fig. 3. Emission spectrum of $Sr_2V_2O_7$:Eu^{3+} phosphor.

Fig. 4 shows the excitation spectrum of $Sr_2V_2O_7$: Dy^{3+} phosphor which gives peak at 349 nm wavelength. Excitation spectrum reveals that a broad excitation band centered at 349 nm, which aroused due to the combination of charge transfer state corresponding to Dy^{3+} -O^{2-} interaction and the charge transfer from the oxygen ligand to the central metal atom inside the vanadate (V – O) host matrix.

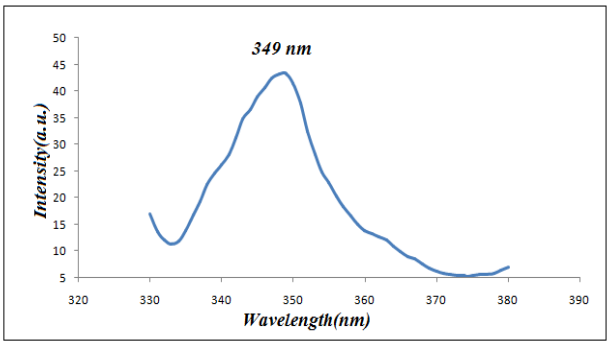

Fig.4 Excitation spectra of $Sr_2V_2O_7$: Dy^{3+} phosphor.

Fig. 5 shows the emission spectrum of $Sr_2V_2O_7$:Dy^{3+} phosphor. In this we observed two peaks one at 484 nm (blue region) and another at 575 nm (yellow region). The blue peak at 484 nm originate due to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition of Dy^{3+} ion and yellow peak a 575 nm originate due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} ion. From fig.5 we can also observe that as we increase the concentration of Dy^{3+} ion the intensity of phosphor increases.

Conclusion

An efficient Eu^{3+} and Dy^{3+} activated $Sr_2V_2O_7$ phosphor is synthesized via solid state diffusion method and confirmed by XRD pattern. Eu^{3+} gives PL emission at 593 nm (orange) and 618 nm (red) region of the wavelength. Dy^{3+} gives PL emission at 484 nm (blue) and 575 nm (yellow) region of the wavelength. All these PL results indicate that prepared Eu^{3+} and Dy^{3+} activated $Sr_2V_2O_7$ phosphors may be good candidates for lamp industry as a solid state lighting phosphor.

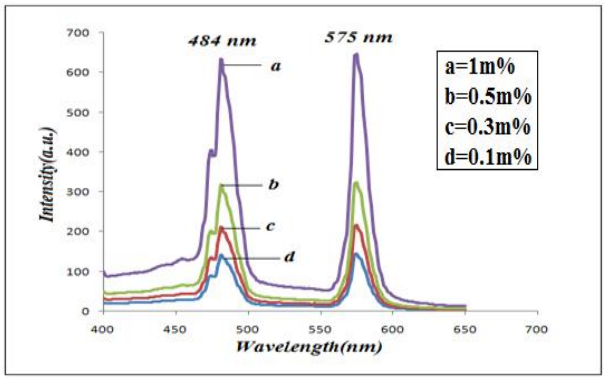

Fig. 5. Emission spectrum of $Sr_2V_2O_7$:Dy^{3+} phosphor.

Acknowledgements

Authors also, thankful to the 2009, Ontario Ministry of Agriculture, Food and Rural Affairs (OMAFRA) – New Directions & Alternative Renewable Fuels Research Program Project number SR9225 for the financial support to carry out this research. Authors would like to acknowledge the University of Guelph, 2009 President's Research Assistantship for providing LC's summer 2010 fellowship.

Reference

1. Blasse, G.; Grabmeter, B.C., Luminescent Materials, Springer-Verlag, Berlin, **1994**.
2. Riwotzki, K.; Haase, M. J. Phys. Chem. B 105 **2001**,12709-12713. **DOI:** 10.1021/jp0113735
3. Chukova,O.; . Nedilko,S.; Moroz,Z.; Pashkovskyi,M. J. Lumin. 102-103 **2003,** 498-503. **DOI:**10.1018/S0022-2313(02)00595-1
4. Brito, H.F.; Malta,O.L.; Felinto, M.C.F.C. J. Alloys Compd. 344 **2002,** 293-297. **DOI:**10.1018/S095-8388(02)00372-9
5. Reisfeld,R.; Zelner,M.; Patra, A. J. Alloys Compd. 300-301 **2000,** 147-151. **DOI:**10.1016/S0925-8388(99)00714-8
6. Zhang, H.J.; Wang, J.Y.; Wang,C.Q.; Zhu, L.; Hu,X.B.; Meng,X.L. Jiang, M.H.; Chow,Y.T. Opt. Mater 23 **2003,** 449. **URL:** http://dx.doi.org/10.1016/S0925-3467(02)00337-3
7. Yan,R.X.; Sun, X.M. ; Wang,X.; Peng,Q. Li,Y.D. Chem. Eur. J. 11 , **2005,**. 2183.
8. ShindeK.N.;Dhoble,S.J.Adv.Mat.lett.**2010**,1(3),254-258 **DOI:**10.5185/amlett.2010.9161.
9. Deshamukh, A.D.; Dhoble, S.J.; Dhoble, N.S. Adv. Mat. Lett. 2(1), **2011**, 38-42. **DOI:**10.5185/amlett.2010.10171
10. Wang, L.S.; Lin,J.; Quan, Z.W. J. Rare Earths 22 (1) **2004,** 91.

11. Wang Y.H., Endo Tadashi, ; He, L.; Wu, C.F. J. Cryst. Growth, 268, **2004,** 568.
12. Nirwan ,F.M. Gundu Rao,T.K. ; Gupta ,P.K.; Pode , R.B. Phys. Status Solidi A 198, **2003,** ***447–456***.
    DOI: 10.1002/pssa.200306632
13. Wang, X.X.; Wang, J.; Shi, J.X.; Su, Q.; Gong, M.L. Mater. Res. Bull. 42 **2007,** 1669-1673.
    DOI:10.1016/j.materresbull.2006.11.029
14. Adrian,K.; Luminescent Materials and Applications, Wiley, England, **2008,** 81–82.
15. Blasse, G. Luminescence and Energy Transfer, Springer-Verlag, Berlin, **2006,** 1–41.
16. Nakajima, T.; Isobe, M. Tsuchiya,T. Ueda, Y. Kumagai, T. Nature Mater. 7, **2008,** 735-740.
    DOI:10.1038/nmat2244
17. Kruzhalov,A.V.; Shul'Gin,B.V.; Gavrilov,F.F.; Vasil'Eva, E.I.; Fotiev, A.A. Khodos,M.Ya.; Krongauz,V.G. Sov. Phys. J. 19 (3) **1976,** 281.
18. Rietveld, H.M. J. Appl. Crystallogr. 2, **1969,** 65.
19. Young (Ed.), R.A. The Rietveld Method, Oxford University Press, **1993**.
    DOI:10.1002/Crat.2170300412
20. Nakatsuka, A.; Ikuta, Y. Yoshiasa, A.; Iishi, K. Acta Cryst. C59, **2003,** i133-i135.
    DOI:10.1107/S0108270103023035
21. Nakajima, T.; Isobe, M.; Tsuchiya, T.; Ueda, Y.; Kumagai, T. J. Lumin. 129 **2009,** 1598-1601.
    DOI:10.1018/j.jlumin.2009.03.029
22. Singh, Roshani; Dhoble , S.J. Bull. Mater. Sci., (in press).
23. Xiu , Z.; Yang , Z.; Lu ,M.; Liu ,S.; Zaang , H.; Chan , G. J.Lumin.128 **, 2008,** 1162.
24. Liang , X.; Zhu , C. ; Yang ,Y.; Yuan , S. ; Chan, G. J.Lumin. 128, **2008,** 1162-1164
    DOI:10.1016/j.jlumin.2007.11.086
25. Nikajima, T.; Isobe, M.; Tsuchiya, T.; Ueda, Y.; Manabe T. Opt. Mater. 32, **2010,** 1618-1621.
    URL: http://dx.doi.org/10.1016/j.optmat.2010.05.021
26. Wei, Z.; Sun, L.; Liau,C.; Yin, J.; Jiang, X.; Yan, C. J. Phys. Chem. B 106**, 2002,** 10610-10617.
    DOI:10.1021/jp025967z
27. Wu, C.; Qin, W.; Qin, G.; Zhao, D.; Zhang, J.; Huang, S.; Lu, S.; Liu,H. appl. Phys. Lett. 82 **, 2003,** 520-522.
    DOI:101063/1.542685
28. Dexpert-Ghys, J. ; Mauricot, R. ; Faucher, M.D. J. Lumin. 27, **1996,** 203-215
    DOI :10.1018/S0022-2313(98)00094-4