

NEW OPTOELECTRONIC DEVICE PHOSPHOR EU CO-DOPED $Zn_2SiO_4:Mn$ GREEN EMITTER

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ABSTRACT

Optoelectronic device [display devices] are called human eye. Phosphor materials in the ceramic form are the inorganic and are silicate phosphors are very good in display devices. Zinc silicate doped with divalent manganese ions is well known for its high luminescence efficiency coupled with excellent color purity and application for lamps and cathode ray tubes as a green phosphor. The present paper reports the photoluminescence and characterization of Mn^{2+} activated Zn_2SiO_4 phosphors co-doped with Eu prepared via solid state reaction method. Analytical grade reagents with purity greater than 99% were used for the synthesis this material. The starting materials are ZnO, SiO_2 and MnO were mixed and ground thoroughly using mortar and pestle prior to this all the materials are weighed as per the required quantities. Then this mixture was fired at $1200^\circ C$ for 2 hours in a muffle furnace. Photoluminescence spectra were recorded at room temperature using Shimadzu-5301-RF Spectrofluorophotometer. The PL emission spectra of $Zn_2SiO_4:Mn$ and $Zn_2SiO_4:Mn, Eu$ emitted at 525nm, addition of Eu in $Zn_2SiO_4:Mn$ enhances the PL intensity by 100%. The mission at 525 nm is due to d-level spin-forbidden transition of Mn^{2+} (${}^4T_1 \rightarrow {}^6A_1$). The phosphors were characterized using XRD, SEM, EDS.

Key Words: Photoluminescence, X-ray diffraction, Scanning electron microscopy.

I. INTRODUCTION

The ceramic materials (Phosphors) should able to work in tough environment surrounded and bombarded by high energy Vacuum Ultra Violet (VUV), UV or electron beam radiations in any discharge tube. The plasma display panel (PDP) is increasingly gaining attention over conventional cathode ray tube (CRT)-based TVs as a medium of large format (60+”) television (TV), particularly high definition TVs (HDTVs). Improvements have been made not only in size but also in other areas such as resolution, luminescence efficiency, brightness, contrast ratio, power consumption, and cost reduction. The formation of a phosphor host and doping process by solid solution is critical and is highly dependent on the reaction temperature and conditions. Since the purity of starting chemicals is very important to the synthesis of phosphors, the required starting chemicals are typically 99.9%, 99.999% in purity. Required amounts of starting ingredients are mixed in the presence of an appropriate flux (if necessary) and fired at high temperatures ($1200^\circ C$) in air or in a controlled atmosphere (N_2 , C, CO, or N_2 with 2-5% of H_2). The luminescence properties of Mn doped zinc silicate nano-crystalline phosphors, already reported as well as known $Zn_2SiO_4:Mn^{2+}$ shows a strong green emission, since we know that Zn^{2+} and Mn^{2+} ions have similar oxidation states, and ionic radius. The tough materials in the ceramic form are the inorganic silicate phosphors; zinc silicate doped with divalent manganese ions is well known for its high luminescence efficiency coupled with excellent color purity and application for lamps

and cathode ray tubes as a green phosphor. Zn_2SiO_4 has been identified as a very suitable host matrix for many rare earth dopant ions with excellent luminescent properties in the blue, green and red spectral zones including its chemical stability. However last past few years, greater attention has been paid to the study of luminescence properties of rare earth ions (Mn^{2+} and Eu^{3+}) doped zinc silicate phosphors in powder and thin film forms with a view to examining their application for flat panel display devices for example as a plasma display panels, field emission displays and thin film electroluminescence devices etc., Therefore Rare earth ions are better candidates for luminescence centers relevant for PDP applications. The luminescence properties of Mn doped zinc silicate nano-crystalline phosphors, already reported as well as known which shows a strong green emission, since we know that Zn^{2+} and Mn^{2+} ions have similar oxidation states, and ionic radius.

II. EXPERIMENTAL

ZnO , SiO_2 and MnO and Eu_2O_3 were mixed and ground thoroughly using agate mortar and pestle prior to this all the materials are weighed as per the required quantities. Acetone is added to get uniform mixing of the oxides while grinding using agate mortar and pestle for 30 minutes. Analytical grade reagents with purity greater than 99% were used for the synthesis this material. Then the mixture was fired for $1200^\circ C$ for 2 hours and PL measurements were made. The received powder phosphors $Zn_2SiO_4:Mn$ and $Zn_2SiO_4:Mn, Eu$ was subjected for PL measurements in air. The powder phosphors are characterized using XRD, SEM, and EDS analysis. All the spectra were recorded at room temperature. The emission and the excitation spectra of the synthesized powders were characterized with a spectrofluorometer (Shimadzu RF 5301 PC) with xenon lamp as excitation source and using a spectral slit width of 1.5nm. All the spectra were recorded at room temperature. To identify the crystal phase, XRD analysis was carried out with a powder

diffractometer (Rigaku-D/max 2500) using $Cu K\alpha$ radiation. The excitations used are mainly 254nm which is resonant radiation of mercury which can be easily produced.

III. RESULTS AND DISCUSSION

3.1 Photoluminescence study

$Zn_{2-x}Mn_xSiO_4$ is a classical green emitting phosphor, and it has been used in many display applications, such as CFL, CRT, PDP etc. This paper reports on $Zn_2SiO_4:Mn$ and $Zn_2SiO_4:Mn, Eu$ green phosphor was synthesized using the solid-state reaction method. The excitation and emission spectra of $Zn_2SiO_4:Mn$ under 254, 261 and 270nm is presented in Fig.1A. The excitation and emission spectra of $Zn_2SiO_4:Mn, Eu$ under 254nm and 270nm is presented in Fig.1B. When Eu is added as co-dopant to $Zn_2SiO_4:Mn$ the PL intensity is increased by 100% when compared to $Zn_2SiO_4:Mn$ phosphor. The PL peak observed at 525 nm in these phosphors suggests their potential use as these green emitting phosphors in display devices. Table 1 shows the 525nm peak intensity under 254 and 270nm excitation wavelengths.

Table 1 525nm peak intensity under different excitation wavelengths

S.No.	Sample Name	525nm peak intensity under	
		$\lambda_{Ex}-254$ nm	$\lambda_{Ex}-270$ nm
1	$Zn_2SiO_4:Mn(1.1\%)$	485	280
2	$Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$	>1000	>1000

The strongest emission at 525nm is attributed to the charge transfer transition of Mn^{2+} due to resonance sensitization of Eu ions. The mission at 525 nm is due to d-level spin-forbidden transition of Mn^{2+} (${}^4T_1 \rightarrow {}^6A_1$). Finally the

experimental data show that 1.1% of Mn concentration in Zn_2SiO_4 and firing in air medium and addition of Eu as co-dopant lead to formation of good $Zn_2SiO_4:Mn$. Therefore we concluded that presence of Eu and SiO_2 concentrations having important role to achieve good PL intensity. $Zn_2SiO_4:Mn$ phosphors have been very important phosphor as a green component in the PDP application. The efforts have been made for the performance of $Zn_2SiO_4:Mn$ phosphors to the CFL application. SEM, XRD and EDAX are shown in the figures bellow.

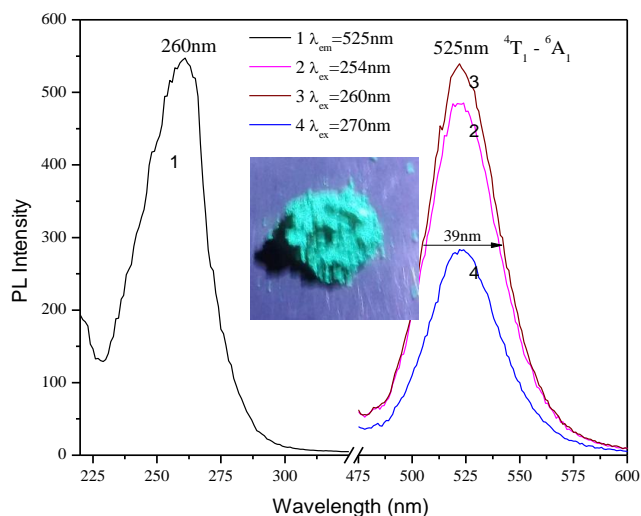


Fig.1A. PL Excitation and Emission Spectra of $Zn_2SiO_4:Mn(1.1\%)$ phosphor

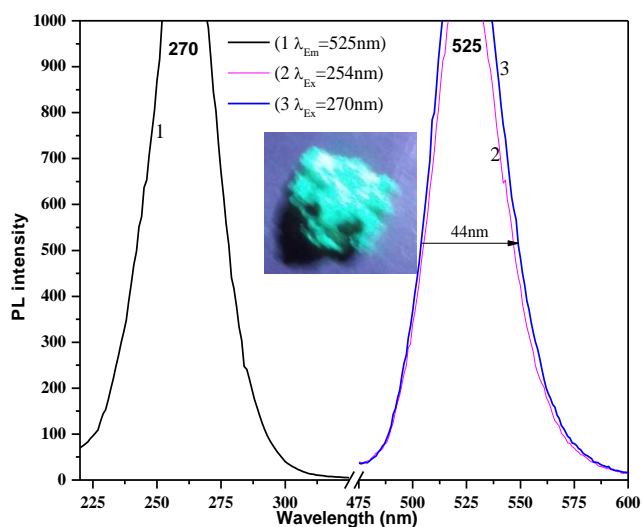


Fig.1B PL Excitation and Emission Spectra of $Zn_2SiO_4: Mn(1.1\%), Eu(1.5\%)$ phosphor

Photographs 1 and 2 (inserted in Fig.1A and 1B) are the $Zn_2SiO_4: Mn(1.1\%)$ and $Zn_2SiO_4: Mn(1.1\%), Eu(1.5\%)$ excited with 254nm 3 watts lamp. The same experimental conditions are maintained to photograph the phosphors. Photo 2 is more brighter than photo 1 which is due the PL out is more than 100% in the $Zn_2SiO_4: Mn(1.1\%), Eu(1.5\%)$ phosphor.

3.2 XRD study

The XRD patterns of $Zn_2SiO_4:Mn(1.1\%)$ and $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ are shown in Fig.2A. and 2B respectively.

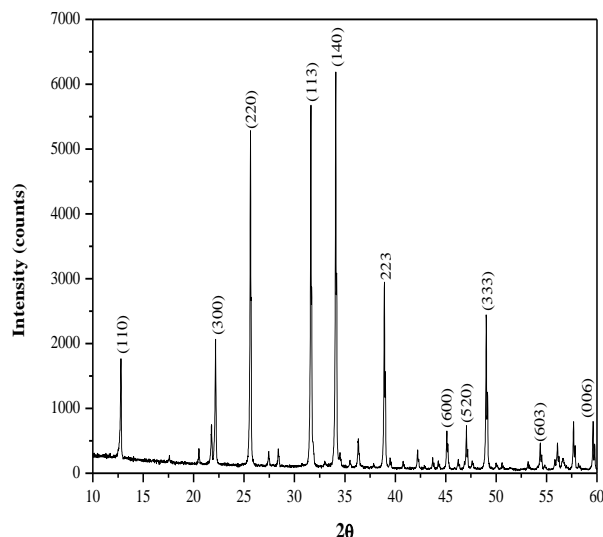


Fig.2A XRD pattern of $Zn_2SiO_4:Mn(1.1\%)$ phosphor

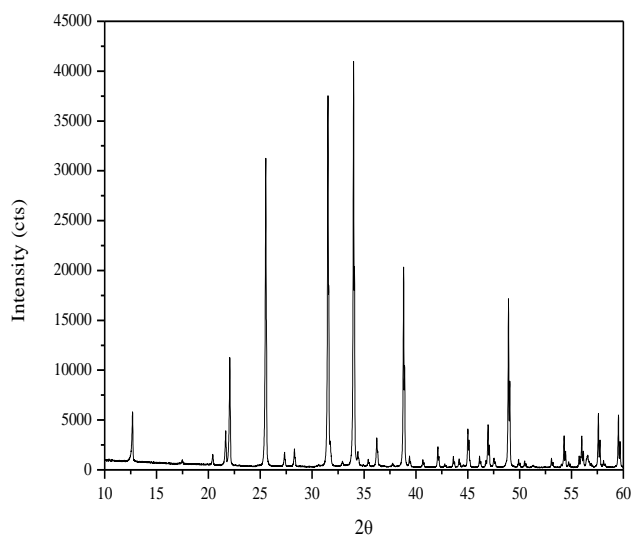


Fig.2B XRD pattern of $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphor

From the XRD pattern it was found that the prominent phase formed is Zn_2SiO_4 , after the diffraction peaks are well indexed based on the JCPDS No 85-0453. Good agreement between the observed and calculated inter-planer spacing

(d-values) suggests that the compound crystallizes in single phase. This reveals that the structure of Zn_2SiO_4 is Rhombohedral with space group $R\bar{3} (148)$. The crystallite size was calculated using the Scherrer equation $D = k\lambda / \beta \cos \theta$, where k the constant (0.94), λ the wavelength of the X-ray (0.154 nm or 1.54 Å), β the full-width at half maxima (FWHM) and θ the Bragg angle of the big XRD peak. The calculated average crystallite size of $Zn_2SiO_4:Mn(1.1\%)$ is ~ 85.5 nm and the $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ is ~ 96.5 nm. From fig.2A & 2B it is found that the diffraction peaks are same for all the phosphors which conclude that the dopant did not affect the host structure except change of the peak intensities ad increase of 12% of crystallite size.

3.3 SEM study

Fig.3A and 3B shows the SEM micrographs of the $Zn_2SiO_4:Mn(1.1\%)$ and $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphors. From the Scanning Electron Micrograph of $Zn_2SiO_4:Mn(1.1\%)$ with the measuring scale is 5microns it appears to be mostly irregular shape with smooth surface having an average basal diameter one to two microns. From SEM micrograph it is observed good particles having mostly diffrent shapes of varying sizes mostly agglomerated together are found in figure 3A.

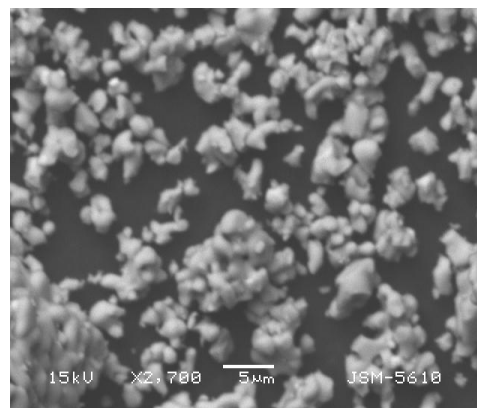


Fig.3A SEM image of $Zn_2SiO_4:Mn(1.1\%)$ phosphor

Fig. 3B shows the SEM micrograph of the $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphor prepared using SSR. From the Scanning Electron Micrograph of $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphor with the measuring scale is 5 microns it appears to be mostly irregular shape with smooth surface having an average basal diameter of one to two microns. From SEM micrograph it is observed good particles having mostly different shapes of varying sizes and agglomerated are found in figure 3B. On comparison figures 3A and 3B it is concluded that the particles are less agglomerated in $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphor. This type of formation may be due to the synthesis technique adopted for preparing the phosphor material.

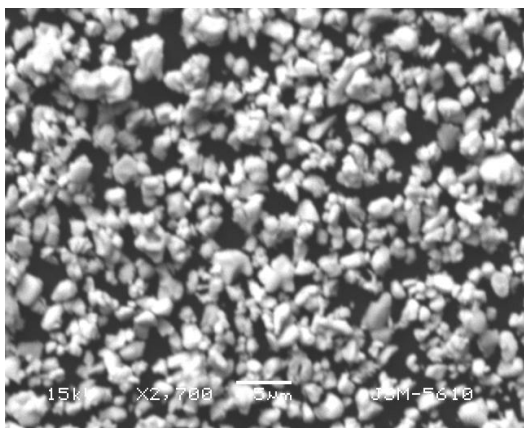


Fig.3B SEM image of $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$

Fig. 4A and 4B are the EDS of $Zn_2SiO_4:Mn^{2+}$ and $Zn_2SiO_4:Mn^{2+} Eu$, wherein there are no other elements observed except base elements. Therefore it is concluded the present phosphor is free of impurities.

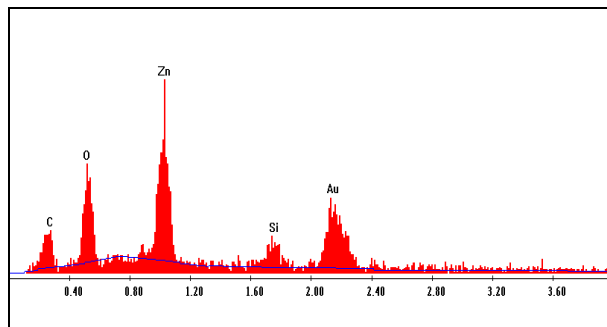


Fig.4A EDS of $Zn_2SiO_4 Mn(1.1\%)$

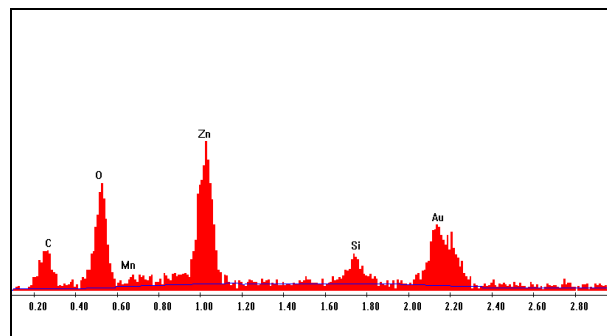


Fig.4B EDS of $Zn_2SiO_4:Mn(1.1\%)Eu (1.5\%)$

The figure-5 is the comparison of the sample holders of RF5301. 1. Is the (black) sample holder diameter is 25mm which is company supplied one. 2, 3 and 4 are the aluminum sample holders developed by us with 10, 6 and 3mm diameters. The present PL measurements were made using 6mm diameter sample holder. However the $Zn_2SiO_4:Mn, Eu$ PL emission goes out of range. This is the novel idea to use the new samples holders to record the PL within the range. However if the Shimadzu RF 5301 PC company can provide the auto ranging it will help the users at a great extent.

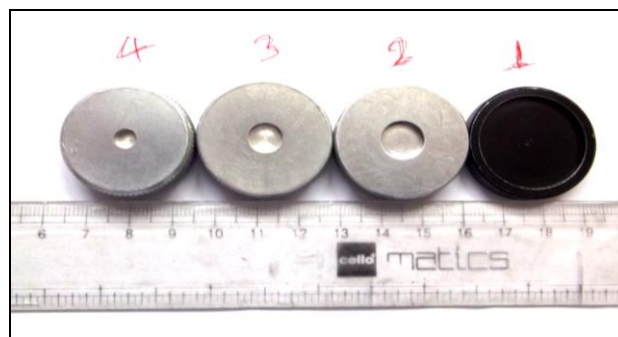


Fig.5 Different sized sample holders

3.4 CIE analysis:

Fig.6 shows the CIE colour co-ordinates of the $Zn_2SiO_4:Mn(1.1\%)$ and $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$ phosphors under 254nm excitation wavelength. The colour co-ordinates of the $Zn_2SiO_4:Mn$ phosphor are $x=0.178$ and $y=0.696$ and for $Zn_2SiO_4:Mn, Eu$ are $x=0.188$, $y=0.671$. From the figure the phosphors emitting green colour and are useful in producing white light in the field of lamps and display devices. The calculated correlated colour temperatures (CCT) are 7829K and 7780K. This allows us to conclude that the Eu doped phosphor is more suitable for display applications as a phosphor.

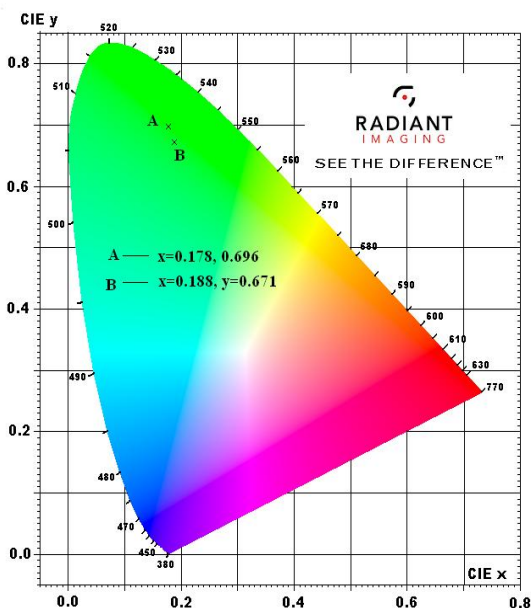


Fig. 6 CIE co-ordinates of the A) $Zn_2SiO_4:Mn(1.1\%)$ and B) $Zn_2SiO_4:Mn(1.1\%), Eu(1.5\%)$

IV. CONCLUSION

Optoelectronic device phosphor materials Zinc silicate doped with Mn and co-doped with Eu phosphors were prepared via high temperature solid state reaction in air medium. Overall results show that the PL intensity monitored at 525 nm with 254 nm excitations displays a good green emission from $Zn_2SiO_4:Mn^{2+}$ Eu phosphor

system The ${}^4T_1(4G) \rightarrow {}^6A_1(6S)$ transition, is directly responsible for the green emission at 525nm. It is concluded the Eu ions sensitizes the 525nm emission in $Zn_2SiO_4:Mn$ by 100%. The novel idea is to use the developed new samples holders to record the PL emission within the range. This concludes us the PL emission intensity is very high in both the samples $Zn_2SiO_4:Mn^{2+}$ and $Zn_2SiO_4:Mn^{2+} Eu$. The $Zn_2SiO_4:Mn^{2+} Eu$ phosphor can be a good candidate for PDP, CFL devices. By using $Zn_2SiO_4:Mn^{2+} Eu$ phosphors the total quantity in the device may be reduced by 40-50% which leads cost reduction of the phosphor component in the optoelectronic device.

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