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Luminescence properties of Zn co-doped Y_2O_3:Mn thin film phosphor for thick ceramic display devices

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Abstract

High-luminance yellow light emitting Zn co-doped Y_2O_3:Mn thin-film phosphor was fabricated employing less expensive sol-gel deposition method using the corresponding metallic complex salts. Addition of Zn in Y_2O_3 enhances the growth of monoclinic phase of Y_2O_3, crystal quality, photo luminescent (PL) and electro-luminescent (EL) emission properties. A high luminance of 2640 cd/m^2 was obtained using a 20 at% Zn doped Y_2O_3:Mn, whereas Zn un-doped Y_2O_3:Mn shows 240 cd/m^2 driven at 1 kHz.

Keywords: EL device, monoclinic Y_2O_3, sol-gel dip-coating, yellow emitting phosphor

1.0 INTRODUCTION

Rare earth and transition metal doped metal oxide powder phosphors are widely used in fluorescent lamps, plasma displays, field emission displays (FED) and white LEDs because of their high chemical stability over the sulfide phosphors [1-2]. However, in recent days, there is a growing trend towards the development of high luminance oxide TFEL devices that consist of binary or multi component oxides as the host materials Ga_2O_3, Y_2O_3 and Zn_2SiO_4, $ZnGa_2O_3$, $CaGa_2O_4$, Y_2O_3-Ga_2O_3,Y_2O_3-GeO_2 controlled chemical compositions, as EL layers [3-8]. Among these, Mn activated monoclinic Y_2O_3 is demonstrated as a new yellow emitting phosphor material for PL and TFEL devices and whereas cubic Y_2O_3 doesn't show any emission. However, the preparation of monoclinic phase Y_2O_3 thin film is tedious and specific preparation condition could be employed at high pressure [9]. Moreover, it is reported that co-doping of zinc ion to rare earth doped phosphors shows a sensible enhancement in the luminescent properties of the phosphor materials [10-15]. ZnO is chemically stable, n-type semi-conductor (Eg,3.3eV), transparent to visible radiation with excitonic emission in the UV region, it is widely used in optonic applications [16-18]. Y_2O_3 is an unsurpassed insulating phosphor host crystal (Eg,6eV) for various rare earth ions and extensively used in high efficiency lighting and display devices due to its inherent advantages of stability towards the high energy irradiations [19-21]. By considering these concepts, in this work, first time, we are reporting the growth of monoclinic phase Y_2O_3 thin film at ambient conditions by co-doping of Zn in Y_2O_3:Mn thin film phosphor using sol-gel deposition method. This method is simple and easy to prepare thin film phosphors for a significant improvement in the luminance for display device applications.

2.0 EXPERIMENTAL

Zn co-doped Mn activated Y_2O_3 thin films were deposited onto a $BaTiO_3$ ceramic substrate by sol-gel deposition method using yttrium acetyl acetonate, zinc acetyl acetonate and manganese di-chloride. The manganese concentration was fixed at 2 at% with respect to the yttrium concentration and the zinc concentration was varied from 5 to 20 at% with respect to the remaining yttrium concentration. In order to make the uniform distribution of metal ions, required amount of the corresponding salts were dissolved in methanol by stirring at room temperature (RT) for 30 minutes in N_2 atmosphere and subsequently, H_2O and HCl were added and stirred for 2 hrs to get clear sol-gel solution. Then the $BaTiO_3$ ceramic sheet substrate was dip coated in N_2 atmosphere and then heated at 600ºC for 10 minutes. This dip coating process was repeated for 15 to 20 times in order to obtain a thickness of about 2 µm. All the as deposited thin films were further post annealed at 1020ºC in a pure Argon atmosphere for 1 hour. In the final TFEL device fabrication process, a transparent conductive Al doped ZnO thin film was deposited on the phosphor thin film and Al electrode is deposited at the back side of the insulating $BaTiO_3$ ceramic sheet. The photoluminescence characteristics of all the post-annealed samples were evaluated using Shimadzu RF-5300 PC fluorescence spectrophotometer. The crystalline structure of Zn co-doped Y_2O_3:Mn thin film emitting layer were investigated by X- Ray diffraction (XRD) using Cukα radiation. The EL characteristics of the TFEL devices driven by an AC sinusoidal wave voltage at a frequency of 1 kHz were measured using a Sawyer-Tower circuit, power meter and conventional luminance meter.

3.0 RESULTS AND DISCUSSION

3.1 XRD Analysis

XRD pattern of Zn co-doped Y_2O_3-Mn thin film deposited at 600°C and post annealed at 1020°C for 1 hour in Argon atmosphere is shown in Fig.1 as a function of Zn concentration. All the XRD patterns are compared with a cubic (JCPDS- 43-1036) and monoclinic phase of Y_2O_3 (JCPDS-47-1274). Most of the diffraction peaks of the Zn co-doped Y_2O_3:Mn thin films can be identified to the monoclinic phase where no Zn addition shows a major cubic phase with a minor monoclinic phase formation. The addition of Zn ion (up to 10 at%), changed the crystal structure from cubic Y_2O_3 to monoclinic Y_2O_3 and further increase in Zn concentration enhances the monoclinic phase with better crystallinity. The crystallinity enhancement by Zn addition was also observed in our earlier report on the Zn co-doped Y_2O_3-Eu red phosphor for efficient CL properties [15].

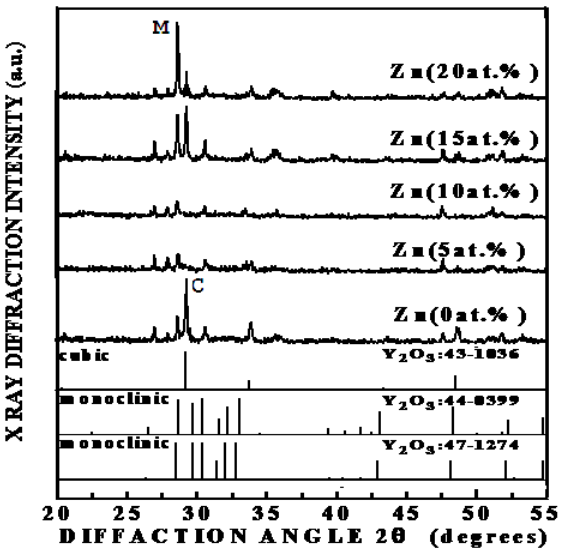

Fig. 1: X-ray diffraction patterns of Zn co-doped Y_2O_3-ZnO:Mn thin film phosphor prepared at various concentration of Zn deposited at 600°C and annealed at 1020°C

3.2SEM Analysis

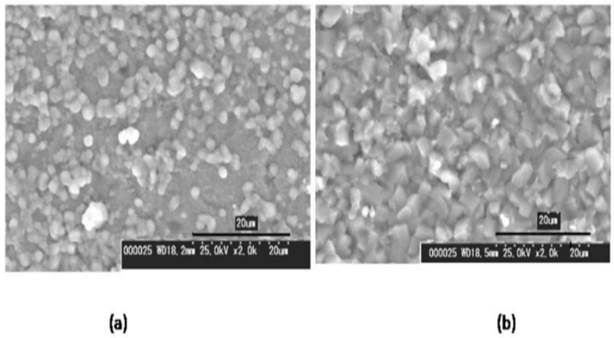

Fig. 2: SEM image of (a) Y_2O_3:Mn and (b) Zn co-doped (20at%) Y_2O_3:Mn thin film.

The micrographic analysis of Zn un-doped and Zn co-doped (20 at%) Y_2O_3:Mn thin film deposited on the thick ceramic $BaTiO_3$ substrate at a deposition temperature of 600°C and post annealed at 1020°C in Argon atmosphere are shown in Fig.2 a and b. It is interestingly observed that for the Zn un-doped phosphor, the particles formed are spherical in shapes in the range of 1-2 microns with a porous structure. However, the zinc co-doped phosphor thin film shows a formation of porous free closely packed particles in the range of 2-3 microns.

3.3 PL Spectra Analysis

The PL excitation and emission spectra of Y_2O_3-Mn (2 at%) doped with various concentrations of Zn at a deposition temperature of 600°C and post annealed at 1020°C in Argon atmosphere is given in Fig. 3a and b. The excitation band shows a broad band excitation which starts from 220 to 350 nm at the emission wavelength of 575 nm. This clearly shows that the manganese excitation originated from an intermixed host excitation viz,Y-O-Zn. However, PL emission spectra of this phosphor thin film show only a narrow band emission at 575 nm at the excitation of 330 nm due to the Mn luminescent center. This yellow emission is due to intrashell d-d transition of $^4T_1$ (^4G)-$^6A_1$(^6S) Mn^{2+} [7]. From the above figure, we can see that there is a drastic improvement of PL excitation and emission intensity when the concentration of the Zn increased in the deposition solution. The increase in PL intensity depends on the Zn content in the phosphor Y_2O_3-Mn thin film, may be due to the improvement in the crystallinity of the monoclinic phase of Y_2O_3 and close packing of deposited particles.

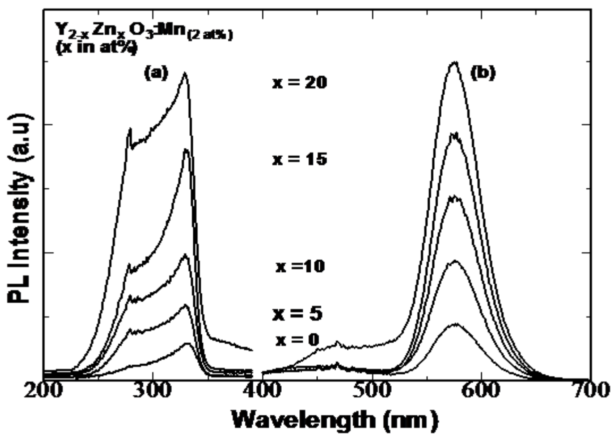

Fig. 3: Photo-luminescent excitation and emission spectra of Y_2O_3:Mn co-doped with various concentration of Zn at 600°C and annealed at 1020°C

3.4 EL Characteristics of Y_2O_3-ZnO:Mn TFEL Devices

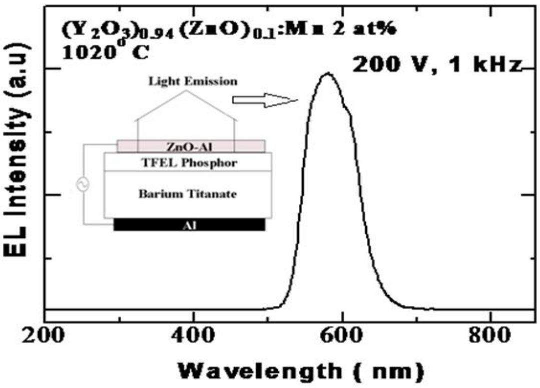

Fig. 4: EL emission spectrum of Zn co-doped (10at%) Y_2O_3:Mn(2at%) thin film phosphor

Fig. 4 shows EL spectrum of the Zn co-doped (10 at%) Y_2O_3:Mn (2 at %) TFEL devices over the $BaTiO_3$ thick ceramic substrate driven by an AC sinusoidal wave voltage (200 V) at a frequency of 1 kHz were measured using a luminance meter. The EL spectrum shows a narrow band emission due to $^4T_1$ (^4G) - $^6A_1$(^6S) transition of Mn luminescent center doped in the Zn co-doped Y_2O_3 thin film. L-V characteristics of Zn co-doped Y_2O_3:Mn thin film as a function of Zn are shown in Fig.5. From the Fig. 5, it should be noted that the obtainable EL characteristics of the TFEL devices using Zn co-doped Y_2O_3:Mn thin films were correlated to the growth of monoclinic phase and its crystallinity as evidenced from enhanced intensity of the diffraction peaks and found to increase as the content of Zn increases. It is observed that the highest L max about 2640 cd/m^2 was obtained in a TFEL device prepared with a ZnO content of 20 at% where as Zn un doped Y_2O_3:Mn shows a low lumen of about 214 cd/m^2 at 1 kHz. The spectrum of yellow emission observed from the Zn co-doped Y_2O_3:Mn TFEL at the ZnO content of 20 at% was nearly same that of standard yellow emitting ZnS:Mn phosphor. The CIE chromaticity color co-ordinate (x = 0.512 & y = 0.438) is not changed at any Zn concentration.

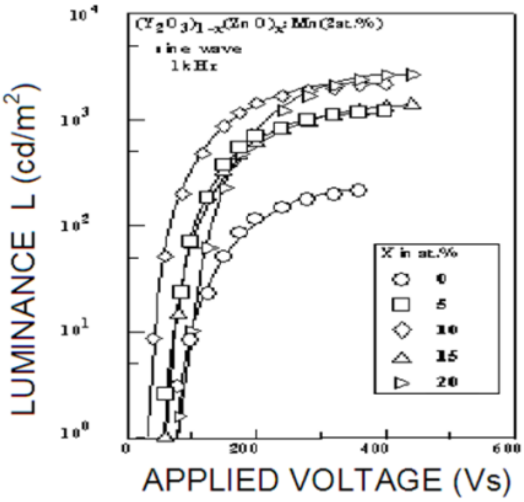

Fig. 5: L-V characteristics of Zn co-doped Y_2O_3-ZnO:Mn thin film phosphor prepared at various concentration of Zn deposited at 600°C and annealed at 1020°C

4.0 CONCLUSION

It is concluded that high luminance yellow emitting monoclinic Y_2O_3:Mn thin film could be easily prepared by co-doping Zn by using sol-gel deposition method on a thick ceramic substrate.The addition of zinc enhances the crystallinity, crystal quality of the phosphor thin film, in which a high photo and electroluminescent emission could be obtained from Mn luminescent center. A high luminance of 2640 cd/m^2 was obtained for the 20 at% Zn co-doped Y_2O_3:Mn thin films, whereas Y_2O_3:Mn without Zn shows 240 cd/m^2 driven at 1 kHz. Zn co-doped Y_2O_3:Mn film shows a very promising phosphor for the fabrication of TFEL devices.

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