MULTICOLOUR EMITTING ZnS:RE TFEL DEVICES

Abstract:

ZnS:Mn TFEL devices emitting yellow light are now commercially available. But, still multicolour emitting devices are lacking in luminescence output. This chapter gives the fabrication details of ZnS:RE,Cl TFEL devices. The various emission bands obtained are assigned to the transitions of RE$^{3+}$ ions. The blue green emitting ZnS:Tb,Cl is found to be the best device among them. The operating voltage of the device has been brought down below 50V using MIS structure for the device with Sm$_2$O$_3$ as insulator. The effect of halides ($F^-$, $Cl^-$, $Br^-$) and oxygen $O_2^-$ on the EL emission spectra ZnS:Pr TFEL device is presented. The device with fluoride dopant has been found to have the maximum efficiency. The halogen compounds of rare earth elements offering efficient luminescent centers are explained to some extent. The PrF$_3$ dopant appears as a promising candidate for EL devices because of its capacity for producing white light emission from single luminescent centre.
6.1 Introduction

TFEL displays are generally recognized as the most aesthetically pleasing among the flat display systems. A TFEL display is an active light emitter, has clearly defined uniformly illuminated pixels and has high contrast because of its low reflectivity yet specular like surface. The TFEL display has become a viable, producible flat-panel display for wide range of applications. Inspite of these advantages, these devices require still higher luminescence output and contrast for use in high ambients upto sunlight and for multi-colour displays.

Various types of luminescent centers such as transition ions, rare earth (RE) ions and donor acceptor pair impurities have been employed in ZnS TFEL devices to obtain multicolour emission \[1,2\]. Due to a wide variety of emission wave lengths possible with rare earth ions in the visible spectrum, extensive investigations have been carried out in recent years in this direction \[2,3,4\]. Earlier workers have noted that in the case of samples doped with RE metals, one obtains bright spots but where halide coactivation (F, Cl) was used, the EL emission
was uniform over the entire surface [5,6].

It is difficult to introduce substitutionally RE ions into ZnS with relatively high concentration because of the mismatch in ion size and charge valance between Zn$^{2+}$ and RE$^{3+}$ ions. A new type of emission centre was proposed by Chase et al. [1] who introduced rare earth fluoride in ZnS. This molecular centre offer several advantages such as possibility of high doping levels and weak coupling with the lattice vibration. Among RE luminescent centers TbF$_3$ dopant is identified as the most efficient emitter (green). The best reported value for TbF$_3$ device is 2400 cd/m$^2$ by Hale et al. [7]. But in literature very few reports on luminescent centers with RE other than Tb exist. Inspite of all efforts, the maximum brightness achieved with these activators is relatively low [8]. These factors motivated the study of ZnS:RE,Cl TFEL devices. The following section gives the fabrication and study of ZnS:RE:Cl (RE = Tb,Sm,Dy,Nd,Er,Eu,Pr) in devices with MISIM and MIS structure. The Sm$_2$O$_3$ insulator layer is found to be effective for low voltage operation and the device parameters are optimised in terms of thickness of active and insulator layer. The last section
of this chapter gives the effect of halide and oxide coactivators on the device performance and emission spectra.

6.2 Device Fabrication

The EL devices with thin film structure of SnO₂—Sm₂O₃—ZnS:RE,Cl—Sm₂O₂—Al (MISIM) and SnO₂—ZnS: RE,Cl—Sm₂O₃—Al (MIS) (shown in Fig. 5.1) were fabricated as described below. The transparent conducting glass plates were prepared by spray pyrolysis of an aqueous solution of SnCl₄ onto a glass substrate kept at 450°C as described in Chapter-II. The SnO₂ coated glass plate having a transmittance above 80% and sheet resistance below 120 Ω/√cm were selected for the fabrication of the devices. The active layer of ZnS:RE,Cl was evaporated onto SnO₂ coated glass substrate using an electron beam gun from ZnS:RE,Cl phosphors prepared in the laboratory by the slurring technique described in Chapter-II. The starting material of ZnS was luminescent grade material from Koch light, England. The Sm₂O₃ insulating layer was evaporated onto this followed by the aluminium back electrode. During the deposition of the insulator and active layer the substrate temperature was maintained at 150°C. After the deposition of insulator layer the
film was annealed at 150°C for one hour. The experimental investigations were carried out using AC TFEL cells having a rectangular area of 0.5 cm². The EL emission and brightness voltage characteristics were studied using the experimental set up described in Chapter-II.

The device performance such as brightness and threshold voltage depends not only on the type of insulating material but also on the film thickness of ZnS layer and insulator thickness. In the case of device with Sm₂O₃ as insulator, the device having an active layer to insulator thickness ratio, \( t_2/t_1 \) lying between 1 and 2 is found to be the optimal condition for the low voltage operation of the MIS TFEL device. Figure 6.1 gives the B-V characteristic of the device with ZnS:Pr,Cl as active layer and Sm₂O₃ as the insulator with different insulator thicknesses keeping the thickness of active layer fixed and also for different active layer thicknesses with insulator thickness constant. It is found that the threshold voltage for onset of emission can be reduced by reducing the thickness of ZnS layer thickness or insulator or both. But reduction of ZnS layer thickness causes reduction in brightness which can be compensated by reducing insulator thickness. The reasons for dependence of brightness and threshold voltage on the
Fig. 6.1. B-V characteristic of the ZnS:Pr,Cl MIS TFEL device with Sm₂O₃ as insulator (a) varying active layer, and (b) varying insulator layer thickness.
active and insulator film thickness in case of device with Eu₂O₃ as described in Chapter-V holds good in this case also. Taking into account of the maximum brightness and low threshold voltage optimal condition is found to be for an active layer to insulator thickness ratio in the range 1-2. Consequently the TFEL devices with MIS structure were prepared with active layer thickness 0.3 μm and an insulator thickness of 0.2 μm.

Sm₂O₃ has been selected as the insulator layer because it has got high dielectric constant of 43 and low loss factor. The film has a transmittance above 90%. The detailed study on dielectric properties of Sm₂O₃ is given in Chapter-IV.

6.3 EL emission characteristics of the devices

6.3.1 ZnS:Pr,Cl.

The EL emission spectra of a typical TFEL device with ZnS:Pr,Cl active layer under 1 KHz excitation frequency is as shown in Figure 6.2. These devices give emission at 450, 500, 580, 615, 680 and 700 nm. The emission spectral characteristics of these devices are found to be more or less independent of excitation frequency. Blue green (500 nm) ³P₀ → ³H₄ and orange (580 nm, 615 nm) ³P₀ → ³H₅,
$^{3}P_{0} \rightarrow ^{3}H_{6}$ transitions dominate this spectrum and the overall emission colour is yellow-orange in appearance. The assignments are based on those of Dieke and Sarup [9]. Unlike the ZnS:PrF$_3$ system [1,10], the PrCl$_3$ doped device has emission at slightly higher wavelength. Luminescence characteristics such as emission and brightness are strongly dependent on the environmental effects. It is expected that emission properties depend on the number of halide ions linked to Pr$^{3+}$ ion, which result in different strength and symmetry of crystal field [11]. In order to have clear picture, further studies on Pr$^{3+}$ emission on halide concentration are necessary.

6.3.2. ZnS:Nd,Cl.

The distinguishing feature of this system is the IR output, which is largest among the Lumocen devices. Though very few reports on ZnS:Nd system are available, Zhong et al. [12] have reported that stimulated emission at 1080 nm can be achieved in DCEL of ZnS:Cu,Nd,Cl thin films by population inversion involving $^{4}F_{3/2}$ and $^{4}I_{11/2}$ energy levels.

Figure 6.3 shows the EL emission spectra of the device with ZnS:Nd,Cl as active layer. Because of the
Fig. 6.2. EL emission spectra of ZnS:Pr,Cl TFEL device with 1 KHz excitation frequency.

Fig. 6.3. EL emission spectra of ZnS:Nd,Cl TFEL device under 1 KHz excitation frequency.
limitation of monochromator and PMT sensitivity the EL emission spectra is recorded only in the visible region. The device has an orange emission colour which results due to the following transitions of Nd\textsuperscript{3+} ions 

\[4_{G_{7/2}} \rightarrow 4_{I_{9/2}} (606 \text{ nm and } 586 \text{ nm}), \quad 4_{G_{9/12}} \rightarrow 4_{I_{9/2}} (488 \text{ and } 500 \text{ nm}) \text{ and } 2_{H_{11/2}} \rightarrow 4_{I_{9/2}} (656, 686 \text{ nm}).\]

6.3.3. ZnS:Sm,Cl.

Samarium is a significant luminescent centre which are of interest for full colour display. ZnS:SmF\textsubscript{3} has orange-red emission [2]. The EL emission of the present device with ZnS:Sm,Cl as active layer appears orange-red. The dominant transitions are occurring at 600 nm (\(4_{G_{5/2}} \rightarrow 6_{H_{7/2}}\)) and 650 nm (\(4_{G_{5/2}} \rightarrow 6_{H_{7/2}}\)). Weak emission line at 570 nm (\(4_{G_{5/2}} \rightarrow 6_{H_{7/2}}\)) is also observed. The EL emission spectra of the device is shown in Fig. 6.4.

6.3.4. ZnS:Eu,Cl.

Unlike other rare earth system ZnS:Eu,Cl device is found to have broad band emission. The \(5_{D_{0}} \rightarrow 7_{F_{2}}\) transition [13] at 610 nm is the dominant one (Fig. 6.5). In addition, there are transitions from the \(5_{D_{0}}\) to some other
Fig. 6.4. EL emission spectra of ZnS:Sm,Cl TFEL device under 1 KHz excitation frequency.

Fig. 6.5. EL emission spectra of ZnS:Eu,Cl TFEL device under 1 KHz excitation frequency.
6.3.5. ZnS:Tb,Cl.

Among the localised emission centers, such as rare earth elements, terbium (Tb) doped zinc sulphide shows the brightest green electroluminescence. All ZnS:Tb devices give rise to transitions which originate in the $^5D_3$ and $^5D_4$ and terminate in the $^7F$ manifold [15]. Emission from $^5D_3$ level is generally weaker and has been shown to decrease with concentration [16]. Figure 6.6 shows the EL emission spectra of ZnS:Tb,Cl device. As can be seen from the EL spectra of the device, it has emissions corresponding to $^5D_4 \rightarrow ^7F_j$ ($j = 3,4,5,6$) transition of Tb$^{3+}$ ion. The emission corresponding to the transition $^5D_4 \rightarrow ^7F_5$ occurring at 505 nm in bluish-green is the most prominent one. The present device with ZnS:Tb,Cl has emission at slightly shorter wavelength than that in the case of ZnS:TbF$_3$ systems [2]. There are marked difference between spectra of ZnS:RE and ZnS:RE F$_3$. It appears the spectral details depend sensitively on sample preparation, concentration of rare earth activator and coactivators.
6.3.6. ZnS:Dy,Cl.

Figure 6.7 shows the EL spectra of a typical ZnS:Dy,Cl TFEL device at 1 KHz excitation frequency. The yellow output of these devices arises from the strong emission from $^{4}F_{9/2} \rightarrow ^{6}H_{13/2}$ transition [17]. In the present case ZnS doped DyCl$_3$ TFEL cells, the type of transitions of Dy ions observed are similar to those appearing in DyF$_3$ doped ZnS TFEL device [1] and Dy doped CaS phosphors [18].

6.3.7. ZnS:Er,Cl.

Among the ZnS:RE system ZnS:Er seems to be very little studied. Xu-mou Xu et al. [19] have calculated the input cross section of Er$^{3+}$ ions in ZnS and this comes to the value about $2 \times 10^{-16}$ cm$^2$. The EL emission spectra of the present device with ZnS:Er active layer is as given in Figure 6.8. The faint green light emitted by this system is the result of the transitions at 530 nm ($^{2}P_{3/2} \rightarrow ^{4}I_{9/2}$ or $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$) and 550 nm ($^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$). In addition there are other transitions at 650 nm ($^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$) [20]. The spectra observed in the case of ZnS:RE Cl$_3$ differ generally in relative intensity of the lines from those observed for
Fig. 6.6. EL emission spectra of ZnS:Tb,Cl TFEL device under 1 KHz excitation frequency.

Fig. 6.7. EL emission spectra of ZnS:Dy,Cl TFEL device under 1 KHz excitation frequency.
Fig. 6.8. EL emission spectra of ZnS:Er,Cl TFEL device under 1 KHz excitation frequency.
bare ions in ZnS [21, 22] and also in some cases from RE F₃ dopants systems [1]. If one makes the assumption that the dominant contribution to the crystal field at the central ion arises from the neighbouring chlorine, it is reasonable to expect that this field will vary from site to site as the molecule distorts to achieve the minimum energy in its cavity within ZnS lattice. On this model, it is possible to account for the large breadth of the lines without invoking strong coupling to the lattice. The effect of halides and oxide coactivation on the emission characteristic of ZnS:Pr system is described at the end of this chapter.

6.4 Brightness voltage characteristics

The brightness-voltage (B−V) characteristics of these devices with ZnS:RE,Cl as active layers and Sm₂O₃ as insulator having MISIM and MIS structure under 1 KHz excitation frequency are shown in Figure 6.9 and Figure 6.10 respectively. Figure 6.11 shows the B−V characteristic of devices with ZnS:Sm,Cl as active layer and MgF₂, Eu₂O₃, Sm₂O₃ and BaTiO₃ as insulators in the MIS and MISIM structure. It is observed that device with insulator having high dielectric constant has low threshold voltage for onset of emission. In the present case the device with Sm₂O₃ as
Fig. 6.9. B-V characteristic of ZnS:RE,Cl MIS TFEL device with Sm$_2$O$_3$ as insulator at 1 KHz.

Fig. 6.10. B-V characteristic of ZnS:RE,Cl MISIM TFEL device with Sm$_2$O$_3$ as insulator at 1 KHz.

Fig. 6.11. B-V characteristic of ZnS:Sm,Cl MIS and MISIM TFEL devices with different insulating layers at 1 KHz excitation frequency.
insulating layer in MIS structure has the lowest threshold voltage. The reasons for this can be explained in terms of the dielectric constant of the insulating material as described in Chapter-V. Nanto et al. [23] have reported low voltage TFEL device with BaTiO$_3$ ceramic sheet as insulator which has very high dielectric constant. However, in the present case the BaTiO$_3$ films show very low dielectric constant. This may be due to impurities and defects and perforation in the film.

The experimental results shown in Figures 6.9 and 6.10 indicate that brightness of rare earth doped ZnS devices could not compete with that of Mn doped devices. The brightness of ZnS:Tb,Cl device, although the best among the rare earth doped devices is still only about 60% of that ZnS:Mn. The devices with ZnS:Eu,Cl and ZnS:Er,Cl are least efficient. But for ZnS:RE,Cl devices there is an optimum concentration and its value is found to depend upon the kind of the activator.

From the B–V characteristics (Figures 6.10, 11) it can be seen that the doubly insulated TFEL device shows a remarkable increase in brightness when the applied voltage exceeds a certain value, whereas in MIS TFEL device the brightness is found to increase steeply and after attaining
a certain brightness value it levels off indicating saturation. The MIS TFEL device has no insulator in between the electrode and ZnS layer. Thus carriers could be readily injected from the electrode or released from the ZnS layer with the result that no carriers will accumulate near the ZnS-electrode interface, whereas in MISIM TFEL device the charge will be stored in ZnS-insulator interface. As a consequence electric field induced by space charge at ZnS-insulator layer is strong as it will superpose with electric field due to the applied voltage [24]. The trapped holes inside the ZnS layer can generate an internal field which increases the probability of electrons tunnelling through the ZnS-insulator barrier. Moreover, the TFEL device being a capacitive load, conduction current which contributes to luminescence is different at high voltages [24]. These factors account for the sudden increase in brightness observed for MISIM structure devices.

6.5 Effect of halides on the EL emission spectra and brightness of ZnS:Pr TFEL devices

Thin film EL devices, though have a number of advantages there are applications that require higher luminescence and contrast for use in high ambience upto
sunlight and for multicolour displays. Thus practical application calls for other colours of emitted light, especially white. In view of this Praseodymium was chosen as dopant in ZnS matrix. The brightness of TFEL structures strongly depends on particular rare earth compound used in the doping [5,6]. Also it is difficult to introduce rare earth ions into ZnS with relatively high concentration because of the mismatch in ion size and charge valance between Zn\(^{2+}\) and RE\(^{3+}\) ions. A new type of emission centre was proposed by Chase et al. [1] who introduced rare earth fluoride in ZnS. This molecular centre offers several advantages such as possibility of high doping and weak coupling with lattice vibration. The present investigation are on the effect of coactivation of halides on the EL spectra of ZnS:Pr. It is well known fact that emission spectra and brightness depend critically on preparation conditions [25]. Thin film electroluminescent devices having low threshold voltage and white like emission have been developed using ZnS:PrF\(_3\) as active layer and Sm\(_2\)O\(_3\) as insulator. The effect of F\(^-\), Cl\(^-\), Br\(^-\) and O\(_2^-\) coactivation of ZnS:Pr TFEL devices on the EL spectra and brightness are investigated here.

The TFEL devices were prepared with SnO\(_2\)-ZnS:Pr-Sm\(_2\)O\(_3\)-Al
having MIS structure. The conducting transparent electrodes were prepared by spray pyrolysis method. The active layer (~0.3 μm) was evaporated by electron beam gun from the phosphors prepared in the laboratory. Then the insulator layer (0.2 μm) Sm₂O₃ was evaporated by electron beam gun. Evaporated aluminium acts as the back electrode. The phosphors for active layer was prepared using luminescent grade ZnS with 3 wt % of Pr, which was introduced in the form of PrF₃, PrCl₃, PrBr₃ and Pr₃O₁₁. Na₂S₂O₃ was used as flux. The phosphor was prepared by slurrying technique and vacuum firing process as described in Chapter-II.

Figure 6.12 shows the EL emission spectra of ZnS:Pr TFEL devices coactivated with F⁻, Cl⁻, Br⁻ and O²⁻. The EL spectra of ZnS:PrF₃ shows two emissive groups that are centered around 500 nm and 650 nm. The former corresponds to \( ^3P_0 \rightarrow ^3H_4 \) and the latter to \( ^3P_0 \rightarrow ^3F_2 \) of \( \text{Pr}^{3+} \) ions. These two groups of spectral emission roughly satisfy the complementary colour relationship. The comparative intensity relationship is such that these combination results in a white appearance. The emission colour is independent of driving voltage and excitation frequency.
Fig. 6.12. EL emission spectra of ZnS:Pr TFEL devices coactivated with $F^-$, $Cl^-$, $Br^-$ and $O_2^-$ under 1 KHz excitation frequency

A- ZnS:PrF$_3$, B- ZnS:PrCl$_3$, C- ZnS:PrBr$_3$, D- ZnS:Pr$_6$O$_{11}$
In the case of ZnS:PrBr$_3$ and ZnS:Pr$_6$O$_{11}$ also the emission shows transition corresponding to $^3P_0 \rightarrow ^3H_4$ at 500 nm and $^3P_0 \rightarrow ^3F_2$ at 650 nms. But in the case of ZnS:PrCl$_3$ system the transition corresponding to $^3P_0 \rightarrow ^3H_5$ and $^3P_0 \rightarrow ^3H_6$ (580 nm and 600 nm) are prominent.

Luminescence characteristics such as emission and brightness are strongly dependent on the environmental effects. It is expected that emission properties depend on the number of halide ion linked to Pr$^{3+}$ ion which result in different strength and symmetry of crystal field \[3\].

Figure 6.13 shows the brightness voltage (B-V) characteristics of these devices. The device with ZnS:PrF$_3$ have maximum brightness while ZnS:Pr$_6$O$_{11}$ is least efficient.

Thus Halogen compounds of rare earth elements offer efficient luminescent centre in TFEL device and this may be due to the following facts: (i) The low solubility of trivalent rare earth ions in ZnS which would prevent one from introducing these ions in concentrations sufficiently large to optimise electroluminescence efficiency. This could be circumvented by the introduction of a neutral entity, (ii) the valance of rare earth ion could be controlled by choosing an appropriate rare earth compound which does not dissociate during evaporation, (iii) since
Fig. 6.13. B-V characteristics of ZnS:Pr TFEL devices coactivated with $F^-$, $Cl^-$, $Br^-$ and $O_2^-$ under 3 KHz excitation frequency.
the excitation of the active ions was assumed to proceed by direct electron impact, the large size of molecular system could serve to increase the excitation cross sections, (iv) in a molecular center weakly coupled to the surroundings, non radiative decay of the fluorescing ion could be reduced in comparison with a system where the ion enters substitutionally. From the above studies, the PrF$_3$ appears to be a promising candidate for application of EL devices because of its capacity of producing white light from a single luminescent centre.
REFERENCES


