EFFECT OF RARE-EARTH DOPING ON ELECTROLUMINESCENCE, PHOTOCONDUCTIVITY AND OPTICAL ABSORPTION PROPERTIES OF (ZN, CD) S PHOSPHORS

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ABSTRACT

(Zn, Cd) S: Tm Phosphor films with thickness in the range 10 to 30 nm have been prepared in an atmosphere of nitrogen. The electroluminescence (EL), photoconductivity and optical absorption properties of these films have been studied systematically. Exponential dependence of EL brightness on excitation voltage as per Alfrey-Taylor relation reveals the existence of acceleration collision mechanism in these films. Further, the El-brightness also changes with the frequency of excitation and concentration of Tm as well. The photo response curves show peak around 2.62 eV corresponding to the direct band gap of ($Zn_{0.45}$, $Cd_{0.55}$) S:Tm films. The optical absorption studies reveal the fundamental absorption edge at 475 nm corresponding to 2.62 eV, which is in good agreement with the photoconductivity studies also.

KEYWORDS: *Mixed Phosphor, Electroluminescence, Photoconductivity, Rare-earth.*

I. INTRODUCTION

The study of phosphor materials is the novel field of the research. The (Zn, Cd) S mixed phosphor material shows wide spectrum of applications due to its ability to show both EL and photoconductivity properties. The (Zn, Cd) S material, with proper proportion is one of the most sensitive photoconductors especially for visible and near infra red radiations at room temperature [1,2]. It is found that, these properties are significantly depend upon the nature and concentration of the activator. Further, Photoconductivity and electroluminescence are concurrent processes and the studies of these phenomena provide substantial information about the electronic transitions in semiconductors [3,4]. Various parameters of (Zn, Cd) S material are investigated by many workers [5, 6,7], but the reports on the properties of materials doped with rare earth ion are rather rare. Therefore, the intrinsic properties of (Zn, Cd) S phosphor doped with different concentrations of Tm have been investigated and the results regarding electroluminescence, photoconductivity and optical absorption are interpreted.

II. EXPERIMENTAL

The compositions of ($Zn_{0.45}$, $Cd_{0.55}$) S: Tm are prepared in thick film forms. The ZnS and CdS powders prepared by the method, described elsewhere [8], have been mixed in the mole proportion 45:55 along with requisite amount of Tm in the form of its solution. The concentration of Tm has

been changed systematically from 0.001 to 1.0 wt% of ($Zn_{0.45}$, $Cd_{0.55}$) S. The mixture is dried and then fired in tubular furnace in N_2 atmosphere at 900 ^oC for one hour. The formation of solid solution was confirmed by X-ray diffraction studies. This phosphor is then mixed with 10 wt% of $CdCl_2$ and 65 Vol % of propylene glycol to form slurry which is then coated on SnO_2 conducting glass using 120 mesh stainless steel screen to form the phosphor film. This film is sintered at 600 ^oC in N_2 atmosphere for 30 minutes. The thickness of the films is found to very from 10 nm to 30 nm.
For electroluminescence (EL) studies, the EL cell consisting of the phosphor film has been excited by alternation voltage up to. 1.5 KV at 100 Hz to 2.5 KHz, obtained from an audio frequency oscillator (Philips GM 230/99) in conjunction with wide band amplifier (Telmax type SP-100). The intensity of EL-emission is measured by using PM tube (Thorn EMI 9781B) coupled with a precession multimeter (HP 34401A). The variation in EL brightness is studied as a function of voltage, frequency of excitation and concentration of Thulium (Tm).

Photoconductivity measurements are carried out by using gap-type cell formed by painting two silver-paste electrodes on the sintered film with the spacing of one millimeter. Ohmic contacts between electrodes and the film are obtained by annealing the coated silver-paste at 373 K for 30 minutes in nitrogen atmosphere. The biasing voltage has been applied to these electrodes using d.c battery and the photocurrent is recorded with the help of multimeter.

Optical absorption measurements are carried out in the wavelength range 200nm to 850nm using UV-VIS-NIR double beam spectrophotometer (Hitachi Model 330, Japan).

III. RESULTS AND DISCUSSION

The electroluminescence (EL) brightness of the compositions under investigation is measured with respect to the variable voltage (Vrms). These measurements are carried out at fixed frequency. The variation of electroluminescence (EL) with excitation voltage is depicted in figure 1.

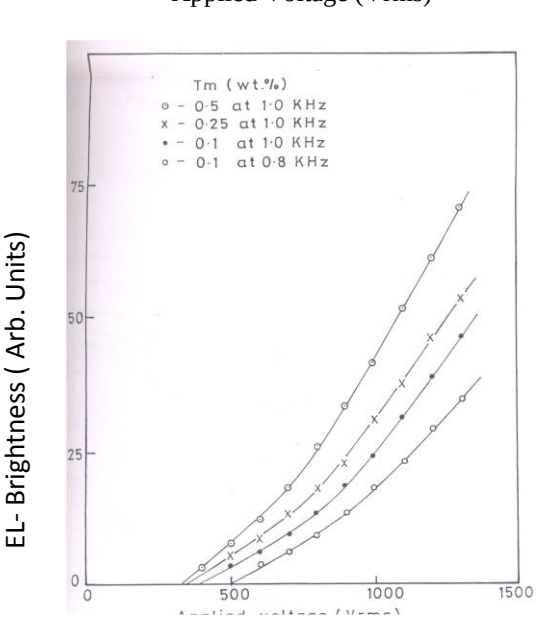

Figure 1: Variation of EL Brightness with voltage for (Zn, Cd) S Tm films

On inspection of figure 1, it is found that, the EL brightness is observed from the particular voltage called Threshold voltage and then shows increasing trend with increase in the applied voltage. The values of Threshold voltage varies with concentration of Thulium (Tm). The trend of EL brightness is essentially same for different concentrations of Tm. However, the magnitude EL brightness varies with Tm concentration. It is also found that, the value of Threshold voltage decreases with increase in Tm Concentration and also with increase in frequency of excitation. The increase in Tm

concentration causes to increase the number of shallow donors in the band gap of the phosphor material, which may be responsible for the decrease of threshold voltage with increase in Tm concentration.

In a.c. EL response, the maximum peak value of the voltage is applied twice in each cycle to the phosphor system. When the frequency of applied field is increased, the impurity ion receives energy at a rapid rate. As a result, it gets excited at comparatively smaller field strengths and hence the threshold voltage decreases with increase in the frequency of applied field. Similar results have been obtained by Todkar et.al [9] for Gd doped Y-Ba-Cu-O superconducting luminophors.

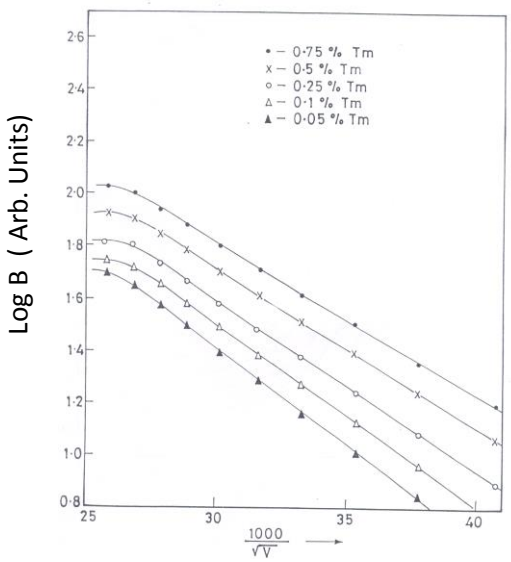

Figure 2: Variation of EL Brightness with excitation voltage at 1 KHz for (Zn, Cd)S Tm films

The dependence of El-brightness (B) on applied voltage (V) is seen from the linearity of log B Vs $1000/\sqrt{V}$ plots (Figure 2), which suggests that the Alfrey-Taylor relation (Eq. 1) is valid in these films.

$$B=B_0 \exp(-b/V^{1/2}) \quad \ldots(1)$$

The existence of such exponential relationship between brightness and voltage indicates that the EL emission in these films results from the potential barrier of Mott-Schottky type and the mechanism of EL is acceleration collision type [10]. Moreover, it is found that the EL Brightness shows deviation from above relation for high voltages, which ensures saturation of the charge carriers. The EL-brightness of these films increases with increase in Tm concentration and no concentration quenching effect is observed. Because, in the Tm^{3+} ions, forming donor levels, partially filled 4f electrons are well shielded by 5s and 5p shells and Tm ions interact very weakly with each other. Consequently, the excitation energy is not transferred to killer centers present in the phosphor and hence no concentration quenching is observed.

Figure 3 shows frequency dependence of EL-brightness of $(Zn_{0.45}, Cd_{0.55})$ S :Tm films. From figure 3, it is seen that the nature of curves is not changed due to change in concentration of Tm. At lower frequencies, brightness increases almost linearly with frequency. At higher frequencies, the increase in brightness with frequency is rapid, may be due to excess charge carriers provided by donors on ionization. At still higher frequencies, the brightness remains almost constant i.e. saturation takes place. These observations confirm the theory of hyperbolic recommendation process given by Curie[11], according to which

$$B = \frac{B_0 n_0 \alpha}{(1 + n\alpha/2f)} \quad \ldots(2)$$

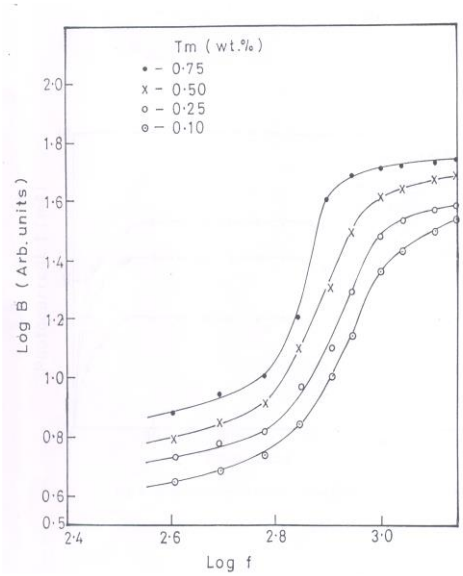

Figure 3: Variation of EL Brightness with excitation Voltage at 1 KHz for (Zn, Cd)S Tm films

Where α is time constant, n is the initial number of free electrons in the conduction band, B is proportionality constant and f is excitation frequency.

At lower frequencies, the life time of excited centers is short compared to the periodicity of applied voltage and factor α in equation 2 becomes large compared to f. Hence ($n_0 \alpha / 2f$) >>1 and therefore equation 2 gives

$$B = 2B_0 n_0 f \qquad \ldots(3)$$

Which shows that the EL brightness is varies linearly with the frequency.

At sufficiently higher frequencies ($n_0 \alpha / 2f$) <<1 and hence equation 2 becomes

$$B = B_0 n_0^2 a = \text{constant} \qquad ..(4)$$

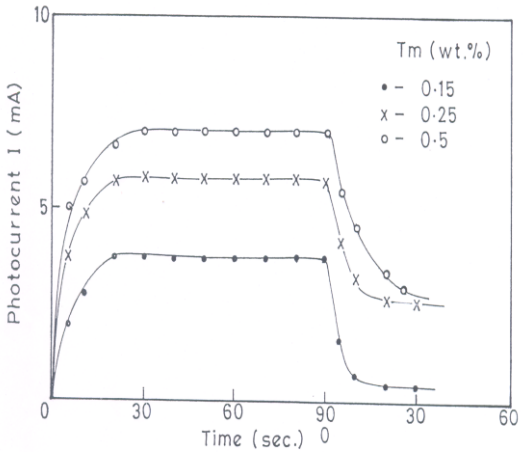

Figure 4 : Rise and decay curves of photocurrent for ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films

This explains the saturation of EL brightness at higher frequencies.

In order to explorer the timing response, the photocurrent is measured with the time of exposure of the film to the light. Figure 4 shows rise and decay curves of photocurrent for ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films. From the curves it is seen that, on exposure of photoconductor to light, the photocurrent initially

increases exponentially in accordance with equation $\sigma = \sigma_0[1-\exp(t/\tau)]$ and reaches to the steady state level. Further, on interruption of light, the photocurrent decays exponentially as per equation $\sigma = \sigma_0[1-\exp(-t/\tau)]$. Where σ is the conductivity, t is time and τ is constant. This slow rise and decay of photocurrent is attributed to the presence of trap levels in the band gap of the phosphor.

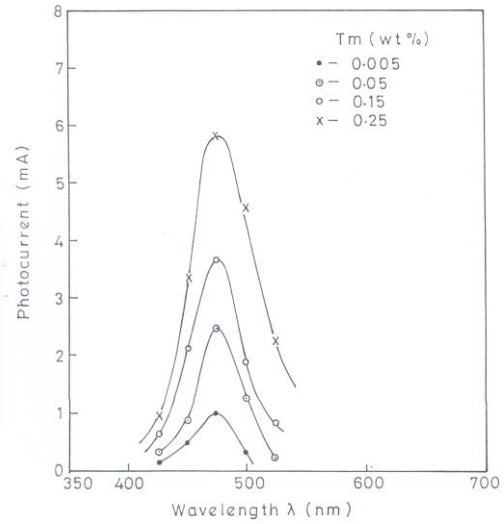

Figure 5: photoconductivity spectral response for ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films

The spectral response of photoconductivity ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films for constant illumination is exhibited in figure 5. It shows that all, the curves have peak photo response around 475nm corresponding to band gap of 2.62 eV of ($Zn_{0.45}$, $Cd_{0.55}$) S. Therefore, intrinsic transition i.e. the optical excitation of valence band electron to conduction band essentially causes peak response. The photo response is found to decrease both on shorter as well as longer wavelength side. The decreasing photo response on shorter wavelength side may be due to absorption of short wavelength radiations in the surface recombination states. The decrease in photo response in long wavelength region is be due to structural imperfection such as cationic vacancies. As the population of these defect levels goes on decreasing above the valence band, the photocurrent decreases with decrease in energy of the illuminating radiations.

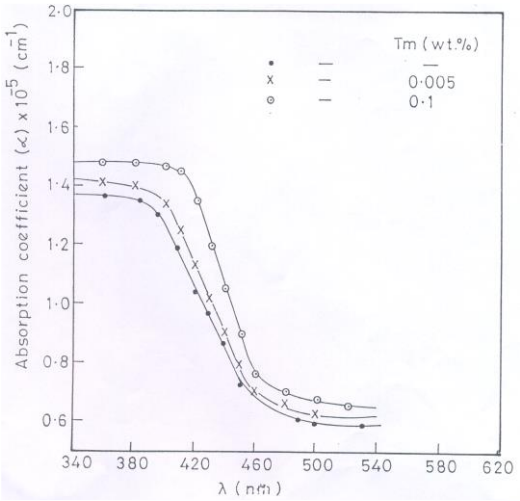

Figure 6: variation of absorption coefficient with wavelength for ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films

Optical absorption studies of ($Zn_{0.45}$, $Cd_{0.55}$) S :Tm films reveal high optical absorption coefficient. The variation of absorption coefficient with wavelength is shown in figure 6. It shows that the optical absorption coefficient (α) is a function of photon energy ($h\nu$). The optical absorption coefficient is of the order of 10^4 to 10^5 cm^{-1} supporting the direct band transitions.[14,15]. The absorption coefficient is found to drop rapidly and the material becomes fairly transparent at longer wavelength. The absorption edge for these films is obtained by extrapolating the steep position of the α Vs λ plot on the wavelength axis. The films show absorption edge at about 475 nm which corresponds to the energy band gap (2.62 eV) of ($Zn_{0.45}Cd_{0.55}$) S.

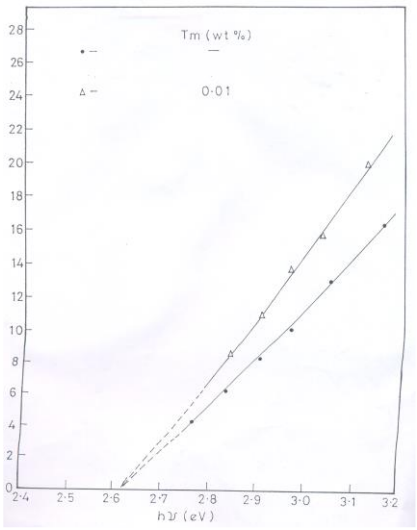

Figure 7: $(\alpha h\nu)^2$ Vs $h\nu$ for (Zn, C)S Tm films

The nature of optical transitions involved in these films can be determined on the basis of the dependence of absorption coefficient (α) on photon energy ($h\nu$). The variation of $(\alpha h\nu)^2$ Vs ($h\nu$) is shown in Figure 7, which is a straight line indicating the transition involved is of direct band to band type[16]. The value of band gap energy is obtained by extrapolating the straight portion to the energy axis at α=0 and it is found to be 2.62 eV which is in good agreement with photoconductivity studies.

IV. CONCLUSION

($Zn_{0.45}$, $Cd_{0.55}$) S :Tm thick films of mixed phosphor material show photoconductivity as well as electroluminescence properties. The exponential dependence of EL brightness on voltage suggests the existence of acceleration collision mechanism. The EL brightness significantly varies with voltage and frequency of excitation and also with the concentration of Tm. On photoconductivity study the band gap energy obtained is 2.62 eV, which suggest the direct type band gap. The optical absorption studies reveal the fundamental absorption edge at 475 nm corresponding to 2.62 eV, which is in good agreement with the photoconductivity studies.

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