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Electro-Optical studies of ZnSe:Tb and ZnSe:(Mn,Tb) Phosphors

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ABSTRACT: ZnSe:Tb and ZnSe:(Mn,Tb) phosphors have been prepared by firing the samples in nitrogen gas atmosphere. Photoluminescence (PL) and electroluminescence (EL) of these phosphors have been studied. The emission of yellow and red bands has been interpreted in terms of different electronic transition. The voltage and frequency variation of EL brightness are in agreement with collision-excitation mechanism, i.e. Schottky barrier at the metal semiconductor interface.

Keywords: Photoluminescence (PL), Electroluminescence (EL), Phosphors, Energy transfer, Schottky barrier, donor-acceptor (D-A) pair.

1. Introduction

Doubly activated ZnS/ZnSe phosphors have been found to possess good electroluminescence (EL) and photoluminescence (PL) emission and the energy transfer between the dopants ions has been explained satisfactorily [1-20]. In ZnSe type phosphors the localized states are better treated as states from the band structure of the pure crystal perturbed by the activators. Mn is widely used as an activator in the luminescent grade ZnS/ZnSe phosphors [1-7, 21]. The present paper deals with Photoluminescence (PL) and electroluminescence (EL) of ZnSe:Tb and ZnSe:(Mn,Tb) phosphors.

Recently, ZnSe phosphors doped with rare earth ions have drawn much attention in view of their application in electro-optical devices [14-16, 18, 21]. These phosphors emit predominantly in the yellow-orange region of the spectrum and the energy transfer is understood to a fair degree of accuracy and reliability. The common feature of all such investigation is that they exhibit emission line corresponding to 4fⁿ configuration of a trivalent ion. The purpose of the present work is to know in what way spectral characteristics of the ZnSe phosphors are affected by the introduction of Mn and Tb ions and also to determine unambiguously the electronic transitions involved in the energy transfer by the photons and the electric field.

Electroluminescence arises due to excitation of luminescent centre (which is created by dopants and host crystal) and subsequent radiative recombination. In the sufficiently high field regions electron ejected into the conduction band attain enough kinetic energy to excite a dopant atom by means of inelastic collision. This collision process is governed by the voltage and frequency applied in addition to other parameters like temperature, concentration of charge, imperfection etc. We study the effect of the alternating voltage on the EL emission at various frequencies in these phosphors. Changes in the intensity of emitted light have been investigated with change in field frequencies at constant applied voltage and the result have been discussed in the light of existing models [1-4].

2. Experimental

ZnSe.Tb₂O₃ and MnCl₂.4H₂O phosphors were well mixed in an appropriate proportion. The samples were fired at (780° ± 20°) C for one hour in nitrogen gas atmosphere [17]. For photoluminescence (PL) studies the phosphors were excited by 3650 Å UV radiations. Then, for electroluminescence (EL) study, the phosphor powder was spread in a condenser type EL cell using castor oil as dielectric. The EL cells were excited by an audio frequency oscillator coupled to a wide band amplifier. A constant deviation spectrograph was used to study the spectral distribution of PL and EL. Light output of PL and EL emission was detected by an RCA IP-21 photomultiplier tube connected with a multiflex galvanometer [4].

3. Results and discussion

3.1 Emission spectra

3.1.1 PL spectra

The PL spectra of ZnSe:Tb and ZnSe:(Mn,Tb) at different concentrations are recorded and are shown in **Fig. 1**. In ZnSe:Tb phosphor maximum emission at 5900 Å is found for Tb concentration of 0.1% (**Table 1**). The position of peak maxima shifts towards lower wavelength side on decreasing concentration of Tb³⁺ ions (**Table 1**). In ZnSe doped with (Mn,Tb) phosphors two peaks around 5750 Å and around 6350 Å have been

recorded in PL spectra are shown in **Table 1** . But for Mn=2%, Tb=0.1% and Mn=1%, Tb=0.001% only one intense orange-red band around 6300 A was found. It has been observed that the peak maxima of PL emission shifted towards lower wavelength side with dopant concentration.

The emission structure changes with intra-pair separation of the centres. When a donor-acceptor pair has small intra-pair separation, it can act as a neutral centre and provide potential attractive to one of two carriers. For a short distance pair of deep acceptor and shallow donor the potential of each centre is perturbed and reduced by the presence of the other in the neighborhood. Therefore, the concentration of the dopants affects donor-acceptor (D-A) pair separation and consequently emission peak appears with change in the concentration of dopant ions. The shifts also show that the dopant ions are at the interstitial site in the lattice [3-5].

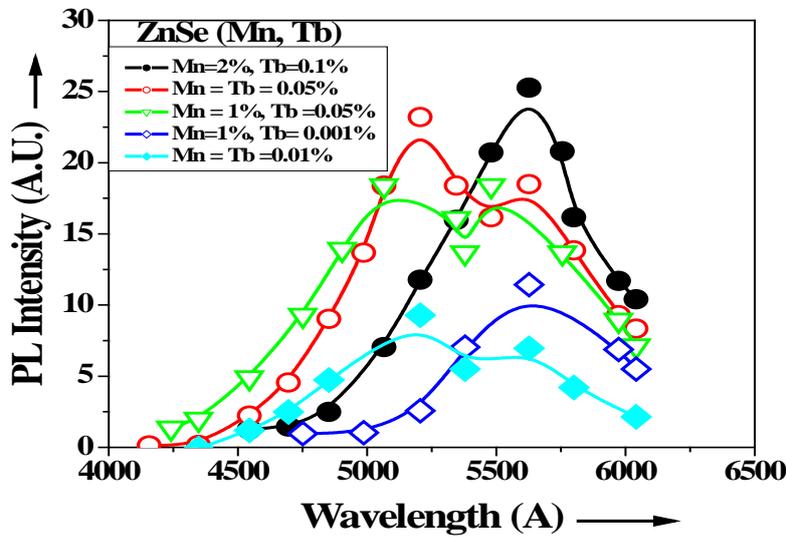


Figure 1: PL Spectra of ZnSe : (Mn,Tb) Phosphor at 300K

Table 1: Characteristics of PL Spectra of ZnSe:Tb and ZnSe:(Mn,Tb) phosphor

Sl. No	Phosphors	Concentration of dopants	PL Spectra		Probable Electronic Transition
			Wavelength (A ⁰)	Intensity (A.U.)	
1.	ZnSe : Tb	Tb=0.1%	5900	28	⁵ D ₄ → ⁷ F ₄
		Tb=0.05%	5850, 6400	23, 16	⁵ D ₄ → ⁷ F ₄ , SA
		Tb=0.01%	5800	10	⁵ D ₄ → ⁷ F ₄
		Tb=0.001%	5750	5	⁵ D ₄ → ⁷ F ₄
2.	ZnSe:(Mn,Tb)	Mn=2%, Tb=0.1%	6300	28	⁵ D ₄ → ⁷ F ₃
		Mn=0.05%, Tb=0.05%	5750, 6350	25, 20	⁴ G→ ⁶ S _{1/2} , ⁵ D ₄ → ⁷ F ₃
		Mn=1%, Tb=0.05%	5700, 6350	20, 20	⁴ G→ ⁶ S _{1/2} , ⁵ D ₄ → ⁷ F ₃
		Mn=1%, Tb=0.001%	6300	13	⁵ D ₄ → ⁷ F ₃
		Mn=0.01% Tb=0.01%	5750, 6400	10, 8	⁴ G→ ⁶ S _{1/2} , SA

3.1.2 EL spectra

The spectral distribution of emitted light from EL cell at different frequencies and voltages of the applied a.c. field are shown in **Fig. 2** and results are tabulated in **Table 2**. EL emission spectra of ZnSe:Tb (for Tb=0.1%) consists of two broad band located at 5850 Å and 6450 Å. The orange-red bands were found to be shifted towards lower wavelength side with increase in frequency. It is observed that this phosphor is a good EL emitter at 2 kHz field frequency (**Table 2**).

The EL emission spectrum of ZnSe:(Mn,Tb) consists of two intense band (**Fig. 2**) having maxima around 5750 Å and 6400 Å for the concentration of Mn=Tb=0.05%, under a.c. field excitation at different field frequencies except dominant orange-red band located at 6450 Å at 6 kHz frequency. The peak maxima of both bands shift towards lower wavelength side with increasing field frequency. This is supposed due to the recombination of electrons at different centres. When the excitation field is applied, the luminescent centres are ionized and electrons will try to occupy the lowest empty centres. If the frequency of excitation is the low, the lowest centers will be fully occupied and recombination will take place at higher centers. This mean the emission will involve less energy i.e. higher wavelengths. Now if the frequency of excitation is increased, the electron will not have sufficient time to redistribute them. Consequently the recombination occurs at low lying centers, which means higher energy i.e. shorter wavelength [16-18].

Therefore, it is found that this phosphor is a good EL emitter at 1 kHz field frequency (**Table 2**). In emission spectra of Mn²⁺ doped phosphors the yellow band is attributed due to ⁴G→⁶S transition within the Mn²⁺ d-d shell (**Table 2**). The emission band around 6400Å in all the phosphors shows a feature of self-activated (SA) emission, which is attributed due to D-A transitions involving deep donor and acceptor centers consisting of zinc vacancy in association with Mn ions.

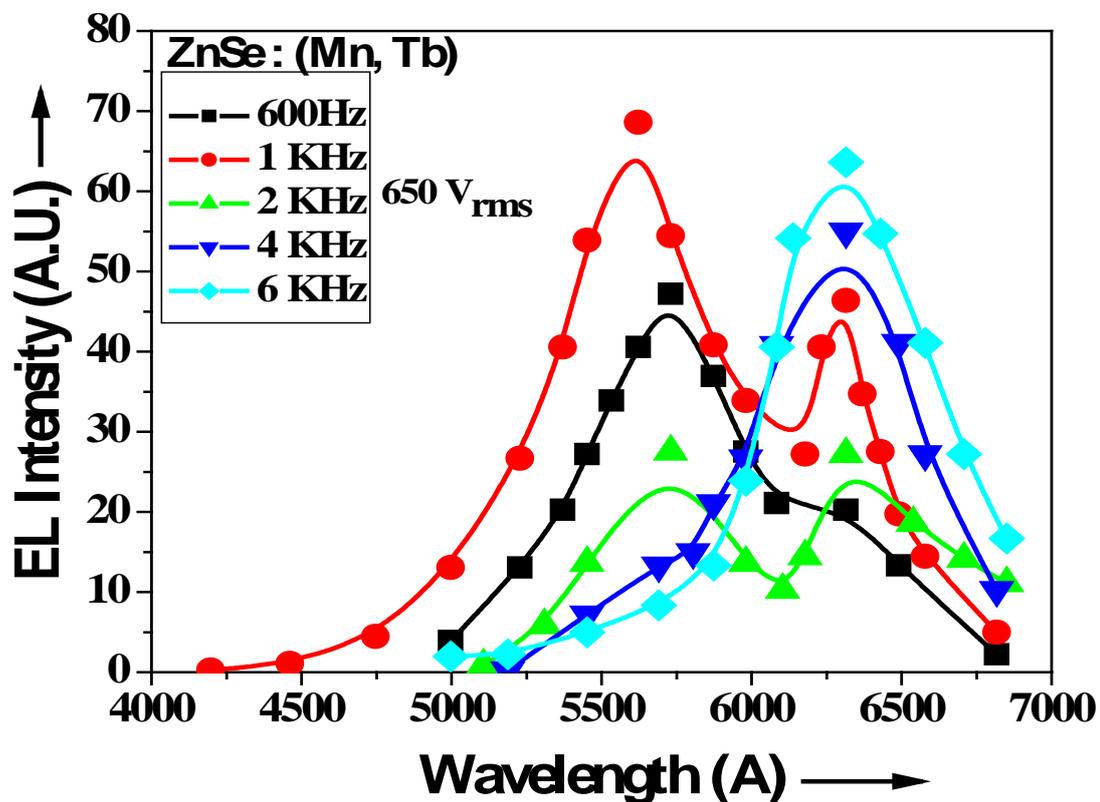


Figure 2: EL Spectra of ZnSe : (Mn, Tb) Phosphor (Mn=Tb=0.05%) at 300K

Table 2: Characteristics of EL Spectra of ZnSe:Tb and ZnSe:(Mn,Tb) phosphors

Sl. No.	Phosphors	Frequency of Applied a.c. field	EL Spectra		Probable Electronic Transition
			Wavelength (Å)	Intensity (A.U.)	
1.	ZnSe : Tb, Tb=0.1%	500Hz	5950, 6450	16, 8	$^5D_4 \rightarrow ^7F_4$ SA
		1kHz	5800, 6350	28, 20	$^5D_4 \rightarrow ^7F_4$ $^5D_4 \rightarrow ^7F_3$
		2kHz	5800, 6350	40, 30	$^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_3$
		4kHz	5750	26	$^5D_4 \rightarrow ^7F_4$
		6kHz	5700, 6500	16, 4	$^5D_4 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_2$
2.	ZnSe: (Mn,Tb) Mn=Tb=0.05%	500Hz	5800, 6400	53, 23	$^4G \rightarrow ^6S_{1/2}$, SA
		1kHz	5700, 6400	75, 50	$^4G \rightarrow ^6S_{1/2}$, SA
		2kHz	5750, 6400	30, 30	$^4G \rightarrow ^6S_{1/2}$, SA
		4kHz	5750, 6400	15, 60	$^4G \rightarrow ^6S_{1/2}$, SA
		6kHz	6450	68	SA

3.2 Voltage and frequency dependence of EL brightness

The EL brightness of the integrated light output as a function of applied a.c. voltage has shown in **Fig. 3**. It is observed that the relation between the log of brightness (B) of the EL condenser and the voltage (V) is expressed by the equation $B = B_0 \exp(-b/\sqrt{V})$, where B_0 and b are constants, which shows that the excitation of EL emission is due to acceleration collision at the Schottky barrier layers in metal semiconductor contact. This can be explained as the electric field directly ionizes the Tb^{3+} ions, which are located below the bottom of conduction band [3, 4, 8, 16].

The thermal energy or phonons also assists in detrapping the electrons from the shallow traps. These electrons are raised to the conduction band, where they got accelerated by positive half cycle of the alternating voltage and till they acquire sufficient kinetic energy to ionize or excite activator centre (Mn^{2+}) by inelastic impact. In the reverse half cycle these electrons recombine with the luminescence centers with the emission of their characteristics radiations. In case of ZnSe:(Mn,Tb) phosphors (representative figure), the plot between log of B versus $V^{-1/2}$ is found to be consists of two straight lines inclined to each other and obeying the relation $B = B_0 \exp(-b/\sqrt{V})$, below and above the points where the bending occurs. This aspect may be due to the presence of different luminescent centers with different activation energies [2, 8].

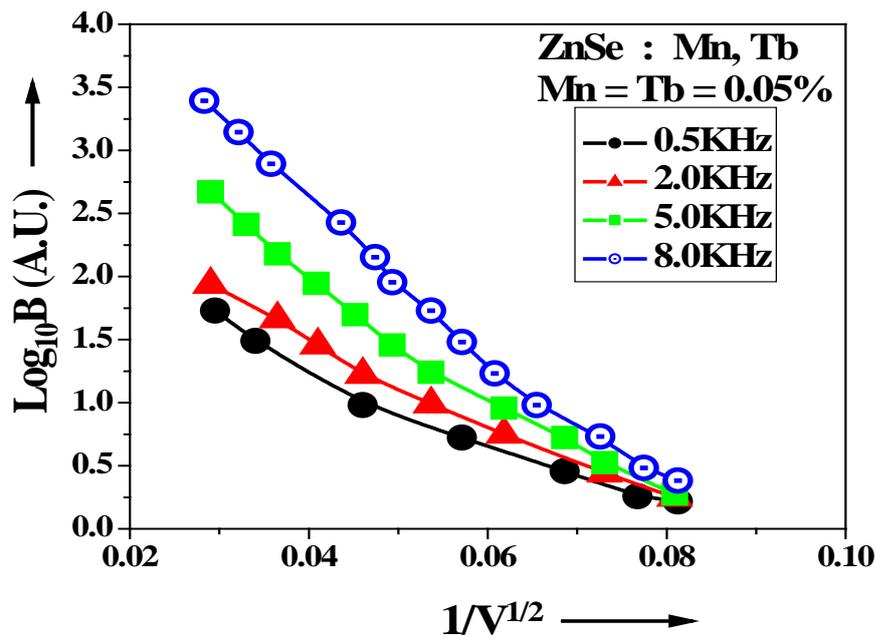


Figure 3: Voltage dependence of EL brightness (B) at various frequencies

Variation of log of mean EL brightness (B) with frequency at different constant voltage has shown in Fig. 4. Generally, it is found that the brightness increases sub-linearly with increasing field frequency. After attaining maximum value or saturation there is a decrease in the brightness on further increasing the field frequency. Such behavior was also obtained in related phosphors [3, 4, 8, 17].

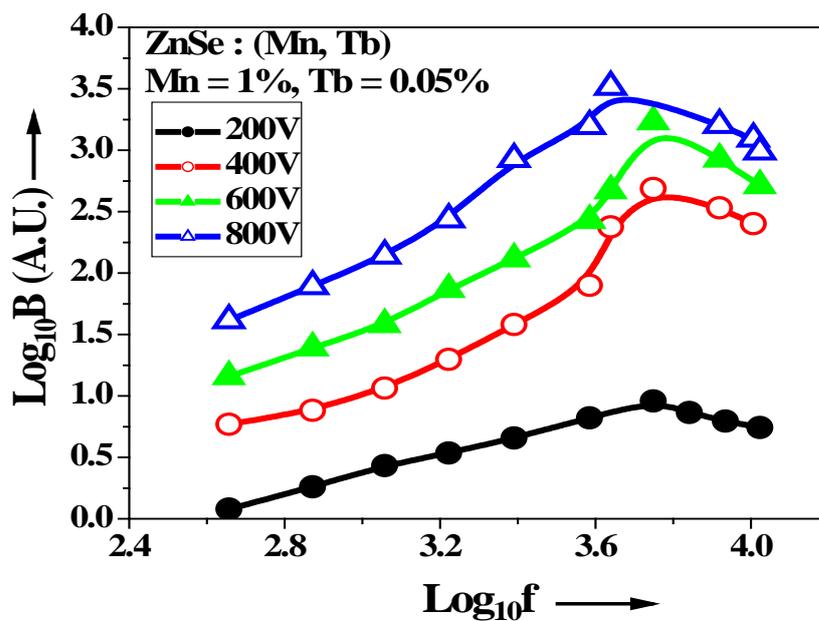


Figure 4: Frequency dependence of EL brightness

4. Conclusions

It is observed that the PL emission bands obtained in the spectra of these phosphors are almost similar to EL emission bands although relative intensities are different. Finally, we have concluded that there are two types of emission bands in PL and EL spectra, first those which are characteristics of ZnSe lattice slightly modified by the lattice ions and second those which are characteristics of impurities Mn^{2+} and Tb^{3+} ions. It is pertinent to point out that the metal phosphor contact Mott-Schottky type barrier is present. EL capacitors of these phosphors having wider distribution are more useful at moderate to high voltage. From the study of frequency dependence of EL brightness, we have concluded that the recombination is inhibited at higher frequencies. Anyway this conclusion is qualitative and further experiments are needed to find its quantitative effect.

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