

Laser-induced down-conversion parameters of singly and doubly doped ZnS phosphors

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Abstract. Singly and doubly doped ZnS phosphors have been synthesized using flux method. Laser-induced photoluminescence has been observed in ZnS-doped phosphors when these were excited by the pulsed UV N₂ laser radiation. Due to down-conversion phenomenon, fast phosphorescence emission in the visible region is recorded in milliseconds time domain for ZnS:Mn while in the case of ZnS:Mn:killer (Fe, Co and Ni) the lifetime reduces to microseconds time domain. Experimentally observed luminescent emission parameters of excited states such as, lifetimes, trap-depth values and decay constants have been reported here at room temperature. The high efficiency and fast recombination times observed in doped ZnS phosphors make these materials very attractive for optoelectronic applications.

Keywords. UV laser excitation; quencher impurities; excited state lifetimes; laser-induced photoluminescence.

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1. Introduction

Fluorescence and phosphorescence studies of luminescent materials doped with various impurities has been reported by a number of earlier workers [1–6] using different techniques employing laser and conventional excitation sources. Transient absorptions have been obtained in powdered samples of ZnS:Ag, ZnS:Cu and undoped ZnS at room temperature by the technique of diffuse reflectance laser flash photolysis [7] where broad featureless absorptions in the 500–850 nm region were recorded for ZnS:Ag and ZnS:Cu. The emission decays in these cases are non-exponential having initial half-lives of 3.1 ms and 0.48 ms for the Ag- and Cu-doped phosphors respectively. The luminescence of ZnS_{1-x}Fe_xS occur over a band between 2400 and 3000 cm⁻¹ which also shows pronounced zero phonon lines at 5 K [8]. Also luminescence output was reasonably independent of the Fe²⁺ concentration, thus indicating that iron is not a killer of its own luminescence. It has been shown [9] that the performance of phosphors for plasma display panels (PDPs) and CRTs is

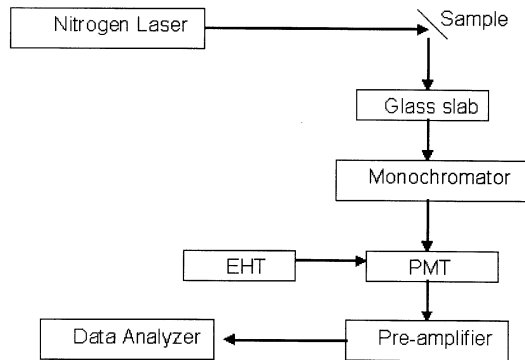


Figure 1. Block diagram of the experimental set-up for recording decay curves.

almost ideal with respect to their efficiencies. However, the decay time of green emitting Mn^{2+} phosphors for PDPs should be reduced further. In the present paper, lifetime values due to Mn^{2+} impurity are reduced to microseconds time domain with the addition of killer dopant (Fe or Co or Ni) to ZnS:Mn phosphors. Thus the lifetime shortening is achieved to get phosphors having fast decay times suitable for PDPs, CRTs and optoelectronic applications.

2. Experimental arrangements

ZnS-doped phosphors with variable concentration of dopants have been synthesized in the laboratory at a firing temperature of $1000 \pm 20^\circ\text{C}$ using the well-known flux method [3,10,11]. Four series of samples A–D were prepared (table 1). The decay of photoluminescence in doped phosphors, following excitation by a short UV N_2 laser pulses, depends on trap-depths introduced by the dopant in the forbidden gap of the phosphor. The analysis of photoluminescence decays reveals valuable information about the ‘centre’ chemistry of the luminescence and trap-depths. Nitrogen laser [11,12] is the most suitable excitation source (wavelength ~ 337.1 nm, pulse width ~ 10 ns and output peak power ~ 200 kW) for photoluminescence decay studies. High photon flux density (10^{19} photons per pulse) of the nitrogen laser is extremely useful to excite the short-lived shallow trapping states. The fast phosphorescence emission from the sample at an angle of 90° to the incident beam was collected by a fast photomultiplier tube (PMT) through an assembly of monochromator and glass slab used as a UV filter (figure 1). The decay signals from the phosphors were recorded by digital storage oscilloscope coupled with computer assembly. The recorded decay curves were analyzed by computer simulations to find out three lifetime values in almost all the samples.

3. Theoretical background

The intensity of luminescent radiation at time t is given as

$$I = I_0 e^{-pt}, \quad (1)$$

where I_0 is the intensity of radiation at cut-off position and the constant $p = 1/\tau$ is the transition probability of the corresponding radiative transition. τ is the lifetime of the excited state from where photoluminescence is monitored by fast PMT, the time spent by the electron in the trap before recombination. A plot of $\ln(I)$ vs. time will be a straight line in the case of single trap of energy, E . From the slope of the line, which provides the value of p , one can calculate the value of trap-depth, E , according to the Boltzmann's equation [3,10,13]

$$p = Se^{-E/kT}, \quad (2)$$

where S is the escape frequency factor ($\sim 10^9 \text{ s}^{-1}$), k is the Boltzmann's constant and T is the absolute temperature.

However, in most of the cases, when one comes across the interaction of radiation with solids, there are trapping levels at different depths which give rise to the different exponential decays superimposed with each other. Such types of decay curves due to the superposition of a number of exponential decays are popularly known as hyperbolic decay curves (figure 2). In the present case, a plot of $\ln(I)$ vs. time does not show a linear relationship because of the superposition of the number of exponential decays. Different components of a decay curve may be considered as emission due to traps of different depths. Thus it is reasonable to assume that as the number of exponentials increase, the decay curve changes from an exponential to a hyperbolic one. The decay curves have been peeled-off into maximum of three components by the peeling off method of Bube [13].

The distribution of traps in the energy band gap of doped phosphor can be studied from the equation [3,10]

$$I = I_0t^{-b}, \quad (3)$$

where b is called the decay constant. The value of decay constant explains the distribution of the trapping states introduced by the dopant within the band gap of the phosphor. If the value of decay constant is unity, the traps introduced by the impurity are uniformly distributed within the band gap of the phosphor. Otherwise there will be nonuniform distribution of the traps.

In an ideal case of uniform distribution of trapping states, one can assume an equal number of traps at all depths.

4. Results and discussion

\ln intensity vs. time is plotted from the decay curve of figure 2 by computer simulations which has been peeled off into three components. The slope of these components gives three probability values (p_1, p_2 and p_3). The lifetime values have been calculated from the relation $\tau = 1/p$. Thus three components of lifetimes (τ_1, τ_2 and τ_3) are extracted from figure 2. The value of p thus found, is substituted in eq. (2) along with other parameters leading to the calculated trap-depth values corresponding to various lifetime values. In these calculations the used value of escape frequency factor is 10^9 s^{-1} . The graph of \ln intensity vs. \ln time (not shown here) is plotted, the slope of which yields the value of decay constant b according to eq. (3). Table 1 shows the values of the excited state lifetimes, trap-depths and

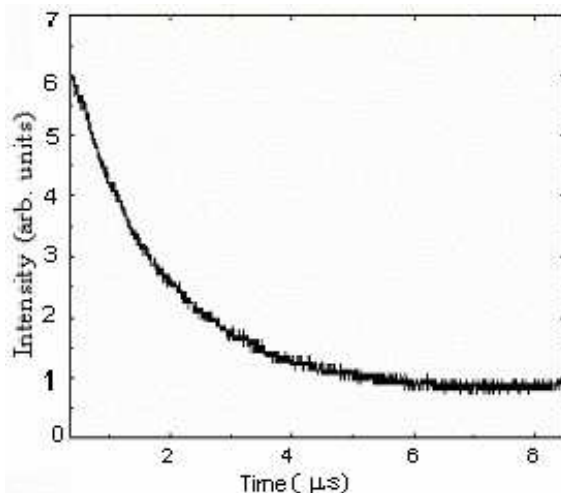


Figure 2. Hyperbolic type of luminescence decay curve for ZnS:Mn (0.05%): Co (0.05%) at room temperature showing three overlapping exponentials.

decay constants for different concentrations of the dopants at room temperature. The excited state lifetimes in the case of ZnS phosphors doped with Mn only are in milliseconds time domain and varies from 0.03 to 1.07 ms and the excited state lifetimes in the case of ZnS phosphors doped with Mn as well as killer impurity individually vary from 0.34 to 25.89 μs at room temperature.

The lifetime values decrease appreciably with the addition of killer impurities in ZnS phosphors doped with Mn. The trapping states which contribute significantly to the photoluminescence, range from 0.267 to 0.359 eV in the case of ZnS:Mn-doped phosphors. When killer impurity is added to ZnS:Mn-doped phosphors, the excitation of the shallow trapping states is dominated over the excitation of the deep trapping states and the trap-depth decreases by considerable amount varying from 0.151 to 0.263 eV. This shows that killer impurities are responsible for quenching the long-period phosphorescence emission from deep trapping states (0.267 to 0.359 eV) and also add their own shallow trapping states (0.151 to 0.263 eV) from which the short-period emission now dominates. However, the decay curve remains hyperbolic and does not change their nature with the addition of the killer impurities.

The trap-depth is maximum (0.359 eV) in the case of zinc sulphide phosphors singly doped with 0.05% of Mn and it is minimum (0.267 eV) in the case of zinc sulphide doped with 0.70% of Mn. The trap-depth is maximum (0.263 eV) in the case of zinc sulphide doubly doped with 0.05% of Mn as well as 0.05% of Fe and minimum (0.151 eV) in the case of zinc sulphide doubly doped with 0.30% of Mn as well as 0.70% of Fe. So it is seen that killer impurities (luminescence killers) such as iron, cobalt and nickel appreciably modify the trap-depths introduced by the dopant Mn.

The levels introduced by Mn in ZnS phosphors which are responsible for millisecond lifetimes are ${}^4T_1-{}^6A_1$. The change in the spin quantum number here is, $\Delta S = 1$. So this transition is forbidden by spin selection rules and the probability

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Table 1. Lifetime, trap-depth and decay constant values for ZnS:Mn and ZnS:Mn:(Fe, Co or Ni)-doped phosphors.

Series	Phosphor: impurity (%)	Lifetime values (μs) at 300 K			Trap depths (eV) at 300 K			Decay constant b
		τ_1	τ_2	τ_3	E_1	E_2	E_3	
A	ZnS:Mn(0.05)	0.16*	0.29*	1.07*	0.310	0.325	0.359	0.99
	ZnS:Mn(0.30)	0.05*	0.24*	0.81*	0.279	0.321	0.352	0.97
	ZnS:Mn(0.70)	0.03*	0.17*	0.72*	0.267	0.312	0.348	0.95
B ₁	ZnS:Mn(0.05):Fe(0.05)	3.09	5.89	25.89	0.207	0.225	0.263	0.76
	ZnS:Mn(0.05):Fe(0.30)	3.05	5.01	24.07	0.207	0.220	0.261	0.72
	ZnS:Mn(0.05):Fe(0.70)	2.07	3.15	15.11	0.197	0.208	0.249	0.92
B ₂	ZnS:Mn(0.05):Co(0.05)	2.06	3.62	11.32	0.197	0.212	0.241	0.80
	ZnS:Mn(0.05):Co(0.30)	1.69	2.52	7.18	0.192	0.203	0.229	0.91
	ZnS:Mn(0.05):Co(0.70)	1.57	2.44	5.79	0.190	0.202	0.224	1.07
B ₃	ZnS:Mn(0.05):Ni(0.05)	2.46	5.54	18.78	0.202	0.223	0.255	0.81
	ZnS:Mn(0.05):Ni(0.30)	2.43	5.03	18.03	0.202	0.221	0.253	0.92
	ZnS:Mn(0.05):Ni(0.70)	2.26	5.01	16.28	0.199	0.220	0.251	0.88
C ₁	ZnS:Mn(0.30):Fe(0.05)	2.89	4.56	20.11	0.206	0.217	0.256	1.23
	ZnS:Mn(0.30):Fe(0.30)	2.69	3.96	19.11	0.204	0.214	0.255	1.44
	ZnS:Mn(0.30):Fe(0.70)	0.34	1.28	9.21	0.151	0.185	0.236	1.33
C ₂	ZnS:Mn(0.30):Co(0.05)	2.07	3.39	16.94	0.197	0.210	0.251	0.81
	ZnS:Mn(0.30):Co(0.30)	1.62	2.39	5.53	0.191	0.201	0.223	1.13
	ZnS:Mn(0.30):Co(0.70)	1.47	2.03	4.77	0.189	0.197	0.219	1.09
C ₃	ZnS:Mn(0.30):Ni(0.05)	2.91	6.77	23.11	0.206	0.228	0.259	0.76
	ZnS:Mn(0.30):Ni(0.30)	2.34	6.07	22.12	0.201	0.255	0.259	0.89
	ZnS:Mn(0.30):Ni(0.70)	2.07	3.43	17.99	0.197	0.211	0.253	0.86
D ₁	ZnS:Mn(0.70):Fe(0.05)	3.94	5.17	25.01	0.214	0.221	0.262	0.81
	ZnS:Mn(0.70):Fe(0.30)	2.39	3.65	21.72	0.201	0.212	0.258	0.89
	ZnS:Mn(0.70):Fe(0.70)	2.11	3.57	20.11	0.198	0.212	0.256	1.18
D ₂	ZnS:Mn(0.70):Co(0.05)	1.78	2.93	9.59	0.193	0.207	0.237	0.84
	ZnS:Mn(0.70):Co(0.30)	1.60	2.73	9.49	0.191	0.205	0.237	0.79
	ZnS:Mn(0.70):Co(0.70)	1.57	2.67	9.26	0.190	0.204	0.236	0.86
D ₃	ZnS:Mn(0.70):Ni(0.05)	2.76	3.26	18.67	0.205	0.209	0.254	1.26
	ZnS:Mn(0.70):Ni(0.30)	1.61	2.25	16.85	0.191	0.199	0.251	1.21
	ZnS:Mn(0.70):Ni(0.70)	1.01	2.06	13.72	0.179	0.197	0.247	1.20

*Lifetime values in milliseconds.

of this transition is very low leading to long lifetime values, i.e. of the order of milliseconds. Due to addition of quencher impurities to ZnS:Mn phosphors there is energy transfer from Mn levels to killer impurity levels and the probability of the transition is found to increase which reduces the lifetime values.

The lifetime values decrease appreciably with the addition of killer impurities in ZnS phosphors doped with Mn. In series A there is considerable decrease in

lifetime values of ZnS:Mn phosphors when concentration of Mn is increased. In series B, C and D there is lifetime shortening when concentration of quencher impurity is increased in ZnS:Mn phosphors. The trap-depth values decrease with increase in concentration of killer impurities in series B, C and D which shows that photoluminescence from deep trapping states is quenched by the quencher impurity. The emission being faster in the present case is from relatively shallow trapping states. The decay constant values show that the distribution of the traps within the energy band gap of phosphors is nonuniform in most of the cases and do not change appreciably with changing dopant concentration.

5. Conclusions

Killer impurities were earlier supposed to be quenchers of luminescence but strong and fast photoluminescence is observed in our investigations. The photoluminescence in the present case is attributed to shallow trapping and fast decaying states due to killer impurities which has been excited efficiently due to the high peak power and short pulse-width of N₂ laser source. The luminescence lifetime of Mn²⁺ ions (ms) (⁴T₁-⁶A₁) from a spin forbidden ($\Delta S = 1$) transition was observed to decrease drastically by more than three orders of magnitude (ms to μ s) on adding quencher impurity to ZnS:Mn phosphors. Thus the need for phosphors having fast decay time has been achieved by the addition of killer dopants to the host ZnS:Mn phosphors. Extra electron may be injected to ZnS:Mn phosphor by the addition of dopant radical ion. The exchange interaction between the extra electron of the dopant and the impurity electron splits the energy levels and makes the former spin forbidden transition as allowed one which leads to fast lifetime of the transition from shallow trapping states.

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