

LIFETIME SHORTENING FROM MICRO TO NANO IN COPPER DOPED CaS AT LIQUID NITROGEN TEMPERATURE

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Copper doped Calcium sulphide phosphors having variable concentrations of killer impurities Fe, Co and Ni have been synthesized and then using laser excitation of samples for their photoluminescence behaviour, their decay-curve analysis has been done. Various strong emissions in these phosphors have been detected and the corresponding excited state lifetimes are measured at liquid nitrogen temperature. Studies have also been carried out to see the effect of killer impurities on the phosphorescence excited-state life times. With the addition of killer impurities appreciable decrease in lifetime values (microsecond to nanosecond) is reported. These studies are quite useful and find applications in the areas like optical memories, sensors, luminescent screens, laser-beam detection and alignment, colour displays, printing, etc. This work is an extension of the work earlier done by Bhatti *et al* (14-16) on CaS phosphors.

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1. Introduction

Life-time analysis using nondestructive techniques is always important regarding fluorescence and phosphorescence due to addition of dopants in the phosphors. Fluorescence and Phosphorescence studies of luminescent materials doped with various impurities were conducted by the earlier workers [1-4] using different techniques. H S Bhatti *et al* has earlier seen the effect of killer impurities on bulk CaS and ZnS phosphors doped with Mn (14-16). They have also studied the effect of killer impurities on ZnS nanophosphors (13) doped with Mn. But as the emission from the phosphor depends upon the nature of the dopant so it is necessary to try as many dopants as we can. As it is reported earlier by Bhatti *et al* that killer impurities have an appreciable effect on the excited state lifetimes so we are trying to see the effect of these killer centers using copper as no body had studied the effect of killer impurities on copper yet. The experimental determination of excited state lifetimes becomes more reliable with modern laser spectroscopic nondestructive techniques and advanced methods of sample preparation [5-7]. This approach yields better results. Pulsed Nitrogen laser having operating wavelength in UV region, short pulse-width, large photon flux density and high repetition rate is quite useful for excitation of shallow trapping states, and to calculate the lifetime values at liquid nitrogen temperature. The decay of luminescence in doped phosphors, following excitation by a short laser pulse, depends on trap-distribution in the forbidden gap of the phosphor. This paper presents quite precise measurements of excited state lifetimes under short laser-pulse excitation at liquid nitrogen temperature. The excited-state lifetime studies find wide industrial applications in diverse fields like photo-luminescent screens,

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laser-beam detection and alignment, colour displays, printing etc; these emissions, in general, being in the visible range.

2. Experimental

Generally phosphors are prepared by the well known flux method[8] but we synthesise the required phosphor by starting with spectroscopic grade non-luminescent CaS and then adding the desired amount of dopants Cu, killer impurities(Fe, Co & Ni) individually and flux(30% sodium sulphate) by weight. The whole mixture is fired in the graphite crucible at 900° C for two hours. The mixture is then cooled and washed with distilled water to remove the residual impurities. Laser induced pulse excitation method (Fig-1) is used to study the PL spectra. Nitrogen laser is the most suitable excitation source (337.1 nm) to irradiate the CaS phosphors having pulse-width of 5-7ns and average power of 10 kW and peak power of 1MW. High photon flux density of the Nitrogen laser is extremely useful to excite the short-lived shallow trapping states. The short-lived phosphorescence from the sample at an angle of 90° to the incident beam was collected by a fast photo-multiplier tube through an assembly of monochromator having a Least count of 1nm and cryostat CF-426(input window of quartz and output window of glass) with temperature controller CTC-2000. The decay signals from phosphors were recorded by digital storage oscilloscope(TDS-1012) and analysed using computer simulations to calculate excited state lifetimes of the phosphors.

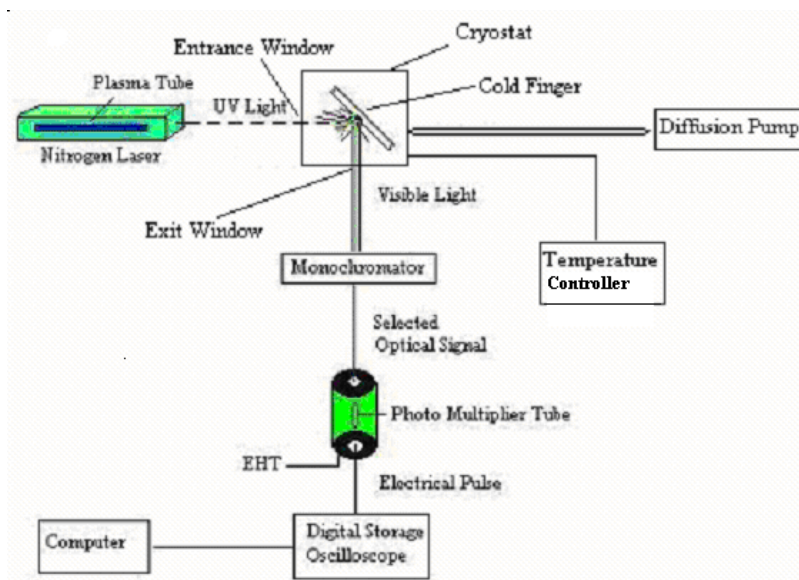


Fig-1 Experimental setup for liquid nitrogen studies

3. Theoretical

When samples are exposed to the laser radiation, the electrons are raised from valence band to excited states. These electrons may return to the valence band with the emission of characteristic luminescent radiation. If 'n' be the number of electrons in an excited state at time, t, and, dn be the number of electrons decaying in time, dt[9-10]. For this decay

$$\frac{dn}{dt} = -pn \quad (1)$$

$$n = n_0 e^{-pt} \quad (2)$$

or, intensity is given by

$$I = I_0 e^{-pt} \quad (3)$$

where 'I' is the intensity of phosphorescence radiation at time, t, and I_0 , the intensity of radiation at cut-off position and the constant 'p' is the transition probability of the corresponding radiative transition. A plot of 'log I vs t' will be a straight line in case of *single set of traps* of energy, E. From the slope of line we can calculate value of trap depth 'E' according to equation:

$$P = S e^{-E/kT} \quad (4)$$

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

However, in most of the cases, when we come across the interaction of radiation with solids, there are trapping levels at many different depths. In an ideal case of uniform distribution, one can assume an equal number of traps at all depths. Under this assumption if n_E be the number of traps in the energy range E and E+dE, the intensity of phosphorescence at any time, t, is given by :

$$I = \int n_E S e^{-E/kT} \exp(-St e^{-E/kT}) dE \quad (5)$$

which on integration yields

$$I = nkT/t(1 - e^{-St})$$

$$I = nkT t^{-1}.$$

However in most of the cases, the distribution of traps, at different depths, is not uniform and is given by equation:

$$I = I_0 t^{-b} \quad (6)$$

where b is called the decay constant.

Table-1 show the values of the excited-state lifetimes for different transitions.

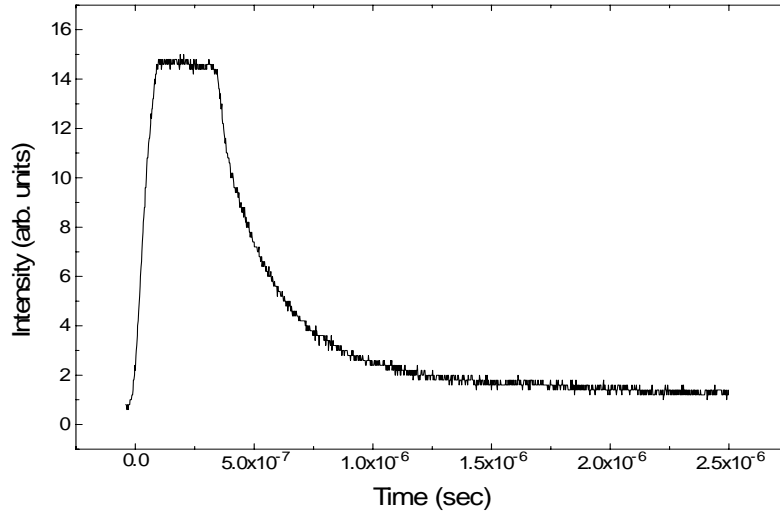


Fig. 2. Decay curve for CaS:Cu(0.1%)Fe (0.1%).

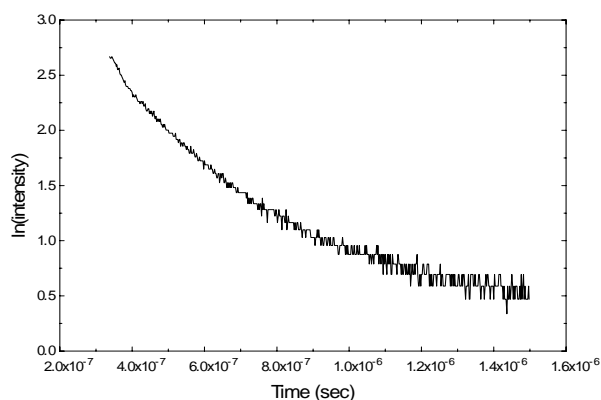


Fig-3 $\text{Log}_e(I)$ Vs time for $\text{CaS}:\text{Cu}(0.1\%)\text{Fe}(0.1\%)$

Table-1

Phosphor: Impurity(%)	Life time values (μs) at 77°K * (nsec)		
	τ_1	τ_2	τ_3
CaS:Cu(0.1%) :Fe(0.05%)	980*	400*	250*
CaS:Cu(0.1%) :Fe(0.1%)	1.03	340*	240*
CaS:Cu(0.1%) :Fe(0.3%)	1.30	340*	240*
CaS:Cu(0.1%) :Fe(0.5%)	50.10	15.53	10.20
CaS:Cu(0.1%) :Fe(0.7%)	52.15	18.35	13.00
CaS:Cu(0.1%) :Fe(1%)	52.17	18.34	13.10
CaS:Cu(0.1%) :Co(0.05%)	2.40	600*	250*
CaS:Cu(0.1%) :Co(0.1%)	2.48	620*	200*
CaS:Cu(0.1%) :Co(0.3%)	2.72	620*	250*
CaS:Cu(0.1%) :Co(0.5%)	45.14	30.67	8.56
CaS:Cu(0.1%) :Co(0.7%)	46.15	29.02	9.20
CaS:Cu(0.1%) :Co(1%)	48.10	30.75	10.12
CaS:Cu(0.1%) :Ni(0.05%)	1.30	320*	240*
CaS:Cu(0.1%) :Ni(0.1%)	2.00	440*	210*
CaS:Cu(0.1%) :Ni(0.3%)	2.72	610*	250*
CaS:Cu(0.1%) :Ni(0.5%)	50.19	17.43	12.11
CaS:Cu(0.1%) :Ni(0.7%)	50.21	20.66	13.43
CaS:Cu(0.1%) :Ni(1.0%)	60.30	18.79	13.10

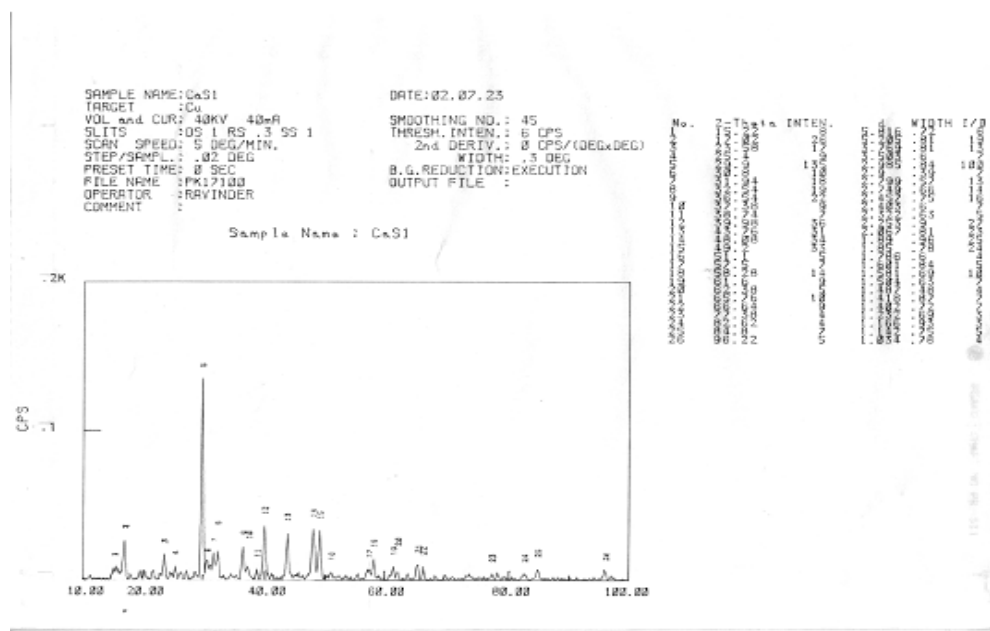


Fig-4 XRD of host CaS

4. Results and discussions

With the addition of killer impurities, lifetime values are found to be in the range of 200ns to 60.30 μ s. Lifetime is maximum in case of Calcium Sulphide doped with 0.1% of Copper and 1% of Nickel. Lifetime is minimum in case of Calcium Sulphide doped with 0.1% of Copper and 0.1% of Cobalt. CaS is a very versatile phosphorescent host material. Quantized semiconductor particle is a novel state of matter for the material science. It is found that the photoluminescence mechanism of doped CaS phosphors is a very complex process. Basically there are two types of luminescence centers involved in the luminescence process of doped phosphors. The first of these is the luminescence center, which is made up of an imperfection and second is the trapping center in which an electron trapped is effectively in an excited state from which a transition to the ground state cannot take place directly. Nature of the luminescence center determines the spectral distribution of emission from the phosphor, whereas the nature of the trapping center is a major factor in determining how the emission will decrease with time after the cessation of excitation.

To understand the internal mechanism going on in the phosphors, the decay curves of phosphorescence (intensity vs. time) were recorded as shown in Figs-2-3 which were hyperbolic in all the cases rather than exponential nature. These hyperbolic decay curves were analysed using computer simulations to find out three lifetime values (τ_1 , τ_2 , τ_3). An interesting feature of the analysis is that the phosphorescence decay becomes faster with

the addition of killer impurities (Fe Co Ni) which were earlier supposed to be only quenchers of luminescence. This unique result is attributed to the use of UV radiation of high power short pulse-width nitrogen laser.

The fast lifetime component (τ_3) is attributed to the shallow trapping states while longest lifetime component (τ_1) corresponds to the decay from the relatively deeper traps. The medium lifetime value (τ_2), corresponds tentatively to the decay from the intermediate levels between the shallow trapping states and deeper traps.

There is lot of increase in the value of lifetimes in case of all the phosphors at higher concentration of killer impurities. It means more deeper traps are involved in the luminescence

with the increase in the dopant concentration, whereas the lifetime values are very less at lower concentration of dopants in comparison to the phosphors doped with higher concentration of killer impurities. It means shallower trapping states are excited at lower dopant concentration. The reduction in the magnitude of trapping states leads to the conclusion that the radiative transitions play a dominant role in the decay processes of these phosphors at lower concentration of killer impurities at liquid nitrogen temperature. The sharp increase in the values of lifetimes or trapping states at a particular concentration of the dopant in case of CaS doped phosphors can be explained due to the decay from deep trapping states introduced in the larger band-gap of these phosphors. Colour of the emission remains the same even after the variation of concentration of killer impurities in the copper doped phosphors. XRD studies show the host material CaS to be cubic(Fig-4).

5. Conclusions

The phosphorescence decay becomes faster(nano-second time domain) with the addition of Fe, Co and Ni, in the doped phosphors as compared to the singly doped phosphors at lower concentration of dopants i.e CaS doped with Cu [11-12 and references there in] . Three lifetime values were observed in all the cases which shows that the decay curves are still hyperbolic in nature even after the addition of killer impurities as compared to the decays in case of singly doped phosphors. Generally shallow trapping states are introduced in the band-gap of the phosphors from which fast lifetime values were observed with an exception of few cases at higher concentration of dopants where deep trapping states were introduced which are responsible for long lifetime components. A decreasing trend of the lifetime values at lower concentration of dopants in comparison to the lifetimes of singly doped CaS phosphors leads to the conclusion that nature of transitions in these phosphors are dominantly radiative in nature due to the addition of the killer impurities at liquid nitrogen temperature.

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