

Laser-induced phosphorescence studies of doubly-doped CaS phosphors

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Effect of killer impurities (Fe, Co and Ni) on excited state life-times in CaS phosphors, doped with copper and having variable concentrations of iron, cobalt and nickel has been studied in this paper. The phosphors have been synthesized, and, then using a nitrogen laser as the excitation source, their decay-curve analysis has been done. Various strong emissions have been detected and the corresponding excited state life-time values measured. These studies are conducted at room temperature. Very interesting results are obtained with the addition of killer impurities in the phosphors with single impurity. Life-time values found to decrease appreciably with the addition of killer impurities (at lower concentration) in the singly doped phosphors. These studies are important as the excited state life-time of the sulphide phosphors prepared by flux method converge to the longer side only, but with the addition of killer impurities at a particular concentration, values of the life-times decreases up to large extent. At higher concentration of killer impurities deeper traps contribute to the phosphorescence, leading to the much higher increase in life-time values.

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Excited state life-time analysis is always important regarding fluorescence and phosphorescence produced due to the addition of dopants in the phosphors. Fluorescence and phosphorescence studies of luminescent materials doped with various impurities were conducted by the earlier workers¹⁻⁴ using different techniques. The experimental determination of excited state life-times becomes more reliable with modern laser spectroscopic techniques⁵⁻⁷. 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 life-time values at room temperature. The decay of luminescence in doped phosphors, following excitation by a short laser pulse, depends on trap-depths in the forbidden gap of the phosphor. This paper presents quite precise measurements of excited state life-times under short laser-pulse excitation at room temperature. This analysis reveals valuable information about the 'centre' chemistry of the luminescence and trap-depths. The sulphide phosphors have wide industrial applications in diverse fields like photo-luminescent screens, laser-beam detection and alignment, colour displays and printing; these emissions, in general, being in the visible range.

Experimental

Sulphide phosphors are generally prepared by the well-known flux method⁸. The required phosphor is synthesized by starting with spectroscopic grade non-luminescent CaS and then adding the desired amount of dopants AR grade Cu, killer impurities (Fe, Co and Ni) and flux (Na₂SO₄) by weight and then the whole mixture is fired in the graphite crucible at 900°C for two hour. The mixture is then cooled and washed with distilled water to remove the residual impurities. Nitrogen laser is the most suitable excitation source (337.1 nm) for phosphorescence studies. 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 (Make: ECIL, Model: SH644W) having rise time of the order of ns through an assembly of monochromator and glass slab as a filter for UV radiation (Fig. 1). The decay signals from the phosphors were recorded and analyzed to calculate excited state life-times accurately up to two decimals.

Theoretical

When samples are exposed to the laser radiation, the electrons are raised from valence band to excited

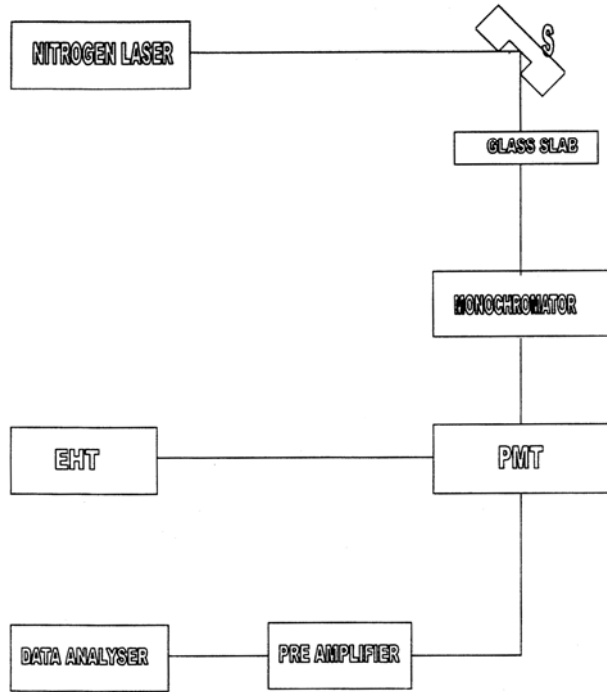


Fig. 1— Block diagram of instrumentation for life-time measurements

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 (refs 9 and 10), then:

$$\frac{dn}{dt} = -pn$$

$$n = n_0 e^{-pt}$$

or, intensity is given by

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

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. From the transition probability we can find out the excited state life-time as $\tau = 1/p$. A plot of $\ln I$ versus 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:

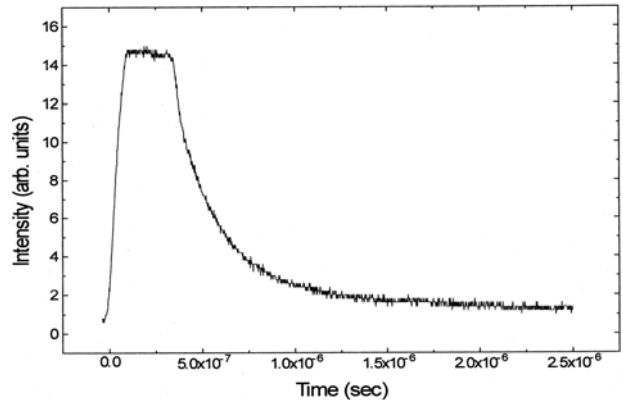


Fig. 2—Decay curve (intensity versus time) of CaS:Cu (0.1%):Fe(0.1%)

$$p = S e^{-E/kT} \quad \dots (2)$$

where S , is the escape frequency factor ($\sim 10^9 \text{ s}^{-1}$); k , the Boltzmann 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 be the number of traps in the energy range, E and $E+dE$, the intensity of phosphorescence at any time, t is given by:

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

which, on integration, yields

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

$$I = nkT t^{-1} \quad \text{for } st \gg 1$$

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

$$I = I_0 t^{-b} \quad \dots (3)$$

where b is called the decay constant and $I_0 = nkT$.

If b is unity then the trap distribution is uniform, but, if it is not unity, then the trap distribution is non-uniform.

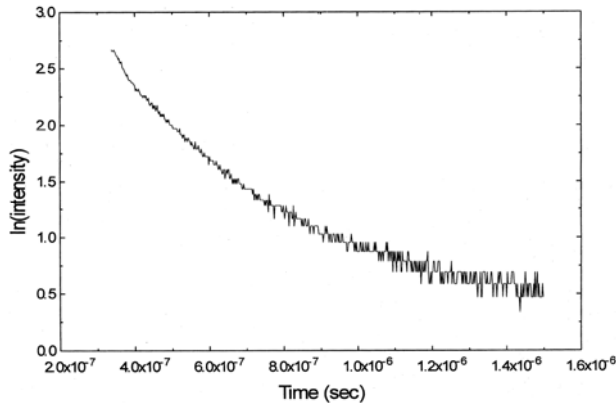


Fig. 3—Log intensity versus time

Table 1—Excited state life-times and emission intensities of CaS(Cu:Fe) phosphors

Phosphor: Impurity(%) Cu:(0.10)	Excited state life-times and emission intensities at 300 K			
	τ_1 (μ s)	τ_2 (μ s)	τ_3 (μ s)	Intensity (arb. units)
CaS:Fe:(0.05)	1.40	0.58	0.22	1.0
CaS:Fe:(0.10)	1.43	0.65	0.30	3.0
CaS:Fe:(0.30)	1.66	0.41	0.13	9.0
CaS:Fe:(0.50)	60.30	18.81	13.05	14.5
CaS:Fe:(0.70)	61.73	19.12	13.24	2.1
CaS:Fe:(1.00)	61.90	19.85	13.77	0.9

Results and Discussion

Figs 2 and 3 show the decay curves: 'Intensity versus time' and 'ln Intensity versus time'. Tables 1, 2 and 3 show the values of the excited state life-times for different transitions.

The different components of a decay curve may be considered as emission due to traps of different depths. Thus, it is reasonable to assume as the number of exponentials increase, the decay curve changes from exponential to hyperbolic decays. The minimum number of exponentials required are three to form a hyperbolic decay curve. The decay curves can be peeled-off into three components by the peeling off method of Bube¹. The results of decay curves can be expressed as:

$$I = I_{01} \exp(-p_1 t) + I_{02} \exp(-p_2 t) + I_{03} \exp(-p_3 t) \quad \dots (4)$$

where P_1 , P_2 and P_3 are the transition probabilities and these can be measured by analyzing the decay curves as discussed above.

Table 2—Excited state life-times and emission intensities of CaS(Cu:Co) phosphors

Phosphor: Impurity(%) Cu:(0.10)	Excited state life-times and emission intensities at 300 K			
	τ_1 (μ s)	τ_2 (μ s)	τ_3 (μ s)	Intensity (arb. units)
CaS:Co:(0.05)	2.50	0.69	0.22	3.0
CaS:Co:(0.10)	2.67	0.73	0.23	13.0
CaS:Co:(0.30)	2.93	0.84	0.23	0.9
CaS:Co:(0.50)	51.11	39.76	12.48	0.5
CaS:Co:(0.70)	50.09	38.26	12.64	0.3
CaS:Co:(1.00)	52.30	39.87	13.92	0.3

Table 3—Excited state life-times and emission intensities of CaS(Cu:Ni) phosphors

Phosphor: Impurity(%) Cu:(0.10)	Excited state life-times and emission intensities at 300 K			
	τ_1 (μ s)	τ_2 (μ s)	τ_3 (μ s)	Intensity (arb. units)
CaS:Ni:(0.05)	2.34	0.55	0.24	4.2
CaS:Ni:(0.10)	2.58	0.58	0.25	13.1
CaS:Ni:(0.30)	3.71	0.73	0.28	13.5
CaS:Ni:(0.50)	52.16	18.34	13.09	14.0
CaS:Ni:(0.70)	50.20	20.67	13.52	3.0
CaS:Ni:(1.00)	51.77	22.15	14.48	2.0

With the addition of killer impurities (Fe, Co, Ni), excited state life-time values are found to be decreased appreciably and are in the range of 0.22 to 61.73 μ s at room temperature. The life-time is maximum in case of calcium sulphide doped with 0.70% of Fe, and, it is minimum, in case of calcium sulphide doped with 0.05% of cobalt, keeping the percentage of copper constant, i.e., 0.10%. The phosphorescence in inorganic phosphors is due to absorption of electrons below conduction band. The thermal energy, at room temperature, is sufficient to empty the shallow traps, which, therefore, become ineffective in phosphorescence decay. That is why faster life-times in case of sulphide phosphors are not easily achievable. To understand the luminescent nature of all the phosphors through phosphorescence decay curve characteristics, the after-glow intensity as a function of time was recorded for all the phosphors. Phosphorescence intensity (I) versus time (t) plot shows the same pattern of decay, i.e., hyperbolic with the addition of multiple killer impurities (Fe, Co, Ni) as is observed in case of single impurity^{11,12}. The 'ln I versus time' plot does not show a linear relationship because of superposition of number of exponential decays. As

the number of exponential distributed traps increases, the decay takes the form of hyperbolic nature due to superposition of their intensities, each of which is varying exponentially with time. The effect of addition of killer impurities shows that excited state life-time decreases as compared to the life-time of the phosphors doped with only Cu^{13} up to a particular concentration but after certain value of concentration life-time values increase appreciable leading to the conclusion that deeper traps contribute to the phosphorescence. The effect of concentration on excited state life-times is very less which suggests that emission is due to the host defect but pure calcium sulphide does not show any luminescence effect. It leads to the fact that the addition of dopants have a perturbation effect on the defects of the host material.

Conclusions

Addition of killer impurities results in decreasing the excited state life-times at a particular concentration. Effect of 'change in dopant concentration on life-times' is, in general, insignificant. It means that the impurities have only perturbation effect on the defects in the host material, which are responsible for phosphorescence emission.

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