ON THE LUMINESCENCE CHARACTERISTICS OF CERIUM AND COPPER DOPED
BARIUM SULPHIDE PHOSPHOR

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Photoluminescence, thermoluminescence and phosphorescence studies of cerium and copper doped BaS phosphors are attempted. Cu^+ centres in BaS lattice activate red emission while Ce^{3+} sensitize the blue emission. Results are explained on the basis of superposition theory involving monomolecular kinetics. In Randall and Wilkins model, the decay and TL studies are found to corelate each other.

Because of the increased potential applications of alkaline earth sulphide phosphors in lasers, LED's, flat panel diplays etc., the development of phosphors with high quantum efficiency is very essential. Although considerable amount of work has been made in this direction, the mechanism of energy transfer and nature of lumiminescence centers in these phosphors are not yet fully understood. Amongst the II-VI compounds BaS is the least studied material. This paper gives an account of photoluminescence (PL), thermoluminescence and decay characteristics of BaS phosphors doped with cerium and copper impurities.

BaS:Cu, BaS:Ce and BaS:Ce:Cu phosphors were prepared by firing the mixture of $BaSO_4$ and dopants along with $Na_2S_2O_3$ as flux and carbon powder as reducing agent [1]. It was observed that the fluorescence efficiency was a maximum for flux concentration at 25% by wt of BaS. The samples in the form of circular disc of 10mm dia and 3mm thickness were exicited using 365nm line of Hg lamp. Fluorescence emission was recorded using 0.5m Jarrel ash monochromator coupled with PMT (PR-1400RF) followed by a pre-amplifier and omniscribe strip chart recorder. For TL measurements the samples were fixed on a specially designed sample holder with provisions for heating the samples at a uniform rate.

All observations were made at room temperature and all the emission spectra were corrected for monochromator dispersion and PMT response. Fig.1 shows the PL emission spectra for some of the typical samples in each series. Pure BaS phosphor shows emission bands at 450nm, 585nm and 613.4nm. In the case of BaS:Cu samples the emission intensity of 450nm band decreases while the band in the red region becomes more intense. The band at 585nm and 613.4nm merges into a single intense band with peak position at 600nm. Another important feature noticed in the emission spectra is that at high concentrations of the dopant, a shoulder band appears at
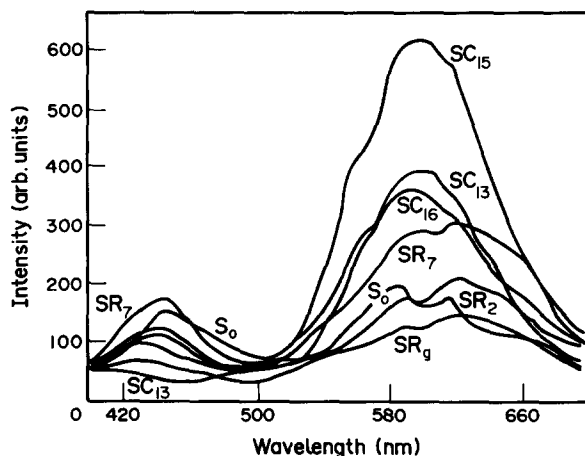

Fig.1. Luminescence emission spectra of pure and doped BaS phosphors.

(S_o - pure BaS, SC - Copper doped BaS, SR - Cerium doped BaS).

560nm. For cerium doped BaS phosphors the band in the orange-red region becomes very broad. However both bands gain intensity as the concentration of the dopant increases. The usual concentration quenching effect is observed in both cases of doped BaS phosphor.

The flux in the form of sodium thiosulphate in the lattice will create more cation vacancies. The recombination of localised holes in these cation vacancy levels with e^-s from conduction band cause the emission of 450nm band. The increase in intensity of this band for BaS:Ce phosphor with increase of dopant concentration also support this assumption. When cerium is doped, it goes as a trivalent cation in the lattice. In fact cerium in the trivalent form in BaS lattice sensitize the blue emission. The band at 613.4nm can be attributed to the annihiliation of

localised e⁻s in the vicinity of anion vacancy and the holes trapped at the level A (Fig.2). The difference between these two band energies gives the location of anion vacancy level and cation vacancy level in the forbidden gap. From these two band positions we obtained the band gap of BaS as ∼ 4eV which agrees well with the earlier reports [2,3]. S^{2-} in the vicinity of cation vacancy and Ba^{2+} in the vicinity of anion vacancy will form a complex $(V_{Ba}2+ +V_S2-)$ giving rise to an additional level B in the forbidden gap. The recombination of holes trapped in this level with e⁻s trapped in V_S2- will give the band in 585nm region.

Copper in BaS latice reduce the population of cation vacancies and this is why as the copper concentration increases, the intensity of blue band decreases and almost disappear at high copper concentrations (at 3.3% wt of BaS). The intense red emisssion at 600nm of BaS:Cu phosphor is due to the transition ^3E_g (3P) ⟶ $^1A_{1g}$ (1S) of Cu^+. A weak transition may also occur due to $^3T_{2g}$(3P) ⟶ $^1A_{1g}$(1S). This appears as the shoulder band at 560nm. As there is no shift in peak positions with increase of the dopant concentration it is further concluded that copper is incorporated substitutionally. In short copper acts as an activator for BaS red emission.

The self-activated BaS shows phosphorescence emission only for about 50 sec while BaS:Ce samples show intense phosphorescence in the green region for about 70 sec or more. But in the case of Cu doped samples eventhough the decay is very small, the afterglow has considerable intensity in orange-red region. The doubly doped samples show intense afterglow and comparitively larger decay time. The presence of Cu^+ enhance the decay time of BaS:Ce phosphor.

Decay studies show that log I – log t (Fig.3a) graph is a straight line with clear discontinuities indicating the hyperbolic nature of decay. Also

$$I(t) = I_o t^{-b} = \underset{m}{\leq} I_{om} \exp(-P_m t)$$

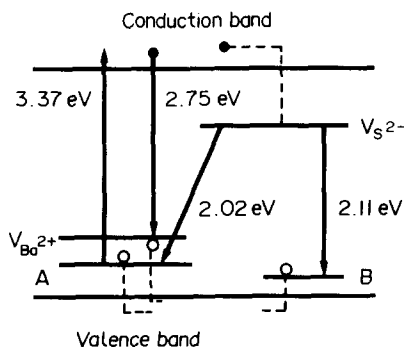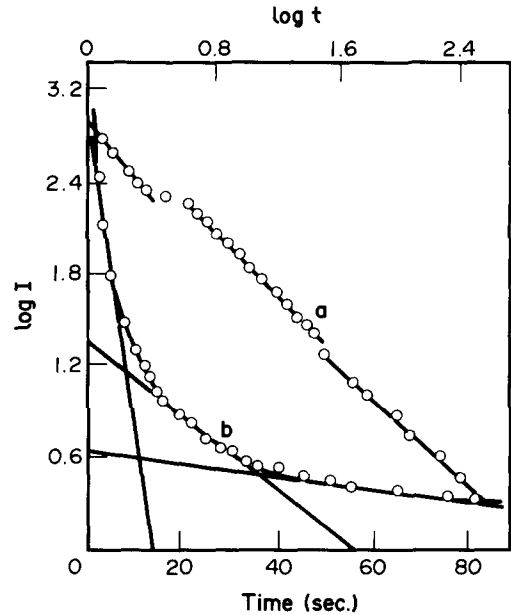Fig.2. Emission model of BaS phosphor.

Fig.3. Decay analysis graphs

(a) log I – log t plot

(b) log I – t plot

where P_m = S exp $(-E_m/KT)$, S the escape frequency factor obtained from TL studies is 10^6/sec (Table 2). The trap depth E_m has been calculated using the peeling off method [4] (Fig.3b) and found to vary from 0.4eV to 0.59eV (Table 1). The values of deay constants 'b' are found to be lying between 0.1 and 1.1 suggesting that the observed decay can be interpreted on the basis of monomolecular superposition theory. Hence the kinetics involved here is of first order which rules out the possibility of re-trapping.

The relative population of trapping level N_n at t=0 can be obtained by extrapolation of log I vs time graph using the relation $N_n (t)_{t=o} = I (t)_{t=o} \tau_n$ where $\tau_n = 1/P$ is the life time of e⁻s trapped in the trap having depth E_m. The ratios $N_n(t)_{t=o} /N_n (t)_{t=5}$ are calculated for the three peeled off components and are given in Table 1. The variation in these values indicates that the deepest traps are more densely filled than the shallow ones. The low values of τ obtained for the slowest exponential are due to the fact that as the time goes on the shallow traps become empty faster than the deeper ones.

In order to draw a conclusion about the type of kinetics involved in the luminescence process, the TL measurements have been made systematically at RT. The samples under study after excitation to a saturation level, were left to decay for about 5 minutes. It was then heated at a uniform rate and the glow curves were plotted (Fig.4).

Table 1   Activation energies and electron population ratios from decay analysis

Sample no.	Con. of the dopant % wt of BaS		Trap depths from peeling off of decay curves (eV)			Electron population ratio for three 'peeled off' components corresponding to		
	Ce	Cu	Slowest exp. eV	IInd exp. eV	Fastest exp. eV	Slowest exp.	IInd exp	Fastest exp.
S_0	0	0	0.53	0.49	0.46	1.01	1.04	1.15
SR_2	0.009	0	0.54	0.50	0.46	1.01	1.03	1.17
SR_4	o.2	0	0.56	0.51	0.44	1.01	1.04	1.18
SR_9	3.6	0	0.55	0.54	0.41	1.01	1.04	1.18
SC_{10}	0	0.01	0.57	0.53	0.50	1.02	1.03	1.25
SC_{13}	0	0.6	0.51	0.47	0.44	1.07	1.18	1.41
SC_{15}	0	3.3	0.51	0.45	0.42	1.02	1.12	1.77
SS_{17}	0.7	0.1	0.50	0.47	0.44	1.04	1.10	1.95
SS_{18}	0.7	0.8	0.50	0.47	0.45	1.07	1.11	2.13
SS_{19}	0.7	3.3	0.52	0.48	0.43	1.02	1.07	3.2
SS_{20}	0.009	3.3	0.53	0.46	0.44	1.02	1.3	1.42
SS_{23}	2.1	3.3	0.49	0.47	0.41	1.09	1.21	∠.5

Table 2   Trapping parameters from TL studies

Sample no.	Trap depth E (eV)					Escape frequency factor 'S' (Sec⁻)	
	Urbach's method	Curie method	Chen's method	Gross-Weiners method	Randall and Wilkins method	Chen's method	Curie method
SS_{17}	0.7	0.58	0.52	0.7	0.46	1.01×10^6	1.31×10^6
SS_{18}	0.78	0.65	0.65	0.51	0.48	0.68×10^6	0.89×10^6
SS_{19}	0.75	0.62	0.48	0.54	0.44	0.05×10^6	$.075 \times 10^6$

Only the doubly doped phosphors show appreciable TL emission with peak temperature (T_m) around 350K. The traps empty as temperature rises the shallow ones first. At each temperature T, those with life times of a fraction of a second or so are responsible for the observed increase in the intensity of the glow curves. The trapping parameters are calculated by different methods [5-9] which agree well with those obtained by R.P. Rao et al [10]. The single peak observed in the case of all samples studied indicates the probability of only one trapping level operative under experimental conditions is associated with these phosphors. Presence of Cu^+ enhances the TL efficiency of BaS:Ce samples. At
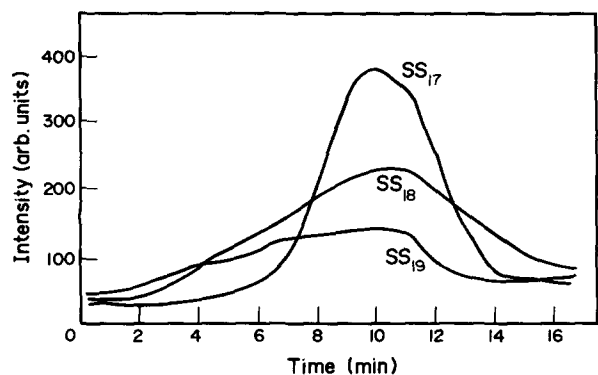
high concentration of Cu^+ however the characteristic Cu^+ emission decreases the probability of electron trapping showing the decrease in TL efficiency.

Electron traps in the forbidden gap are due to the host lattice point defects. Vacancies of Ba^{2+} and S^{2-} are responsible for the formation of such metastable states. Decay studies show that doping of Ce^{3+} enhances decay time. Copper doped phosphors show comparitively shorter decay time. This is due the fact that cerium enhances vacancy population while the characteristic emission of Cu^+ reduces the role of vacancies in luminescence emission. Simultaneous incorporation of Cu^+ and Ce^{3+} will populate deeper traps more efficiently.

Fig.4. TL emission spectra of some typical phosphors

(SS - doubly doped BaS)

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