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Nature of traps in CaS:Bi:Pd phosphors

Luminescence behaviour of alkaline earth sulphide phosphors activated with one or more impurity elements has been studied by many workers. Recently, studies on CaS phosphors co-activated with Bi^{3+} and various rare earth elements have been reported [1-3], and the effect of ferromagnetic impurity on the behaviour of CaS:Bi phosphors has been investigated by Zope and Walunjkar [4]. The thermoluminescence behaviour of CaS:Bi:Pd phosphors has also been studied and reported previously by the present authors [5]. However, these studies have been mainly devoted to the determination of trap depths and the spectral distribution of luminescence radiation and very little is known about the nature of traps in these phosphors. In this letter we report photo- and thermoluminescence studies carried out on CaS:Bi:Pd phosphors with a view to investigating the physical and chemical nature of traps responsible for the luminescence.

CaS:Bi:Pd phosphors containing varying concentrations of Bi and Pd were prepared by thermal reduction of purified gypsum, as described earlier [5]. Half the amount of the prepared samples was sulphurized in an atmosphere of H_2S at 900° C for $2\frac{1}{2}$ h. The samples studied are listed in Table I.

Fig. 1 shows typical decay curves for the sulphurized and unsulphurized samples. It is evident that the nature of the decay in both cases is similar, but the phosphorescence intensity in the case of sulphurized samples has decreased considerably. In the thermoluminescence study it is found that sulphurization does not give rise to new glow peaks and the peak position and shape of the glow curves also remain essentially unaltered. However, sulphurization has the effect of reducing the thermoluminescence intensity considerably (Fig. 2). These results indicate that sulphurization does not modify the mode of decay or the shape of the glow curves, but it certainly does cause a reduction of trapping levels responsible for photo- and thermoluminescence.

From decay and glow curves, the activation energies for sulphurized and unsulphurized samples were determined. The activation energies

TABLE I Experimental details and values of E for sulphurized samples

Sample no.	Concentration of Bi (wt %)	Concentration of Pd (wt %)	Values of E from "peeling off" of decay curves (eV)			Values of E from glow curves (eV)	
			Slowest exponential	Second exponential	Fastest exponential	First peak	Second peak
S4	0.00	0.001	0.63	0.52	0.48	0.66	—
S13	0.00	0.25	0.64	0.55	0.52	0.64	—
S17	0.005	0.00075	0.58	0.50	0.41	0.58	—
S31	0.01	0.00075	0.52	0.44	0.39	0.52	0.61
S45	0.05	0.00075	0.51	0.48	0.45	0.55	—
S57	0.1	0.00	0.55	0.46	0.42	0.55	0.73
S61	0.1	0.0025	0.53	0.47	0.43	0.57	—
S64	0.1	0.01	0.55	0.46	0.42	0.59	0.69
S66	0.1	0.05	0.56	0.45	0.41	0.58	—
S69	0.1	0.25	0.52	0.44	0.41	—	—

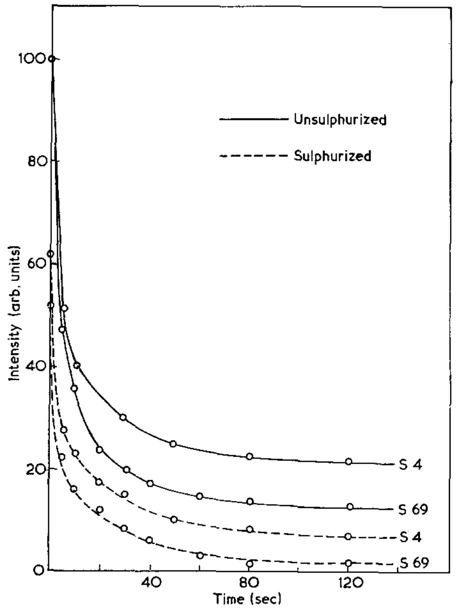

Figure 1 Decay curves for sulphurized and unsulphurized samples.

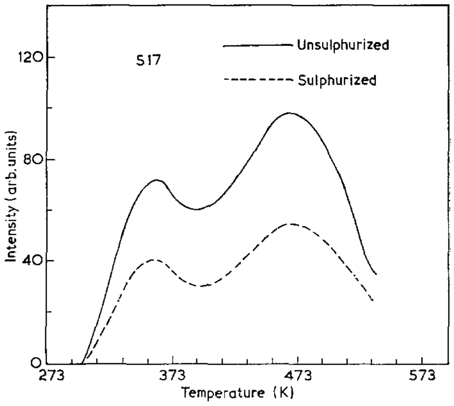

Figure 2 Glow curves of a sample before and after sulphurization.

from decay curves were estimated by the peeling-off procedure. The decay curve was split into three exponentials. Activation energies corresponding to each exponential were determined from the slopes of the straight lines on the semi-log plot of the intensity against time. The values thus obtained are given in Tables I and II. The initial rise method [6] was used to calculate the activation energies from glow curves. As the glow peaks were overlapping, it was necessary to isolate them. This was achieved by the method suggested by Bettinali *et al.* [7]. Thermoluminescence intensity was plotted against temperature and values of E were determined from the slopes. The activation energies thus obtained are given in Tables I and II. It should be mentioned that as certain glow peaks were weak and/or overlapped excessively they could not be isolated, and thus their activation energies could not be determined. A comparison of the E values contained in Tables I and II indicates that there is no significant effect of sulphurization on the activation energy. This implies that sulphurization does not influence the relative distribution of trap densities revealed by photo- and thermoluminescence measurements.

These results suggest that beyond all reasonable doubt, the traps are associated with defects in the host lattice which are likely to be the sulphur vacancies. This is further supported by the variation in E of unsulphurized samples with activator concentration [5]. The variation obtained is small and unsystematic, indicating that addition of activators only modifies the relative importance of traps and not their mean

TABLE II Values of E for unsulphurized samples

Sample no.	Values of E from "peeling off" of decay curves (eV)			Values of E from glow curves (eV)	
	Slowest exponential	Second exponential	Fastest exponential	First peak	Second peak
S4	0.65	0.53	0.50	0.65	—
S13	0.68	0.57	0.53	0.67	—
S17	0.55	0.46	0.42	0.60	—
S31	0.52	0.43	0.39	0.49	0.60
S45	0.52	0.49	0.44	0.58	0.67
S57	0.54	0.46	0.43	0.57	0.74
S61	0.54	0.47	0.43	0.57	0.72
S64	0.53	0.46	0.41	0.56	0.67
S66	0.54	0.46	0.41	0.55	—
S69	0.52	0.45	0.41	—	—

depths [8]. This implies that the trapping levels are not associated with the activators, but that they are the defects in the host lattice. This investigation suggests that these defects are likely to be sulphur (S^{2-}) vacancies.

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Coefficient of thermal expansion of sulphamate nickel electrodeposits

At Sandia Laboratories, Livermore, electroplating is used to join metals that are difficult to join by conventional techniques [1-3]. A taper is cut on the metals to be joined, then they are mated and held together while electroplating is used to fill the triangular segment created by the tapers. Of the deposits used to provide the "filler material" of the joint, nickel has found the most usage.

Ideally, the thermal coefficient of expansion of a deposit used for a joining application should match that of the other materials comprising the joint. This is particularly true for applications at elevated temperatures where distortion could occur due to differential expansion of components of the joint. Very little published information is available on this property for nickel electrodeposits. Brenner *et al.* [4] published data for nickel deposits produced in a Watts solution and Safranek and Schaer [5] for deposits produced in a sulphamate solution. Since an application existed wherein a plated joint was to be part of a structural configuration subjected to temperature variations between room temperature and 300° C, thermal coefficient of expansion data were obtained in our laboratory for sulphamate nickel deposits.

Two sulphamate plating solutions were used. They were of the same composition but differed in volume and age. Chemical formulation and operating conditions are presented in Table I. Nickel tubes were electroformed by plating on aluminium and then dissolving the aluminium in hot caustic solution. The tubes had an outside diameter of 9.5 mm (0.376 in.), a wall thickness of 0.5 mm (0.020 in.), and a length of 51 mm (2 in.).

After electroforming, a tube was placed in the bottom of a 0.91 m (3 ft) long closed-end quartz tube. A quartz rod, connected to the core of a Linear Variable Differential Transducer (LVDT) was placed on top of the nickel tube. The top end of the quartz tube was attached to the case of the LVDT. A chromel–alumel thermocouple was

TABLE I Composition and operating conditions for nickel sulphamate solutions

Code	A* and B†
Nickel	81 g l^{-1}
Nickel sulphamate	450 g l^{-1}
Boric acid	40 g l^{-1}
Surface tension	38 dyn cm^{-1}
pH	3.8–4.0
Anodes	Sulphur depolarized
Current density	268 A m^{-2}

*Solution volume was 40 litres. Electrolysis time was 6 Ahl^{-1}.

†Solution volume was 120 litres. Electrolysis time was greater than 250 Ah l^{-1}.