ESR and thermoluminescence studies of bismuth doped calcium sulphide phosphors

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Thermally stimulated luminescence (TSL) and electron spin resonance (ESR) studies were carried out on bismuth doped CaS phosphor synthesized by using solid-state reaction technique. The defect centers formed in CaS:Bi were studied using the technique of electron spin resonance. The thermoluminescence glow curve shows two peaks at about 400 and 505K. Irradiated CaS:Bi exhibits ESR lines due to defect centers. Thermal annealing behaviour of the phosphor indicates that one of the defect centres correlates with the TSL peaks at 400 and 505K. The center is characterized by an isotropic g-value of 2.0034 and is assigned to a F+ center.

[Keywords: Electron spin resonance, Thermoluminescence, CaS phosphor, Defect centre]

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1 Introduction
Numerous applied studies of luminescence materials based on alkaline earth sulphides (ASE) have been performed over the past several years. Calcium sulphide is known as an excellent host material of phosphors and many investigations on the luminescence properties of CaS:Bi3+ phosphors, sometimes with co-activators, have been made. Bismuth is a well-characterized impurity center in sulphides. Lushchik et al and Lehmann (in 1972) prepared some CaS phosphors activated with Bi3+ or other Tl3+-type ions and investigated the optical properties of the phosphors obtained. Their investigations however intend to give a survey of the results and do not show the details. The purpose of this work is to correlate ESR and TSL studies in CaS:Bi. In recent years a number of researchers have worked on sulphate based phosphors and with the help of ESR studies different radicals were observed. However to the best of our knowledge, correlation between ESR and TL studies in bismuth doped sulphides have received little attention.

Intrinsic lattice defects can be created either by doping CaS with impurities requiring a charge compensation or by damaging the crystal lattice. The former way results in various complexes of intrinsic defects and impurities. The latter way also gives a multiple interacting defects in the damaged crystal lattice, where unusual ionic and electron hole processes take place.

In the present paper, a report is made on the basis of thermoluminescence (TL) and electron spin resonance (ESR) studies. The defect centers formed in CaS:Bi system using the technique of ESR have been studied. The defect centers are related to the process of TL in phosphors. It has been observed that the release of holes/electrons from defect centers at characteristic traps initiate luminescence process characteristic traps initiate luminescence process in these materials.

2 Experimental Details
Sample Preparation — Calcium sulphide phosphor was obtained using solid-state reaction with control bearing between activator (bismuth, 0.1 mole %) and calcium sulphate using Na2SO4 as flux and fired at 1000 °C in a muffle furnace for 2 hr. AR grade carbon powder was used as reducing agent during synthesis. After heat treatment, the resultant powder was pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in preparation. The photograph of the
sample was checked for proper crystallization of the powder using X-ray diffraction technique. The details of phosphor preparation are the same as reported earlier\textsuperscript{2,10,11}.

**TL and ESR measurements** — Thermoluminescence glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (EMI 6255 S), dc amplifier and a millivolt recorder. ESR measurements were carried out on a Varian E112 E-line Century series X-band ESR spectrometer. TCNE ($g = 2.00277$) was used as a standard for $g$-factor measurements. Step heat treatments were performed to follow the decay and evolution of the defect centers. These were carried out \textit{in situ} in the ESR cavity using the Varian variable temperature accessory.

### 3 Results and Discussion

Figure 1 shows a typical TSL glow curve for CaS : Bi at test gamma exposure of 225 Gy. The TSL glow peaks are appearing around 400 and 505K. The TL intensity of 505K is less as compared to the prominent peak. Therefore, only one type of strong defect center was generated and the hole and electron recombination took place at 400K due to the release of traps at this temperature.

Unirradiated sample exhibits a number of ESR lines due to impurities. The ESR spectrum after gamma irradiation (30 kGy) in CaS:Bi recorded at room temperature is shown in Fig. 2(a). The scan range has been selected to record only the lines in the vicinity of free-electron resonance. The ESR line, close and to the left of the TCNE ($g = 2.0028$) marker is due to a defect center (center I). Center I appears to exhibit a single ESR line with principal $g$-value 2.0034 and a line width of 3 G. A likely trapping center which can be formed in a system like CaS:Bi is the F$^+$ center (an electron trapped at an anion vacancy). This center was first observed by Hutchison\textsuperscript{12} in neutron irradiated LiF. In LiF, a single broad line (line width $\sim$ 100 G) with a $g$-factor 2.008 was observed. A similar center has been observed in other systems, notably in alkali halides after X-ray or gamma irradiation. The main characteristic features of such a center is: (1) a small $g$-shift, which may be positive or negative, (2) a large line width and (3) saturation properties characteristic of an inhomogenously broadened ESR line. The large line width arises from an unresolved hyperfine structure.

The F$^+$ center consists of an electron occupying an anionic vacancy formed by the removal of a negative ion from the lattice. Hyperfine interactions with the nearest-neighbour cations account for most of the line widths. Defect center I formed in the present system is characterized by a small $g$-shift and the line width, however, is relatively small. The center also does not exhibit any resolved hyperfine structure.

On the basis of these observations and considerations of the characteristic features of the defect centers likely to be formed in a system such as CaS:Bi,

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Fig. 1 — TL glow curve of CaS : Bi phosphors exposed to gamma ray (225 Gy)

Fig. 2 — (a) ESR spectrum of irradiated CaS : Bi system at room temperature, (b), (c) and refer to spectra from annealed samples at 493, 553 and 623 respectively
center I is tentatively assigned to a F\(^+\) center. An intense signal at \(g = 2.0032\) observed in X-ray irradiated CaS at room temperature has been attributed to the F\(^+\) center (Ghosh et al.\(^{13}\)).

The stability of center I was measured using the step-annealing technique. The thermal annealing behaviour of the F\(^+\) center (Fig. 3) shows different temperature regions where there is a reduction in intensity of the corresponding ESR line. The first region from 373K to around 408K is likely to arise from recombination of charges, released from unknown traps, at F\(^+\) center sites. This annealing region appears to correlate with the observed TL peak at 400K. The subsequent annealing region is from approximately 393 to 483K. It is observed that this region is not related to any of the TL peaks. The next annealing region from 528 to 613K is not well-defined and is likely to correlate with the observed TL peak at 505 K. This region also appears to arise from recombination of charges, released from unknown traps, at F\(^+\) center. The F\(^+\) center has been observed to decay completely at 713K.

4 Conclusions

Based on the results presented above, the following conclusions may be highlighted. A defect center formed in gamma irradiated CaS:Bi system is tentatively assigned to a F\(^+\) center. The TL peaks at 400 and the 505 K appear to correlate with the F\(^+\) center.

References