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Review
The preparation and thermoluminescence of alkaline earth sulphide phosphors

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The present article offers a review of the material preparation and thermoluminescence (TL) of alkaline earth sulphide phosphors. Different methods of material preparation and characterization of alkaline earth sulphides in the form of polycrystalline powders, films, single crystals and pellets are described. In the process of impurity doping, the role of flux is explained. The general theory of TL and the different methods used to calculate the trapping parameters (E and s) from the TL glow curves are presented. The effects of impurities, flux, grain size, preparative parameters etc. on the TL of these materials are reported. The types of traps and trapping parameters obtained by various workers are given. Considering the results presented by various authors, possible impurity complexes are proposed. The potential applications of these phosphors in TL and OSL dosimetry, cathode ray tubes, electroluminescence panels and infrared sensors are briefly discussed.

1. Introduction

Alkaline earth sulphides (AES) have been known for a long time as versatile and excellent phosphor materials. These are traditionally known as "Lenard Phosphors". Luminescence and optoelectronic properties of II^B–VI^A compounds such as ZnS, ZnSe, CdS and CdSe have been extensively studied and used in several optoelectronic devices. Systematic investigations have not been made in detail on alkaline earth sulphides of the same group (II^A–VI^A) because of their chemical instability in the presence of atmospheric moisture and poor reproducibility. But recently, these sulphides (AES) have attracted the attention of many workers in view of their potential applications in radiation dosimetry, TV screens, cathode ray tubes, EL panels, infrared detectors etc. They posses NaCl (fcc) crystal structure and thus offer themselves as good host materials in the preparation of industrial phosphors by incorporating different impurities (activators and coactivators). Because of their wide band gaps (3.8–4.5 eV), the excited states of dopants are not densely distributed between the valence and conduction bands. These sulphides when doped with certain impurities such as rare earths produce emission in ultraviolet to near infrared regions. It is well known that the dopants, depending on their nature, may act as trapping/recombination/luminescence centres in the system and their energy storage properties can be suitably controlled. Apart from the role of impurities, the native defects which develop in the material under normal thermodynamic considerations as well as those produced during preparation when the impurities are incorporated, also play a dominant role in controlling the energy storage properties.

Energy storage properties such as thermoluminescence (TL) or thermally stimulated luminescence (TSL), thermally stimulated conductivity (TSC), thermally stimulated exo-electronic emission (TSEE) etc. of a system are generally studied under excitation with different types of ionizing radiations such as ultraviolet, X-rays and γ-rays. TL is a well known technique used by several workers [1–3] to investigate and understand the electronic processes involved in the energy storage properties related to point defects as well as impurities in the phosphor systems. In the TL phenomena, the material is exposed to electromagnetic or ionizing or particle radiation, where a fraction of the energy is stored in the material. Depending on the nature of the exciting radiation, free carriers and/or lattice defects such as vacancies and interstitials may be generated. As a result, due to the trapping of charge carriers at suitable sites or centres, incident radiation energy is stored in the phosphors during the process of excitation. It is generally believed that when the sample is heated to temperatures above the excitation temperature, electrons and holes which escape from their related traps recombine radiatively producing TL emission.

The TL phenomena in alkali halides which have a simple structure have been well understood, and the information is also profitably used to establish relationships with the different types of colour centres [4, 5]. Although the colour centre phenomenon in AES systems has not been well established [6–8], the reported data on TL directly or indirectly indicate the major role of the native defects in the processes involved. The results on TL reviewed in the following

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section illustrate the involvement of the native defects and their complexes associated with impurities.

Although several hundred papers have been published so far on the preparation and study of various properties of these sulphides, there does not seem to be an agreement on the results of the studies, even on the same material. An attempt has been made in this paper to review the work done on the preparation and thermoluminescence of AES in recent years. The review is divided into two parts; the first part dealing with the different methods of material preparation and the second dealing with the TL phenomena and the various effects of TL on alkaline earth sulphides.

2. History

On 28th October 1663, Sir Robert Boyle, one of the founders of modern chemistry, presented his observations on "Glimmering Light" concerning a diamond warmed in the dark, to the Royal Society. He wrote:

> "I also brought it to some kind of Glimmering Light, by taking it into Bed with me and holding it a good while upon a warm part of my Naked Body."
> "To satisfy myself, whether the Motion introduc'd into the Stone did generate the Light upon the account of its producing Heat there, I held it near the Flame of a candle, till it was qualify'd to shine pretty well in the dark."

In 1705, Oldenberg [9] described the phenomenon of TL in minerals. The theory on TL along with the description of measurements was reported for the first time by Urbach [10]. Extensive research work on TL was carried out by Randall and Wilkins [11] and Garlick and Gibson [12], on silicates, phosphates and on other related materials. Studies on alkaline earth sulphides (SrS) activated with rare earths like samarium, neodymium and palladium were reported in the last century by Lenard [13] and Haitinger [14]. Interest in the alkaline earth sulphides really began after the discovery of infrared stimulation and sensitized luminescence by various workers in the 1940s [15–17]. During World War II, research on luminescence was pursued for the development of cascade phosphors, like CaS:Ce, for radar applications and infrared sensitive materials like SrS:Eu,Sm for infrared photography. The thermoluminescence phenomena are the basis for one of the most important methods of modern dosimetry [18]. Daniels [19] suggested that the TL could be used fruitfully in radiation dosimetry. Since then, a number of books, papers and patents have appeared on the preparation and TL of alkaline earth sulphides.

3. Material preparation

3.1. Introduction

Alkaline earth sulphide phosphors were prepared by several workers [20–24] in the past. Most of the preparation procedures involved reduction processes of host sulphates by using carbon or hydrogen or H_2S as a reducting agent. However, the stability of these phosphors was poor and in most of the cases only 80–90% yield was obtained [25]. Recently several papers have appeared on luminescence and related aspects of alkaline earth sulphides [26–41] where different methods of preparation have been described. It has been pointed out by Lehmann [33] and Kato *et al.* [41] that these materials when properly prepared and activated with suitable impurities may become efficient phosphor systems for many optoelectronic applications.

Normally these sulphides are prepared by firing the host sulphates or carbonates or oxides with reducing agent in the temperature range 800 to 1200° C under different controlled ambient atmospheres and for a duration of 1 to 4 h. The optimum yields of sulphides in the end product could be obtained by making several trials by varying the temperature and duration of firing, adding different reducing agents and flux materials. Different methods used in the preparation of these alkaline earth sulphides in the form of powders, films, single crystals and pellets by various workers are described below.

3.2. Different methods of material preparation

3.2.1. Polycrystalline powders

3.2.1.1. Carbon reduction. This is a commonly used procedure where the host sulphates are mixed with required quantities of carbon

$$XSO_4 + 2C \rightarrow XS + 2CO_2 \qquad (1)$$

where X = Ca, Sr, Ba or Mg, and fired at specified temperatures in ambient atmospheres or in a vacuum. Rao [42] prepared BaS by reducing $BaSO_4$ with various grades of carbon like activated charcoal, glucose carbon, purified carbon and spectroscopic grade pure carbon in air as well as in N_2 atmosphere. A better yield of BaS was obtained with purified carbon and spectroscopic grade pure carbon. A proper reducing atmosphere was maintained throughout the process by burning a sufficient quantity of carbon in a separate crucible in order to minimize the formation of oxide on the exposed surface. Addition of small quantity of carbon to the charge was found to be very efficient in inhibiting the diffusion of oxygen in the host lattice [43]. Fine carbon powder prepared from sucrose was also used to prepare SrS. The charge was fired for 1.5 h at 900° C under vacuum (10^{-3} torr) [44]. Rawat and Ranade [45] reduced $CaSO_4$ with carbon in an atmosphere of stagnant air. Purified N_2 was also used in the reduction of $SrSO_4$ with carbon [46]. Air tight graphite crucible was used in the preparation of SrS:Hf [47]. Rabotkin and Stroganova [48] synthesized sulphides by reducing hyposulphite with carbon at 1200° C with limited access of air. Most of the Indian authors had followed the method described by Bhawalkar [21] where CaS was prepared by heating gypsum $CaSO_4 \cdot 2H_2O$ (mineral available in India) with carbon and flux at 950° C for 2 h in a reducing atmosphere.

In general, the charge consisting of the respective sulphate and required amount of carbon for the reduction process, in some cases with added dopants along with flux materials, is fired in a muffle or tubular furnace at desired temperature (say 950° C) for 1 to 3 h in ambient atmosphere (N_2 or Ar). The schematic

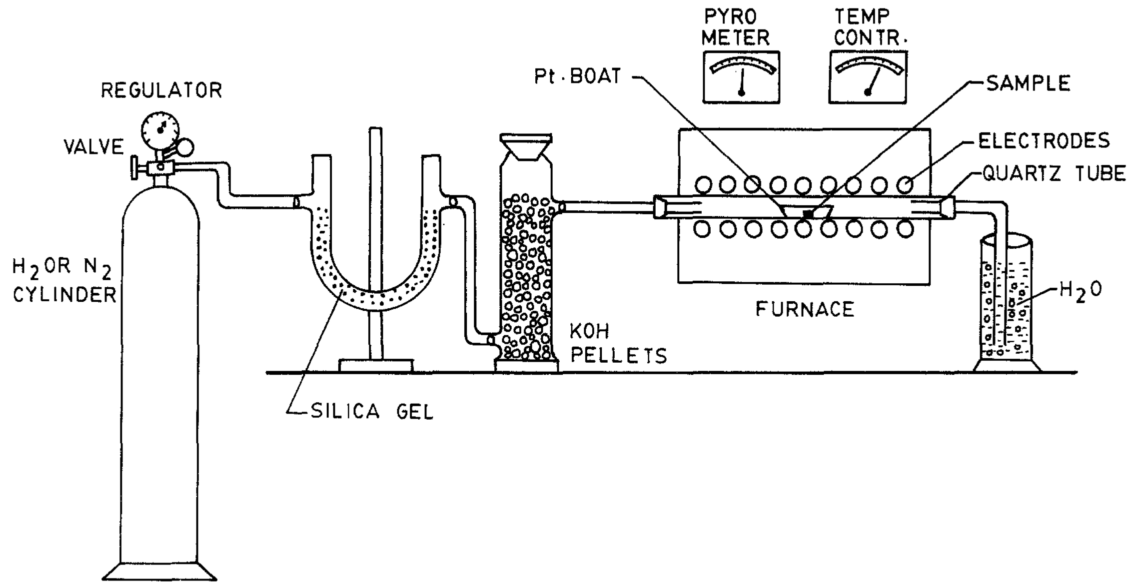


Figure 1 Schematic of the tubular furnace used in the preparation of BaS phosphors.

diagram of the tubular furnace used in the processes of reduction is shown in Fig. 1.

3.2.1.2. Hydrogen/sulphur reduction. Sulphides are prepared by passing H_2 over heated alkaline earth sulphate or by firing carbonates in presence of an excess of sulphur at appropriate temperatures. The following are possible chemical equations:

$$X\mathrm{SO_4} + 4\mathrm{H_2} \rightarrow X\mathrm{S} + 4\mathrm{H_2O} \qquad (2)$$

$$X\mathrm{CO_3} + 2\mathrm{S} \rightarrow X\mathrm{S} + \mathrm{CO_2} + \mathrm{SO_2} \qquad (3)$$

The advantage of this method over carbon reduction is that the unwanted impurities from carbon are minimized. However, it needs repetition of the process to ensure the complete reduction. Silica chips were used to increase the sample area in contact with H_2 and thereby improving the reaction efficiency [49]. Asano *et al.* [50] prepared CaS by reducing $CaSO_4$ with pure hydrogen. BaS was prepared by reducing $BaSO_4$ in a stream of hydrogen and had a 97–98% degree of phase purity [51]. According to Wachtel [52], CaS was prepared by reduction of $CaSO_4$ with H_2 at 400° C followed by firing in dry H_2S. BaS was also prepared from the hydrosulphide ($Ba(SH)_2$) by heating in a stream of forming gas (8% H_2 and 92% N_2) to a temperature of 900° C for several minutes. Goldman and Romanenko [53] synthesized SrS from $SrCO_3$ and S in the presence of CaF_2 flux at 900 to 1000° C in neutral atmosphere (N_2 or Ar). CaS was also prepared and activated with erbium in the presence of sulphur [54].

Well developed and non-aggregated CaS and SrS particles of larger size (Fig. 2) were prepared by using a sulphurizing flux method [39, 41]. The alumina crucible containing a mixture of sulphur and either sodium carbonate, and/or potassium carbonate was placed in a large alumina crucible and the space between the two crucibles was filled with carbon to avoid oxidation of the reactants and products. The crucible with its contents was heated to about 800 to 1200° C under normal atmosphere for 0.2 to 72 h. After cooling, the mass was crushed to a fine powder and then the flux was removed by dissolving and washing with cold deionized water. It was found that the average particle size increased with higher firing temperature and longer reaction time (Fig. 3). Because of the good crystallinity and larger particle size, the phosphors prepared by the above method are relatively stable against atmospheric H_2O and CO_2. Since BaS and MgS are highly hygroscopic, it is difficult to prepare them using the flux method.

3.2.1.3. H_2S reduction. In this process, alkaline earth sulphates or carbonates or oxides are reduced to sulphides by passing a stream of H_2S at 900 to 1100° C for 1 to 3 h. The following are the possible chemical reactions:

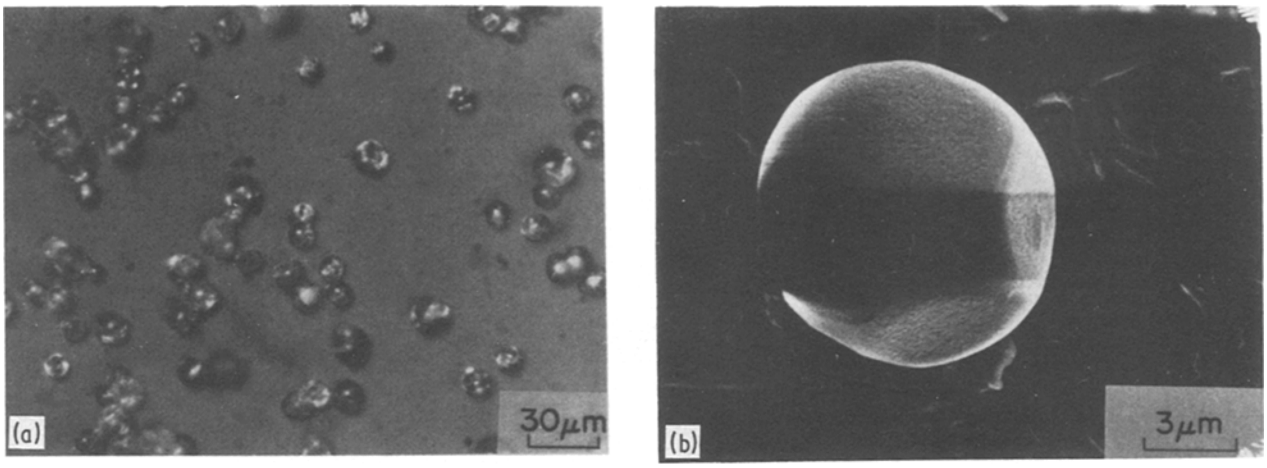
$$3X\mathrm{SO_4} + 4\mathrm{H_2S} \rightarrow 3X\mathrm{S} + 4\mathrm{SO_2} + 4\mathrm{H_2O} \qquad (4)$$

$$X\mathrm{CO_3} + \mathrm{H_2S} \rightarrow X\mathrm{S} + \mathrm{CO_2} + \mathrm{H_2O} \qquad (5)$$

$$X\mathrm{O} + \mathrm{H_2S} \rightarrow X\mathrm{S} + \mathrm{H_2O} \qquad (6)$$

The quality of the final product depends on the purity of host as well as H_2S. Purified $SrCO_3$ was sulphurized by heating at 1000° C for 40 min in a stream of $N_2 + H_2S$ [55]. They estimated the weight loss for the conversion process to be 81%. Yokono *et al.* [56] prepared CaS samples by firing $CaCO_3$ for 2 h at 1200° C in a stream of H_2S. CaS phosphor was synthesized for a DC electroluminescence cell by using $CaCO_3$ [57] and also from hydrosulphides. A later process [58] yielded phosphor with low oxide contamination and low particle size distribution. For CaS : Mn phosphor prepared in a H_2S atmosphere, the amount of manganese incorporated is less than for those fired in air and this seems to indicate the formation of manganese compounds on the surface [59]. Lehmann [60] prepared sulphates of calcium, strontium and barium from the purest available nitrates and then converted to the respective sulphides by firing them in an atmosphere of H_2 and H_2S.

3.2.1.4. Carbon disulphide (CS_2) reduction. Host sulphates are reduced to sulphides with the help of CS_2. CS_2 vapours are passed on heated sulphates



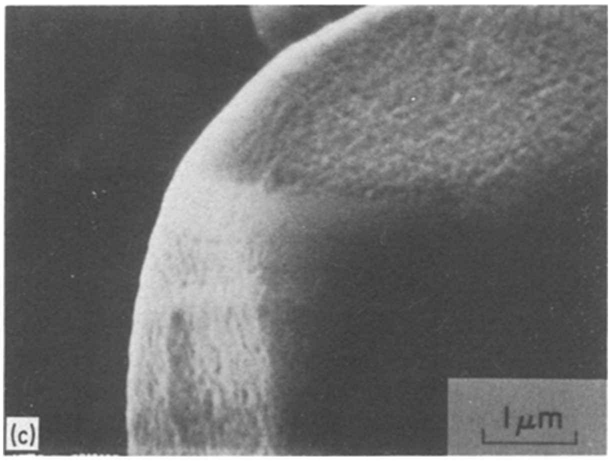


Figure 2 (a) optical and (b, c) SEM micrographs of as-prepared CaS : Eu phosphors [39].

through a stream of argon or helium gas for a few hours at the desired temperatures. It was found that the yield is greater than that of other methods. In order to obtain pure MgS powder, Asano *et al.* [61] used purified $MgSO_4$ as a starting material. The MgS was prepared by reduction of $MgSO_4$ powder in a mixed stream of N_2 and CS_2 at 750° C for 3 h. Fine powders of sulphates are prepared and are spread in the form of a thin layer on platinum through CS_2 bubbles to create a reducing atmosphere [62]. Other reducing atmospheres like H_2 and CO were also tried but they did not reduce all the sulphate satisfactorily. $CaSO_4$ and $SrSO_4$ were also reduced to respective sulphides in a CS_2 saturated helium atmosphere [63]. A different method was developed for the preparation of these sulphides by homogeneous precipitation from a single solution by Avinor *et al.* [64]. Here, a solution of alkaline earth sulphamate was prepared by dissolving the carbonate in sulphamic acid solution. The solution was first purified by the precipitation method with H_2S and then rendered slightly alkaline by adding ammonia and the last trace of heavy metals was extracted by a solution of dithiazone in CCl_4. The sulphate after adding the activator solutions was reduced to sulphide by heating at 1000° C in a stream of H_2S.

3.2.2. Films

The preparation of thin films of these alkaline earth sulphides is very difficult because of their high vaporization temperature, instability in air and high activation temperature in obtaining luminescent films.

3.2.2.1. Evaporation. Zollweg [65] prepared thin films of sulphides and selenides of these systems on the inside walls of sealed ampoules of corning glass or fused quartz by evaporating barium, strontium metals and reacting with H_2S gas at about 390° C. George and Eugene [66] have described a slightly modified procedure for preparation of the films. The samples were prepared first by evaporating a small amount of the desired alkaline earth metal onto the substrate and then introducing sulphur on top of this. Sulphur with a high vapour pressure was kept in an ampoule in a side arm until the complete evaporation of the alkaline earth metal film had taken place. The ampoule was then broken open and sulphur vapour admitted to the tube. The entire tube was then placed in an oven and baked to form sulphide. MgS : Ce films were prepared by baking MgO : Ce films in H_2S atmosphere at 950° C for a few hours [67]. According to Mortin and Schamber [68], vapours of metal atoms (calcium, strontium and magnesium) and sulphur atoms were mixed at high temperature and then frozen to a low temperature substrate. Metal sulphide molecules form over only a small range of vapour to gas mixture ratios. If the concentration is too low, the atoms are isolated from one another but at high concentrations the vapour components condense into microcrystals.

3.2.2.2. Sputtering. Thin films of CaS were prepared by cathode sputtering [69, 70] using CaS pellets as sputtering specimens. The specimen was bombarded with a beam of 20 keV neon ions, the incident ion current density was 10 mA cm^{-2}. In the evaporation technique described by Levshin *et al.* [71], the luminescence grade CaS or SrS was evaporated on quartz or fluorspar substrate in a conventional vacuum bell jar (10^{-5} to 10^{-6} torr). The evaporation was carried out from a tungsten boat heated to 1700 to 1800° C. After removing the oxides from the jar, the tungstate evaporator received the charge of sulphide. Evaporation was carried out after 20 min of annealing at 1300 to 1400° C.

3.2.2.3. Sedimentation. Rao [72] prepared MgS phosphor films by an entirely different method called

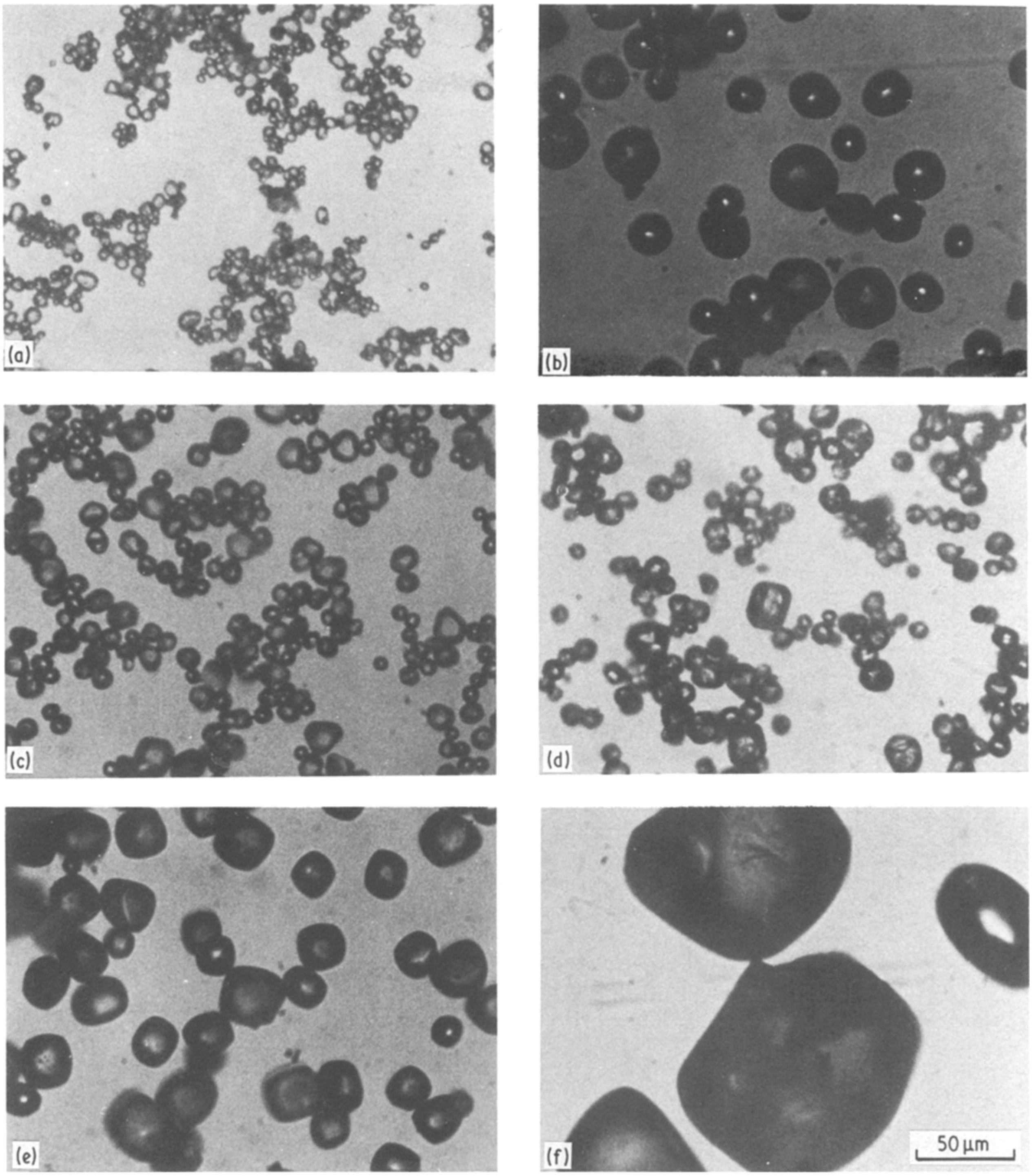


Figure 3 Photomicrographs of particles of CaS : $Ce_{0.001}$ prepared using the flux mixture of Na_2CO_3 and sulphur at different firing conditions (a) 900° C for 6 h; (b) 900° C for 72 h; (c) 1000° C for 4 h; (d) 1000° C for 12 h; (e) 1100° C for 4 h; (f) 1100° C for 72 h. [41]. Reprinted by permission of the Electrochemical Society Inc.

"sedimentation". Absolute alcohol containing fine particles of MgS was poured on well cleaned glass substrates. After the settlement of the particles, the alcohol was removed from the bath and then the films were dried for a few hours at 100° C. The films were protected from the atmospheric moisture by coating them with Dow Corning 805 polymer. It is observed that the films obtained by this method are uniform. The scanning electron microscope studies show the uniformity and the texture of the films (Fig. 4).

3.2.3. Single crystals

It is always necessary to grow single crystals to study the physical properties and to understand the behaviour of these sulphides in various applications. It is well known that these sulphides have high melting temperatures (for example T_{mel} = 2430° C for SrS). The proper control of high vapour pressure under high T_{mel}, prevention of impurity contamination from the crucible and oxidation, hydroxidation and carbonation during the growth are major problems. Since the investigations of Keller [73], many workers [74–80] have been trying to grow single crystals of these sulphides. SrS single crystals were grown from melt (Sr) and vapour (S) in a graphite crucible at 2150° C [74]. Single crystals were grown in a carbon arc

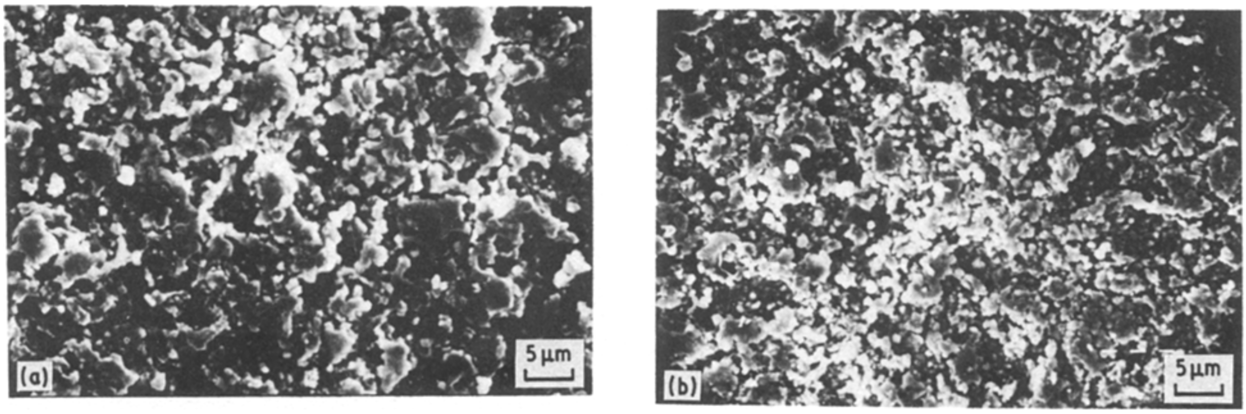


Figure 4 Scanning electron micrographs of polycrystalline films of (a) MgS : Eu and (b) MgS : Ce phosphors.

furnace operating in an argon atmosphere to prevent the spontaneous conversion of BaS to $BaSO_4$. Most of the melt in which single crystals were formed was very dark. A close investigation by X-ray diffraction showed that these thin plates like crystals were due to the formation of barium monosulphide. Single crystals of BaS were also grown using a plasma torch-tip fusion process similar to the Varnoulli processes used for growing sapphires [75]. The gas used was a mixture of argon and H_2 with about 50 vol % of H_2. The H_2 was induced to reduce oxides that could form or might already be present. CaS single crystals were prepared, by taking chemical vapour transport using iodine at a concentration of $1\,\mu g\,mm^{-3}$ of growth over a temperature difference 1200 to 800° C [77].

Kaneko *et al.* [76, 78] succeeded in growing single crystals of CaS, CaSe, SrS, SrSe, BaS and BaSe as large as 3 to 5 mm diameter and about 100 mm long by the float zone method using a xenon-arc image furnace. Photographs of BaS single crystals prepared by the float zone method are shown in Fig. 5. For CaS (T_{mel} = 2600° C) it was necessary to increase the lamp current up to the maximum attainable value of 4.5 kW. From the optical spectra [79], they observed that these crystals have fairly good stoichiometry and chemical purity. Also from SEM studies, it was proved that the crystals do not contain any voids or bubbles. The main advantages of this technique are its efficient and rapid operation, fairly good stoichiometry of crystal due to the prompt heating at a small hot spot, and high purity crystals free from impurity contamination from the crucible and the ambient atmosphere.

3.2.4. Pellets

The electrical properties such as conductivity, thermoelectric power, dielectric constant etc. of these sulphides have been studied by compacting the polycrystalline powders into pellets. The studies on the pellets could be carried out as on the crystals by manipulating the density of the pellet to that of the crystal with the help of a "packing factor", which is the ratio of pellet and crystal density. Pellets of CaS were made from powder under an argon atmosphere and sintered at 1550° C for 6 h under a H_2S/H_2 gas mixture providing partial presence of sulphur [80]. In order to prevent the oxidation of the samples during sintering, the pellets were surrounded by CaS powder in an alumina boat [81]. BaS [82] pellets were made by compacting the phosphor in powder form ($\sim 75\,\mu m$) under a constant pressure of $825\,kg\,cm^{-2}$ for 8 h at room temperature (300 K) and it was observed that their packing factor varied from 0.7 to 0.8.

3.2.5. Mixed systems

The studies on mixed systems of II^B–VI^A compounds like (ZnCd)S, (ZnCd)Se and (ZnCd)Te lead to many optoelectronic device applications [83, 84]. Systems like (Ca Ba)S, (CaSr)S, (BaSr)S and (Ca Ba Sr)S have also exhibited interesting features [85, 86]. The preparation of these systems is as simple as for monosulphides; appropriate proportions of two or three

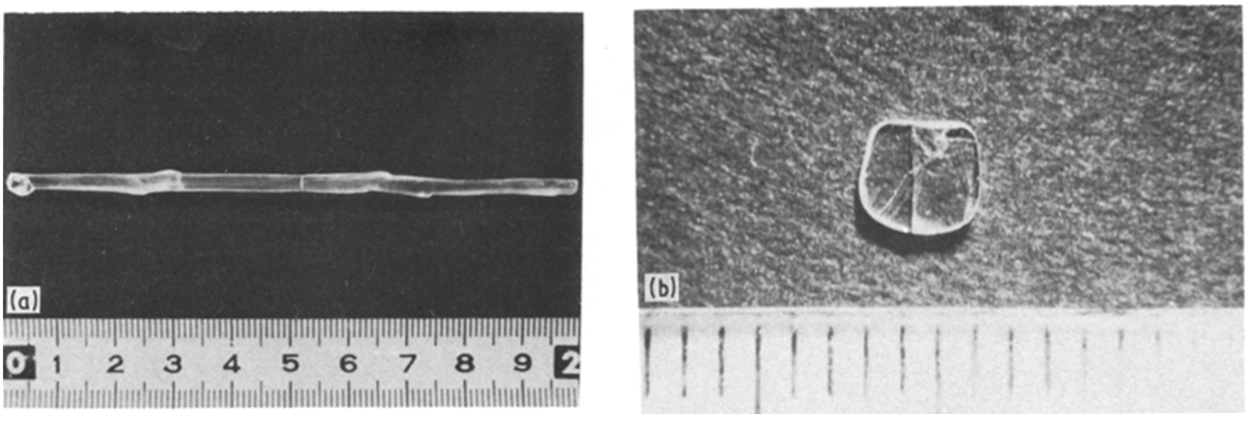


Figure 5 Photographs of BaS single crystals prepared by the float zone method using a Xenon-arc image furnace, (a) a side view perpendicular to the ⟨0 0 1⟩ growth direction, and (b) the (0 0 1) cleavage surface showing the (1 0 0) and (0 1 0) facets. [78].

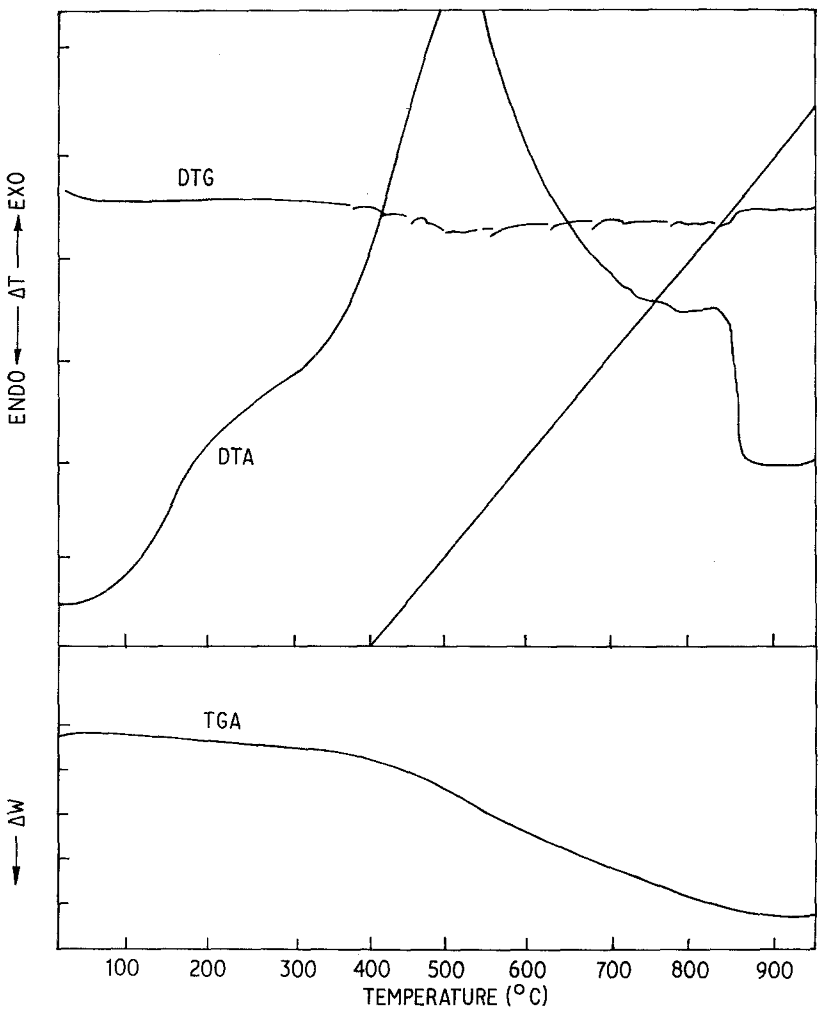


Figure 6 DTA, TGA and DTG of BaS prepared in air by carbon reduction process. DTA = DTG = $\frac{1}{10}$.

sulphates or carbonates are mixed with impurities and flux, and then fired at suitable temperatures.

3.3. Characterization

3.3.1. Thermal analysis

Better yields of sulphide could be obtained by varying different parameters such as firing temperature, duration of firing, reducing agent and ambient atmosphere. Thermal analysis like DTA, TGA, DTG etc. are used to determine the optimum values of the above parameters [42]. Thermal analysis of BaS prepared by reducing $BaSO_4$ with pure carbon is shown in Fig. 6. From the figure it could be concluded that the reduction process started from 400° C, attained a maximum at 550° C, and ended at around 850° C.

3.3.2. X-ray diffraction

The different phases present in the material in addition to the host sulphide could be detected from X-ray diffraction data. The X-ray diffractograms of BaS prepared from $BaSO_4$ with carbon and with hydrogen (Fig. 7) are of the same nature. The data obtained were compared with the standard data available in the Data File [87]. Most of the lines obtained represent the BaS phase only. The lines of other possible compounds like sulphates (unreduced), oxides and carbonates are not observed in the spectrum. The spikes

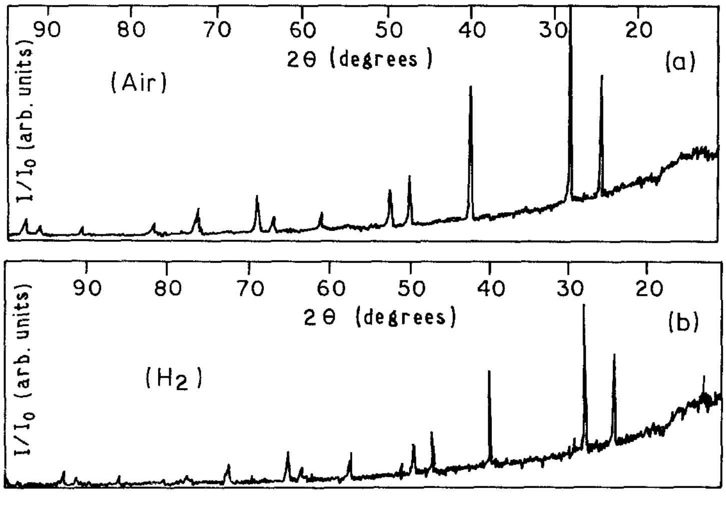


Figure 7 X-ray diffraction patterns of polycrystalline BaS prepared in (a) air and (b) hydrogen.

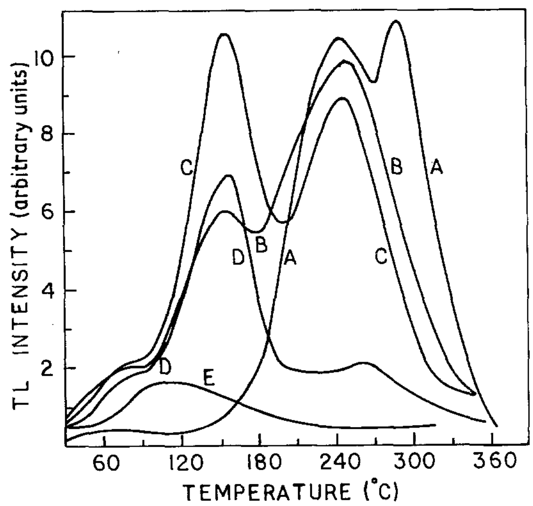


Figure 8 TL glow curves of $BaSO_4$ and BaS irradiated by X-rays (30 kV, 10 mA) for 10 min at 30° C, (A) $BaSO_4$, heat treated at 950° C for 2 h. BaS prepared reducing $BaSO_4$ by (B) charcoal carbon (C) glucose carbon (D) purified carbon and (E) purified hydrogen.

with low intensity might be due to noise in the detection systems of the X-ray diffractometer or due to trace impurities present in the starting chemicals (sulphate, carbon etc.). X-ray diffraction analysis is also used to detect the formation of solid solutions in binary and ternary mixed systems.

3.3.3. Thermoluminescence

Thermoluminescence (TL) could also be used successfully to understand the state of reduction. Generally alkaline earth sulphates and sulphides exhibit specific glow maxima. The amount of sulphate and/or sulphide present in the final product could be estimated by comparing the heights and/or area of respective TL glow curves. As an example, TL glow curves of $BaSO_4$ and BaS prepared from same $BaSO_4$ with different reducing agents are shown in Fig. 8.

3.3.4. Electron microscopy

Various workers estimated the grain sizes and their distribution of these sulphides, with the help of scanning electron microscope (SEM) studies. It is also possible to know whether the doped impurities really entered into the lattice or remained in the mechanical mixture. The impurities doped in the material at lower temperatures have been observed as a minute particle under SEM. The conductivity of these sulphides and dopants varies considerably and it is easy to identify them by SEM. For example in Fig. 9a a copper particle appeared as a part of the mechanical mixture whereas Fig. 9b shows the uniform distribution of particles in the material doped at higher temperatures. Spectrographic analysis is also used to find out the impurities as well as to estimate different compounds in a particular sulphide.

3.4. Impurity doping

The doping (incorporation) of impurities into the host lattice (*X*S) could be carried out in two ways; namely (1) the impurities are added to the starting chemicals such as sulphates or carbonates before the reduction process, or (2) the impurities are added to sulphides and then fired in the presence of flux materials. It was suggested that flux could be avoided by firing the mixture of sulphide (*X*S) and sulphate (XSO_4) in a particular ratio in the presence of CS_2 [88]. Incorporation of activators and coactivators in the phosphor depends on the firing temperature, duration of firing, firing atmosphere and the flux material. Elements such as phosphorus, scandium, manganese, nickel, copper, calcium, arsenic, yttrium, silver, cadmium, gadolinium, indium, tin, antimony, lanthanum, gold, lead, bismuth etc. are considered as activators in AES phosphors. Six activators, namely oxygen, manganese, copper, gadolinium, cadmium and antimony, do not require any coactivator although the presence of the coactivator may improve the efficiency of the phosphor. Generally halides (VII) and alkalides (I), introduced into the lattice from the flux during the preparation act as coactivators. In contrast to the impurities such as copper, bismuth etc. the characteristic luminescence of RE ions are due to the deep lying partially filled shells. The energy states of "f" electrons are well screened by the electrons of the outer shell. They are least affected by the crystal lattice field and closely resemble the free ions. Elements such as iron, chromium, cobalt etc. diminish the luminescence efficiency, and are known as "killers". The exact amount of impurity (concentration) that has entered into the lattice is rather difficult to estimate. In cases, calculations are made on the assumption that the total amount of impurity added before firing has entered into the lattice. One should consider the

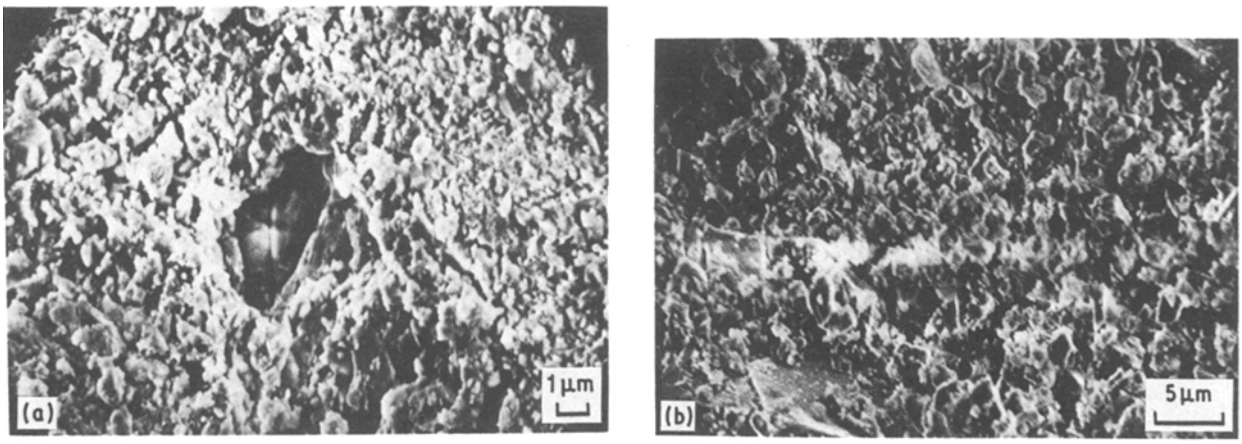


Figure 9 (a, b) Scanning electron micrographs of BaS phosphor powders.

lattice parameters of both host and impurities before doping.

3.5. Role of flux

The role of flux materials in the preparation of industrial phosphors is well known. The flux materials are used during the activation (doping) of these sulphides, to act as a medium for the incorporation of impurities into the lattice and also to reduce the firing temperatures. Generally, alkalis or alkaline compounds such as sulphates (Na_2SO_4), carbonates (Na_2CO_3), halides (NaF, NaCl, CaF_2), etc. are used as flux materials. The halide and/or alkali ions from these compounds entered into the lattice along with activator. In the literature, it is mentioned that the luminescence efficiency is increased with addition of a specific type of flux. However, the flux added does not play an important role in the "critical" concentration. Above the critical concentration, the fluxes degrade the efficiency by forming a cluster with the activator. It is also possible that the residual flux in the final product can be removed by dissolving in a suitable solvent. Well separated and larger grain size SrS and CaS phosphors were obtained by using a sulphurizing flux such as thiosulphate or a mixture of sodium carbonate and sulphur [39].

Series of samples of CaS : Zr were prepared using NaCl, KCl, $CaCl_2$, $MgCl_2$ and $Na_2S_2O_3$ fluxes. In each series, the quantity of flux was varied, keeping the concentration of the activator as a constant [89]. Varma [90] and Chakarvarti *et al.* [91] prepared CaS : Zr in presence of Na_2SO_4, NaF, K_2SO_4 and KF fluxes. Singh *et al.* [92] studied the effect of flux (Na_2SO_4 or NH_4Cl) on TL of CaS and SrS doped with copper, arsenic and phosphorus. Borax was also used as flux in the preparation of BaS : Cu [93]. At longer durations of firing (> 90 min.), the phosphor became progressively reddish in colour, which might be due to the formation of a borax–copper complex in the course of firing. These fluxes NaF, Na_2SO_4 and CaF_2 were used in the preparation of Ca(S, Se)Sn^{2+} phosphor by Yamashita and Asano [94] and it was found that CaF_2 was more effective. Samples of BaS were prepared with various amounts of copper and bismuth along with different quantities of NaCl flux in the range 0 to 40% [95].

4. Thermoluminescence

4.1. Introduction

Among the different experimental techniques employed to study the energy storage properties of phosphors, thermoluminescence (TL) or themally stimulated luminescence (TSL) has been widely used to investigate the nature and distribution of traps. The storeability and related luminescence phenomena which involve trapping and radiative recombinations respectively can be reasonably understood by considering the various results on TL, TL spectra and bleaching characteristics. Such studies on the various aspects of thermoluminescence of alkaline earth sulphide phosphors have been made by several workers in the past and some of the essential findings are summarized in this review. In order to understand the role of impurities and their relationship with the point defects, the author had undertaken a comprehensive work in which alkaline earth sulphide phosphors were prepared and their TL, TL spectra, radioluminescence, electrical conductivity, thermally stimulated conductivity (TSC) and dielectric properties were studied by exciting them with different ionizing radiations. The theory, experimental details and the results on TL and TL spectra of alkaline earth sulphide phosphors obtained by the author and others are described in the next section.

4.2. Theory

The mechanism of TL is complex and, although general theoretical models can be postulated, difficulties arise when specific materials are considered. Thermoluminescence involves two steps. In the first step, the material is excited with ionizing radiations like UV, X-rays, γ-rays or particle radiations at a fixed temperature. In the second step, the excitation is interrupted and the sample is heated at a particular rate of heating. With the progress of heating, the sample emits light. The intensity of emission varies with temperature giving a number of maxima. Other thermally stimulated methods such as TSC and TSEE which are measured along with TL are complementary [96].

4.2.1. A general model for TL

The production of TL in a sample by exposure to ionizing radiation may be divided into two stages: (i) electron and/or hole trapping, and (ii) electron and hole recombination with photon emission.

The energy band configuration for each stage explained below is shown in Fig. 10. Ionizing radiation is absorbed in the material and free electrons are produced. This is equivalent to transferring electrons from the valence band to the conduction band (A). These electrons are free to move through the crystal (B), but if trapping levels such as (T) are present the electrons may be trapped (C). The production of free electrons is associated with the production of free holes which may also migrate via the valence band (b) and may be trapped (c). Many hole centres are thermally unstable and may decay rapidly at room temperature (d). The trapped electrons will remain in the traps provided they do not acquire sufficient energy to escape. This will be determined by the trap depth and temperature of a particular material. If the temperature of the material is raised, trapped electrons may acquire sufficient thermal energy to escape (D). Released electrons may recombine with holes at the luminescence centre (L) and emit visible or UV photons (E_p). With electron capture and delayed recombination with a hole at the (L) centre is the mechanism of TL. As the phosphor is heated, the probability of releasing any particular electron is increased and at some temperature there is virtual certainty of its release. The emission (TL) will thus start to increase, go through a maximum and then decrease again to zero. The intensity of emitted light with temperature is known as a TL glow curve.

The nature of trapping states as well as the kinetics

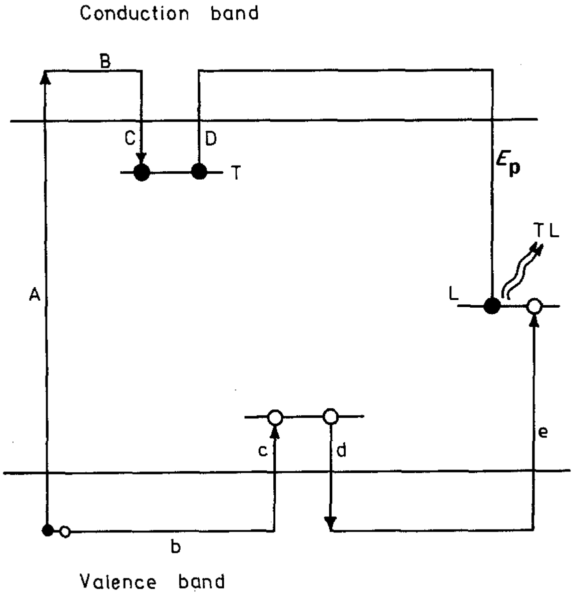


Figure 10 A simple energy band model for thermoluminescence. ●, electron; ○, hole.

involved in the recombination phenomenon can be understood from the TL results. Utilizing the information, the trapping parameters, namely trap depths (E) and frequency factor (s) can be calculated by using different techniques.

4.2.2. *Different methods of analysis to calculate the trapping parameters*

The first theoretical treatment for an isolated TL peak contributing electrons to the conduction band in the process was given by Randall and Wilkins [11]. They assumed that (i) glow peaks corresponding to different trapping levels do not overlap, (ii) no retrapping occurs in the processes of TL emission and (iii) the life time (τ) for recombination is so small that $dn/dt \ll n/\tau$ where n is the concentration of the electrons in the conduction band. Further, assuming the frequency factor $s = 10^9\,\text{sec}^{-1}$, they derived a simple equation for trap depth $E = 21\,kT_m$ where k is Boltzmann's constant and T_m is temperature maximum. Urbach [97] had, however, derived another simple equation as $E = T_m/50$ for $s = 10^7\,\text{sec}^{-1}$ much earlier than Randall and Wilkins.

By using different rates of heating, the TL glow curves have been recorded for the same systems of phosphors and the trapping parameters E and s have been calculated by Booth [98], Bohun [99] and Hooganstraaten [100], using the relation

$$E = (kT_{m_1} - T_{m_2})/(T_{m_1} - T_{m_2}) \ln (\beta_1 T^2_{m_2}/\beta_2 T^2_{m_1}) \qquad (7)$$

where T_{m_1} and T_{m_2} are the temperatures corresponding to the glow maxima and β_1 and β_2 are the corresponding rates of heating.

Methods have also been suggested by using the complete glow curve (possible only in the case of an isolated/single glow peak) where depending upon the shape of the glow curve the parameter $\mu g = \delta/w$ will be calculated in which $\delta = T_2 - T_m$, the fall of half width and $w = T_2 - T_1$ the total half width, and T_1 and T_2 are the temperatures at which the TL intensity I falls to half of that at temperature T_m. The formulae frequently used in the calculation of E and s by the total curve methods are given below:

1. Growssweiner [101] proposed the equation for I order kinetics as

$$E = (1.51\,kT_mT_1)/(T_m - T_1) \qquad (8)$$

Chen [102] modified the same formula by replacing 1.51 with 1.41 for better accuracy, in the case where $s > 10^7\,\text{sec}^{-1}$ and $E/kT_m > 20$.

2. The trap depth values were obtained [103, 104] by approximating the area under the glow curve to a triangle as

$$E = kT^2_m/(T_2 - T_m) \quad \text{for I order kinetics} \quad (9)$$

$$E = 2kT^2_m/(T_2 - T_m) \quad \text{for II order kinetics} \quad (10)$$

Chen suggested, in this case, the multiplying constants as 0.978 and 0.853 respectively, for better accuracy.

3. Theoretically, Halperin and Braner [105] have developed formulae for the determination of trapping parameters by considering the luminescence emission as mainly due to two kinds of recombination process. In one, the recombination takes place via the conduction band and in the other the electrons raised to an excited state within the forbidden gap below the conduction band recombine with the holes.

The above methods are applicable only for well isolated (single) glow peaks as mentioned earlier. Different methods proposed by various workers have been reviewed by Shalgaonkar and Narlikar [106]. In the case of complex TL patterns, before applying the methods described above, the overlapping glow peaks have to be separated by using thermal, optical and analytical methods.

4.3. Experimental procedures

4.3.1. *Excitation*

The phosphor samples are normally excited, by an ionizing radiation source such as UV, X-ray, γ-ray etc. UV excitation is carried out by using a high pressure mercury lamp (< 100W) or a xenon lamp (> 100W) and filters of specific wavelengths. The samples are always fixed at a distance from the source and focused by using a quartz lens. For the purpose of X-ray irradiation, the samples are mounted near the exit window of the X-ray unit at a fixed distance from the target. Depending on the nature of target and operating conditions (voltage, current etc.), the dose varies from 1 mR to several kR. The dose to the sample could be varied by changing the distance between the sample and the target and duration of exposure. γ-ray sources like Co^{60}, Cs^{137} etc. are used to excite the phosphors. The excitation energy depends on the nature of the isotope and its half life time. Samples packed in aluminium foil are placed near to the source which is generally installed at a depth of a few metres below the ground. The samples are also excited with low energy electrons by placing them in the path of an electron beam from a demountable cathode ray tube which are usually operated at a few kV.

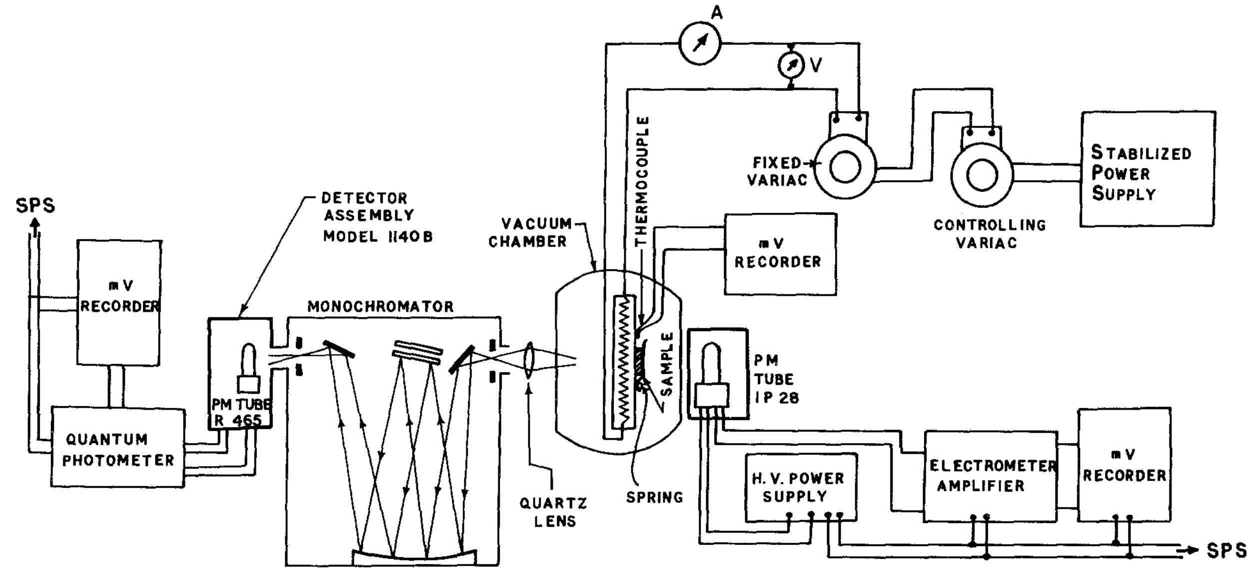


Figure 11 Schematic of the set up used for recording TL and TL spectra.

4.3.2. Detection system

A schematic diagram of the detecting systems along with its accessories is shown in Fig. 11. After irradiation (ultraviolet/low energy electrons/X or γ-rays) the samples are mounted on the sample holder and heated at a certain rate of heating inside a vacuum chamber. The luminescence output during the heating is fed to a photomultiplier tube, normally operated between 500 and 1000 V, and the photocurrent has been measured using an electrometer amplifier. The amplifier output as well as the thermo e.m.f. sensed by the thermocouple are recorded simultaneously on X–Y or by two mV recorders.

4.3.3. TL spectra

The spectral composition of the TL emission at each glow peak temperature has been measured by using a grating monochromator, and a detector assembly. The detector assembly unit contained the PM tube and its associated circuitry of the input amplifier, discriminator and a mV recorder. A schematic diagram of the equipment used to record the TL spectra is also included in Fig. 11. Arrangements are made to maintain the temperature of the sample within $\pm 3^\circ$C around the glow maximum (T_m). The TL spectra are replotted after normalizing with spectral response of the grating and PM tube.

4.3.4. Automation

After the successful use of this TL technique in radiation dosimetry, its applications developed extensively. Consequently there has been a vast growth towards automation, with the result that many automatic TL readers have appeared in the commercial market. These automatic readers mainly consist of a heating system and a light detecting system. Heating of the sample could be carried out in many ways, for example, by controlled planchat heating, the heater block method, hot gas heating, RF heating, optical heating, or laser heating etc. The light detection system could be divided into three parts, namely (i) light collecting system (ii) light detector and signal amplifier and (iii) signal conditioning system [107].

The first commercially available automatic system for TL dosimetry was the Harshaw Model 2271 [108], followed by the models 2276 and 8000 TLD, being the second [109] and third [110] generations, respectively. In addition to these, Teledyne Isotopes 9100, Pitman 605, TNO hot gas, Therados TLD–10, Victorien 2810, Studsvik, Saphymo TLD 20 etc. are a few examples of commercially available automatic TLD readers. Saphymo TLD 20 has been used in the present investigation to record TL of MgS phosphors; Fig. 12 shows a schematic diagram of this.

4.3.5. Optical bleaching and thermal cleaning

In the case of optical bleaching experiments, the irradiated samples are exposed either to monochromatic light or to specific regions of wavelengths using filters from a mercury or tungsten lamp. In thermal cleaning, samples are heated at a uniform rate by the pre-adjusted programme up to the desired temperature in darkness and then brought to room temperature (RT) quickly under vacuum. After the sample attains RT, the residual TL is recorded.

4.4. TL glow curves

Most of the earlier work on AES had been on the emission and related properties with UV excitation. Meagre information is available on similar studies with X-ray and γ-ray excitations. Most of the earlier work on these lines is available in general books [111–117]. In the following sections, the recent work on TL of AES phosphors is described.

From the various publications, it appears that most of the work is on TL of these sulphides doped with impurities such as copper, bismuth, silver, manganese, aluminium, lead etc. The influence of various flux materials had become a part of these investigations in every case. Studies on AES doped with impurities such

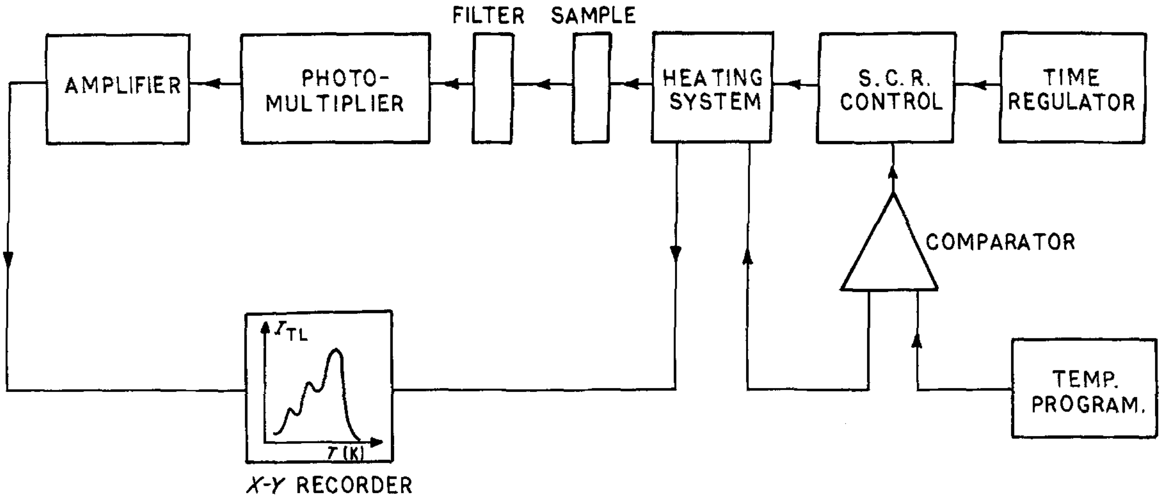


Figure 12 Schematic diagram of Saphymo TLD–20.

as antimony, tin etc. as well as rare earth impurities have also gained equal importance. In most cases, the TL was recorded by exciting the phosphor with UV (330–400 nm) at LNT (76° K) or at RT (300 to 303° K). The trapping parameters like trap depth E and frequency factor s were calculated from the glow curves by various workers, adopting the equations described in Section 4.2.2. Results of all the investigations essentially deal with

1. the nature of TL glow curve prior to material preparation and dopants,
2. the nature of traps and thermal activation energy associated with the traps, and
3. relation of traps with the defects (point). Results by various workers on TL of AES phosphors are summarized below.

4.4.1. The role of impurities

Alkaline earth sulphides in the pure state do not exhibit any TL even with high energy radiations like X-rays. Various workers observed the variations such as area under the glow curve, trap depth, temperature maximum (T_m) etc. after doping with various impurities (dopants). Vij and Mathur [118] observed that the TL intensity increases first with the increase of activator (cerium) concentration and then decreases with further increase; the maximum intensity was at around 0.4% of cerium. The decrease in intensity with the increase of cerium was due to the large number of levels produced which might give radiationless transitions. They found that CaS : Ce and CaS : Bi exhibit good TL but not CaS : Ce, Bi. The presence of bismuth and cerium provided a number of localized levels spaced at smaller energy differences, thereby giving the means to the electrons to return to ground state by smaller radiationless transitions. Due to this fact, even a very efficient activator can act as a killer, but it may not be the same in the case of other impurities. The TL of CaS doped with various impurities is given in Fig. 13 [119]. It is observed that different glow maxima depend on the nature of activating impurity. The trap depth values calculated from glow curves with IR stimulation are given in Fig. 13. In case of copper and zirconium doped CaS and SrS, copper acts as a principal activator [120]. In case of CaS : Bi,Pd Lawangar *et al.* [121] observed a variation in the shape and relative intensity of TL glow curves, with an increase of bismuth and palladium. The variation of palladium

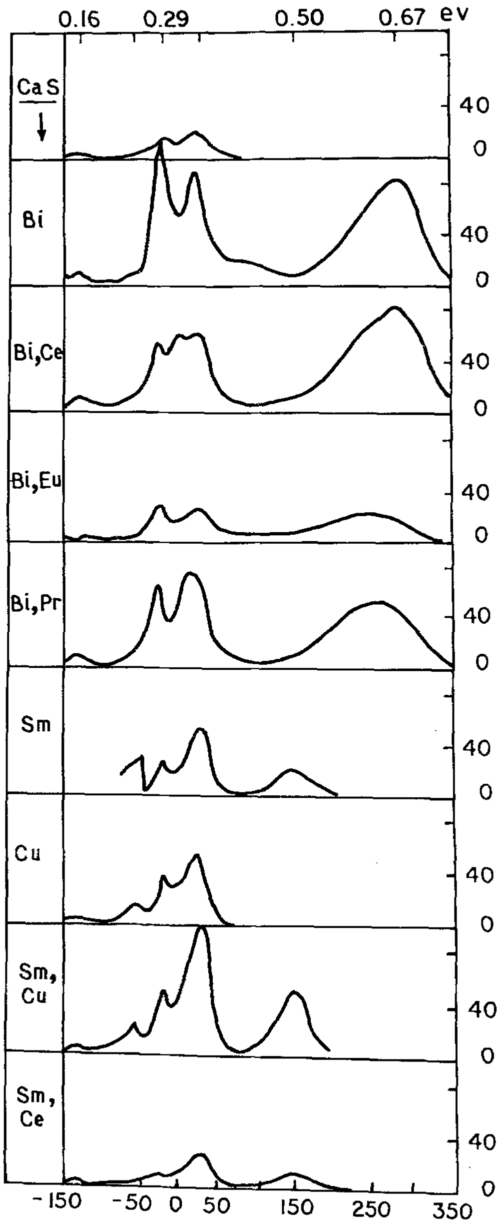


Figure 13 TL glow curves of CaS phosphors doped with bismuth, copper, cerium, europium, samarium and their combinations [119].

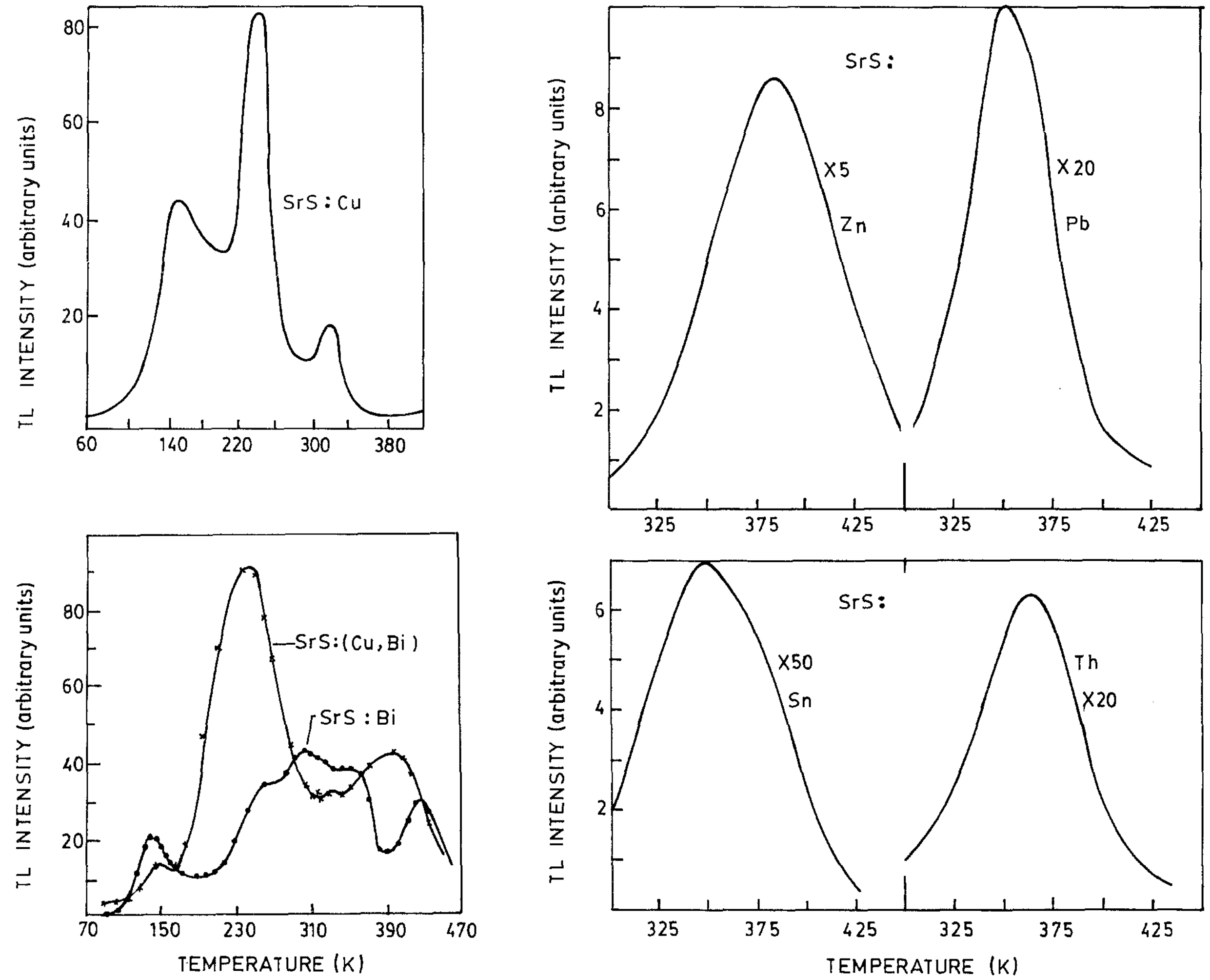


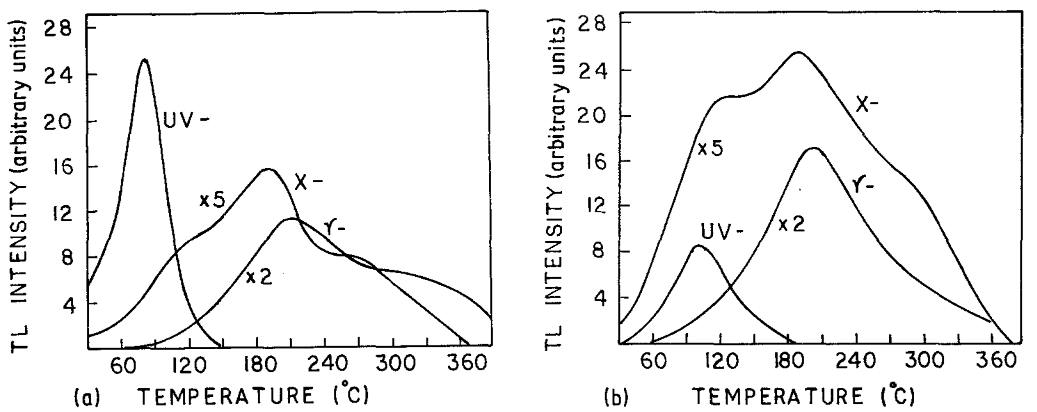
Figure 14 TL glow curves of SrS phosphors doped with copper, bismuth, tin, zirconium, thorium and lead [46, 124 and 125].

concentrations has a relatively greater effect on the intensity of the second peak suggesting that deeper traps are affected with the increase of palladium. Addition of palladium to CaS : Bi had the effect of increasing the population of traps corresponding to a lower temperature peak. The area under the glow peak is proportional to the concentration of cerium in CaS : Ce [122]. At concentrations lower than 0.05%, the overall efficiency was reduced due to decrease in the number of luminescence centres. Cerium and chlorine may aid the formation of defects. Cerium plays a predominant role in CaS as a sensitizer, increasing TL efficiency by more than one order of magnitude. Incorporation of silver in CaS markedly affects the relative intensity of glow peaks [123]. SrS doped with zirconium, antimony, lead or thorium exhibits TL glow curves of different glow maxima and areas could be due to a distribution of trap density [124]. TL glow curves of SrS doped with copper, bismuth, tin, terbium, zinc and lead are shown in Fig. 14. CaS doped with manganese, cerium and samarium did not show any significant changes. The shoulder developed in the low temperature side indicated that the centre of gravity of the traps shifted towards the shallow side [126].

The TL glow curves of BaS : Cu, BaS : Bi and BaS : Cu,Bi, phosphors prepared by varying the concentrations of bismuth and copper in the range 0.001 to 0.5 wt % are shown in Figs 15 and 16. There is no regular variation of TL intensity, but the intensities increase with increase of concentration up to a certain concentration and then decrease with further increase. This is due to the well established phenomenon of concentration quenching [115]. The variation in TL patterns of BaS : Bi phosphors recorded after exciting the samples with UV, X-ray, γ-ray and low energy electrons is shown in Fig. 17. The TL of MgS phosphors, prepared by doping with all possible dopants including rare earth elements, was recorded after exciting with UV and X-rays. The TL glow curves of the same are shown in Figs 18 and 19. It is observed that the samples exhibited TL maxima corresponding to respective dopants.

4.4.2. Nature of traps

In order to identify the electron and hole traps responsible for the TL emission, one has to look for the centres and/or regions which will act as places for stabilizing the trapped electron as well as the trapped hole centres. Most of the workers concluded that the traps responsible for TL emission are associated with a host lattice such as sulphur ion vacancies in AES phosphors. The traps are due to defects incorporated during preparation and trapped in the host material (CaS) [127]. As the concentration of dysprosium in CaS : Bi increases the centre of gravity of the traps shifts towards the shallower side. The electronegativity and the ionic radii of these rare earth ions are likely to



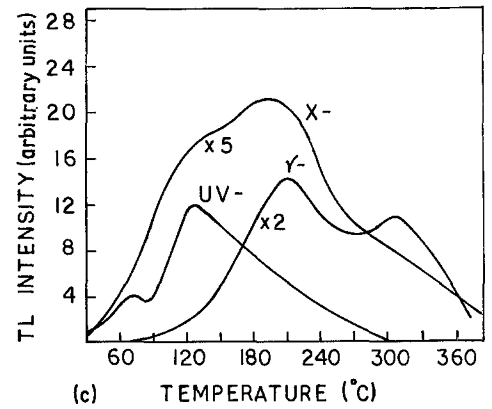


Figure 15 TL glow curve of BaS phosphors doped with (a) copper, (b) bismuth and (c) copper and bismuth.

occupy the substitutional sites in the CaS lattice [127]. The observed differences in the peak temperatures and area under the glow curves in phosphors doped with different materials could be due to the distribution in the trap density. The flux and activator concentration did not affect the traps associated with the host lattice. But when fluorides from flux get associated with sulphur, ion vacancy and trapping states are formed as in the case of CaS : Zr. The extra positive charge might lower the electronic energy levels of neighbouring calcium ions [128]. It has been established that anion (sulphur ion) vacancies (associated with impurities like copper) in II–VI compounds of ZnS type, exhibit magnetic resonance spectra [129] and in the same way reports exist for CaS suggesting that such variables act as effective traps [130]. To explain the TL results on copper and bismuth doped BaS phosphors, the author has considered the role of defects such as $[V_S]^{2+}$, $[V_S - Cu_{Ba}]^{+}$ and $[Bi_{Ba}]^{+}$ as possible trapping sites for electrons and $[Cu_{Ba} - V_{Ba}]^{2-}$ and $[V_{Ba} - Bi_{Ba}]^{-}$ for holes (square brackets indicate the effective charge of the centre.) The trap depth values (0.4 to 0.6 eV) and monomolecular process of low temperature glow peak indicated that the involved electron and hole traps are located near each other. The TL traps related to the high temperature glow peaks, exhibited by BaS phosphors excited with X- or

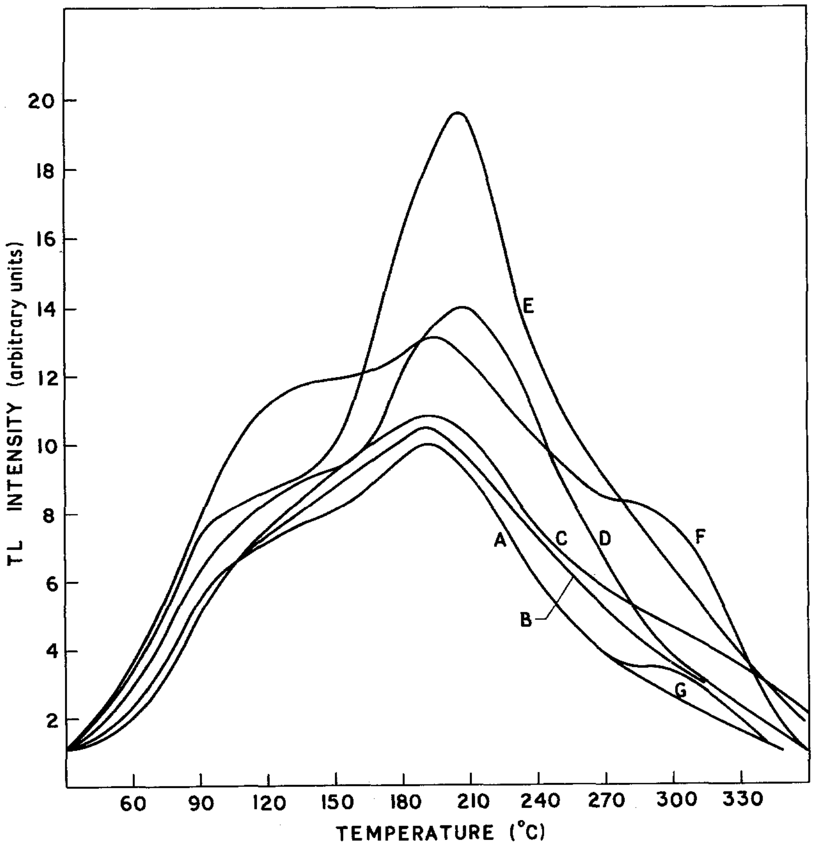


Figure 16 TL glow curve of BaS phosphors doped with different concentrations of bismuth. wt % = A, 0.005; B, 0.023; C, 0.058; D, 0.173; E, 0.231; F, 0.347; G, 0.463.

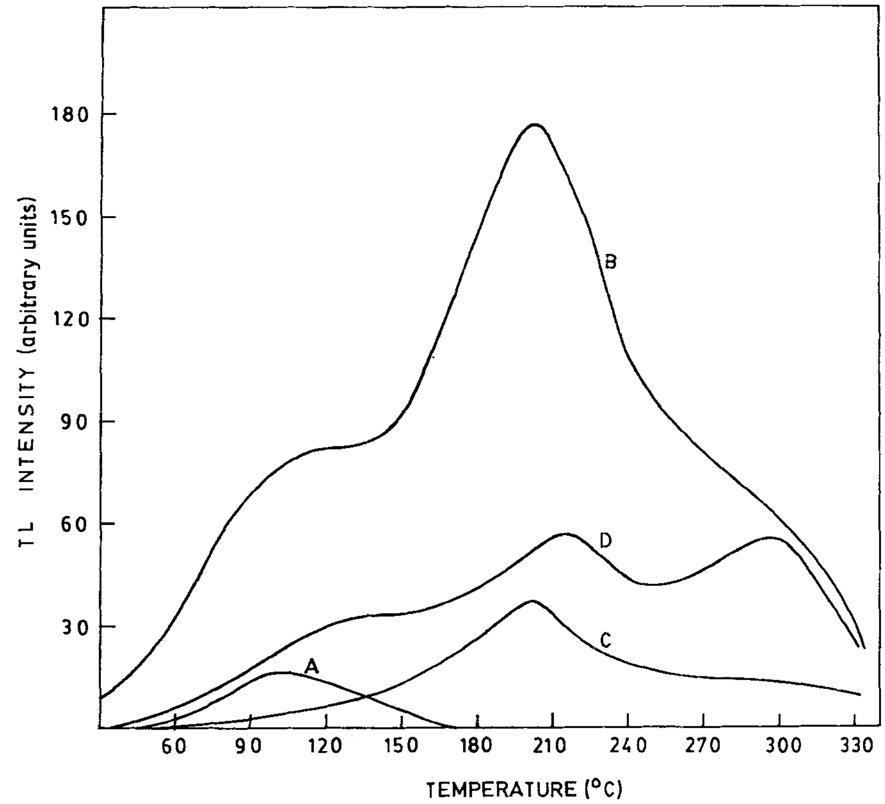


Figure 17 TL glow curves of BaS:Bi phosphors after exciting with A, UV; B, X-rays; C, γ-rays and D, low energy electrons.

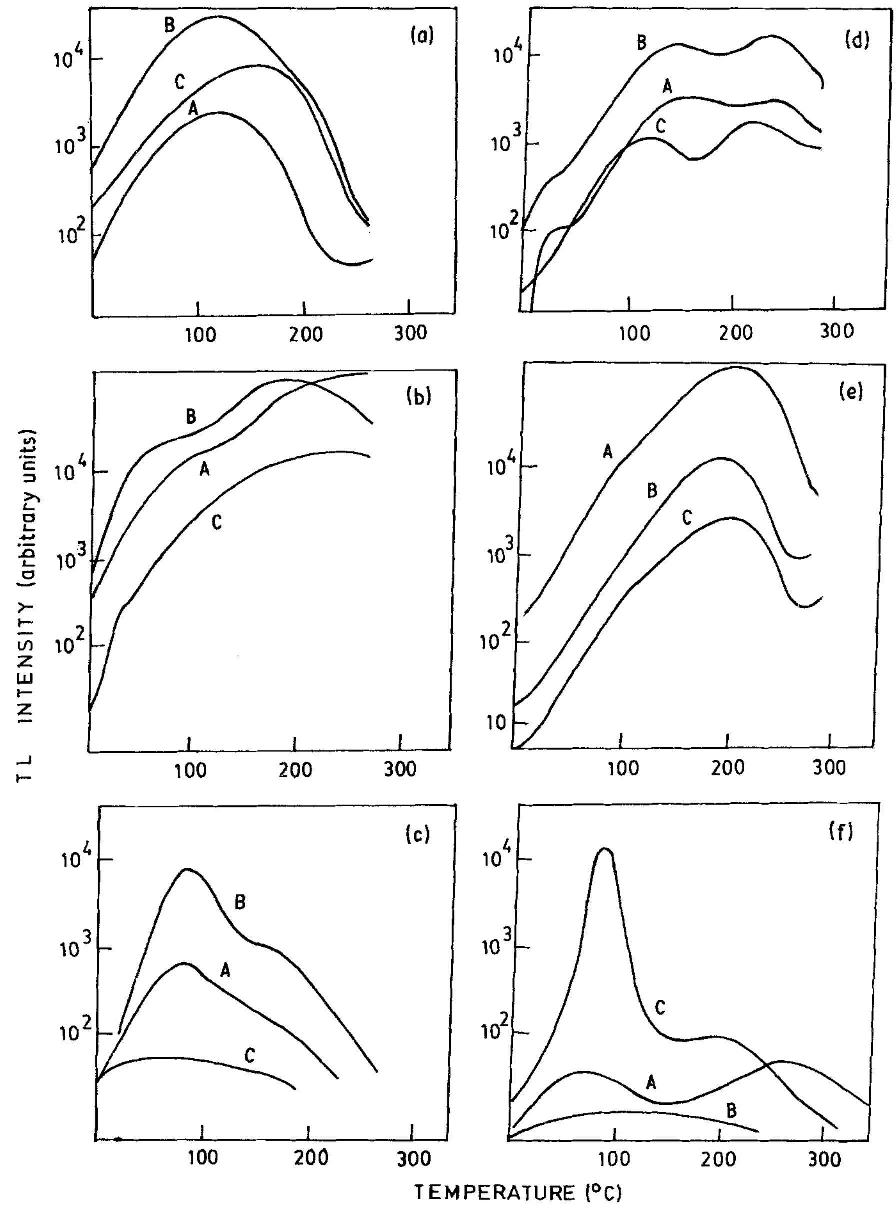


Figure 18 TL glow curves of MgS phosphors doped with (a) terbium, (b) samarium, (c) copper, (d) manganese, (e) cerium and (f) bismuth. A, day light (6 h); B, UV (5 sec) and C, X-rays (25 mR).

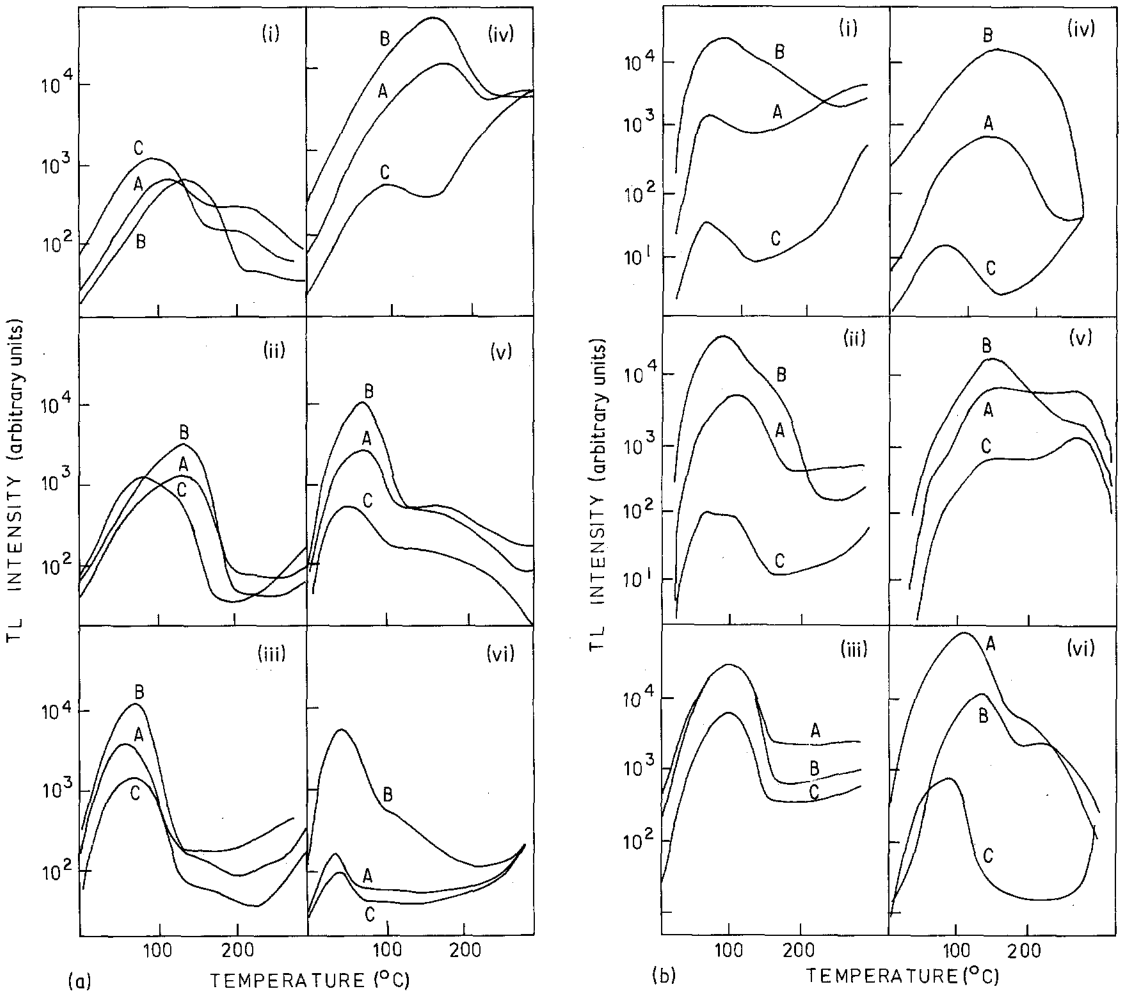


Figure 19 (a) TL glow curves of MgS doped with (i) europium (ii) europium, bismuth (iii) europium, terbium (iv) cerium, bismuth (v) cerium, europium and (vi) manganese, samarium. A, day light (6 h); B, UV (5 sec) and C, X-rays (25 mR). (b) TL glow curves of MgS doped with (i) manganese, bismuth (ii) manganese, terbium, (iii), managese, europium (iv) terbium, copper (v) samarium, europium and (vi) manganese, cerium. A, day light (6 h), B, UV (5 sec) and C, X-rays (25 mR).

γ-rays or low energy electrons, might be attributed to the distribution of trapped hole and electron centres involving the defect complexes in some manner or other. Levshin and Pipines [131, 132] studied the trapping levels in CaS and SrS phosphors by thermoluminescence and exoelectronic emission. The low temperature peak, which could not be exhibited by TL, may thus be due to the hole traps or to insufficient energy of activated electrons to escape from the traps.

4.4.3. Trapping parameters

The calculation of trapping parameters from afterglow decay and TL glow curves is a common feature in the study of luminescence properties. The trapping parameters (trap depth, E and frequency factor, s) calculated by various authors for alkaline earth sulphide phosphors doped with different impurities are shown in Table I. In general, monomolecular kinetics (1st order) implies that the process of retrapping is neglible and the traps should be situated very close to the luminescence centre. The complex TL patterns are resolved into single peaks by adopting the thermal cleaning technique [100, 161, 162], the analytical method [163] and optical bleaching or photostimulation [164]. For example, resolution of a complex glow curve of X-irradiated BaS : Cu phosphors, by the thermal cleaning technique as well as the analytical method, is shown in Fig. 20. Agnihotri and Ranade [128] could not find any systematic variation in the values of E and s with activator (Zr) concentration in CaS : Zr but the value of E decreased from 0.8 to 0.7 eV with the increase of zirconium concentration. This indicates that activator atoms were perturbed. A little variation is observed in the values of E and s in case of CaS : Zr prepared with different fluxes [91]. With the increase of cerium concentration in CaS, the value of S varies between 10^8 and $10^{10}\,\text{sec}^{-1}$ which is less than the frequency of crystal vibration ($10^{13}\,\text{sec}^{-1}$ for CaS) for several orders of magnitude. This fact shows the presence of a small transition probability on the temperature emptying process [122].

The storage of electrons and their distribution in traps and trapping parameters have been determined from the studies of TL glow curves of SrS : Eu,Sm phosphors by Keirin-Markus [165] after γ-irradiation. Levshin and Orlav [166] studied the thermal activation process in CaS : Bi phosphors after exposing excited phosphors to various intensities of IR.

4.4.4. Effect of flux

While preparing the phosphor, the flux materials are generally used to incorporate the dopants into the matrix so that luminescence efficiency could be

TABLE Ia Trapping parameters of alkaline earth sulphide phosphors calculated from TL glow curves: ultraviolet excitation.

Sample	Glow maximum T_m (K)	Trap depth E(eV)	Frequency factor s (sec^{-1})	Reference
BaS : Cu	310	0.73	1.0×10^{10}*	133
BaS : Cu	353	0.55	2.0×10^{6}	35
BaS : Bi	333	0.59	–	134
BaS : Bi	377	0.54	2.0×10^{6}	35
BaS : Bi	375	0.49	2.8×10^{4}	135
BaS : Ce	345	0.54	1.0×10^{6}	136
BaS : Sm	346	0.55	1.0×10^{6}	
8BaS : Ce, Sm	348	0.55	1.0×10^{6}	
BaS : Eu, Sm	373	0.50	1.0×10^{7}	137
CaS : Cu	330	0.75	1.5×10^{10}*	138
CaS : Bi†	112	0.22	1.24×10^{8}	139
	141	0.30	1.85×10^{9}	
	163	0.32	3.2×10^{8}	
	197	0.39	3.4×10^{8}	
CaS : Bi	353	0.61	3.5×10^{5}	140
CaS : Bi	350	0.68	–	127
CaS : Ag	333	0.84	–	123
	393	1.00	–	
CaS : Ce	334	0.82	1.0×10^{10}*	118
CaS : Ce†	160	0.12	1.0×10^{3}	141
	225	0.32	1.0×10^{5}	
	320	0.74	1.0×10^{9}	
	350	1.10	1.0×10^{14}*	
CaS : Sb		0.55		142
		0.67		
CaS : Tm†	131	0.25	2.5×10^{8}	140
	199	0.39	2.4×10^{8}	
	276	0.57	5.9×10^{8}	
CaS : As	380	0.55	1.0×10^{9}	143
	445	0.65	1.0×10^{9}	
CaS : Tb	343	0.5 to 0.8‡		144
CaS : Nd	335	0.71	1.0×10^{9}	145
CaS : Dy	340	0.7	–	146
CaS : Pd	348	0.7	–	147
CaS : Zr	380	0.7 to 0.8‡	1.0×10^{9}	128
CaS : Zr	365	0.72	1.0×10^{9}	120
CaS : Zr	365	0.72	2.4×10^{9}	148
CaS : Zr	350	0.74	1.0×10^{9}	90
CaS : Zr	350	0.72 to 0.75§	1.0×10^{9}	91
CaS : Cu, Al	353	0.70	–	92
CaS : Cu, Cl	348	0.70	–	
CaS : Cu, Cl	350	0.81	1.0×10^{8}	127
	379	1.24	1.0×10^{12}	
CaS : Cu, Zr	328	0.76	1.0×10^{10}	120
CaS : Bi, Dy	353	0.55	1.0×10^{6}	140
CaS : Bi, Tm	338	0.59 to 0.77‡	$0.1\text{-}45 \times 10^{8}$	32
CaS : Bi, Tm	129	0.20	1.0×10^{7}	139
	154	0.30	1.3×10^{8}	
	166	0.32	2.2×10^{8}	
	205	0.39	1.3×10^{8}	
CaS : Bi, Pd	343	0.52 to 0.66‡	10^{5}–10^{6}	146
	473	0.61 to 0.73‡	10^{4}–10^{6}	
CaS : Bi, Pd†	165	0.27 to 0.40¶	10^{7}–10^{10}	149
	270	0.36 to 0.55¶	10^{5}–10^{7}	
CaS : Pb, Mn	375	0.79	–	150
CaS : P, Cl	343	0.70	–	92
CaS : Ag, Cl	358	0.70	–	
CaS : Zr, Dy	360	0.70	1.0×10^{9}	27
CaS : Zr, Gd	330	0.70	1.0×10^{9}*	151
	360	0.76	1.0×10^{9}*	
CaS : Zr, Mn	380	0.6 to 0.9‡	–	157
CaS : Mn, Ce, Sm	345	0.65 to 0.69‡	–	126
	370	0.58 to 0.68‡	–	
SrS : Cu	325	0.75	1.0×10^{10}*	138
SrS : Cu	327	0.74	1.0×10^{10}*	120
SrS : Cu†	154	0.36	1.0×10^{10}*	125
	264	0.58	1.0×10^{10}*	
	319	0.76	1.0×10^{10}*	
SrS : Bi†	145	0.56	1.0×10^{10}*	125
	250	0.58	1.0×10^{10}*	
	400	0.60	1.0×10^{10}*	

TABLE I continued

SrS : Bi	332	0.77	10^{10}*	133
SrS : Bi	353	0.7 to 0.8‡	10^{9}–10^{10}	153
SrS : Pb	355	0.62	–	124
SrS : Th	355	0.62	–	
SrS : Sn	375	0.66	–	
SrS : Zr	375	0.66	–	
SrS : Zr	338	0.70	10^{10}*	154
SrS : Ho	330	0.70	5.0×10^{9}	155
SrS : Hf	340	0.70	2.3×10^{9}	47
SrS : Cu, Bi†	140	0.33	10^{10}*	125
	240	0.58		
	320	0.76		
	400	0.94		
SrS : Cu, Zr	327	0.74	10^{10}	120
SrS : Mn, Zr	340	0.71	8.5×10^{8}	156
MgS : Eu, Sm	353	0.50	–	152
	533	0.71	–	

*second order kinetics or assumed from other data.
†excitation at LNT.
‡wrt activator concentration.
§wrt flux content.
¶different methods of calculation.

TABLE Ib Trapping parameters of alkaline earth sulphide phosphors calculated from TL glow curves: X-rays

Sample	Glow maximum T_m (K)	Trap depth E(eV)	Frequency factor s (sec^{-1})	Reference
BaS : Cu	389	0.38	1.7×10^{3}	135
	463	0.63	1.6×10^{5}	
	547	0.87	1.6×10^{6}	
BaS : Bi	385	0.36	3.6×10^{3}	135
	473	0.61	4.6×10^{5}	
	571	1.04	3.5×10^{7}	
BaS : Cu, Bi	493	0.38	2.6×10^{3}	135
	471	0.68	3.0×10^{5}	
	559	0.81	3.7×10^{5}	

TABLE Ic Trapping parameters of alkaline earth sulphide phosphors calculated from TL glow curves: γ-rays

Sample	Glow maximum T_m (K)	Trap depth (eV)	Frequency factor s (sec^{-1})	Reference
BaS : Cu	476	0.88	1.6×10^{5}	158
	568	0.91	8.9×10^{6}	
BaS : Bi	486	0.67	1.2×10^{5}	158
	570	1.10	1.1×10^{8}	
BaS : Ce	365	0.47	1.0×10^{5}	136
BaS : Sm	362	0..52	1.0×10^{3}	
BaS : Cu, Bi	471	0.47	4.7×10^{5}	
	591	0.68	8.4×10^{4}	158
BaS : Ce, Sm	365	0.47	1.0×10^{8}	136
CaS :	650	1.30	–	159

TABLE Id Trapping parameters of alkaline earth sulphide phosphors calculated from TL glow curves: low energy electrons

Sample	Glow maximum T_m (K)	Trap depth E(eV)	Frequency factor s (sec^{-1})	Reference
BaS :Cu	401	0.56	–	35
	453	0.74	2.35×10^{5}	
	552	0.82	–	
BaS : Bi	487	0.66	2.9×10^{5}	160
	561	1.10	3.5×10^{7}	

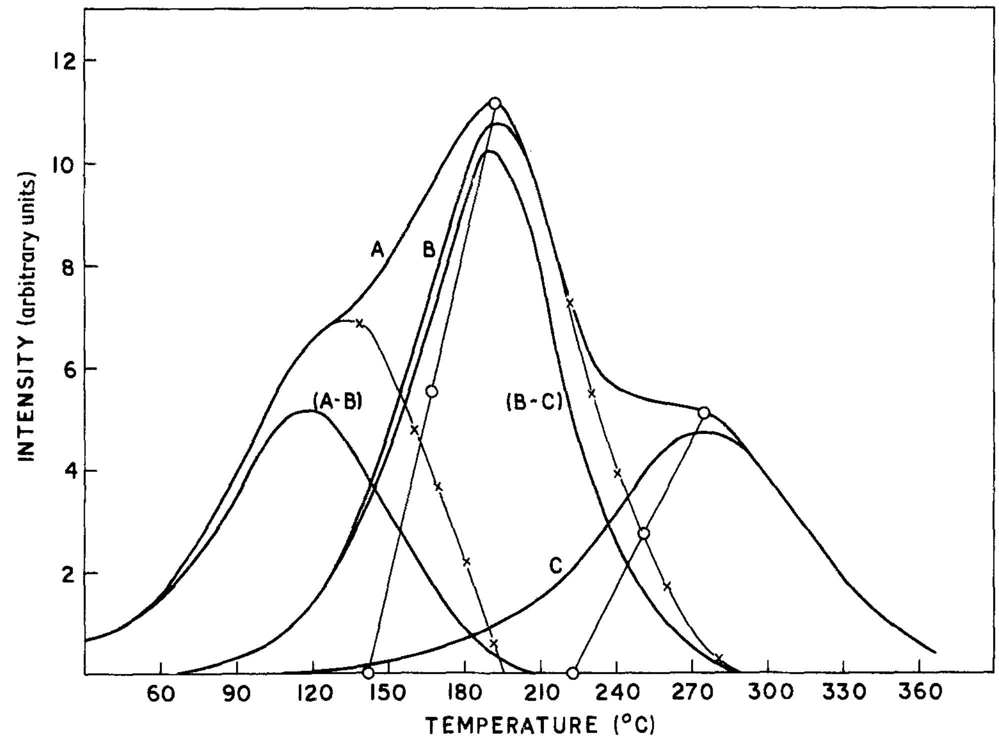


Figure 20 Analysis of Tl glow curve of BaS : Cu phosphors irradiated by X-rays at 30° C for 10 min. (—) Thermal clearing; (-x-) Rao's technique.

improved. Generally, flux does not introduce any new trapping states. Glow maximum (T_m) and shape of the glow curve have changed with flux but there is no significant variation with the amount of flux [148]. This indicates that flux serves to alter the relative importance of different groups of traps and not their mean trap depth. The emission has been affected because the atoms of flux cluster around the activator atoms and bring about changes in the number of centres. It is observed that fluxes do not only facilitate the even distribution of activator ions into the base lattice (of CaS : Bi prepared with Na_2SO_4 and $LiCO_3$ fluxes), but also to a large extent change the course of reaction and structure formation of the basic substance [167]. Varma [90] has observed an increase in T_m with the increase of flux and then a decrease with further increase of flux content.

It was assumed that the number of deeper traps increased with flux and then decreased with further flux content. The low temperature peak (332 K) remains unaffected by the quantity of flux (Na_2SO_4) used in the preparation of SrS : Bi phosphors while the high temperature peak (423 K) varies with the quantity of flux [168]. In the case of BaS : Cu phosphor, the TL yield increased with the increase of flux (NaCl) up to 25 wt % and then decreased with further increase of flux [95]. The broad nature of glow maxima gradually reduced and at the optimum value of flux content (curve 5 of Fig. 21) well defined glow maxima were observed. The variation in TL glow curve of BaS : Cu (0.01 wt %) phosphor prepared in the presence of different amounts of NaCl flux is shown in Fig. 21. The nature of increase in the intensity of the glow peak at 180° C (related to the presence of copper) as well as the total area under different glow curves with the increase flux content are also shown as an inset in the same figure (Fig. 21).

4.4.5. Effect of grain/particle size

While considering the industrial applications of

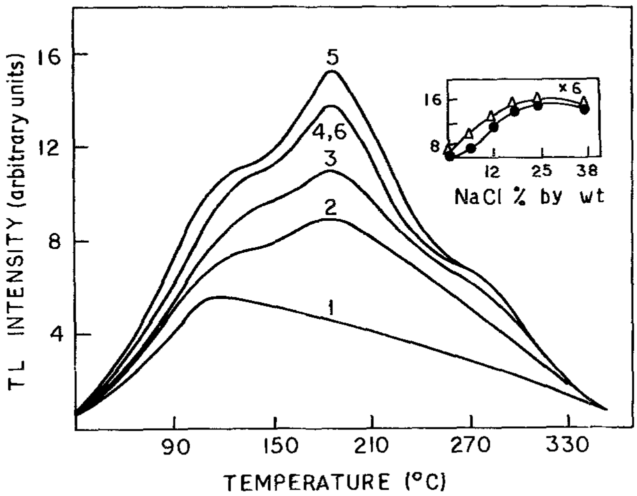


Figure 21 TL glow curves of BaS : Cu (0.01 wt %) phosphors prepared with different quantities of NaCl flux. (●) 180° C peak; (△), total area. NaCl (wt %): (1) 0.0, (2) 6.4, (3) 12.9, (4) 19.3, (5) 25.7 and (6) 38.6.

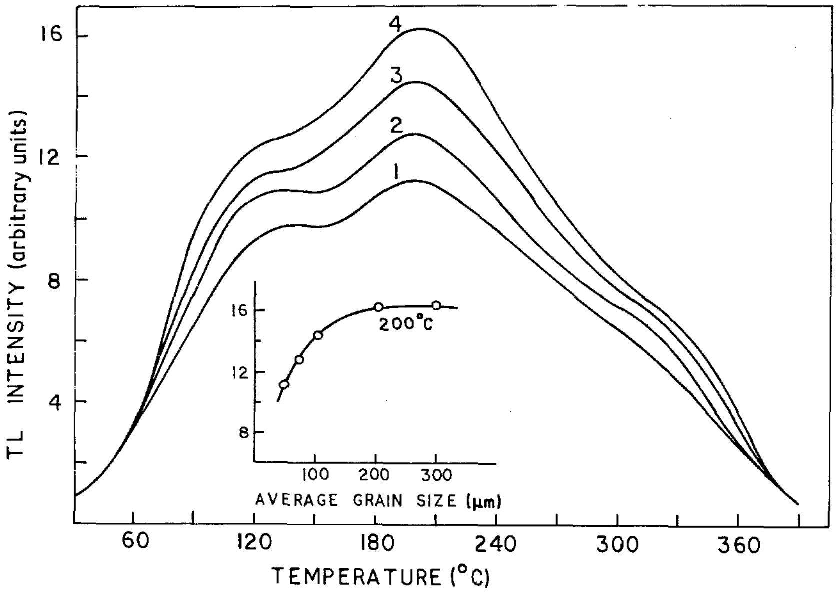


Figure 22 TL glow curves of BaS : Bi (0.36 wt %) phosphors of different particle sizes. (1) 45 μm; (2) 75 μm; (3) 106 μm; (4) 212 and 300 μm.

polycrystalline phosphors in fluorescent lamps, screens, luminescent paints and radiation dosimetry, the effect of grain size on the light output has to be especially studied and estimated. Information on a similar study of the effect of grain size on TL of AES phosphors is very little. The powders obtained in the reduction process were ground in a pulverizer and brought to various particle sizes using sieves of different mesh numbers. Rao [169] reported that the TL output decreases with the decrease of grain size. In Fig. 22, the results on TL glow curves of a typical sample BaS : Bi (0.36 wt %), where all three TL glow peaks are well defined, are presented for different grain sizes. The effect of grain size on the glow peak at 200° C which is related to bismuth impurity is also shown as an inset in Fig. 22. The increase in TL yield with grain size could be understood considering the phenomenon of scattering by which a major fraction of incident radiation is lost due to scattering by smaller grains, thus making available less excitation energy to the bulk of the material.

4.4.6. Optical bleaching

Alkaline earth sulphide phosphors are sensitive to daylight. It is essential to study the effect of visible light on TL characteristics of these sulphides. Most of these AES phosphor materials are excited with visible light to a greater extent than UV. The effect of daylight on MgS phosphor before its irradiation with UV and X-rays are shown above in Figs 18 and 19. In general, a decrease in TL output is observed with the increase of exposure time and all the glow peaks are reduced in the process; the samples cannot, however, be bleached completely even if they are exposed to light for much longer durations. It has been further noticed that in the process of optical bleaching the low temperature glow peaks have been completely removed and the high temperature glow peaks reduced gradually with the increase of exposure time [170]. The effect of visible light on the TL of X-irradiated BaS : Cu phosphors is shown in Fig. 23. The nature of bleaching observed for one glow peak around 190° C is shown as an inset in the same figure. It indicates the decrease of intensity in two stages, the fast decay at the rate of $\sim 10^{-3}\,\mathrm{sec}^{-1}$, followed by the slow decay at the rate of $\sim 10^{-5}\,\mathrm{sec}^{-1}$. The bleaching of stored energy in UV excited samples is not regular because of the fact that both destruction and creation of traps occur with visible light.

4.4.7. TL decay (fading)

The fading behaviour of TL with storage for different durations of time is an important parameter in TL dosimetry. After irradiation, the samples are stored in darkness for different lengths of time and their TL studied. The TL output becomes negligibly small in case of UV excited BaS after a few minutes of storage (Fig. 24a). In case of X- and γ-ray irradiated samples, sufficient TL emisssion could be observed even after a few days of storage time. It was reported that the fading is small in the case of annealed CaS : Bi phosphors [171]. The TL glow curves recorded for irradiated samples of BaS : Cu, Bi and BaS : Bi after storing for different lengths of time are shown in Figs 24 and 25. With the increase of storage time, the low temperature glow peak is observed to get destroyed earlier than the high temperature glow peaks. The low temperature peaks are suppressed because the shallower traps get destroyed with the time of storage. The trend in the fall of the intensity of the high temperature peaks is shown as an inset in Fig. 24, which indicates a two-stage process, each one being exponential in nature. Thus, these results are similar to those obtained in the case of optical bleaching except for the fact that the bleaching occurs faster in the latter case.

Vij and Mathur [118] observed peak shift with decay time in case of CaS : Ce from 334 to 375 K. This effect may be due to the broad distribution of trap depths which are responsible for the release of electrons from the traps as they may have two kinds of energies; one kind of energy is the result of thermal vibrations of the lattice and the other is due to interaction taking place between electrons trapped at the same depth.

4.4.8. Effect of preparative parameters

The storability of a phosphor can be improved by

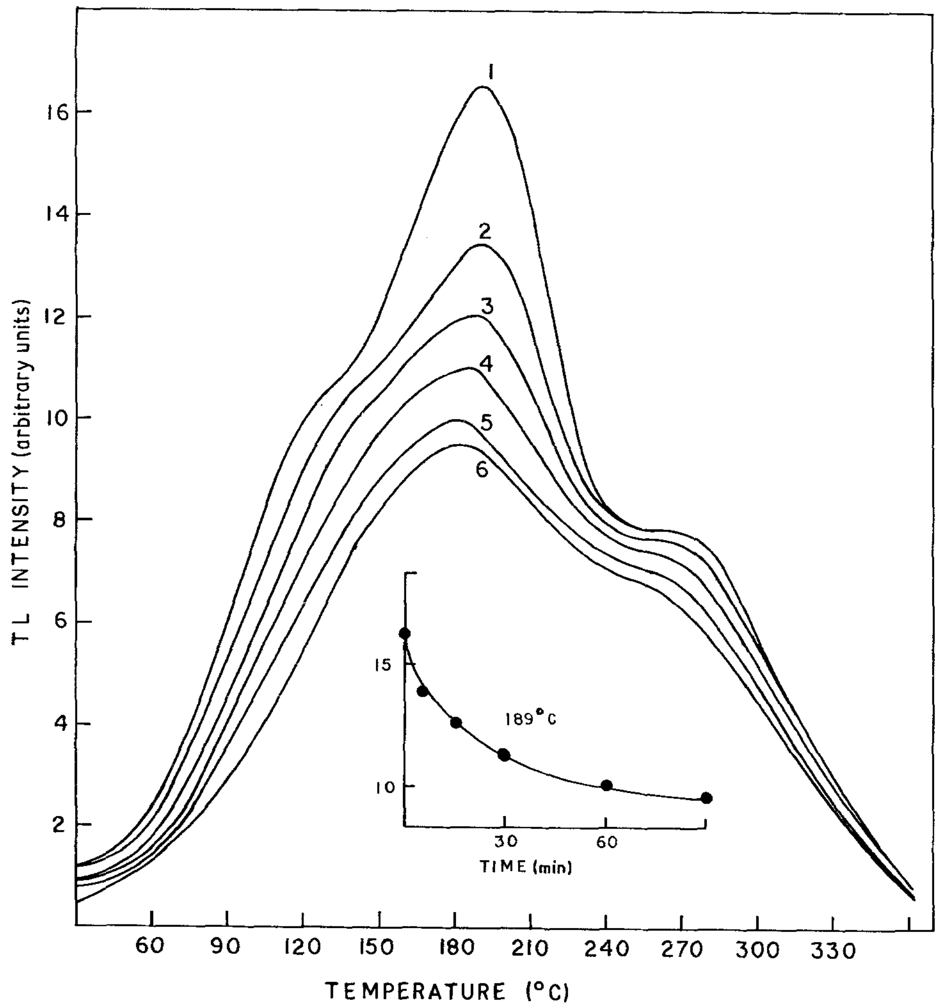


Figure 23 The effect of visible light (400 nm) on TL glow curves of BaS : Cu (0.01 wt %) phosphors. (1) unbleached; (2) bleached for 5 min; (3) 10 min; (4) 30 min; (5) 60 min; (6) 90 min.

varying the preparative parameters such as duration of firing, rate of cooling, ambient atmosphere etc.

1. In the preparation of AES, optimum values of firing temperature and duration of firing could be obtained from the other data like DTA, DTG etc. In the preparation of BaS : Cu, it is found that TL yield is more for samples fired at 950° C for 90 min (an optimum value). The samples prepared for more than

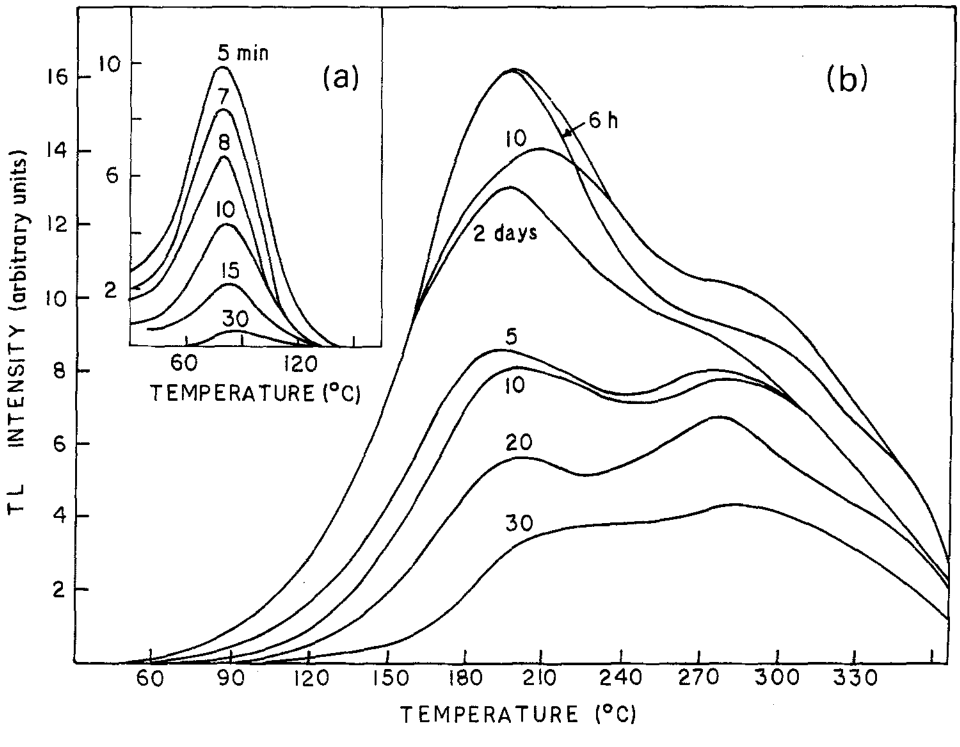


Figure 24 TL glow curves of (a) BaS : Cu, and (b) BaS : Cu, Bi phosphors stored in dark after (a) UV and (b) γ-ray irradiations.

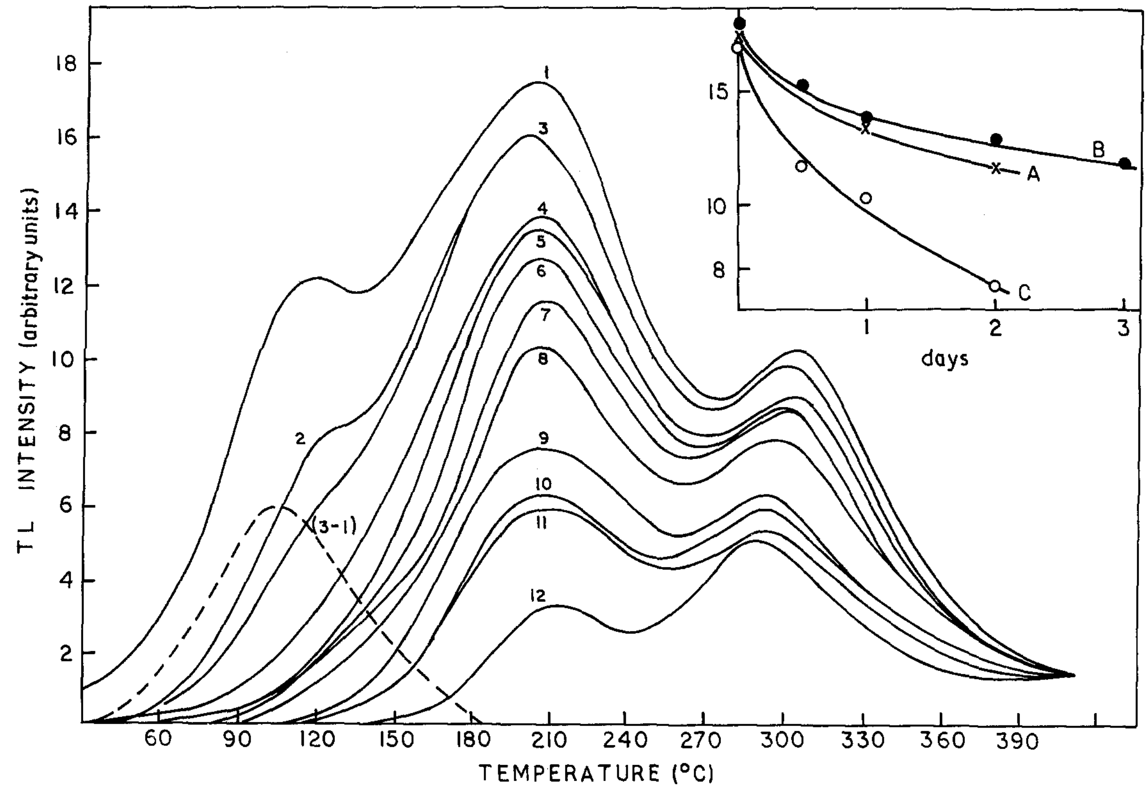


Figure 25 TL glow curves of BaS : Bi (0.23 wt %) phosphors stored in dark after X-irradiation. Inset: TL decay of (A) BaS : Cu, (B) BaS : Bi and (C) BaS : Cu, Bi after X-irradiation. (1) 8 min, (2) 16 min, (3) 30 min, (4) 1 h, (5) 3 h, (6) 6 h, (7) 12 h, (8) 1 day, (9) 2 days, (10) 6 days, (11) 10 days, (12) 30 days.

90 min exhibit poor TL output. The particle size of phosphors increases with the increase of duration of firing. The TL yield diminishes with the increase of particle size. This effect might also be due to the formation of a maximum number of defects during the sample preparation for a particular duration.

2. After the reduction process, the phosphor samples were cooled at various rates of cooling. In general, it was observed, the TL yield is more with a fast rate of cooling. Vij and Mathur [172] have observed that the slow cooled (50° h^{-1}) samples of CaS : Ce exhibited low intensity of TL as compared to

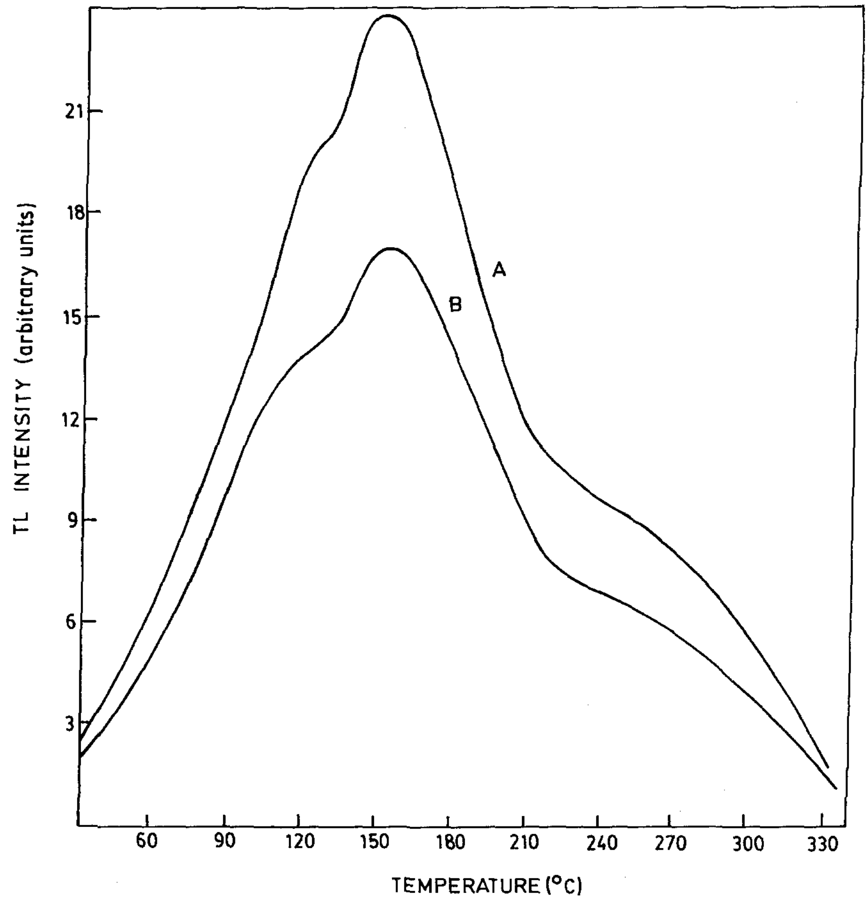


Figure 26 TL glow curve of BaS : Cu (0.01 wt %) phosphors cooled at different rates of cooling after the reduction process, (A) fast and (B) slow cooling.

the fast cooled one. Fig. 26 shows the TL glow curves of BaS : Cu cooled at different rates of cooling. The increase in TL output with decrease of rate of cooling is again due to the formation of defects. At the firing temperature, the lattice has a large density of defects which tends to freeze during fast cooling, while in slow cooling, the lattice has sufficient time to adjust itself and come to an equilibrium state corresponding to that particular temperature. This means that a smaller density of defects and consequently less traps are produced in the slow cooling process. Kanari [46] concluded that the TL intensity is more for samples prepared under purified N_2 than those prepared in air. The samples prepared in sulphurizing atmospheres such as H_2S have exhibited less TL yield when compared to the phosphor prepared by other processes [156, 140]. It may be due to the decrease of sulphur ion vacancies during sulphurization. It is also found that sulphides formed with dopants are deposited on the surface of the phosphor instead of entering into the lattice.

4.4.9. Growth curves

The nature of growth or build up of TL growth curves is an important parameter in the study of radiation dosimetry. The behaviour of TL of AES with different radiation doses from UV, γ-ray, X-ray or particle radiations have not been studied as extensively as $CaSO_4$ and CaF_2. The effect of irradiation dose (X-ray) was studied for samples of BaS doped with copper and bismuth of different grain sizes [173]. All the samples independent of grain size exhibited the same number of TL glow maxima as with the increase of irradiation dose. In case of BaS : Cu, the glow peak at 190° C attains saturation after 15 min of irradiation (X-rays) while in the case of BaS : Bi and BaS : CuBi the saturation is observed after 30 min of irradiation (X-rays). Such clear saturation behaviour has not been indicated for the other high temperature peaks. TL glow curves of BaS : Bi obtained for different times of X-ray exposure are shown in Fig. 27. The growth curves of various glow peaks are also shown in the same figure as an inset. In the case of CaS : Bi, CaS : Bi, T_m [139] and CaS : Bi, Dy [140], the linear growth in TL has been observed up to 10 min of UV exposure.

4.5. TL spectra

The TL emission spectrum has not been studied by many workers due to the problems associated with detection of weak emission and the control of steady temperature (T_m) during the detection. TL spectra of several samples of BaS doped with coper and/or bismuth were studied by Rao [135]. Some of the typical spectra are shown in Fig. 28. The emission indicates overlapping bands in the wavelength region (350–400, 425–500 and 525–550 nm). The most prominent emission band has been observed in the wavelength region 350 to 450 nm in all the samples independent of activator. A slight shift is found in the band maxima towards the longer wavelengths with increase of T_m. It is concluded from the above results that the emission may be associated with the transitions involving radiative recombination between released electrons for the donor-like centres and the trapped hole centres.

4.6. TL of mixed systems

Binary and ternary systems of alkaline earth sulphide phosphors like (CaBa)S, (CaSr)S, (BaSr)S and (CaBaSr)S have been prepared and doped with different concentrations of copper, bismuth, cerium and samarium. The typical glow curves of the above systems are shown in Fig. 29. A well isolated peak at 180° C is observed in case of (BaCa)S : Cu phosphors. From the fading and linear energy transfer (LET) studies, it is concluded that this peak is the most suitable for radiation dosimetry.

5. Discussion

The preparation procedures developed in recent times

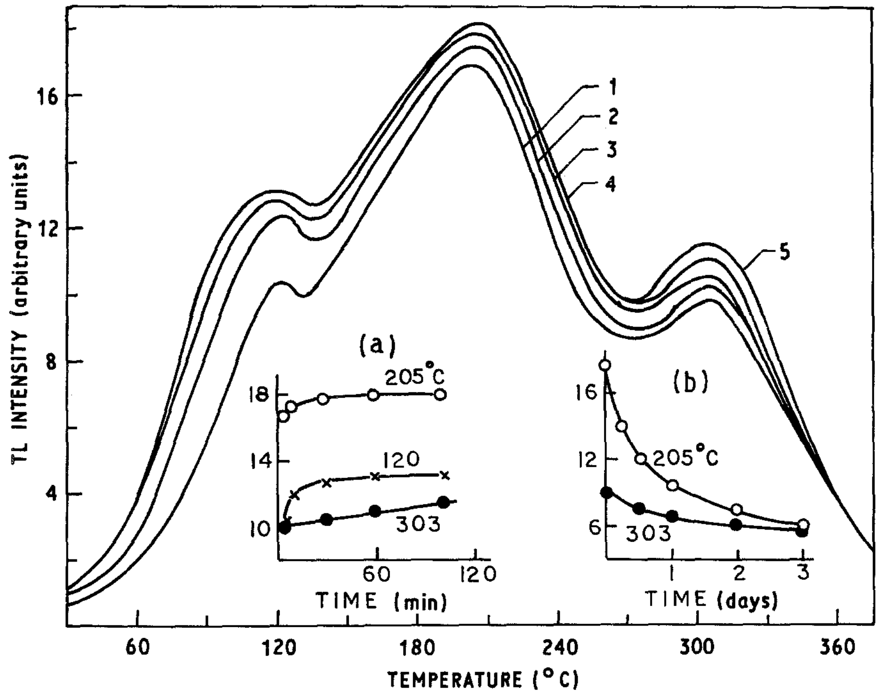


Figure 27 TL glow curve of BaS : Bi (0.23 wt %) obtained for different X-ray exposures, (a) growth and (b) fading curves. (1) 5 min, (2) 10 min, (3) 30 min, (4) 60 min, (5) 100 min.

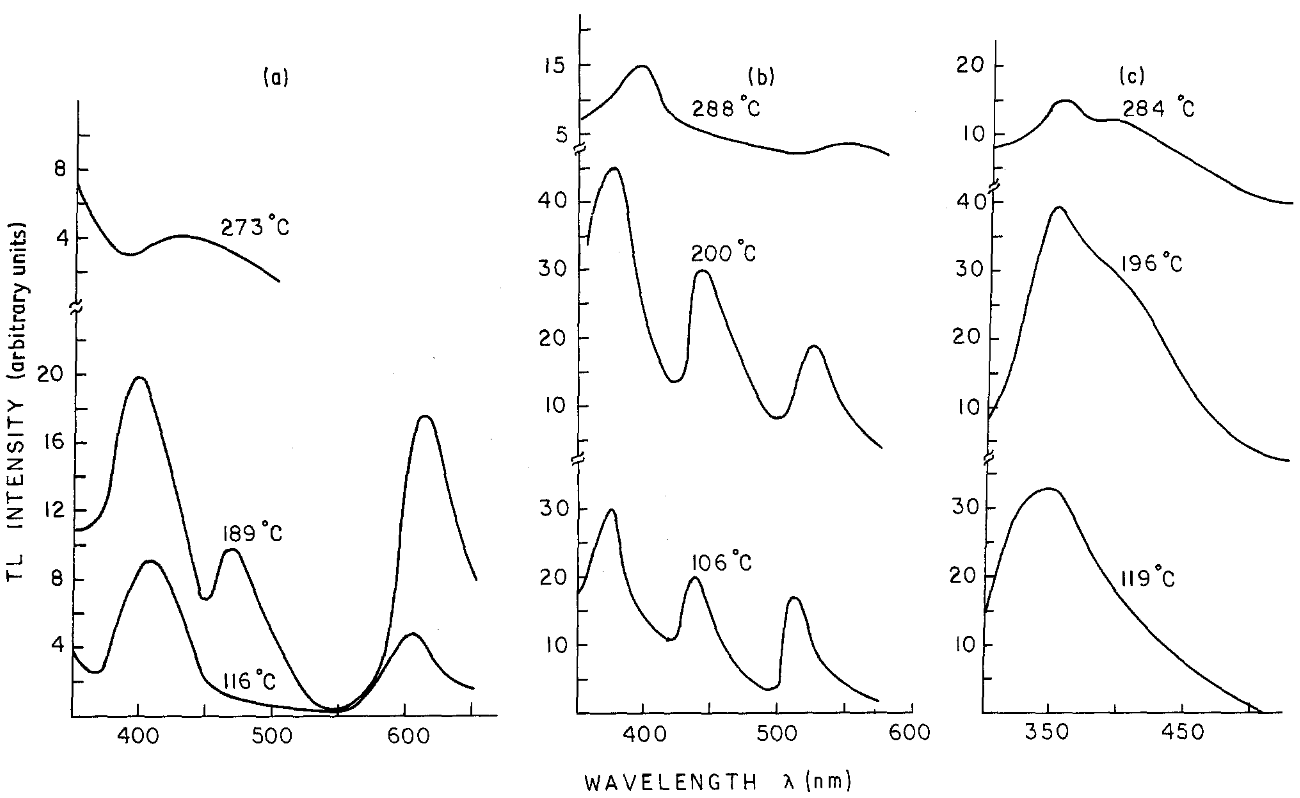


Figure 28 TL spectra of X-irradiated (a) BaS : Cu, (b) BaS : Bi and (c) BaS : CuBi.

have proved that efficient AES phosphors could be prepared and used in several optoelectronic devices. Since the preparative parameters vary from system to system, they could be ascertained with the help of DTA, TGA etc. Due to the potential application of these phosphors in the manufacture of CR tubes for colour television, extensive work has been carried out on material preparation during 1982–85 and most of the details are available from various patents. The efficiency of this system of phosphors has been improved by doping the phosphor with various impurities (dopants) in the presence of suitable fluxes under ambient atmospheres.

These sulphides, in general, show less ionic character than the alkali halides (the fractional ionic character of NaCl is 0.94 and of MgS is 0.79 [174]). It is observed that a strong similarity between the alkali halides and alkaline earth sulphides exists [175]. Rambakh [176] proposed a cycle where one can calculate the crystal lattice energy of alkaline earth sulphides, provided the lattice energy of the corresponding alkali halide is known. Although the ionicity of this system of phosphors is low compared to alkali halides, most of the defect controlled properties like luminescence are explained by representing these materials on ionic models only as divalent analogues of alkali halides like NaCl [177].

It has been generally reported that during the preparation of II–VI compounds, no stable interstitial type of defects (similar to Frenkel type) acting like donors or acceptors are observed in significant concentrations, and in almost all the cases of activating impurities, the results could be explained on the basis of their substiutional incorporation either on the cation or anion sites depending upon the nature of the impurity. The possible types of charge compensation in case of BaS : Cu, BaS : Bi and BaS : Bi, Cu phosphors prepared in the presence of NaCl flux, are shown in Fig. 30, and are explained elsewhere [160]. As indicated in Fig. 30 these impurities and the related lattice vacancies (for charge compensation) formed during the preparation of the phosphor may remain either isolated or randomly distributed, or form complexes depending upon the concentration of the impurity in the material and the temperature of activation. The impurities and their associated defects create localized levels in an otherwise forbidden energy region of the host lattice which will act, depending upon their nature, as electron and/or hole traps as well as recombination centres. The concentration of such trapped electron and/or hole centres depends not only on the concentration of the impurities but also upon the type of excitation source used for the purpose of irradiation, and accordingly the TL yield and related energy storage phenomena get modified. From the results on dielectric constant [82, 178] and electrical conductivity [179, 180], neutral complexes like $[\mathrm{Bi}_{\mathrm{Ba}}\text{–}\ \mathrm{V}_{\mathrm{Ba}}\text{–}\mathrm{Bi}_{\mathrm{Ba}}]^0$ $[\mathrm{Cu}_{\mathrm{Ba}}\text{–}\mathrm{V}_{\mathrm{S}}\text{–}\mathrm{Cu}_{\mathrm{Ba}}]^0$ and $[\mathrm{Bi}_{\mathrm{Ba}}\text{–}\mathrm{Cu}_{\mathrm{Ba}}]^0$ in BaS : Bi, BaS : Cu and BaS : Cu, Bi respectively were proposed. The results on TL and after glow decay of these samples gave ample support to the above proposed complexes [181].

6. Applications

6.1. TL dosimetry

The potential application of alkaline earth sulphides in radiation dosimetry has been proposed by various workers. SrS : Sm, Eu was used for detection of γ-ray radiation by Keirin-Marcus [165]. A high temperature (200° C) peak in TL of CaS : Bi (0.05%) was suggested for monitoring ultraviolet light without any pre-irradiation [38, 171]. The area and height of the

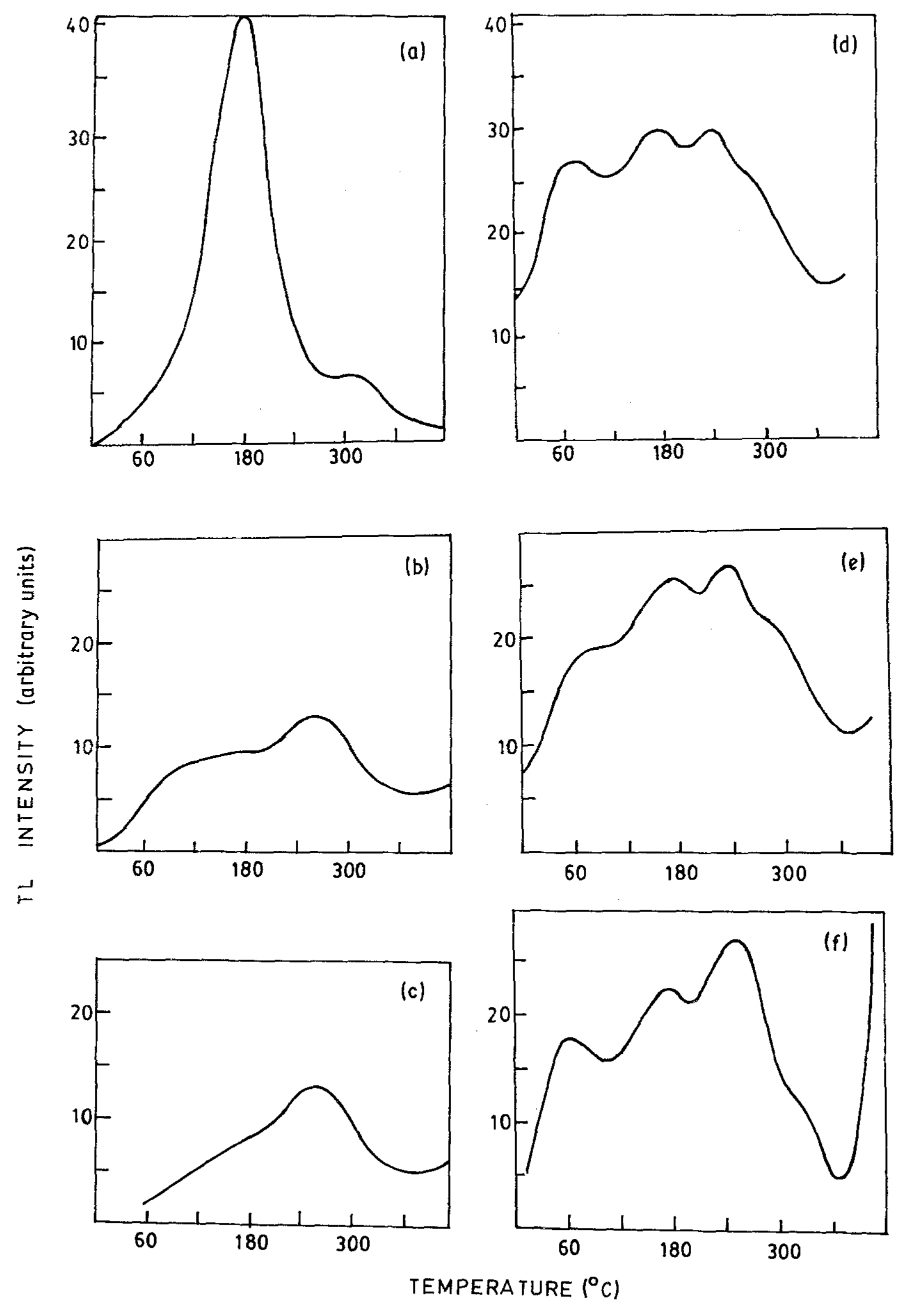


Figure 29 TL glow curves of (1) (Ba, Ca)S : Cu, (2) (Ba, Ca)S : Bi, (3) (Ba, Ca)S : Cu, Bi (4) (Ba, Ca, Sr)S: Cu, (5) (Ba, Ca, Sr)S : Bi and (6) (Ba, Ca, Sr) Cu, Bi.

dosimetric peak increased linearly with the exposure up to 2000 sec from UV lamp of 253.7 nm. It was proposed that the high temperature glow peak (303° C) exhibited by BaS : Cu, Bi could be used fruitfully to asses the X-ray doses [173]. The peak was stable with moderate fading with duration of time and its height increased linearly with X-ray dose up to 20 kR. Mixed systems such as (BaCa)S : Cu gave a stable peak at 180° C with X-ray exposure. The linear increase with dose rate was obtained in the peak height and area. The fading rate was also less when compared to BaS : Cu, Bi [86].

6.2. OSL dosimetry

The application of optically stimulated luminescence (OSL) of alkaline earth sulphides to dosimetry was suggested first by Antonov-Romanovski *et al.* [182]. Sanborn and Beard [62] synthesized sulphides of calcium, strontium and magnesium, and doped with europium and samarium. All the three systems exhibited the same sensitivity to γ-radiation (Co^{60}). It was concluded that out of all the systems, MgS (i) had the ability to detect 10 mR or lower, (ii) was more readily stimulated by IR light, (iii) had a satisfactory signal-storage stability and (iv) had a relatively low discharging temperature and was more suitable for γ-ray dosimetry. A detailed study was carried out by Rao *et al* [183-185] on OSL of MgS which has effective atomic number (Z_{eff}) equal to 14.5 nearly close to Z_{eff} of commonly used TLD materials. The time required to empty the traps was about 50 nsec. In stimulation spectra of MgS, a peak was obtained at around 1.07 μm which is very close to the emission of YAG : Nd laser (1.06 μm). After exciting with ionizing radiations such as UV, X-rays or γ-rays, the samples were fired with fine beam of laser and the emission was displayed on a CRO screen. By measuring the area or the height of the peak, the energy stored in the material could be estimated.

6.3. Electroluminescence (EL) cell

Due to large size of alkaline earth ions, it is easy to dope them with various impurities. This makes these sulphides to be excellent host materials suitable for EL

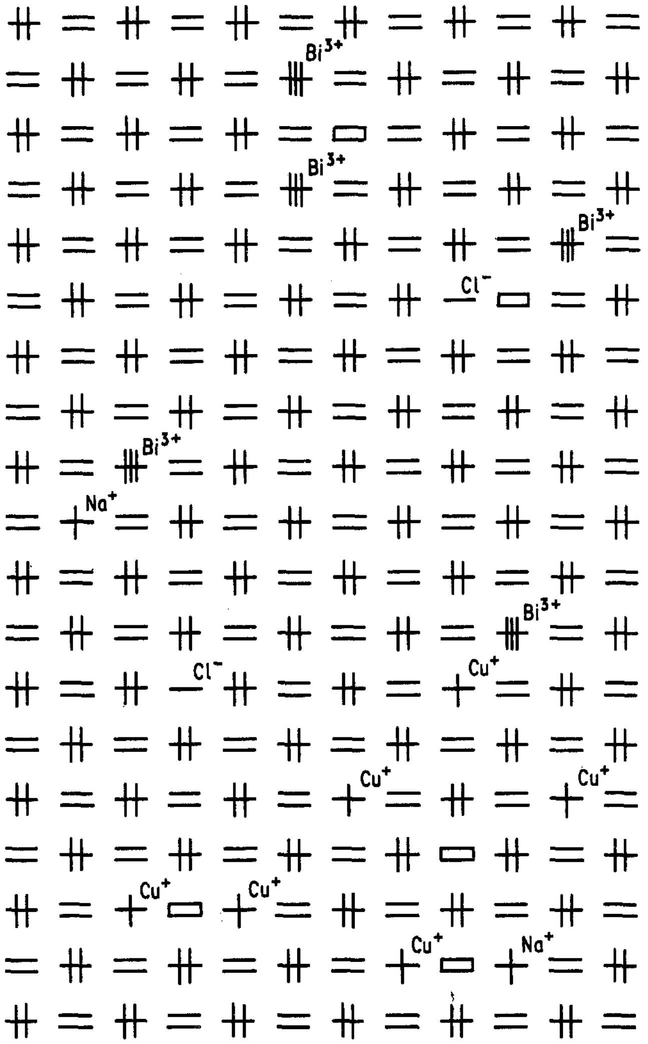


Figure 30 The possible types of charge compensation in BaS : Cu, BaS : Bi and BaS : Cu, Bi phosphors. ++ Ba^{2+}; = S^{2-}; □ vacancy; | | effective charge. $[V_s]^{2+}$, $[V_{Ba}]^{2-}$, $[Bi_{Ba}]^{+}$ and $[Cu_{Ba}]^{-}$.

panels. These sulphides doped with different impurities emit a variety of colours in the EL displays. EL of these phosphors was studied by many workers [54, 57, 186-192]. Vecht *et al.* [57] fabricated a direct-current (DC) EL cell by deposition of the phosphor with a suitable binder, onto a glass substrate coated with a conducting material (SnO_2), etched to the desired configuration. Tin oxide and aluminium formed an anode and a cathode, respectively. With applied voltages of 90 to 100 V, 40 to 25 ft L was achieved over 1000 h for CaS : Ce and 40 to 30 ft L for SrS : Ce phosphors. An EL emitting device was obtained by sandwiching a multilayer structure consisting of an insulator thin film between a phosphor film of CaS/SrS : Ce or Eu, of which one is transparent [190].

6.4. Cathode-ray tubes

In recent times, cathode ray tubes of higher brightness are desired for project TVs. These AES systems are attaining more attention because of their small current saturation at higher voltages [193–200]. A number of TV screen phosphors containing alkaline earth sulphides have been synthesized by many TV manufacturers. Portable TV screens, normally operated at low voltages, are also fabricated with ZnS : RE and SrS : RE. The details are generally available in the various patents published in recent years. For example, a fluorescent screen for colour picture tube having excellent light emitting efficiency and contrast has been prepared using an aqueous dispersion containing CaS based phosphors and a photo sensitive resin. The inner surface of a face plate panel of a picture tube was coated with a compound containing CaS : Ce green phosphor coated with 0.075 wt % of SiO_2 30, poly 3, a surfactant 0.1 and H_2O 32 parts, dried, image wise exposed to Hg lamp at 1.5 mW cm^{-2} for 5 sec and developed with H_2O to form a CaS phosphor layer. The layers of blue and red phosphor were formed in the same way using a conventional poly(vinyl-alcohol) and ammonium dichrometer photoresist. The screen so obtained was overcoated with an organic film (lacquering), subjected to aluminium backing treatment and heated at 430° C for 30 min (the above process is reproduced here from the abstract) [199].

6.5. Paints

In the manufacturing of paints, BaS has been used as an excellent pigment. Luminescent paints have been developed using BaS doped with RE impurities and trace impurities of radioactive elements. Luminescent plastic articles have also been prepared by incorporating both luminescent and fluorescent pigments like CaS and ZnS in plastics [201].

6.6. IR sensors

This system of phosphors has been found efficient in converting infrared (IR) radiation to visible light [202]. It has been observed that the characteristic emission with IR was due to the dominant activator (cerium or europium) while the stimulability and storeability have been due to the secondary activator (samarium) [203]. Leveshin *et al.* [119] had observed IR stimulability for CaS doped with cerium, samarium, bismuth, europium, praseodymium and copper in different combinations when they were pre-excited by UV and then exposed to IR in the region 0.8 to 1.2 μm. Rao *et al.* [204] have suggested that BaS:RE was an excellent IR stimulable phosphor.

7. Concluding remarks

Alkaline earth sulphides are very versatile phosphor host materials. These sulphides produce different characteristic emission of different activators and co-activators and it is possible to prepare hundreds of different phosphors with different properties. Solid solutions of these sulphides as well as with ZnS or CdS further increase the number of possible variations. Their band gaps are comparatively large so that the excited states of dopants are not densely distributed between valency and conduction bands. These host crystals provide different environments around the impurities.

In recent years, many methods have been developed to prepare efficient AES phosphor materials and attempts are being made to use them in several optoelectronic devices. Well crystallized and large size particles prepared by the sulphurizing flux method are relatively stable in water and exhibit high luminescence efficiency. Properly prepared AES phosphors could be competent with the well established II^B–VI^A compounds such as ZnS, ZnSe, CdS, CdSe etc. in potential applications for optoelectronic devices as well as for other TL dosimetry materials.

Thermoluminescence (TL) has been used by many workers to understand the nature of point defects and impurities in such phosphors. Most of the conclusions are that the traps responsible for luminescence emission are associated with the host lattice such as sulphur ion vacancies. Many of the interpretations had been speculative, without much experimentation. The trapping parameters (E and s) calculated from TL glow curves by various authors were not in agreement even for the same materials. No constructive work has been carried out so far to calculate E and s from the complex glow patterns, particularly in AES phosphors. To understand the electronic processes, one has to study low temperature TL, monochromatic TL (MTL), phototransfer TL (PTTL), TL spectra and other complementary measurements such as TSC, TSEE, ESR optical absorption etc.

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