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Review

Luminescence and related properties of magnesium sulphide phosphors

N. SINGH, D. R. VIJ
Physics Department, Kurukshetra University, Kurukshetra 132 119, India

Magnesium sulphide (MgS) belongs to the class of alkaline earth sulphides. It has been found to be an excellent host material to obtain phosphors which can be used in radiation dosimetry as optically stimulated luminescence and thermoluminescence dosimeters, in radiography as infrared sensors, etc. With a view to understanding its various uses, fundamental studies such as emission, absorption and excitation spectra, decay of luminescence, thermoluminescence, etc., have been carried out by various workers. However, no effort has been made to review these studies scattered throughout the literature; an attempt has been made to fill that gap in this paper.

1. Introduction

Alkaline earth sulphides (AES), although not widely studied, are known to be efficient, versatile and excellent phosphor host materials. AES phosphors are utilized in various fields [1–4], such as radiation dosimetry, i.r. sensing devices, lasers, detection panels, etc. Rare earth doped alkaline earth sulphides have recently received renewed attention for their potential applications as alternating current thin film electroluminescence (ACTFEL) and laser discriminators [5].

Lehmann [6, 7] was first to report the results of a detailed and systematic study of CaS doped with a large number of activators and coactivators. CaS, activated with rare earth elements, was found to be an excellent host material for efficient cathode-ray tube phosphors. The question of ZnS-like properties, such as light emission efficiencies, of CaS and SrS doped with rare earth ions has attracted attention for their possible use in full colour electroluminescent thin film displays, also indicated by theoretical calculations [8].

Magnesium sulphide (MgS), one of the alkaline earth sulphides, possessing a f.c.c. structure, had been almost completely neglected until a recent investigation by Mathur *et al.* [9], in which phosphors with MgS as host material, activated with rare earth elements, were used in radiation dosimetry as optically stimulated luminescence (OSL) dosemeters, and in radiography as i.r. sensors.

These phosphors have been found to possess thermally stable traps and can be optically stimulated by both a 1.06 μm YAG:Nd and an In–Ga–As–P laser, giving the capability of fast reading in addition to an increase in sensitivity and life expectancy.

However, no attempt has been made to review the luminescent and related characteristics of MgS phosphors when doped with various impurities, allowing assessment of their use for varied applications. The authors report here information, that has been found scattered in the literature, about various aspects, for example, methods of preparation, the role of impurities, luminescent and related properties, etc., exhibited by these phosphors. The possible use of these phosphors in solid-state dosimetry is also discussed.

2. Preparation techniques

Polycrystalline materials can be prepared by a variety of techniques, each producing characteristic products. Materials of low crystallinity and high surface area have been found to be extremely moisture and atmosphere sensitive, whereas the more crystalline materials are surprisingly inert.

Lehmann [7] prepared MgS powder by firing luminescence grade $MgCO_3$ in argon loaded with CS_2. Desired impurities were added to the pre-fired sulphide before the final firing step. Samples were fired in small amounts (a few grams) either in open quartz boats in flowing H_2S or in capped quartz tubes containing, in addition to the phosphor, some free sulphur, which were surrounded by argon for 1–2 h at 1200 °C. Rao [10] prepared MgS phosphors by reducing $MgSO_4$ (E. Merck, Germany) with pure CS_2 in an argon atmosphere at 900 °C for 90 min and then doping with different quantities of the rare earth elements Eu, Sm and Ce. In the process of doping, MgS and $MgSO_4$ (4:1 by weight) were mixed with the required amounts of rare earth oxides and fired at 900 °C. Yamashita and Asano [11] and Donker *et al.* [12] prepared pure host MgS by reduction of $MgSO_4$ with CS_2 and H_2. Phosphors were then prepared by heating the obtained sulphide with a calculated amount of the metal sulphide of the desired impurity in a crucible at about 1000 °C for 40–50 min in a

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stream of $N_2 + H_2S$. Chakrabarti *et al.* [4] synthesized MgS from anhydrous magnesium sulphate by CS_2 reduction in the presence of argon. The reduction was complete in about 2 h. MgS was mixed with the desired dopant and fired at 1150 °C in the presence of flowing argon bubbled through concentrated H_2SO_4.

3. Experimental studies

The emission spectra of cathodoluminescence [7] of Cu, Ag and Au in MgS were measured on thin powder layers excited in a demountable cathode-ray tube by 10 kV electrons at approximately 1 $\mu A\,cm^{-2}$ current density, either at room temperature or cooled to near 80 K. The luminescence was observed through a quartz window, with a quartz prism Beckman DU monochromator and a 1p28 photomultiplier tube in quartz glass. The mode of excitation (electron beam or short-wave u.v.) was found to have little effect on the spectra. Rao [10] excited the phosphor films by 10 kV electrons at approximately 0.5 $mA\,cm^{-2}$ in a demountable cathode-ray tube at 300 K. The emission from the excited samples was recorded with a Bausch and Lomb monochromator and photomultiplier tube. OSL measurements and the spectral dependence of TL were taken [4] using an optical multichannel analyser. Signal: noise ratio was improved by cooling the silicon diode arrays to − 25 °C. Prior to an OSL measurement, the sample was u.v. irradiated at room temperature and the low-temperature peak was then annealed out to ensure that the luminescence was stimulated from deep traps only. A 1.06 μm YAG:Nd laser and an In–Ga–As–P diode laser were used for optical stimulation. Yamashita [13] measured the emission spectra by the conventional method, i.e. the sample was excited by the monochromatic ray from a high pressure mercury lamp. In the measurements of the excitation spectra three types of light sources – a Hanau D 200 F deuterium lamp, a xenon arc lamp and a halogen lamp – were used depending on the excitation wavelength. The energy of the monochromatic light incident upon the sample was measured by means of a vacuum thermopile. For wavelengths shorter than 320 nm it was measured by means of the excitation spectrum of sodium salicylate. Recently, the diffuse absorption spectra of pure MgS powders at 80 and 293 K have been studied by Yamashita [14].

The measurements of decay curves of Tl^+ type ions in MgS as a function of temperature from 4.2 to 150 K have been carried out by Donker *et al.* [12] using three different set-ups. Each set-up, in principle, had an exciting source, a monochromator and a detection system. Rao [15, 16] has studied TL and dosimetric properties of MgS activated by one or more elements using the usual procedure of first exciting the phosphor with u.v. or X-rays and then recording the TL output.

4. Results and discussion

4.1. Emission, absorption and excitation spectra

Pandey *et al.* [17] have theoretically predicted MgS to be an indirect band gap material, with both CaS and SrS direct gap materials. Stepanyuk *et al.* [18] have also calculated electronic structure and optical properties of MgS by the self-consistent Linear Augmented Plane Wave (LAPW) method. Lehmann [7] observed the influence of the coactivators on the emission spectrum of MgS activated with Cu, Au and Ag. According to his investigations Cu-activated alkaline earth sulphides are normally efficient phosphors (Fig. 1). Quantum efficiencies of photoluminescence of about 50% or more and energy efficiencies of cathodoluminescence of 10–15% can routinely be obtained. The only exceptions are materials containing Cl, Br or I, which perform very poorly; MgS:Au is non-luminescent. All attempts to make luminescent MgS:Au phosphors with or without added coactivators (tested: F, Cl, Br, I, Li, Na, K, Rb and P) failed. Failure was considered to be due to the fact that the gold ion was too big (ionic radius = 0.137 nm) to replace the small Mg^{2+} ion (0.065 nm) in the MgS lattice. Silver was also found to be an inefficient activator in MgS, with any coactivator, and efficiencies of photo- and of cathodoluminescence rarely reached about 10 and 1%, respectively. However, silver does enter the lattice, as evidenced by emission spectra clearly different from those caused by copper (Fig. 1).

Ce induced two emission bands, at about 523 and 590 nm, in MgS [19]. As observed by Asano *et al.* [20], the excitation spectrum had a band at about 254 nm. The emission of Eu in MgS consisted of a single emission band originating from the intra-ionic transitions in Eu^+ ion. The peak position was at about 592 nm at 300 K and remained unchanged at 80 K. Nakao [21] reported an excitation spectrum consisting of two main bands at about 251 and 489 nm. With increasing concentrations of Eu^+ ions an additional band at 285 nm appeared.

Spectral dependence of emission of the high-temperature TL peak (200 °C) in MgS:Ce, Sm and MgS:Eu, Sm has been reported by Chakrabarti *et al.* [4]. In both phosphors the nature of the TL emission was similar, and the emissions at 569, 609 and 657 nm were identified as Sm^{3+} transitions to $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ ground states, respectively. Optically stimulated emission of MgS:Ce, Sm gave a doublet, peaking at 527 and 580 nm, which was identified as Ce^{3+} transitions to $^2F_{5/2}$ and $^2F_{7/2}$ ground states, respectively (Fig. 2). The OSL emission of MgS:Eu, Sm peaked at 586 nm. This emission was due to a transition to the $^8S_{7/2}$ ground state of Eu^{2+} (Fig. 2). The clearly distinguishable OSL spectra are characteristic of activator ions Ce^{3+} or Eu^{2+} present in the sample. However, they are stimulated from the same sensitizer Sm^{2+} ions. This is clear from the identical stimulation spectrum in each case. Stimulation spectra have peaks at ca. 1070 nm, which makes these materials ideal OSL phosphors to be stimulated by a YAG:Nd laser at ca. 1064 nm. There is experimental evidence [22] that the luminescence mechanism and charge trapping in MgS is dependent on dopant concentration.

Yamashita [13] has reported that in the emission spectra of MgS:Cu, Cl_2 (0.1 mol %), the peak at 472 nm at 293 K shifted to 488 nm at 16 K (Fig. 3). The

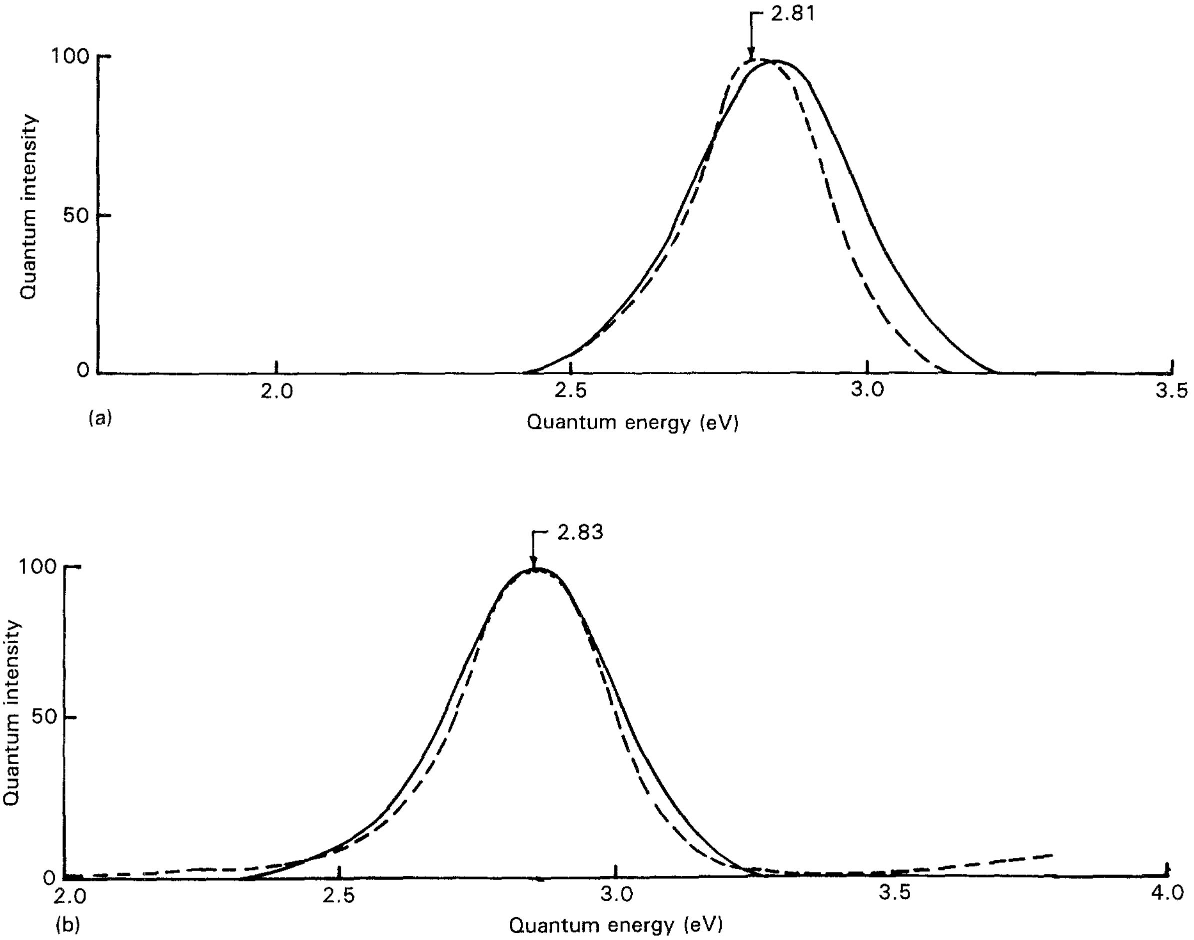

Figure 1 Emission spectra of MgS activated by (a) copper and sodium (1% added) [MgS:Cu(0.01%), Na]; (b) silver and potassium (1% added) [MgS:Ag(0.02%), K]. ——, Room temperature; – – –, ca. 80 K. [Figs 7 and 8 of W. Lehmann, *J. Electrochem. Soc.* **117** (1970) 1389.]

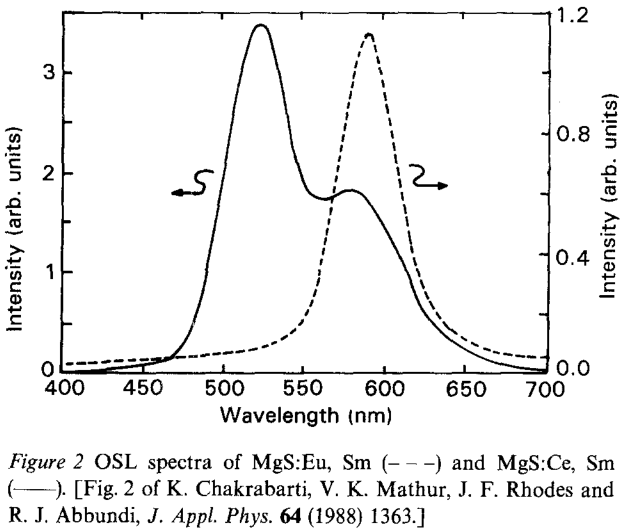

Figure 2 OSL spectra of MgS:Eu, Sm (– – –) and MgS:Ce, Sm (——). [Fig. 2 of K. Chakrabarti, V. K. Mathur, J. F. Rhodes and R. J. Abbundi, *J. Appl. Phys.* **64** (1988) 1363.]

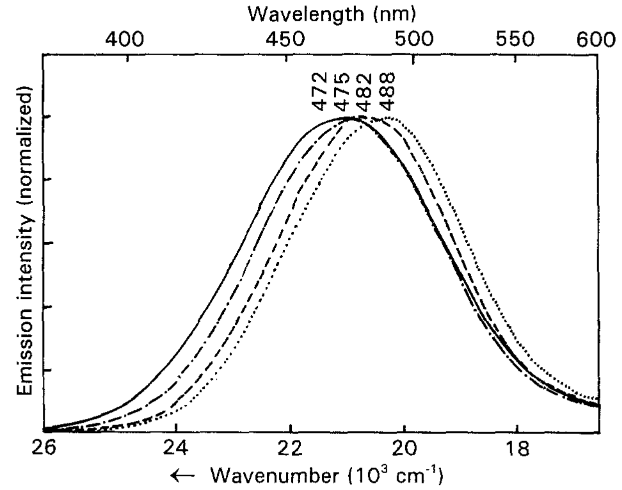

Figure 3 Photoluminescence spectra of MgS:CuCl$_2$ (0.1 mol %) at various temperatures under excitation at 296.7 nm. ——, 293 K; –·–·, 201 K; – – –, 80 K; ····, 16 K. [Fig. 2 of N. Yamashita, *Jpn. J. Appl. Phys.* **30** (1991) 3335.]

Cu$^+$ emission showed concentration quenching at higher Cu$^+$ concentrations ($\geqslant 0.5$ mol %). He concluded that the Cu$^+$ centre formed in alkaline earth sulphides is independent of the valence number of the added copper and that the Cl$^-$ ion does not affect the Cu$^+$ centre. The negative effect of coactivator aluminium on the luminescence efficiency due to contamination was appreciable. MgS:Cu$^+$, Al^{3+} phosphor activated with 0.5 mol % Al$_2$S$_3$ was not luminescent with u.v. excitation.

The excitation spectrum of MgS:Cu$^+$ consisted of two Cu$^+$ bands at 272 and 302 nm. The excitation efficiency of the two Cu$^+$ bands was enhanced with increasing activator concentration from 0.1 to 0.2 mol %. The direct excitation of Cu$^+$ ions was less efficient than the indirect excitation. The excitation efficiencies of MgS:Cu$^+$ at low temperatures was two orders of magnitude smaller than those of SrS:Cu^+, CaS:Cu^+ and BaS:Cu^+. The excitation efficiency of MgS:Cu^+ increased slightly with an increase in temperature, whereas those of the other three phosphors were virtually independent of temperature.

Yamashita [14] has also reported the diffuse absorption and diffuse reflection spectra of pure MgS at 80 and 293 K. The diffuse absorption spectra had the fundamental absorption edge near 4.6 eV and exhibited two (apparent) peaks at 5.49 and 5.21 eV at 80 K, and 5.33 and 5.06 eV at 293 K.

Rao [10] has reported results about cathodoluminescence emission of MgS activated with elements like Eu, Ce and Sm individually, and he tried to assign the various bands to different transitions. Asano *et al.* [23] have observed the emission spectra of MgS:Mn^{2+}, which consisted of a single band whose peak was about 695 nm. Emission spectra of MgS:Bi at 80 and 300 K have been studied by Asano and Yamashita [24, 25]. According to them, the emission consists of two bands having peaks around 428 and 446 nm at 80 K, and a single band with peak around 440 nm at 300 K. The excitation spectra has been studied at 80 K only, and three peaks around 324, 348 and 417 nm have been reported by these authors. They have also observed [26] the emission spectrum of MgS:Pb at 300 K, which consisted of a single band peaking at around 379 nm, and the excitation spectrum, which consisted of three bands with peaks about 280, 307 and 358 nm. According to them [27] the emission spectrum of Sm^{3+} activated sulphides consists of six groups of lines at about 565, 605, 650, 710, 790 and 900 nm at 300 K. The peak positions varied little with the host lattice and were found to shift slightly towards shorter wavelengths with an increase in the lattice spacing of the host material.

4.2. Luminescence decay times

Donker *et al.* [12] measured the luminescence decay times of Tl^+ type ions in MgS (Fig. 4). A single exponential decay curve was recorded for MgS:Sb^{3+} with a decay time at 4.2 K of 1.05 ms. The measurement of the fast decaying component in the emission of MgS:Sb^{3+} was attempted under the A-band (415 nm). The observed emission signal was extremely weak. The decay time observed at 4.2 K (about 7 ns) was of the order of the exciting pulse duration (about 5 ns). The low intensity of this fast decaying emission signal was attributed, on the one hand, to the rather low energy per pulse of the excitation source, and, on the other hand, to the fact that the $^3P_1$ population generated by the exciting pulse relaxes for the larger part to the $^3P_0$ level, and only for a very small part directly to the ground state $^1S_0$. Hence, the emission observed for MgS:Sb^{3+} at 4.2 K can be attributed, for a small part,

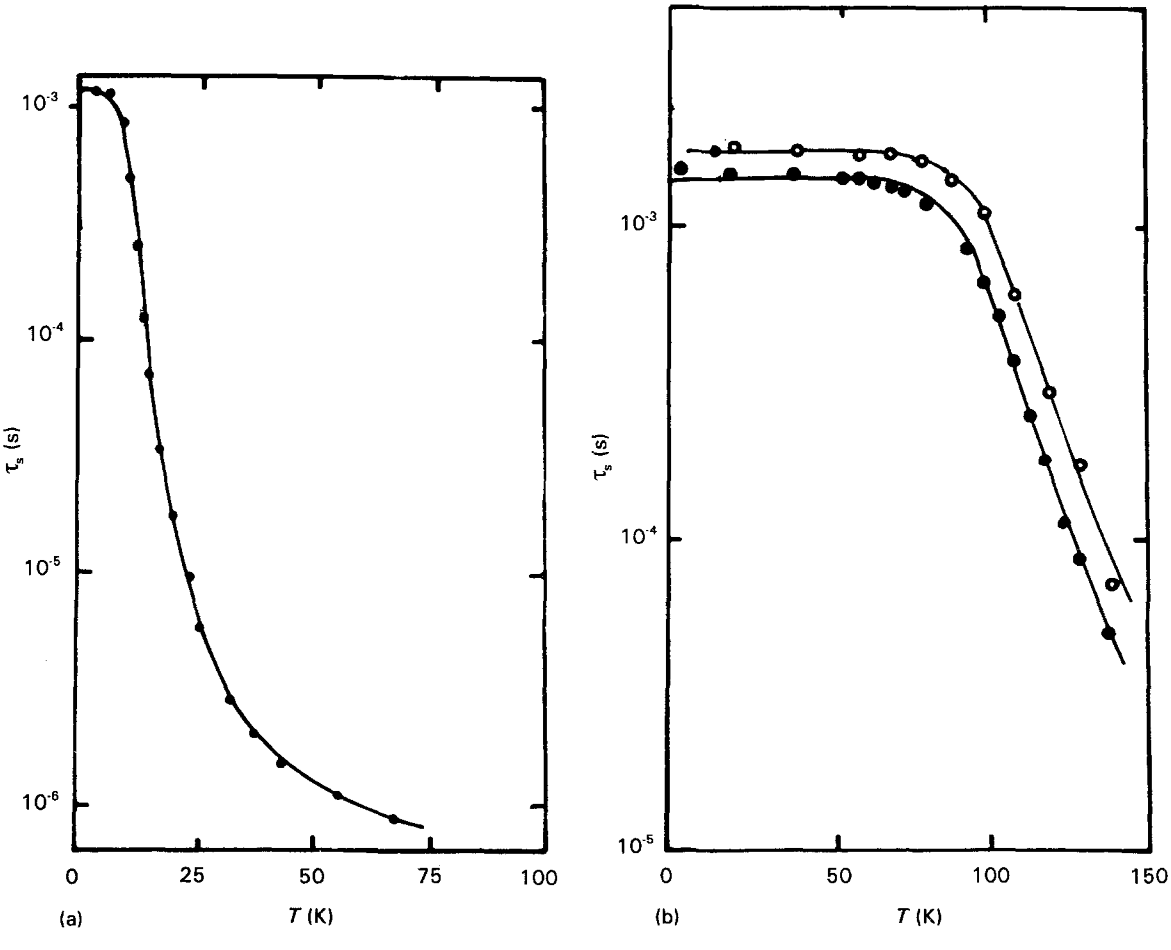

Figure 4 Temperature dependence of the luminescence decay time of (a) MgS:Sb^{3+}; (b) ●—●, MgS:Pb^{2+} and ○—○, MgS:Bi^{3+}. The solid curves give the best fits of the experimental data. [Fig. 2 of H. Donker, N. Yamashita, W. M. A. Smit and G. Blasse, *Phys. Status Solidi* (*b*) **156** (1989) 537.]

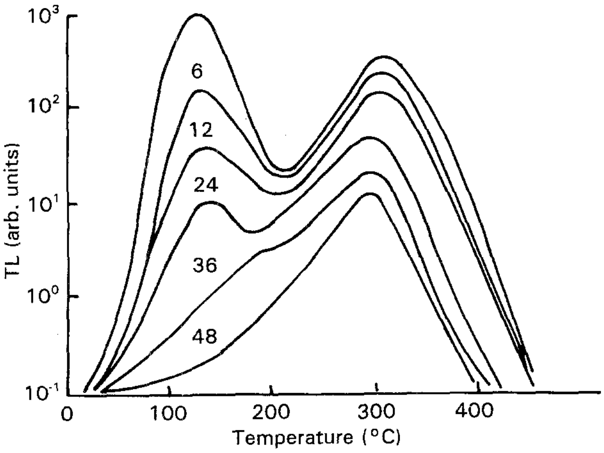

Figure 5 TL glow curves of MgS:Eu, Sm phosphors after various storage periods in the dark. Period (in h) is marked on the curves. [Fig. 1 of R. P. Rao, *Rad. Prot. Dosimetry* **17** (1986) 403.]

to the $^3P_1 \rightarrow {}^1S_0$ emission (fast decaying component) and for the larger part to the $^3P_0 \rightarrow {}^1S_0$ emission (slow decaying component). The decay curves for MgS:Pb^{2+} at low temperatures are composed of two components, but only the slow component could be accurately measured in Donker *et al.*'s work. The emission of MgS:Bi^{3+} at low temperatures was composed of two components. The decay time of the fast decaying component of CaS:Bi^{3+} under the A-band (410 nm) excitation was 12 ns at 4.2 K and 10 ns at 100 K, showing that the lifetime of the $^3P_1$ state was extremely short and almost independent of temperature. The decay time associated with the yellow emission band in MgS:Mn, as reported by Ghosh *et al.* [28], was found to be 4 ms.

4.3. Thermoluminescence dosimetric studies

Rao [15] has observed two glow maxima at 130 and 308 °C in the TL glow curve of MgS:Eu, Sm (Fig. 5). The low temperature peak decreased with an increase in the duration of storage time and disappeared completely after 48 h. Therefore, the fading of the high temperature peak was not significant after 48 h. The peak height of the 308 °C peak irradiated with X-rays as function of time increased linearly up to 5.28×10^{-4} C kg^{-1} and then attained saturation. This peak could be used to monitor X-ray exposures in the range 6–500 μC kg^{-1}. A detailed study was carried out by Rao *et al.* [29, 30] on the OSL of MgS, which had an effective atomic number (Z_{eff}) equal to 14.5, close to Z_{eff} of TLD materials used commercially. The time required to empty the traps was about 50 ns. In stimulation spectra of MgS a peak was obtained at ca. 1.07 μm, very close to the emission of the YAG:Nd laser (1.06 μm). After exciting with ionizing radiations, such as u.v., X-rays or γ-rays, the samples were irradiated with a fine beam of laser and the emission was displayed on a CRO screen. The energy stored in the material could be estimated by measuring the area or peak height.

5. Concluding remarks

Several methods exist for preparation of hundreds of phosphors from a MgS host. These phosphors have been put to a variety of uses, ranging from dosimetry to laser discrimination at laboratory levels. Recently, Albin *et al.* [31] have developed a new concept for an erasable optical memory using MgS:Eu as a stimulated electronic transition (SET) medium. The SET process has several advantages as compared to magneto-optic and phase charge processes. However, there is still a need to put effort into commercializing phosphors based on MgS, thereby extending their utility to other walks of life, such as environmental pollution, health programmes, agriculture, etc.

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