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Luminescence studies of $MgSO_4$:Dy phosphors

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The lyoluminescence (LL) in $MgSO_4$:Dy phosphors has been studied. Thermoluminescence (TL) and photoluminescence (PL) have also been studied to understand the mechanism of LL. $MgSO_4$ phosphors containing different concentrations of Dy (0.05-1.0 mole%) have been prepared by solid-state diffusion method. The maximum LL intensity is observed for 0.05 mole% of Dy in $MgSO_4$. TL glow curves of $MgSO_4$:Dy phosphors are complex and peaks around 110, 150 and 220°C are observed. The effect of post-irradiation annealing on the LL shows that with removal of 220°C TL peak, the LL intensity decreases markedly. LL and TL intensity of $MgSO_4$:Dy phosphors have also been recorded for different γ-doses. PL studies conducted on the sample show that Dy^{3+} ion acts as the luminescence center in $MgSO_4$ phosphor.

Keywords: Lyoluminescence, Thermoluminescence, Photoluminescence, Magnesium sulphate

1 Introduction

The luminescence produced during dissolution of irradiated materials to certain solvent is known as lyoluminescence (LL) and has been investigated by many workers for use in dosimetry application[1-2]. Several organic and inorganic materials possess the LL property and the most widely studied LL materials have been alkali halide[3], sacrides[4] and aminoacid[5]. With inorganic materials such as alkali halide, the reaction of trapped electrons from F centers is responsible for the light emission. In the case of some organic materials trapped free radicals are involved in the process of LL. Lyoluminescence and thermoluminescence (TL) are two different types of luminescence and materials exhibit these phenomena only after irradiating the sample to some high-energy radiation like x- or γ-rays. The intensity of LL and TL signal is the measure of absorbed dose in sample.

Sulphates are known to be good materials for radiation dosimetry. $CaSO_4$:Dy is one of the phosphor that is increasingly utilized in TL radiation dosimetry[6]. In recent years a series of magnesium sulphate phosphors have been prepared and their TL characteristics studied and it was proposed that in these phosphors large defect complexes are produced which include intrinsic imperfections and dopants and these complexes could be regarded as basic elements in TL multistage process[7-9]. Many TL materials also show LL property. Only a few studies have been made on the LL in sulphate based phosphors[10]. In the present paper, lyoluminescence (LL) results in $MgSO_4$:Dy phosphors have been reported and the mechanism of LL using thermoluminescence (TL) and photoluminescence (PL) characteristics has been studied.

2 Materials and Methods

$MgSO_4$ phosphors containing different concentrations of Dy (0.05-1.0 mole%) were prepared by solid-state diffusion method. $MgSO_4$ and Dy_2O_3 were mixed as per the concentration of Dy ion in $MgSO_4$ and crushed for 1 h, then heated at 400°C for 2 h. The mixture was again crushed for 1 h and fired at 800°C for 24 h, then slowly cooled to room temperature. All the chemicals used in the present investigation were of AR grade. The XRD pattern of prepared material is shown in Fig. 1. XRD data of prepared $MgSO_4$:Dy^{3+} phosphor matched well with standard data of JCPDs (File no. 01-072-1259)[11]. The prepared phosphors were used for further study. The samples were exposed to γ-rays from a ^{60}Co source having dose rate of 930 Gyh^{-1}. Lyoluminescence was studied with the usual set-up consisting of a LL cell, photomultiplier tube (Hamamatsu 931 B), amplifier and recorder. Double distilled water was used as the solvent. In all the measurements 5 mg of sample and 2

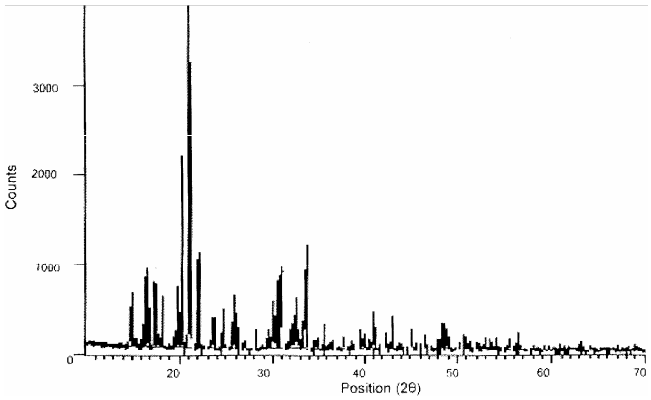

Fig. 1 — XRD pattern of $MgSO_4:Dy^{3+}$ phosphor

ml of solvent was used. For TL measurements a routine TL set-up (Indotherm) was used and glow curves were recorded by heating the sample with 90° cm^{-1}. The PL emission spectra of the samples were recorded by using fluorescence spectrophotometer (Shimatzu RF-530 XPC). Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3 Results and Discussion

Figure 2 shows the glow curves of $MgSO_4$:Dy for the LL intensity as a function of time. The maximum LL intensity is observed for 0.05 mole% of Dy in $MgSO_4$ and it decreases with further increase in concentration of dopant. The LL glow curves show one prominent peak and small shoulder during dissolution. These glow curves indicate that two types of luminescence centers developed during γ-ray irradiation and they are released during dissolution of phosphors in solvent. It is also noticed that the undoped $MgSO_4$ shows very weak LL intensity.

Figure 3 shows the TL glow curves of $MgSO_4$:Dy phosphors after γ-dose of 930 Gy. TL glow curve of $MgSO_4$:Dy (0.05 mole%) phosphor shows two prominent TL peaks around 110 and 220°C. New TL peak appears around 150°C with further increase in concentration of dopant. Enhancement/ decrement in TL intensity with slight shifting of TL peaks is also observed with increase in concentration of dopant. TL glow curves show that peaks are complex and composed of several traps. The TL intensity of 110°C peak increases with concentration of dopant and seems to saturate at higher concentration; however, the intensity of 220°C peak increases with concentration of Dy, attains optimum value at 0.1 mole% and then decreases with further increase in concentration of Dy. By comparing the variation of

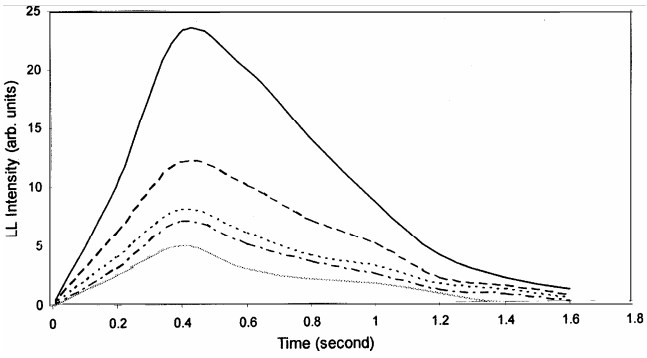

Fig. 2 — LL glow curves of $MgSO_4$:Dy phosphors:(—) 0.05 mole%; (– –) 0.1 mole%; (**…**) 0.2 mole%; (–·–) 0.5 mole%; (…) 1.0 mole%, (γ-dose 930 Gy)

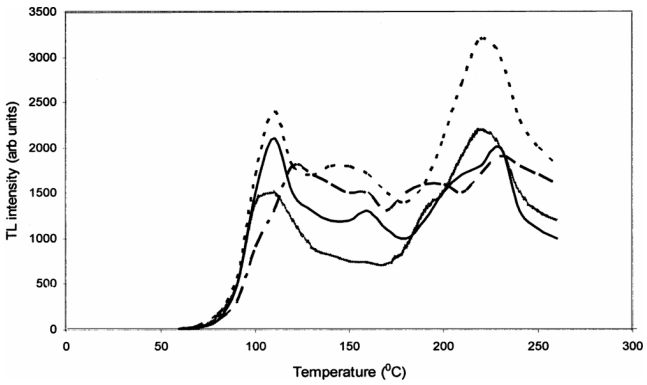

Fig. 3 — TL glow curves of $MgSO_4$:Dy phosphors:(·····) 0.05 mole%; (– –) 0.1 mole%; (—) 0.2 mole%; (— - —) 0.5 mole%; (γ-dose 930 Gy)

LL and TL intensity it has been found that the LL intensity is optimum for the samples having concentration of Dy 0.05 mole% and in the TL glow curve of this sample TL peaks around 150°C are missing. It seems that the growth of TL peaks around 150°C inhibit the enhancement of LL intensity in $MgSO_4$:Dy phosphors.

In order to know the thermal behaviour of traps involved in LL excitation, the influence of post irradiation annealing on the LL of $MgSO_4$:Dy (0.05 mole%) has been studied (Fig. 4). The post irradiation annealing at 150°C for 15 m does not affect the LL intensity, however the LL intensity decreases markedly (about 80%), if the LL glow curve is recorded after removal of TL peak of 220°C. This shows that the traps corresponding to 220°C TL peak are more responsible for LL excitation but the role of other traps could not be ignored.

Figure 5 shows the relative peak LL and TL intensity (220°C) as a function of γ-irradiation. It is seen that the peak LL intensity increases linearly with

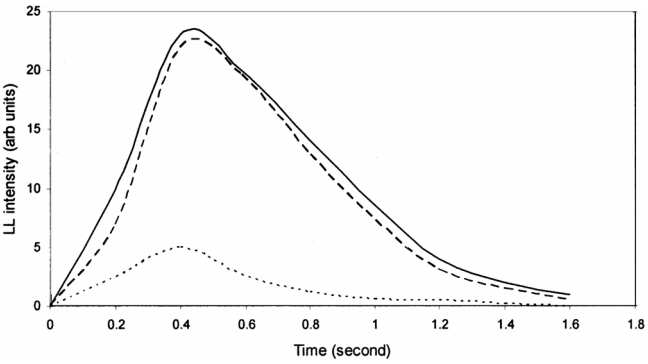

Fig. 4 — LL intensity of γ–irradiated $MgSO_4$:Dy(0.05 mole%) phosphor after γ-dose of 930Gy:(—) without any thermal treatment; (– –) after post-irradiation annealing at 140°C; (….) after post-irradiation annealing at 230°C

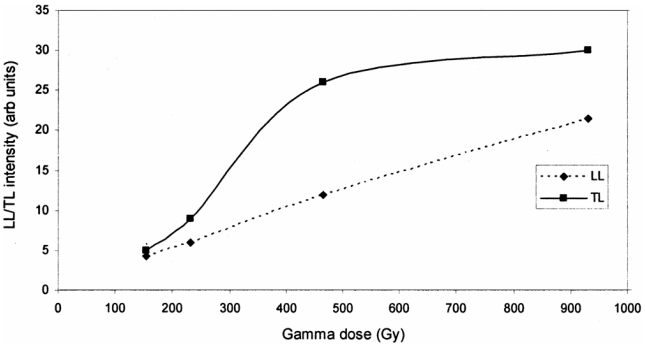

Fig. 5 — Dependence of peak LL (----) intensity and TL (—) intensity (220°C) of $MgSO_4$:Dy (0.05 mole%) phosphor on (γ-dose 930 Gy)

γ-dose given to the samples, however TL intensity of 220°C peaks seems to saturate above 500 Gy.

For considering the candidature of $MgSO_4$:Dy phosphors in LL/TL dosimetry, it is necessary that the filled trap in the phosphors should be stable and does not decay upon storage under usual conditions. It is found that the fading in intensity of 220°C TL peak is only 6% when the TL glow curve was recorded 1 month after γ-irradiation.

In order to identify the nature of luminescent centers, the PL of $MgSO_4$:Dy phosphors were recorded using fluorescence spectrometer (Shimatzu RF-530 XPC). Emission and excitation spectra were recorded using a spectral width of 1.5 nm and are shown in Fig. 6. The emission spectrum after excitation by 247 nm shows prominent bands at 486 and 580 nm, which are characteristics of Dy^{3+} ions due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions respectively. Therefore it is clear that the Dy^{3+} ion acts as the luminescence center in $MgSO_4$ phosphor.

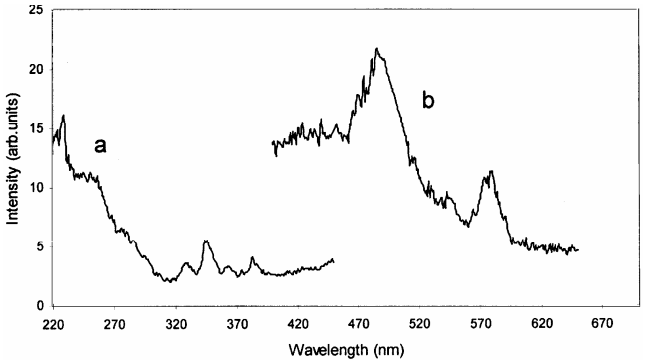

Fig. 6 — Excitation (a) and emission spectrum (b) of $MgSO_4$:Dy (0.05 mole%) phosphor

Various kinds of defects are present in the alkaline earth sulphate phosphors and doping of rare earth in this influence only the relative population of these traps. $MgSO_4$:Dy^{3+}, $MgSO_4$:Eu^{3+} and $MgSO_4$:Tm^{3+} phosphors exhibit similar TL glow peaks and these should be related to the intrinsic imperfections in $MgSO_4$ substance, such as sulphur-oxy radicals and Mg^{2+} vacancy[9,12]. During heating SO_4^{2-} radicals are re-formed and excited states of Dy^{3+} ions are formed simultaneously and TL emission occurs.

When irradiated $MgSO_4$:Dy samples are dissolved in distilled water as a solvent. The LL is observed due to release of trapped energy during dissolution as per the mechanism suggested by Arinkar *et al.*[13]

$$e^-_{(\text{trapped})} + \text{Water} \rightarrow e^-_{\text{aq}} \quad \ldots (1)$$

$$e_{\text{aq}}^- + X \rightarrow X_{\text{aq}}^* \quad \ldots (2)$$

$$X_{\text{aq}}^* \rightarrow X_{\text{aq}} + h\upsilon \quad \ldots (3)$$

where $X = SO_4^-$, SO_3^-, O_3^-, O_2^- etc.

It is possible that steps (2) and (3) occur togeather without the intermediate state X_{aq}*. A similar mechanism was also suggested by Ahnstrom[14].

4 Conclusions

The γ- irradiated Dy activated $MgSO_4$ shows LL when dissolved in water. $MgSO_4$:Dy (0.05 mole%) phosphor shows maximum LL intensity. The LL intensity increases linearly with γ-irradiation. The TL glow curves of $MgSO_4$:Dy samples are complex. The traps corresponding to 220°C TL peak are more responsible for LL excitation and growth of TL peaks around 150°C (with increase in concentration of dopant) suppresses the LL intensity.

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