Effect of Sm$^{3+}$ as co-dopant in CaSO$_4$:Dy,P TLD phosphor

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Abstract
CaSO$_4$:Dy,P and CaSO$_4$:Dy,P,Sm thermoluminescence (TL) phosphors have been prepared by acid method and their TL glow curves and photoluminescence (PL) excitation and emission spectra are recorded. PL emission bands at 565, 599 and 613 nm were observed for CaSO$_4$:Dy,P,Sm under the excitation wavelength 402 nm. Dosimetric peak is observed around 246°C at high temperature. Co-doping of Sm$^{3+}$ in CaSO$_4$:Dy,P enhances its TL intensity by a factor of 1.11.

Keywords: Thermoluminescence, phosphor; CaSO$_4$:Dy,P; photoluminescence

INTRODUCTION

Singly doped CaSO$_4$ phosphors have been studied in detail in the past[1]. Rare earths, especially Dy or Tm doped CaSO$_4$ thermoluminescent phosphors are widely used in radiation dosimetry. Two models have been proposed for the thermoluminescence (TL) mechanism in CaSO$_4$ based thermoluminescent phosphors. Nambi et al. extended the model based on redox reactions proposed by Merz and Pershan for CaF$_2$:RE phosphors as well as Nambi et al. also suggested another model (energy transfer model), which was later supported by Morgan and Stoebe [2-10]. Tomita and Tsutsumi showed that the TL emission spectrum of pure CaSO$_4$ has a maximum at about 335 nm. According to the energy transfer model, there is no direct recombination at the RE site but the energy of electron–hole recombination is transferred to RE$^{3+}$. However, no direct proof has been reported so far[11-18]. In the present study, in addition to change in surface morphology, considerable improvement has been observed in the case of thermoluminescence intensity of the as prepared phosphors. This can be seen from the comparison graph of standard CaSO$_4$:Dy and CaSO$_4$:P,Dy,Sm$^{3+}$ phosphors. It is worth mentioning here that thermoluminescence(TL) intensity is 1.11 times greater in case of CaSO$_4$:P,Dy,Sm$^{3+}$ phosphors prepared via slightly modified acid distillation method than standard CaSO$_4$:Dy TLD phosphor. The photoluminescence (PL) characteristics of almost all phosphors are also good though slight variations have been observed. In this paper, the effect of co-doping CaSO$_4$:Dy,P with Sm is investigated.

EXPERIMENTAL

For the preparation of CaSO$_4$:Dy,P,Sm phosphors all starting materials used were of analytical grade. CaSO$_4$:Dy,P,Sm phosphors were prepared by following the method described by Yamashita et al. The sample phosphors thus prepared were repeatedly washed with double distilled water to remove the traces of acid. Phosphors were annealed at 973 K. The concentration of P used was 1mol%. The concentration of Dy$^{3+}$ used was 0.1mol% but concentration of Sm ion(s) was varied from 0.05mol% to 0.5mol%. The maximum thermoluminescence (TL) intensity was observed for the composition 1mol%P, 0.1mol%Dy$^{3+}$ and 0.1mol%Sm$^{3+}$.

The photoluminescence (PL) emission and excitation spectra of the samples were recorded by using a RF-5301PC SHIMADZU Spectrofluorophotometer. TL glow curves were recorded with the usual set up Nucleonix (TL–1009) Reader. SEM micrographs were obtained using JEOL,6380A Scanning Electron microscope.

RESULTS AND DISCUSSION

Photoluminescence Characteristics

Photoluminescence emission spectra fig.1 of CaSO$_4$:Dy,P,Sm phosphor under excitation wavelength 402 nm($^4H_{5/2} ightarrow ^4F_{7/2}$), sharp emission peaks are observed at 565nm and 599 nm emission wavelength. The emission spectra observed at excitation wavelength 402 nm consists of 565 nm ($^4G_{5/2} ightarrow ^4H_{5/2}$), 599 nm ($^4G_{5/2} ightarrow ^4H_{7/2}$) and 613 nm ($^4F_{3/2} ightarrow ^4H_{5/2}$) respectively. The dominant transitions are $^4G_{5/2} ightarrow ^4H_{5/2}$ (565nm) and $^4G_{5/2} ightarrow ^4H_{7/2}$ (599nm)[2,3].

Fig. 1. Photoluminescence emission spectra of CaSO$_4$:Dy,P,Sm phosphor. Emission spectra consist of 565, 599 and 613 nm wavelengths observed at 402 nm excitation wavelength.

Thermoluminescence (TL) Characteristics

Figure 2 shows the typical TL glow curves of the CaSO$_4$:Dy,P,Sm phosphors exposed to gamma radiations from $^{60}$Co source at room temperature. Thermoluminescence of the phosphor materials was recorded using Nucleonix TLD reader. The TL characteristics of the as prepared phosphors are nearly similar to the TL characteristics of the standard CaSO$_4$:Dy TLD phosphor. The TL intensity of the phosphor material prepared by slightly modified acid distillation method is 1.11 times greater than the standard CaSO$_4$:Dy TLD phosphor. This is really significant improvement observed in TL intensity. Hence it seems reasonable to suggest that there is some degree of sensitization taking place in CaSO$_4$:Dy,P,Sm phosphors. Fig.3 depicts the intensity wise comparison between
standard and as prepared phosphors. No doubt contribution to thermoluminescence from intrinsic defects present in the CaSO₄ lattice is enhanced by the addition of rare-earths but some recent investigations suggest that change in surface morphology of the bulk material can also prove effective.

**CONCLUSION**

Rod type structures of CaSO₄: Dy, P, Sm phosphors have been obtained. As expected, characteristic photoluminescence emission and excitation spectra been observed for Sm³⁺ in CaSO₄: Dy, P, Sm phosphors. Co-doping of Sm³⁺ in CaSO₄: Dy, P phosphor increases the TL intensity by a factor of approximately 1.11.

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**REFERENCES**


Only TL intensity of 246 °C peak has increased.