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Effect of Sm³⁺ as co-dopant in CaSO₄:Dy,P TLD phosphor

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Abstract

CaSO₄: Dy,P and CaSO₄: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 CaSO₄: Dy,P,Sm under the excitation wavelength 402 nm. Dosimetric peak is observed around 246°C at high temperature. Co-doping of Sm³+ in CaSO₄:Dy,P enhances its TL intensity by a factor of 1.11.

Keywords: Thermoluminescence, phosphor; CaSO₄:Dy,P; photoluminescence

INTRODUCTION

Singly doped CaSO₄ phosphors have been studied in detail in the past[1]. Rare earths, especially Dy or Tm doped CaSO₄ thermoluminescent phosphors are widely used in radiation dosimetry. Two models have been proposed for the thermoluminescence (TL) mechanism in CaSO₄ based thermoluminescent phosphors. Nambi et al. extended the model based on redox reactions proposed by Merz and Pershan for CaF₂: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 CaSO4 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 RE3+. 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 CaSO₄:Dy and CaSO₄:P,Dy,Sm³⁺ phosphors. It is worth mentioning here that thermoluminescence(TL) intensity is 1.11 times greater in case of CaSO₄:P,Dy,Sm³⁺ phosphors prepared via slightly modified acid distillation method than standard CaSO₄: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 CaSO₄:Dy,P with Sm is investigated.

EXPERIMENTAL

For the preparation of CaSO₄:Dy,P,Sm phosphors all starting materials used were of analytical grade. CaSO₄: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 Dy³⁺ 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%Dy³⁺ and 0.1mol% Sm³⁺.

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 Electronmicroscope.

RESULTS AND DISCUSSION Photoluminescence Characteristics

Photoluminescence emission spectra fig.1 of CaSO₄:Dy,P,Sm phosphor under excitation wavelength 402 nm($^6H_{5/2} \rightarrow ^4F_{7/2}$) , 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 ($^4G_{5/2} \rightarrow ^6H_{5/2}$), 599 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$) and 613 nm ($^4F_{3/2} \rightarrow ^6H_{9/2}$) respectively. The dominant transitions are $^4G_{5/2} \rightarrow ^6H_{5/2}$ (565 nm) and $^4G_{5/2} \rightarrow ^6H_{7/2}$ (599 nm)[2,3]

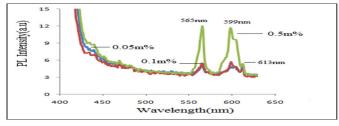


Fig 1. Photoluminescence emission spectra of CaSO₄:Dy,P,Sm phosphor. Emission spectra consist of 565, 599 and 613 nm wavelengths observed at 402 nm excitation wavelength.

Thrmoluminescence(TL) Characteristics

Figure 2 shows the typical TL glow curves of the CaSO₄:Dy,P,Sm phosphors exposed to gamma radiations from ⁶⁰Co 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 CaSO₄: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 CaSO₄: 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 CaSO₄: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.

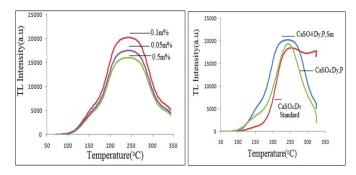


Fig 2. TL glow curves of CaSO₄:Dy,P,Sm(P=1mol%;Dy=0.1mol%;Sm=0.05,0.1,0.5mol%) phosphor exposed to gamma radiations from ⁶⁰Co source at room temperature.

Fig3. Comparison for glow curves of standard CaSO₄:Dy TLD phosphor , CaSO₄:Dy,P; CaSO₄:Dy,P,Sm(P=1mol%;Dy=0.1mol%;Sm=0.1mol%) phosphors.

SEM micrographs of CaSO₄:Dy,P,Sm phosphors.

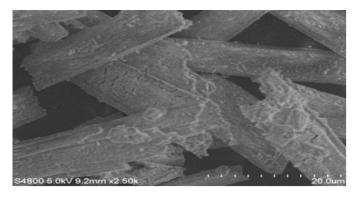


Fig 4. SEM micrographs of CaSO₄:Dy,P,Sm phosphors

From the micrograph (Fig.4) it can be seen that particles of CaSO₄:Dy,P,Sm have shaped like long bars with porous type surfaces and with appreciable diameter. This is obviously different from the morphological characteristics of CaSO₄:Dy and CaSO₄:Dy,P reported till date. Since thermoluminescence is very complicated process it is not yet clear if this morphological change has made any impact on TL of this phosphor. It is to be pointed out here that particle size in each case falls in the micro range which is considered very favorable for thermoluminescence characteristics of a phosphor material. Recently, some nano-TL phosphors have also been reported. These nano-phosphors are suggested to have possible applications in dosimetry of heavy charged particles [18-20].

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.

Only TL intensity of 246 °C peak has increased.

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