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Annealing effect on thermoluminescence (TL) glow curve of $Ca_{0.99}SO_4:Eu_{0.005}Dy_{0.005}$ phosphor

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$Ca_{1-x-y}SO_4:Eu_x,Dy_y$ ($0 < x < 0.04$, $0 < y < 0.04$) phosphors were prepared and characterized by XRD. The samples were well crystalline and exhibit orthorhombic structure. The phosphor $Ca_{0.99}SO_4:Eu_{0.005}Dy_{0.005}$ was found having highest TL intensity. The phosphor was annealed at different temperatures. All the TL glow curves have one prominent peak at 420K. TL intensity for this peak was found decreasing when the phosphor was annealed at a particular temperature for different durations.

Key words: Thermoluminescence, XRD, annealing, sensitivity.

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Introduction

Amongst TL phosphors, sulphates have been very popular for use in radiation dosimetry. Sulphate-based radiation dosimetry materials doped with RE (rare earth) ions, have been prepared (either single or double doped) and are extensively investigated due to their high luminescence.[1-22] In the family of sulphates, $CaSO_4$ phosphors, because of its high sensitivity, ease of preparation and stability of response in adverse climates, have already been very popular for use in radiation dosimetry, personnel dosimetry and environmental monitoring.[23-25] In the presence of certain suitable impurities, particularly rare earth ions, $CaSO_4$ phosphor shows efficient thermoluminescence. There are many works on TL, ESR, PL and various display applications of $CaSO_4$:RE.[26-33]

One of the most important among these is $CaSO_4$ activated with Dy^{3+}. $CaSO_4$:Dy is a unique inorganic phosphor material used in plasma display panels.[26] Another phosphor in $CaSO_4$ series, which has been widely studied, is $CaSO_4$:Eu.[34-36] Out of the different factors influencing the characteristics of TL phosphors, annealing is one of the most effective one. Many researchers reported that pre and post-irradiation annealing affects the glow curve structure and fading pattern of TL phosphors. Many researchers observed changes in TL glow curve structure of $CaSO_4$:Dy phosphor with the increase in annealing temperature.[37,38] Till now no paper is published on TL of $CaSO_4$ doped with both Eu and Dy. In this paper the effect of annealing on the TL glow curve structure and fading of the prepared $Ca_{0.99}SO_4:Eu_{0.005}Dy_{0.005}$ phophor is reported.

Materials and Methods

Method of preparation

Different phosphors of $Ca_{1-x-y}SO_4:Eu_x,Dy_y$ ($0 <$

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x < 0.04, 0 < y < 0.04) were prepared by taking 1 gm of analytical reagent (AR) calcium chloride ($CaCl_2$. $2H_2O$) and different amounts of (AR) europium oxide (Eu_2O_3)and dysprosium chloride ($DyCl_3$. $6H_2O$). In this method Eu_2O_3 is dissolved in AR hydrochloric acid (HCl) and then mixed with $CaCl_2$. $2H_2O$ and $DyCl_3$. $6H_2O$ which were dissolved in deionized water. Then, Ammonium sulphate [$(NH_4)_2SO_4$] had been added to this solution in the presence of ethanol. $(NH_4)_2SO_4$ was added drop wise to the solution until the formation of precipitates were completed. The precipitates were separated and washed many times to remove the ethanol and kept in oven at 373 K for 2 hours. The dried precipitates were crushed and sieved to obtain fine mesh powders. The samples were further annealed at 873 K for 1 hour. The sample with Eu = 0.5 at% and Dy = 0.5 at% was found having the highest TL intensity and had been divided into several parts and subjected to annealing treatment at 873, 973, 1073 and 1173 K for 1 hour.

Characterization

The identification of phases in the synthesized compounds of $Ca_{1-x-y}SO_4:Eu_x$, Dy_y (0 < x < 0.04, 0 < y < 0.04) had been carried out by X-ray diffraction studies using PAN alytical X-ray diffractometer with Cu-$K\alpha_1$ (λ = 1.5406 Å) radiation having Ni filter, operated at 40 kV and 40 mA at a step size of $\Delta 2\theta = 0.02°$ over the angular range $20° \leq 2\theta \leq 80°$ and comparing the interplanar distances and intensity values with those of the corresponding standard peaks using JCPDS files.

The thermoluminescence glow curves of the samples were recorded with the instrument (model TL 1404) consisting of a kanthal strip heated directly using temperature programmer, a photomultiplier (RCA 931A PMT), a DC amplifier and a millivolt recorder. TL glow curves are recorded with linear heating rate of 2.17K sec^{-1}, taking 2-5 mg sample in each measurement.

Results and Discussion

X-ray diffraction study

Figure 1 shows the XRD patterns of $Ca_{1-x-y}SO_4:Eu_x,Dy_y$ (0 < x < 0.04, 0 < y < 0.04) samples annealed at 873 K. The sharp diffraction peaks can be perfectly indexed to the highly purity and crystallinity of $CaSO_4$. All the XRD patterns are fitted well with the orthorhombic structure of $CaSO_4$ (JCPDS no. 80-0787). Fig. 2 shows the XRD patterns of $Ca_{0.99}SO_4:Eu_{0.005}$, $Dy_{0.005}$phosphor an-

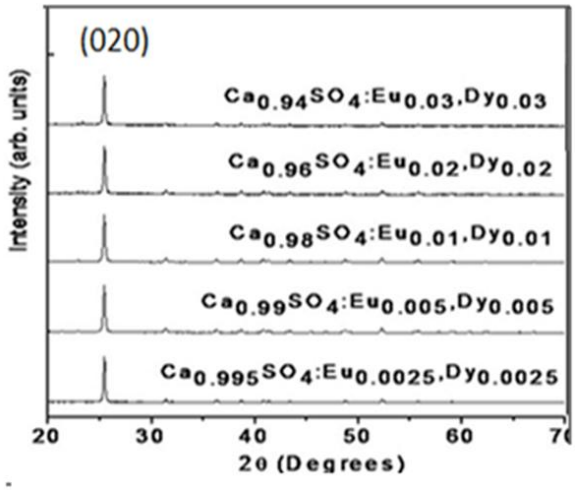

Figure 1 | XRD patterns of $Ca_{1-x-y}SO_4:Eu_x,Dy_y$(0 < x < 0.04, 0 < y < 0.04) samples annealed at 873 K.

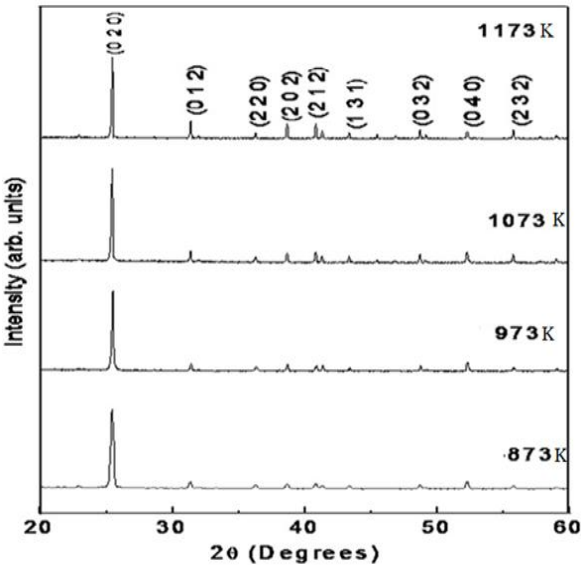

Figure 2 | XRD patterns of $Ca_{0.99}SO_4:Eu_{0.005},Dy_{0.005}$ phosphor annealed at different temperatures.

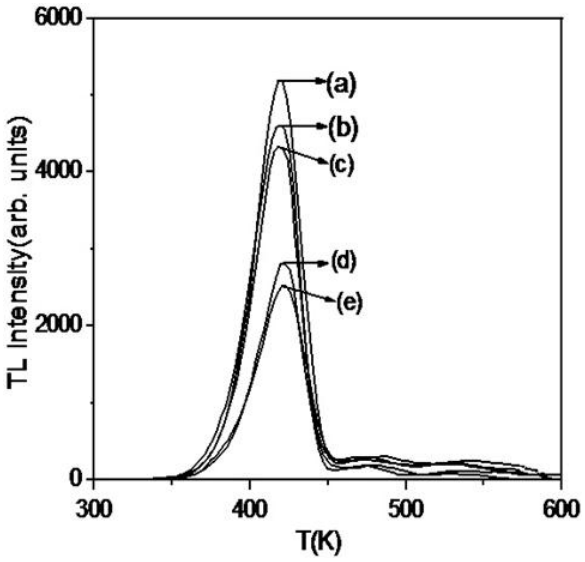

Figure 3 | TL glow curves of $Ca_{1-x-y}SO_4:Eu_x$, Dy_y, (0<x<0.04, 0<y<0.04) annealed at 873 K and irradiated with 150 Gy of γ-ray [x, y = (a) 0.5 at%, 0.5 at%, (b) 0.25 at%, 0.25 at% (c) 1 at%, 1 at%, (d) 2 at%, 2 at%, (d) 3 at%, 3 at%].

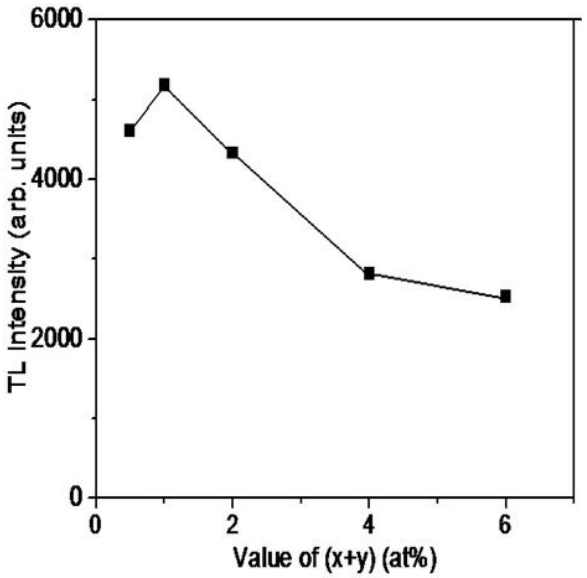

Figure 4 | TL intensity of the prominent peak at 420 K of $Ca_{1-x-y}SO_4:Eu_x,Dy_y$ versus dopant concentrations (x+y).

nealed at different temperatures ranging from 873-1173 K for 1 hour.

Thermoluminescence study

Concentration effect. Figure 3 shows the TL glow curves of $Ca_{1-x-y}SO_4:Eu_x,Dy_y$ ($0 < x < 0.04$, $0 < y < 0.04$), annealed at 873 K and irradiated with 150 Gy. It is observed from the figure that the phosphor $Ca_{1-x-y}SO_4:Eu_x,Dy_y$ has the highest TL intensity for x = 0.5 at% = 0.005 and y = 0.5 at% = 0.005. All the TL glow curves have the same structure, having one prominent peak at around 420 K and two peaks at around 475 and 540 K, the intensities of these glow peaks being very low compared to the prominent peak. The appearance of three peaks in the glow curves shows that three different sets of traps are being activated due to γ–irradiation for all concentrations of Eu and Dy within temperature range of 320-604 K. Fig. 4 shows the variation of TL intensity of the prominent peak at 420 K with change of sum of dopant concentrations (x+y). It is seen that each TL glow curve has one prominent peak at around 420 K and two shoulder peaks at around 475 and 540 K.

Effect of pre-irradiation annealing temperature and duration on TL glow curve. Figure 5 shows the TL glow curves of $Ca_{0.99}SO_4:Eu_{0.005}Dy_{0.005}$ annealed at different temperatures and irradiated with 150 Gy of γ–rays. The glow curve exhibits a dosimetric peak P_1at 420 K and two very low intensity peaks P_2 and P_3 at around 485 and 540 K respectively. As shown in fig., there is no drastic change in the glow curve structure with the annealing temperature. Table 1 shows the relative TL intensities of the peaks and the corresponding peak height ratio (dosimetric peak to high temperature peaks). As the annealing temperature increases, intensities of peaks also increase. But the TL intensity of the peak at 420 K for the annealing temperature 973 K is almost same with the 1073 K which shows the crystal/defect structure stability of $CaSO_4$:Eu, Dy even at such a high temperature. Bakshi *et al.*[37,38] observed con-

siderable change in TL glow curve structure of $CaSO_4$:Dy with post preparation annealing in the temperature range 300-850°C and 650-1000°C. With increasing annealing temperature, intensity of dosimetric peak at 240°C reduces, whereas the low temperature satellite peak increases. Their study indicates that post irradiation annealing of this phosphor should be carried out in the temperature range 650-700°C in order to maintain the dosimetric properties for further application in radiation dosimetry.

To check effect annealing duration on glow curve structure as well as TL intensity, $Ca_{0.99}SO_4$:$Ey_{0.005}Dy_{0.005}$ phosphor has been annealed at 700°C for 1, 3 and 4 hours. The recorded glow curves are shown in Figure 6. TL intensity of the prominent peak decreases with annealing duration. For the annealing duration of 4hours, the glow curve becomes more complex, appearing one more peak in the lower temperature side (≈376 K).

To check the effect of annealing on fading of $Ca_{.99}SO_4$:$Ey_{.005}Dy_{.005}$ phosphor, samples annealed at different temperatures were stored at room temperature for different durations. Figure 7 (a) shows the fading pattern of peak P_1 at Tm = 420 K in phosphor annealed at 873 K. TL intensity reduces by 20% in four days, which remains constant up to 7^{th} day of storage. After that the intensity is further decreased by 27% and then remains constant during experiments. As shown in Figure 7 (b), the fading of the sample annealed at 973 K is very fast. TL intensity reduces by 40% in 7 days The sample annealed at 1073 K shows 34% fading in 4 days remains constant for 4 days, after which it fades very fast (Fig. 7 (c)).

Conclusion

The newly prepared$CaSO_4$ phosphor activated with different concentrations of Eu and Dy have its maximum TL intensity for Eu = 0.5 at% and Dy = 0.5 at%. XRD pattern shows that the phosphors have orthorhombic structure (JCPDS NO. 800787). The effects of annealing temperature on the TL glow curves have been discussed. Unlike $CaSO_4$:Dy, as reported by many researchers, there is no considerable change in the glow curve structure of $CaSO_4$:Eu,Dy. The sample annealed at 1173 K has the highest TL intensity. If the annealing duration increases the TL glow curve becomes more complex, i.e. peaks in the lower temperature side appears.

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