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# Mixed influence of copper and some f-block elements on thermoluminescence intensity of $CaSO_4$: Dy, P phosphors

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## ABSTRACT

Very little data on copper co-doped $CaSO_4$: Dy and $CaSO_4$: Dy, P phosphors seems to have been reported so far. In the present study the influence of copper and rare earths co-doping on thermoluminescence intensity of $CaSO_4$: Dy, P phosphor has been investigated. Acid evaporation re-crystallization method was adopted for the synthesis purpose. Phosphors were characterized by scanning electron microscopy (SEM), photoluminescence (PL) and thermoluminescence (TL) techniques. Results obtained through this study are of mixed nature. In some cases TL intensity is either greater or nearly equal to standard $CaSO_4$: Dy while in other cases it is half or rather weak in comparison to standard $CaSO_4$: Dy phosphor. Copper was found to suppress temperature peak structure above 300 $^oC$. SEM micrographs of $CaSO_4$: P, Dy, Cu, RE phosphors show that the particle size is in the micrometer range, 1 to 5 μm approximately. The systematic study carried out in this work is solely novel as no such report existed before. From this study it is clear now that by co-doping multi-impurities simultaneously to enhance TL characteristics of $CaSO_4$: Dy phosphor is no longer useful because it proved otherwise. 

**Keywords:** Copper; glow curve; thermoluminescence; phosphor.

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## Introduction

Thermoluminescence (TL) is a process of giving off light by a material under constantly increasing temperature, which has been previously irradiated by highly ionizing radiations. $CaSO_4$: Dy is a highly sensitive material and it has been studied extensively. This phosphor was first introduced and synthesized by Yamshitta et al. Glow structure of $CaSO_4$: Dy is nearly simple and its fading is almost negligible. It has got better chemical durability and thermal stability. This phosphor due to its high sensitivity finds a broad range of use as TLD phosphor in dosimetric applications including environmental and personal monitoring. $CaSO_4$: Dy has also shown good signal storage capacity and is more sensitive than LiF: Mg, Cu, P and its other phosphor brothers. Due to all these good TLD properties, it feels always interesting to look for new co-doping/ doping so that further TL sensitization in this outstanding phosphor could be brought about. The attempts to improve characteristics and to study thermoluminescence mechanisms of $CaSO_4$: Dy are continued up to present day **[1-9]**. A very extensive comparative study is reported by Lakashmanan et.al concerning the features of newly designed $CaSO_4$: Dy: crystal morphology, glow curve shape, emission spectra, dependence of sensitivity, detection threshold, storage stability, sensitivity to UV, and other features on activator concentration, grain size etc **[10]**.

Monovalent copper has drawn attention for its luminescent property due to $3d^9 4s^1 \rightarrow 3d^{10}$ transition of $Cu^+$ ions. Suggestions have been made to employ $Cu^+$ luminescence in many applications such as lasing, X-ray imaging, blue component of full color electroluminescent display devices and thermoluminescence dosimetry **[11]**. So far, very limited studies seem to have been reported on Cu doped $CaSO_4$:Dy. In this connection it is of interest to mention some Cu doped thermoluminescence materials such as LiF: Mg, Cu, P and $Li_2B_4O_7$: Cu. These are some of the thermoluminescence materials which unlike the majority of TL materials show a linear TL dose response relationship without supralinearity **[12-17]**. Srivastava et al studied thermoluminescence of $CaSO_4$: Dy co-doped with copper **[18]**. The purpose of this study i.e., co-doping $CaSO_4$: Dy, P with Cu and other rare earths was to see if there could be any further sensitization of thermoluminescence (TL) in $CaSO_4$: Dy, P phosphor. Hence if sensitization takes place which in turn will enhance sensitivity and may improve other characteristics as well. However, the scenario was quite opposite, i.e. TL sensitivity was found to decline with the adoption of multi-impurities in $CaSO_4$: Dy system. It is believed that these different dopants (Cu and $RE^{3+}$ ions) might have created defects which acted as luminescent killers. The systematic study carried out in this work is solely novel as no such report existed before.

## Experimental

### *Materials*

The starting materials we used are $CaSO_4$(Qualigens Excel R 99.5%), $(NH_4)H_2PO_4$(MerckGR99%),$CeO_2$(S.D.Fine-99%), $Dy_2O_3$(S.D.Fine-99%), Sulphuric Acid (S.D.Fine AR-98%), $Sm_2O_3$ (Lobha ChemicalsAR-99%), $Eu_2O_3$(Lobha Chemicals AR-99%), $Tb_4O_7$(Lobha Chemicals AR-99%),$Nd_2O_3$(Lobha Chemicals AR-99%), $Er_2O_3$(Lobha Chemicals AR-99%)$Pr_2O_3$(Lobha Chemicals AR-99%) and $CuSO_4$(Lobha Chemicals AR-99%). All the above mentioned chemicals are manufactured in India.

### *Acid evaporation method*

In order to prepare $CaSO_4$: P, Dy, Cu, RE phosphors all starting materials used were of analytical grade. $CaSO_4$: P, Dy, Cu, RE phosphors were prepared by dissolving the desired starting materials in hot $H_2SO_4$. After the completion of process, the system was allowed to cool to room temperature. Finally, the product at room temperature was taken out. The sample phosphors thus prepared were repeatedly washed with double distilled water to remove the traces of acid. The sample phosphors were then dried at 353 K for 3 hours. In this way the phosphors were prepared and made ready for further characterizations. Then annealing procedure was followed. Some phosphors were annealed at various temperatures up to 1073K for 1 h following this preparation. However, annealing at 973 K was found to be suitable for obtaining high thermoluminescence (TL) intensities. These were used in the further experiments. For doping with phosphorus, $NH_4H_2PO_4$ was added to the sulphuric acid. The concentration of P used was 1mol%. The concentration of copper was varied from 0.02 to 0.5m%. The highest TL intensity was obtained at 0.05m% Cu so we used the same concentration for co-doping with rare earths in $CaSO_4$: P, Dy, Cu, RE phosphors. The concentration of $Dy^{3+}$ used was 0.1mol% but concentration of other rare earth ion(s) was varied from 0.05mol% to 0.5mol%.

### *Characterization*

The characterizations we have carried out to study these phosphors are Photoluminescence, Thermoluminescence and Scanning electron microscopy. The photoluminescence (PL) emission & excitation spectra of the samples were recorded by using a RF-5301PC SHIMADZU Spectro fluorophotometer with 150W Xenon Lamp and measuring wavelength range 220-750 nm. Spectral resolution range is between 1.5 to 5nm. The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral resolution of 1.5 nm. A $\gamma$ -rays of $^{60}Co$ were used for irradiation of the samples. The amount of dose imparted to the samples was 3.75 Gy. The samples were irradiated for 30 seconds. TL glow curves were recorded with the usual set up Nucleonix (TL – 1009), consisting of a small metal plate heated directly using a temperature programmer, photomultiplier tube (PMT), dc amplifier and millivolt recorder. The same amount of sample in the form of fine powder was heated each time at a rate of $5^0$C/s. For comparison TL glow curve of commercially available $CaSO_4$: Dy TLD phosphor was also recorded under identical conditions. SEM micrographs were obtained using JEOL, 6380A scanning electronmicroscope.

## Results and discussion

### *Photoluminescence (PL)*

Since photoluminescence results of $CaSO_4$: Dy, P, Cu, RE phosphors are almost identical to that of $CaSO_4$: Dy, P, RE phosphors **[19, 20]**. Therefore we shall restrict our PL discussion to $CaSO_4$: Dy, P, Cu, Ce phosphors only. **Fig. 1**(**A**) and (**B**) show PL excitation and emission spectrum of $CaSO_4$: Dy, P phosphors. Again in **Fig. 1(C) and (D)** PL emission spectrum $CaSO_4$: Dy, P, Cu, Ce phosphors is shown. Characteristic $Dy^{3+}$ emission in the form of bands around 481 and 573nm corresponding to transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is seen in all cases. It is seen that the PL intensity of $CaSO_4$: Dy, P, Cu, Ce has decreased markedly when co-doped with Cu and $Ce^{3+}$ ions together in comparison with $CaSO_4$: Dy, P, Ce **[19, 20]**. Excitation of $Dy^{3+}$ in $CaSO_4$ : P, Dy consists of narrow bands between 300 nm to 400 nm corresponding to transitions within the 4f shell. In $CaSO_4$: Dy, P, Cu, Ce, there are additional bands on both sides of 295 nm; namely 258nm, 328nm, 352,365 and 389nm.We chose 295 nm for excitation since it is more intense and broad amongst them **[19-22]**. The $Ce^{3+}$ emission is around 309 and 329 nm which overlaps fairly well with the $Dy^{3+}$ excitation. $Ce^{3+}$ thus sensitizes the $Dy^{3+}$ emission in $CaSO_4$. Also we see that $Cu^{+}$ emission (356 nm) lies in the same region and in this way serves as an additional bridge to transfer energy to $Dy^{3+}$ ions which in turn give emission around 481, 571 and 613 nm. It thus shows that the doped impurities are in the desired i.e. $Dy^{3+}$, $Cu^{+}$ and $Ce^{3+}$ forms. Additionally we have recorded emission spectrum of $CaSO_4$: Dy, P, Cu, Ce phosphors under 258 nm excitation. At 258 nm excitation wavelength 356 nm emission peak corresponding to $3d^94s^1 \rightarrow 3d^{10}$ transition of $Cu^{+}$ ions was found to be dominant on the rest of the peaks **Fig. 1 (D)**. As per theoretical considerations, addition of foreign ions (such as $Cu^{+}$, $Dy^{3+}$ and $Ce^{3+}$) results in the introduction of additional charge which must be compensated, e.g.by creation of cation vacancies. Alternatively, phosphorus which replaces hexavalent **S** ions can be used as a charge compensator **[20]**.

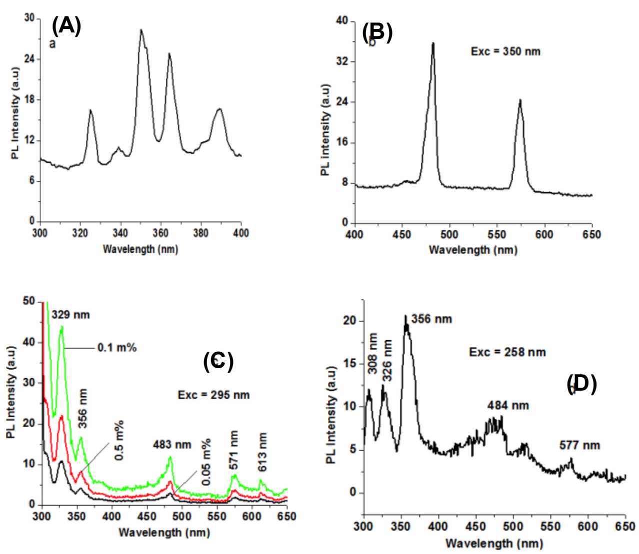


**Fig. 1.** PL excitation (A) and emission (B), (C), (D) spectra of $CaSO_4$: P, Dy and $CaSO_4$: Dy, P, Cu, Ce phosphor phosphors.

*Thermoluminescence (TL)*

*$CaSO_4$: Cu*

**Fig. 2(A)** shows typical glow curves observed for Cu doped CaSO4 phosphor. Thermoluminescence (TL) glow curves were recorded after irradiation with γ -source from $^{60}$Co using Nucleonix (TL – 1009) TLD reader. It is seen that glow curves consist of two peaks one at 152 $^0$C and another at 252 $^0$C. The intensity of 152 $^0$C peak is comparatively higher than 252 $^0$C hump. From dosimetric point of view the 252 $^0$C hump is important. The appearance of two peaks in the glow curve indicates that there are possibly two kinds of trapping sites, one which is shallower leading to the peak at 152 $^0$C temperature and the other which is deeper leading to the peak at 252 $^0$C. With increase in Cu content in $CaSO_4$ thermoluminescence intensity showed well enhancement but got concentration quenched just after 0.05m%Cu. The thermoluminescence intensity of $CaSO_4$: Cu was found to be less than that of standard $CaSO_4$: Dy TLD phosphor, **Fig. 2(B)**.

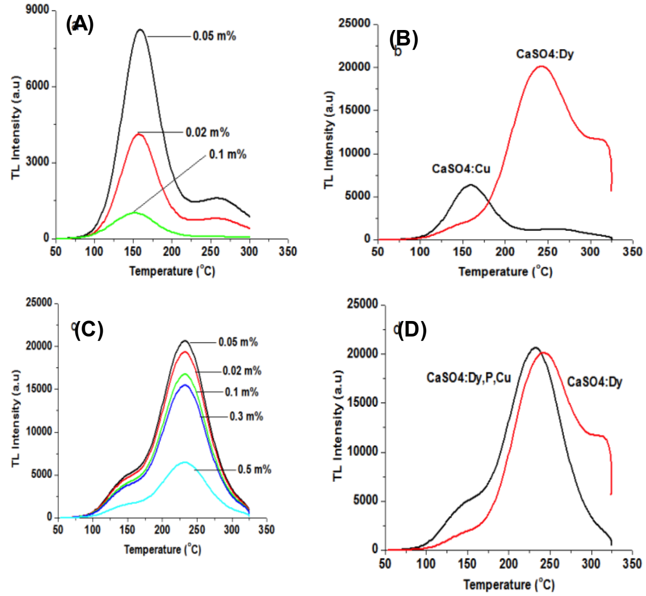


**Fig. 2.** TL glow curves (A), (C) along with comparative glow curves (B), (D) of $CaSO_4$: Cu, $CaSO_4$: Cu, P, Dy and $CaSO_4$:Dy phosphors.

*$CaSO_4$: Dy, P, Cu*

In **Fig. 2(C)** glow curves of $CaSO_4$: Dy, P, Cu are shown. The shape of the glow curve is almost the same as that of Dy doped standard $CaSO_4$ phosphor. Here again the glow curves consist of two peaks: 141$^o$C temperature peak and 232$^o$C temperature peak. In this case thermoluminescence intensity of higher temperature peak is greater as compared to lower temperature peak. It is known that doping of Cu in $CaSO_4$: Dy suppresses thermoluminescence. But it was observed that Cu did not suppress the thermoluminescence up to concentration 0.05m% Cu when doped in $CaSO_4$: Dy, P. However, thermoluminescence intensity was found to decrease as the concentration of copper exceeded the value of 0.05m%. This may be attributed to concentration quenching effect. The glow curve nature of $CaSO_4$: Dy, P, Cu is almost similar to standard $CaSO_4$: Dy TLD phosphor **[19]**. The thermoluminescence intensity of $CaSO_4$: Dy, P, Cu was found to be greater by a factor of 1.08 than standard $CaSO_4$: Dy TLD phosphor, **Fig. 2(D)**. Hence it sounds reasonable to suggest that Cu helps in sensitization in $CaSO_4$: Dy, P phosphor. Also from the old literature it is suggested that Cu doping in CaSO4: Dy trims the glow curve structure **[18]**. But one disappointment is here, that is temperature peak structure above 300 $^0$C is totally suppressed. This feature is observed in all phosphors which we have reported in this paper.

*CaSO4: Dy, P, Cu, Ce*

Glow curves observed for Cu & Ce co-doped $CaSO_4$: Dy, P phosphor is given in figure 3(a).This phosphor was given a dose of gamma radiations from $^{60}$Co at room temperature. TL readout was carried out using Nucleonix TL Reader with constant heating rate 5 degree per second. It is obvious from the figure that as the concentration of Ce was varied, the intensity of thermoluminescence glow curves also changed. The highest intensity was observed for the composition 0.1m% Dy, 0.05m% Cu, 1m% P and 0.1m% Ce. These results show quite good conform to the old literature which suggests that cerium decreases thermoluminescence in $CaSO_4$: Dy when doped in higher concentration. Moreover, there was seen a slight shift in peaks towards lower temperature side. This may be attributed to incorporation of Cu into the host lattice as per the old literature **[2, 18, 20]**. Overall, it seems as if co-doping of copper and Ce together perturbs the trap environment around 240-250 $^0$C peak which results in decline in peak height of dosimetric peak. Not only this we see complete elimination of temperature peak above 300 $^0$C. Nearly same behavior is seen all cases to follow. The thermoluminescence intensity of $CaSO_4$: Dy, P, Cu, Ce was found to be half to that of standard $CaSO_4$: Dy TLD phosphor, **Fig. 3(a)**.

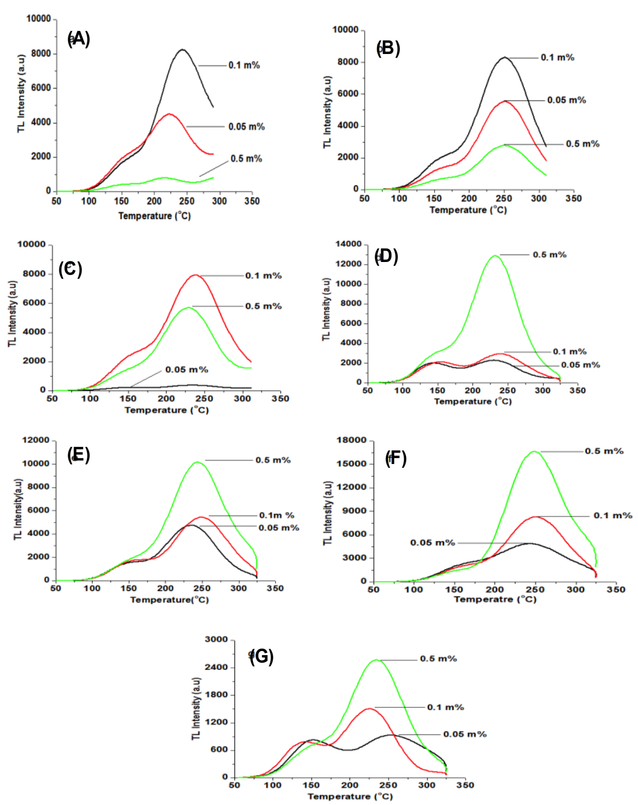


**Fig. 3.** TL glow curves of (A) $CaSO_4$: Dy, P, Cu, Ce, (B) $CaSO_4$: Dy, P, Cu, Eu, (C) $CaSO_4$: Dy, P, Cu, Tb, (D) $CaSO_4$: Dy, P, Cu, Sm, (E) $CaSO_4$: Dy, P, Cu, Nd, (F) $CaSO_4$: Dy, P, Cu, Pr, and (G) $CaSO_4$: Dy, P, Cu, Er phosphors; P=1m%, Dy=0.1m%, Cu = 0.05m% $RE^{3+}$ = 0.05m%, 0.1m%, 0.5m% (RE= Ce, Eu, Tb, Sm, Nd, Pr, Er).

*$CaSO_4$: Dy, P, Cu, Eu*

Dy, P, Cu and Eu co-doped $CaSO_4$ phosphors were given a dose of $^{60}$Co gamma radiations at room temperature and the resulting TL glow curves are shown in **Fig. 3** (**B**). From the results presented here it is evident that thermoluminescence (TL) of $CaSO_4$:Dy,P,Eu phosphor shows well enhancement in TL intensity up to the concentration of 0.1m% Eu afterwards it starts decreasing. The fall in TL intensity could be attributed to what is known as concentration quenching effect. Thermoluminescence (TL) characteristics of $CaSO_4$: Dy, P, Cu, Eu are almost similar to that of standard $CaSO_4$: Dy TLD phosphor. Even under different dopant concentrations no change was observed in glow curve structure. In the present investigation under UV excitation europium has shown $Eu^{3+}$ oxidation state in $CaSO_4$ lattice with peaks at 595 & 617 nm **[19]**. Bapat **[23]** studied the fluorescence of $CaSO_4$: Eu phosphor. Fluorescence emission in unirradiated sample consisted of a broad band at 385 nm attributed to $Eu^{2+}$ and another group of lines at 597, 625 and 700 nm attributed to $Eu^{3+}$ ions. Their spectral studies after a gamma ray dose of about $10^2$ Gy as well as after 500 $^0$C, 0.5 h post-irradiation heating showed that the $RE^{2+}$ fluorescence decreases after erasing the TSL i.e. post-irradiation anneal while the fluorescence corresponding to $RE^{3+}$ increases in the process. The value of $RE^{2+}$ and $RE^{3+}$ fluorescence after erasing TSL is the same as that observed before irradiation. According to Bapat **[23]** this observation confirms that the major TSL in $CaSO_4$: RE phosphor is due to the process of reduction and oxidation of RE dopant. Hence as per the earlier reports, it could be predicted here, that after gamma irradiation $Eu^{3+}$ has changed its oxidation state to $Eu^{2+}$ which is considered fruitful for dosimetry **[23-27]**. The highest TL intensity was obtained at 0.1m% Eu. In comparison with standard $CaSO_4$: Dy TL intensity of $CaSO_4$: Dy, P, Cu, Eu has decreased drastically, fig.4 (b). Hence it could be said that by employing Cu & Eu together as co-dopants in $CaSO_4$: Dy, P, Cu, Eu phosphor not much sensitization has taken place. Furthermore, it looks as if co-doping of copper and Eu together perturbs the trap environment around 240-250 $^o$C peak which results in decrease in peak height of dosimetric peak. Not only this we see complete suppression of temperature peak structure above 300 $^0$C. Almost same response is seen in other cases as well.

*$CaSO_4$: Dy, P, Cu, Tb*

Glow curves of $CaSO_4$: Dy, P, Cu, Tb phosphor co-doped with P, Cu and Tb are depicted in **Fig. 3(c)**. This phosphor was given a dose of gamma radiations from $^{60}$Co source at room temperature. Comparison of glow curves of $CaSO_4$: Dy, P, Cu, Tb and standard $CaSO_4$: Dy phosphors are also given in **Fig. 4(C)**. In this phosphor we saw that with change in Tb concentration TL intensity showed good enhancement. However, thermoluminescence intensity was found to be half to that of standard $CaSO_4$: Dy phosphor. Thermoluminescence was found to quench just after 0.1m% $Tb^{3+}$. Also no high temperature peaks above 300 $^0$C were observed for the as prepared phosphor. Moreover, from the TL glow curves of $CaSO_4$: Dy, P, Cu, Tb phosphor, **Fig. 3(C)** it is obvious that shape is very much similar to standard $CaSO_4$: Dy phosphor. Although the actual TL mechanism is somewhat complicated but it sounds good to infer from the results reported here that further TL sensitization is deterred in $CaSO_4$: Dy, P, Cu, Tb phosphor by co-doping with Cu and Tb ions together. Besides suppressing high temperature peak structure (350 $^0$C), we see that as if behavior of $CaSO_4$: Dy, P, Cu, Eu phosphor is repeated here **[2, 19]**. It is noted here that this feature is exhibited almost by all phosphors reported in the current investigation so it will not be mentioned again and again.

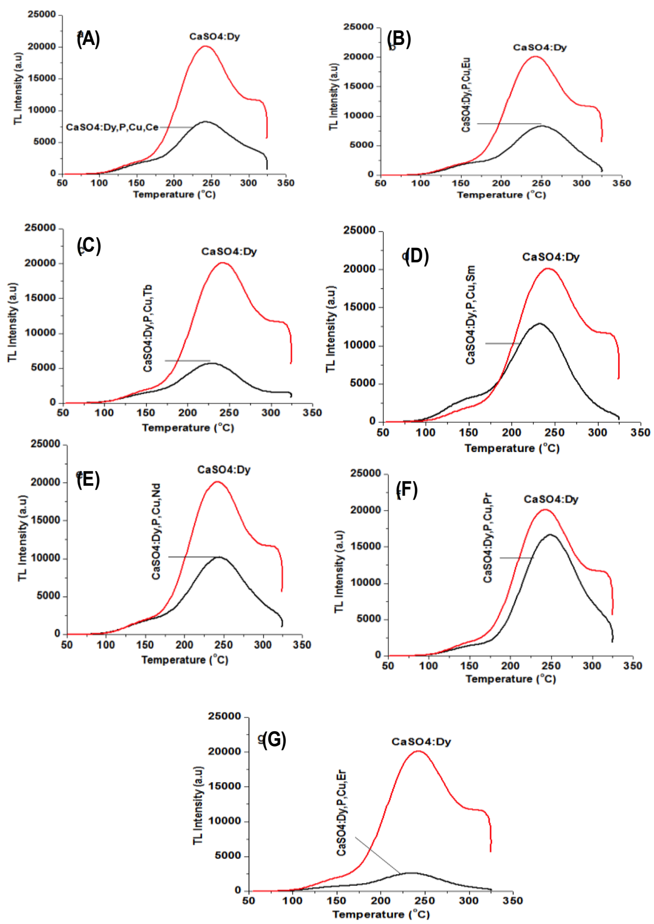


**Fig. 4.** Comparative TL glow curves of (A) $CaSO_4$: Dy,P,Cu, Ce, (B) $CaSO_4$: Dy,P,Cu, Eu, (C) $CaSO_4$: Dy,P,Cu, Tb, (D) $CaSO_4$: Dy,P,Cu, Sm, (E) $CaSO_4$: Dy,P,Cu, Nd, (F) $CaSO_4$: Dy,P,Cu, Pr and (G) $CaSO_4$:Dy,P,Cu,Er phosphors.

*$CaSO_4$: Dy, P, Cu, Sm*

**Fig. 3(D) and 4(D)** show the typical TL glow curves of $CaSO_4$: Dy, P, Cu, Sm and standard $CaSO_4$: Dy TLD phosphors respectively. Both these phosphors were irradiated with gamma radiations from $^{60}$Co source at room temperature. After recording the TL glow curves of $CaSO_4$:Dy,P,Cu,Sm phosphor it was found that with increasing concentration of Sm TL intensity also increased and no concentration quenching was observed up to 0.5m% Sm. However, the total thermoluminescence intensity was found to be less than the intensity of standard $CaSO_4$: Dy phosphor. The maximum TL intensity of $CaSO_4$:Dy,P,Cu,Sm was obtained for the composition at 0.1m%Dy, 1m%P, 0.05m%Cu, 0.5m%Sm. Glow curve structure of $CaSO_4$:Dy,P,Cu,Sm is very much similar to standard $CaSO_4$:Dy phosphor. The thermoluminescence intensity of $CaSO_4$: Dy, P, Cu, Sm is less by a factor of 0.64 than standard $CaSO_4$: Dy TLD phosphor. Although the actual TL mechanism is somewhat complicated but it sounds good to conclude from the results reported here that TL sensitization is not very much improved in $CaSO_4$: Dy, P by co-doping with Cu and $Sm^{3+}$ ions together **[2, 19]**.

*$CaSO_4$: Dy, P, Cu, Nd*

Neodymium is considered a very good activator which exhibits a significant role in the laser applications but some earlier investigations suggest that a good energy transfer could take place if used as a co-activator in TL phosphors **[2, 19]**. As can be seen in the **Fig. 3(E)** typical glow curves of $CaSO_4$: Dy, P, Cu, Nd phosphor obtained after recording the thermoluminescence with Nucleonix TLD reader. The phosphors were given a dose of gamma radiations from $^{60}$Co at room temperature. It was observed that glow curve structure of $CaSO_4$: Dy, P, Cu, Nd is no different from the standard $CaSO_4$: Dy phosphor. Also it is obvious from the figure that with addition of co-dopant in higher concentration thermoluminescence intensity increased but was found comparatively lower than that of standard $CaSO_4$: Dy phosphor, **Fig. 4 (E)**.

For comparison TL glow curve of standard $CaSO_4$: Dy TLD phosphor is also given in **Fig. 4(E)**. It could be seen in **Fig. 3(E)** that with the increase in concentration of Nd thermoluminescence did not quench even for 0.5m% the highest concentration we used in the very phosphor. Since we have used concentration only up to 0.5m% Nd and may be beyond this concentration thermoluminescence show quenching effect. Therefore it can be said that TL of $CaSO_4$: Dy, P shows almost good sensitization when co-doped with copper and neodymium. This is very well supported by earlier investigations which suggest that there is likely a good energy transfer between recombination centers and the Nd ions **[9, 19]**. The highest TL intensity was observed for $CaSO_4$:$Dy_{0.1m\%}P_{1m\%}Nd_{0.5m\%}$ phosphor and the same phosphor has been drawn for comparison with standard $CaSO_4$: Dy TLD material. In this comparison it is clear that $CaSO_4$: Dy, P, Cu, Nd TL phosphor has intensity less by a factor of 0.5 than the standard $CaSO_4$: Dy TLD phosphor. Hence again we say that a poor sensitization in $CaSO_4$: Dy, P phosphor has occurred when co-doped with copper and Nd ions together. Moreover it can be said while taking a look at the glow curve structure of $CaSO_4$: Dy, P, Cu, Nd is vey alike to that of $CaSO_4$: Dy TLD phosphor.

*$CaSO_4$: Dy, P, Cu, Pr*

Praseodymium is also a very good activator which is mostly known in up-conversion phosphors but some earlier investigations suggest that a good energy transfer could take place if used as a co-activator in TL phosphors. **Fig. 3(F)** shows the typical glow curves of $CaSO_4$: Dy, P, Cu, Pr phosphor observed after recording the thermoluminescence using Nucleonix TLD reader with a constant heating rate $5^0$C per second. $CaSO_4$: Dy, P, Cu, Pr phosphors were irradiated with gamma radiations from $^{60}$Co source at room temperature. TL glow curve of standard $CaSO_4$: Dy TLD phosphor is also given for comparison, **Fig. 4(F)**. As is evident from the figure that thermoluminescence intensity raises with change in concentration of dopant ($Pr^{3+}$). TL intensity reaches maximum at 0.1m% Pr afterwards it begins to diminish. Although small but in this case too TL intensity of $CaSO_4$: Dy, P, Pr is less by a factor of 0.83 than the TL intensity of $CaSO_4$: Dy TLD phosphor. For the composition of $CaSO_4$:$Dy_{0.1m\%}$,$P_{1m\%}$,$Pr_{0.1m\%}$ phosphor highest thermoluminescence intensity was observed and for the same composition comparison with standard $CaSO_4$:Dy TLD phosphor has been drawn. In the light of the results presented here it could be suggested that very little sensitization of TL in $CaSO_4$: Dy, P takes place when co-doped with copper and Praseodymium ions **[2, 19]**.

**Table 1.** TL intensities of $CaSO_4$:Dy,P,Cu,$RE^{3+}$ (RE= Ce, Eu, Tb, Sm, Er, Pr, Nd) phosphors in comparison with standard $CaSO_4$:Dy and previously reported phosphors. Major Temperature peaks are also given in the table.

| Name of Phosphor | Temperature Peak | TL Intensity (a.u) | Intensity Ratio Peak height-wise |
|---|---|---|---|
| $CaSO_4$:Dy (Standard) | 240 °C | 20000 | ------- |
| CaSO4:Dy,P | 227 °C | -------- | 1.5 |
| CaSO4:Dy,P,Eu | 250 °C | -------- | 1.11 |
| $CaSO_4$:Cu | 159 °C | 6354 | 0.31 |
| $CaSO_4$:Dy,P,Cu | 232 °C | 20634 | 1.03 |
| $CaSO_4$:Dy,P,Cu,Ce | 242 °C | 8224 | 0.41 |
| $CaSO_4$:Dy,P,Cu,Eu | 251 °C | 8301 | 0.41 |
| $CaSO_4$:Dy,P,Cu,Tb | 228 °C | 5697 | 0.28 |
| $CaSO_4$:Dy,P,Cu,Sm | 232 °C | 12896 | 0.64 |
| $CaSO_4$:Dy,P,Cu,Nd | 244 °C | 10182 | 0.50 |
| $CaSO_4$:Dy,P,Cu,Pr | 248 °C | 16658 | 0.83 |
| $CaSO_4$:Dy,P,Cu,Er | 234 °C | 2572 | 0.12 |

### *$CaSO_4$: Dy, P, Cu, Er*

Chemistry of erbium is attractive when it comes to study of optical properties. It is a very good activator and is mostly known in up-conversion phosphors but some earlier investigations suggest that a good energy transfer can be made if used as a co-activator in TL phosphors. It is disappointing here to say that we could not get a characteristic photoluminescence spectra of erbium ions under UV excitation. Therefore no photoluminescence spectrum for $Er^{3+}$ was recorded. In the **Fig. 3(G)** given below shows typical glow curves of $CaSO_4$: Dy, P, Er phosphor obtained after a pre-exposure to gamma radiations from $^{60}Co$ source at room temperature. TL glow curves were recorded using Nucleonix TLD reader. For comparison, TL glow curve of $CaSO_4$: Dy, TLD phosphor is also shown in **Fig. 4(G)**. As can be seen in the **Fig. 4(G)**, the glow curve nature of $CaSO_4$: Dy, P, Cu, Er is almost similar to $CaSO_4$: Dy, TLD phosphor. With increase in Erbium concentration it was seen that TL intensity increased but very slowly and was found to be drastically lower than $CaSO_4$: Dy. So in order to enhance the TL intensity, here it is possible to go beyond 0.5m% Er. It is again to be remarked here that Morgan and Stoebe state that some rare earth ions such as $Ce^{3+}$, $Gd^{3+}$, $Ho^{3+}$, $Er^{3+}$, $Yb^{3+}$ and $Lu^{3+}$ do not activate the TL mechanism efficiently in $CaSO_4$. But their later investigations suggest that out of these ions, $Ho^{3+}$, $Er^{3+}$ are still receiving the energy from the recombination centre; however, non-radiative decay processes for these ions have been shown to be more likely and no TL is then observed **[2, 19]**. The maximum TL intensity was obtained at 0.5m% Er. For $CaSO_4$: $Dy_{0.1m\%}$,$P_{1m\%}$,$Cu_{0.05m\%}$,$Er_{0.5m\%}$ composition of phosphor TL glow curves showed highest intensity. In the light of the results presented here it could be concluded that not very much sensitization of TL in $CaSO_4$: Dy, P has taken place when co-doped with copper and erbium ions together. From the above obtained results it is quite clear that by employing multi-impurities simultaneously in $CaSO_4$: Dy system did not improve thermoluminescence sensitivity. It was observed that thermoluminescence sensitivity of as prepared phosphors is rather poor as compared to earlier work on the same system. In $CaSO_4$: Dy, P, RE multi-impurity system incorporation of different dopants might have generated traps/defect centers which acted as luminescence killers or they made the absorbed energy to dissipate non-radiatively. The data of previous and present work is compiled in **Table 1**.

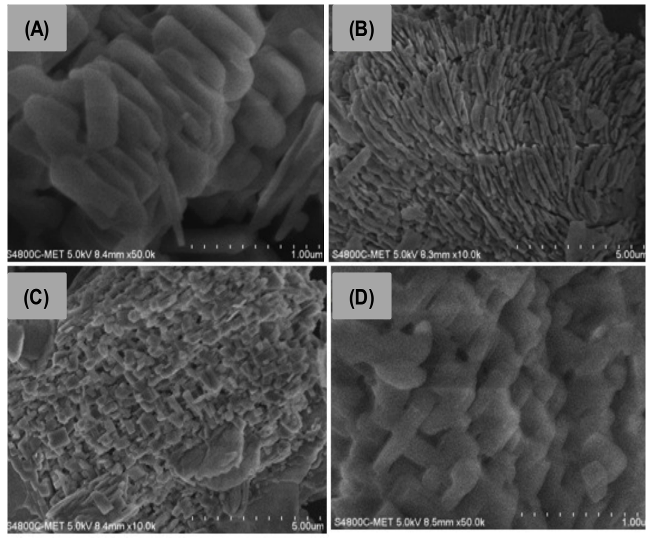


**Fig. 5.** SEM images of $CaSO_4$: Dy, P, Cu, RE.

### *SEM Micrographs of $CaSO_4$:Dy, P, Cu, RE Phosphors*

From the SEM micrographs (**Fig. 5**) it is seen that particles of $CaSO_4$: Dy, P, Cu, RE have shaped like small cement slabs with sharp surfaces. Obviously they posses some well defined geometry. As could be observed in the figure that there is a well organized packing of grains and hence of atoms. Presumably some sort of densely packed arrangement is reflected from the SEM micrographs recorded for this material. Since thermoluminescence is a very complicated process and it is not yet clear if this morphological change has made any impact on TL intensity of this phosphor. So, not much can be said about the morphological contribution if any taking place in this phosphor. However, it is to be pointed out here that particle size in each case falls in the micro range which is generally considered very suitable for thermoluminescence characteristics of a phosphor material. Nano- TL phosphors have also been investigated recently. But the UV response of these nano-phosphors was found to be very poor as compared to microcrystalline phosphors. These nano-phosphors are suggested to have possible applications in dosimetry of heavy charged particles **[28-31].** Nevertheless, nano-materials have other potential applications and they can be prepared by various synthesis routes **[32-34]**.

## Conclusion

Co-doping of Cu and $RE^{3+}$ ions in $CaSO_4$: Dy, P host has been found to be successful as is revealed by the photoluminescence spectra. By the co-doping of Cu and

$RE^{3+}$ ions together in $CaSO_4$: Dy, P phosphor not very much improvement in thermoluminescence intensity has taken place. For example, co-doping of Cu in $CaSO_4$: Dy, P increases the TL intensity by a factor of 1.08 and when Cu and Pr together were co-doped in $CaSO_4$: Dy, P TL intensity was found to be less by a factor of 0.83 than the standard $CaSO_4$: Dy phosphor. Likewise, TL intensity of $CaSO_4$: Dy, P, Cu, Sm is less by a factor of 0.65 than the standard $CaSO_4$: Dy phosphor. For other phosphors TL intensity was either half of or rather weak relative to standard $CaSO_4$: Dy, nevertheless, nature of glow curve structure is retained in every prepared phosphor. From SEM images it is obvious that the particles of $CaSO_4$: Dy, P, Cu, RE phosphors look quite stacked together.

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