Study of TL characteristics of CaSO₄: Dy phosphor with fly ash for thermoluminescence dosimeter application

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Abstract. In recent past fly ash is only being treated as waste and a source of air and water pollution but is in fact an eco-friendly and economically beneficial resource material for various applications and has also proven its worth over a period of time. The utilization of fly ash in several novel researches will also paves the path for systematic disposal of this waste material. The present paper involves the study of Thermoluminescence (TL) of different compositions of fly ash collected from National Thermal Power Corporation, Korba, Chhattisgarh, INDIA with (CaSO₄: Dy) Phosphor. Thermo luminescence Dosimeters are regarded as the badge which absorbs the radiation when persons having TLD badges are exposed to radiation. We have to investigate and compare the glow curve behavior of pure phosphor and 10 %, 20 % and 30 % fly ash doped phosphor when it is exposed to gamma irradiation Cs¹³⁷.

1. Introduction
The phenomenon of thermoluminescence (TL) is widely used for measurement of radiation doses from ionizing radiations viz. x-rays, γ rays and β particles. Dosimeters based on luminescence phenomenon are also used for measurement of radiation doses from neutrons. The application of the phenomena of TL for the dosimetry purpose was first proposed by an American scientist F. Daniels. Subsequently, various phosphors were developed by various laboratories and manufacturing of these phosphors was undertaken by various commercial companies. These are being used in personnel, environmental and medical dosimetry. TL is the emission of light from a wide band gap material called phosphor during heating, which has already been exposed to ionizing radiations (x, β, γ rays and neutrons). During irradiation of phosphor, the electron-hole pairs are generated, which while mobile in the phosphor can be trapped at the metastable energy levels which exist in the forbidden gap due to vacancies, defects or by the addition of impurities/dopants to the host material. [1]

When ionizing radiation is incident on an insulating crystal some of the deposited energy is stored in the lattice at defect sites, colour centres, etc. Upon heating the crystal, this stored energy is released and a fraction of it may be emitted as visible light. This is called thermoluminescence. Within certain limitations, the amount of light emitted is proportional to the radiation dose previously absorbed by the TL material.
Various types of materials can be examined for both low dose dosimetry and high dose dosimetry. Low dose dosimeters can be used for medical applications while high dose dosimeters are useful in various fields such as medical & pharmaceutical industries, research laboratories based on high energy accelerators, etc. Hence, we are here focusing on the examination of low dose behavior of Gamma Irradiation source on the phosphor sample mixed with different percentages of fly ash.

2. Experimental
The fly ash used in this experiment was collected from the Super Thermal Power Station, Korba which is situated on the banks of the confluence of rivers Hasdeo and Ahiran. Korba is the power capital of Chhattisgarh State in India. The source of coal for the power plant is Kusmunda & Gevara Mines. There are total five samples prepared in this investigation. Out of five four samples are based on fly ash and one is based on pure phosphor. CaSO₄: Dy phosphor and Teflon mixture in the weighted ratio of 1:3 is prepared using Liquid Nitrogen by Solid State Sintering Method. CaSO₄: Dy Phosphor and CaSO₄: Dy Phosphor is doped with 10%, 20% and 30% of fly ash and pure fly ash sample are exposed to Gamma Irradiation source of (Cs¹³⁷) varies from low dose range of 1000-4000 mR or 8.77 mGy to 35.08 mGy. TL glow curves of γ-ray irradiated samples were obtained using a Nucleonix 1009I TL reader in the temperature range of 20 °C to 300 °C with a heating rate of 5 °C/sec.

3. Result analysis and discussion

3.1 XRD Analysis
The XRD properties of the samples were obtained using a Bruker D2 Phaser diffractometer. The value for 2θ in a range from 10° to 80° is taken with an increase of 0.01° per sec. The XRD diffraction of fly ash doped CaSO₄: Dy phosphor is shown in figure 1(a) below. This XRD data is compared with standard JCPDS data of 100% fly ash in figure 1(b) and CaSO₄: Dy Phosphor in figure 1(c) and it is almost well matched with it. Due to some impurity or system’s issue noise is created in sample [2]. The “d” value is calculated by the Bragg’s formula by assuming λ value for X-rays.

![Figure 1](image-url)
3.2 TL Glow curve Analysis

The TL techniques are used worldwide for the determination of radiation dose. The TL intensity should be linear with increasing the duration of radiation exposure in such a way that the value of doses absorbed by the material could be easily predicted. The below figures 2(a), 2(b), 2(c) & 2(d) shows the glow curves of 5 different samples given in the Table: 1 at different \( \gamma \)-ray irradiation doses i.e., 8.77 mGy, 17.54 mGy, 26.31 mGy and 35.08 mGy respectively of Cs\textsuperscript{137}.

In figure 2(a) all the samples of fly ash and phosphor are exposed to 8.77 mGy (1000 mR) dose of Cs\textsuperscript{137}. Here we have recorded highest peak for P+FA20% sample and after that P+FA10% sample analogy with the peaks of traditional phosphor material. In Figure 2(b) all samples were exposed to 17.54 mGy (2000 mR) dose. Here again P+FA20% sample shows highest intensity peak but not in analogy with phosphor material. While peak of sample P+FA30% possess nearby intensity with phosphor material and sample P+FA10% shows constant peak as it posses during the 8.77 mGy exposure.

Figure 2(c) shows that, with increment in the dose the intensity also increases with the samples with the increasing percentage of fly ash in it. All the samples were showing clear individual peaks at 26.31 mGy (3000 mR) dose. Highest peak is recorded with the sample P+FA30%, then P+FA20% shows higher intensity while sample P+FA10% shows a little bit hump in comparison with the traditional phosphor. While in the figure 2(d) all the fly ash samples shows lower intensity in analogy with the phosphor when exposed to 35.08 mGy (4000 mR). P+FA30% shows quite clear single peak with a little hump in the intensity.

The matching of JCPDS Cards shows orthorhombic crystalline phase is indicated by planes of CaSO\textsubscript{4}:Dy. Only some major peaks are observed due to the mixing of fly ash in the CaSO\textsubscript{4}:Dy Phosphor. Three major peaks are observed in the XRD pattern indicating the presence of main component of fly ash like SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and CaO phases which are dominant in the fly ash composition.
Table 1. Composition of various samples.

| S.No. | Sample Name | Phosphor | Fly Ash |
|-------|-------------|----------|---------|
| 1     | PP          | 100 %    | 0 %     |
| 2     | PFA         | 0 %      | 100 %   |
| 3     | P+FA10%     | 90 %     | 10 %    |
| 4     | P+FA20%     | 80 %     | 20 %    |
| 5     | P+FA30%     | 70 %     | 30 %    |

Figure 2. TL Glow Curves of Phosphor and Fly Ash samples at different γ-doses ranging from 8 - 35 mGy.

For sample P+FA10%, figures 3(a), 3(b) and 3(c) shows nice linear and individual peaks and figures 3(a) and 3(c) shows nearly the same intensity as it is desired intensity at a particular given dose. Apart from it The figures 3(d) and 3(f) of sample P+FA30% shows very nice single peaks but behaves considerably low with respect to the exposure of desired doses.
Figure 4 show the response of sample P+FA10% at all different doses. We can see in figure 4 that at low doses of 8.77 mGy and 17.54 mGy sample show intensity nearly equal to the desired value. While even at 26.31 mGy and 35.08 mGy we have got quite clear and individual peaks.

![Figure 3](image)

**Figure 3.** Individual Glow Curve peaks of sample P+FA10% and sample P+FA30% at different doses.
3.3 TL Dose Response Curve Analysis
The linear response arises from the recombination of localized entity which is an electron/hole pair and acts as a trapping center. The unoccupied electron/hole trap is suppressed during the linear response of the TL glow curve. Variation in the peak temperature position was observed with a change in radiation dose value. [5]

The linear fitting curve and TL dose response curve of fly ash, phosphor and fly ash composites exposed to low dose range of ~ (8 to 35) mGy respectively are shown in figures 5(a) and 5(b). Here PFA shows very nice linearity in initial and end points and also shows probability of showing positive response with respect to higher dose than 35.08 mGy as the intensity goes on increasing with increasing doses. Here in figures 5(a) and 5(b) sample P+FA10% shows linear patch near lower temperature zone and at high temperature zone as well but it started bending toward low intensity nearby 35.08 mGy. Sample P+FA20% initially loses its linearity and shows higher intensity than the phosphor material but in later part after 26.31 mGy it again get back into linear patch as sample PP in figure 5(a). Sample P+FA30% shows a small hump in between but apart from it shows linear curve with highest peak at higher dose value.
Figure 5 (a) and Figure 5 (b)

Figure 5. Linear fit and TL dose response curve of all samples to different γ-doses ranging from 8 - 35 mGy at 300 °C temperature.

The number of luminescence and trapping centers has increased linearly inside sample P+FA10% and P+FA30% with increasing the dose values and has given rise to enhanced TL intensity. [5] Thus, a good fit linear curve of both samples from figure 5(a) and figure 5(b) suggests that P+FA10% and P+FA30% is likely to favorable material for used as an TL dosimeter at low dose range from ~ (8 to 35) mGy.

3.4 Analysis of Trapping Parameters

Several models have been applied to describe the TL process that arose in materials. The easiest one, named first order kinetics, assumes a thermal release of an electron from trap centers is followed by recombining with a hole in the recombination centers. In this model, the probability of the electron being retrapped is assumed to be impossible. While the second order model considers two possibilities are granted to the electrons upon the thermal release: recombine with holes or retrap again. An empirical model has been suggested to describe the situation when the TL peak of neither first order nor second order are satisfied, named general order kinetics. [6] Specific details of the trap and recombination centers provide valuable information about the material properties, defects, and history of radiation absorbed. This information is found in the trap parameters of the centers.

The parameters include the activation energy $E_a$ (eV), the kinetic order of TL processes b, the initial concentrations of trapped charges $n_0$ (cm$^{-3}$), the frequency factor $S$ (s$^{-1}$). The TL glow curves are usually analyzed also by assuming different b values using many different methods. We can apply Glow Curve Deconvolution (GCD) method, Chen’s Peak Shape method, Initial Rise (IR) method, Three Point Analysis (TPA) method, Whole Glow Curve method, Peak Position method, Isothermal Decay method, Curve Fitting method and many more but here we are focusing on initial four methods described above in this paragraph.
3.4.1 Chen’s Peak Shape Method

Using this method we can calculate the activation energy ($E_A$), frequency factor ($S$), kinetic order ($b$), lifetimes of the peaks is calculated. Here we need to estimate three temperatures required for Chen’s Peak Shape equations those are $T_M$, $T_1$, $T_2$ where $T_1$ and $T_2$ were temperatures at half intensity of glow curve in both the side of $T_M$ which is the maximum peak temperature. Using the value of $\tau$, $\delta$, and $\omega$ which can be evaluated as $\tau = T_M - T_1$, $\delta = T_2 - T_M$ and $\omega = T_2 - T_1$ respectively. Then we can find the geometrical shape factor $\mu = \delta/\omega$.

The value of $E_A$ can be calculated using the values of $E_\tau$, $E_\delta$, and $E_\omega$ where

$$E_\tau = \frac{(1.51kT_M^2)}{\tau - 1.58(2kT_M)} \quad (1)$$

$$E_\delta = \frac{(0.976kT_M^2)}{\delta} \quad (2)$$

$$E_\omega = \frac{(2.52kT_M^2)}{\omega - 2kT_M} \quad (3)$$

Where $T_M$ = peak temperature at the maximum TL intensity, $T_1$, $T_2$ = temperatures on either side of $T_M$, corresponding to the half-maximum intensity and $k$ is the boltzman’s Constant.

The calculation of trapping parameters using Chen’s Peak Shape method is shown in the Table: 2 below.

[7]

**Table 2.** Trapping parameter by Chen's peak shape method of the fly ash sample exposed to Cs$^{137} \gamma$-irradiation.

| Sample    | Peak Temperature (°C) | Order of Kinetics (b) | Geometrical Form Factor (µ) | Activation Energy (eV) | Frequency Factor S (s$^{-1}$) | Lifetime of Peak (τ) |
|-----------|-----------------------|-----------------------|-----------------------------|------------------------|-----------------------------|---------------------|
| P+FA30% 35.08 mGy | 287.15 | 1.47 | 0.19 | 1.16 | 3.85x10$^{11}$ | 8.02 x10$^{-2}$ |
| P+FA30% 26.31 mGy | 249.87 | 2.74 | 0.48 | 0.77 | 1.08x10$^{6}$ | 12.3 x10$^{2}$ |
| P+FA20% 17.54 mGy | 261.19 | 2.2 | 0.42 | 0.61 | 4.71x10$^{6}$ | 12.3 x10$^{2}$ |
| P+FA20% 8.77 mGy | 266.61 | 2.22 | 0.38 | 0.78 | 1.75x10$^{6}$ | 10.1 x10$^{2}$ |
| P+FA10% 26.31 mGy | 269.22 | 1.73 | 0.37 | 0.68 | 1.84x10$^{7}$ | 12.1x10$^{2}$ |
| P+FA10% 17.54 mGy | 292.69 | 0.8 | 0.1 | 1.53 | 6.21x10$^{14}$ | 6.6 x10$^{2}$ |
| P+FA10% 8.77 mGy | 265.8 | 1.43 | 0.38 | 0.63 | 5.22x10$^{6}$ | 13.5 x10$^{2}$ |

3.4.2 Initial Rise Method

This method is based on the approximation that total rate change of trapped charges in initial rise part for temperature less than maximum peak temperature $T_M$ of any glow curve is constant with respect to change in temperature. This method is only application on single glow peak of any curve. Here activation energy is independent of order of kinetics thus TL intensity $I$ is proportional to exp ($-E/kT$) and can be written as $I(T) = R^2 \exp(-E/kT)$

Where $I(T)$ is the intensity with temperature $T$, $k$ is the boltzman’s Constant, $E$ is the activation energy, $T$ is the temperature of glow curve and $R^2$ is the regression constant having value of 0.9997. We can get the value of activation energy $E_A$ by getting a slope in the plot of ln $I(T)$ vs $(-E/kT)$. First 11 data sets were taken to plot the graph and the value of glow curve peak temperature having intensity $I$ was chosen in such a way that it belongs to (10-15) % of maximum peak intensity $I_{M}$. [5]
Figure 6. Plot of $1/kT$ Vs ln(I) for Initial Rise Method of different samples exposed to different $\gamma$-Irradiation Cs$^{137}$ source.
Table 3. Trapping parameter by IR method of the fly ash sample exposed to Cs\(^{137}\) \(\gamma\)-irradiation.

| Sample    | Peak Temperature (°C) | Activation Energy (eV) |
|-----------|-----------------------|------------------------|
| P+FA30%   | 35.08 mGy             | 287.15                 |
| P+FA30%   | 26.31 mGy             | 249.87                 |
| P+FA20%   | 17.54 mGy             | 261.19                 |
| P+FA20%   | 8.77 mGy              | 266.61                 |
| P+FA10%   | 17.54 mGy             | 292.69                 |
| P+FA10%   | 8.77 mGy              | 265.8                  |

The calculation of trapping parameters using Initial Rise method is shown above in the Table 3.

3.4.3 Glow Curve Deconvolution (GCD) Method

It is quite difficult to analyze a glow curve having more than one TL glow peak instead of single peak glow curve. In order to minimize and simplify the difficulty some mathematical expressions are defined by Vasilis Pagonis, George Kitis and Claudio Furetta of first, second and general order kinetics so that we can estimate theoretical values of activation energy \((E_A)\), order of kinetics \((b)\) and frequency factor \((S)\) those are:

For first order of kinetics

\[
I(T) = I_M \exp \left[1 + \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right) \frac{T^2}{T_M^2} \left(1 - \frac{2kT_M}{E}\right) \exp \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right) - \frac{2kT_M}{E}\right]
\]  

(5)

For second order of kinetics

\[
I(T) = 4I_M \exp \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right) \left[\frac{T^2}{T_M^2} \left(1 - \frac{2kT_M}{E}\right) \exp \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right) + 1 + \frac{2kT_M}{E}\right]^2
\]

(6)

and for general order kinetics

\[
I(T) = I_M \left(\frac{b}{kT} \frac{T-T_M}{T_M}\right) \left[1 + (b-1) \frac{2kT_M}{E} \exp \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right) + (b-1) \left(1 - \frac{2kT_M}{E}\right) \left(\frac{T^2}{T_M^2} \exp \left(\frac{E}{kT} \frac{T-T_M}{T_M}\right)\right)\right] - \frac{k}{b-1}
\]

(7)

\[
FOM = \sum p_{|y_{\text{expt}} - y_{\text{fit}}|} \sum p_{y_{\text{fit}}}
\]

(8)

Where \(I(T)\) is the TL peak intensity calculated from above equations at temperature \(T\), \(I_M\) is the highest TL peak intensity at a particular temperature \(T_M\) and \(k\) is boltzman’s constant. [8]

Equations (5), (6) and (7) are used to generate a theoretical glow curve on the basis of some parameters like highest peak temperature of single peak glow curve, order of kinetics and activation energy. TL parameters of theoretical glow curve can be estimated by using Chen’s Peak Shape method and Initial Rise method.

The value of activation energy \((E_A)\) calculated by Chen’s Peak Shape method can be substituted in the equation (9) to find the value of frequency factor \((S)\). The equation for \(S\) is

\[
S = \frac{BE}{kT_M} \exp \left(\frac{E}{kT_M}\right) \left[1 + (b-1) \frac{2kT_M}{E}\right]
\]

(9)

All the calculated trapping parameters using GCD method is given below in the Table 4.
Table 4. Trapping parameter by GCD Method of the fly ash samples exposed to Cs\textsuperscript{137} γ-irradiation.

| Sample      | Peak Temperature (°C) | Order of Kinetics (b) | Activation Energy (eV) | Frequency Factor \( S \) (s\textsuperscript{-1}) |
|-------------|-----------------------|-----------------------|------------------------|-------------------------------------------------|
| P+FA30% 35.08 mGy | 287.15               | 2.68                  | 1.16                   | 4.12\times10^{11}                                |
| P+FA30% 26.31 mGy | 249.87               | 9.71                  | 0.34                   | 2.71\times10^{4}                                |
| P+FA20% 17.54 mGy | 261.19               | 7.28                  | 0.4                    | 7.84\times10^{4}                                |
| P+FA20% 8.77 mGy  | 266.61               | 7.57                  | 0.59                   | 4.21\times10^{6}                                |
| P+FA10% 26.31 mGy | 269.22               | 5.57                  | 0.43                   | 8.89\times10^{4}                                |
| P+FA10% 17.54 mGy | 292.69               | 0.62                  | 1.39                   | 3.34\times10^{13}                               |
| P+FA10% 8.77 mGy  | 265.8                | 3                     | 0.42                   | 5.46\times10^{4}                                |

4. Conclusion
Fly Ash mixed CaSO\textsubscript{4}: Dy Phosphor has a orthorhombic crystalline structure confirmed by matching the JCPDS XRD data. TL response dose response shows the sample P+FA10% shows nearly equal intensity as the traditional phosphor materials. Linear fit and linearity curves indicate that the sample P+FA10% and P+FA30% shows much more linear pattern. The activation energy calculated by the Chen’s Peak Shape method and GCD method were quite in analogy for P+FA10% sample. Here is very small gap between the \( E_A \) value calculated from experimental and theoretical methods. The frequency factor calculated by different methods is very much of same order. Thus the study suggests that P+FA10% sample are expected to show promising behavior if employed in radiation dosimeter applications at low dose. Apart from that we also suggest P+FA10% sample along with PFA sample which shows most linear curve with respect to dose applied to be exposed to high dose value for the identification of its high dose application as well.

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