Electron life time ($\tau$) in trap levels of Dy$^{3+}$ activated calcium aluminate: Implications in TL dosimetry

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Abstract. RE$^{3+}$ (Rare Earth) activated calcium aluminates (CaAl$_2$O$_4$) form an excellent class of phosphors for various applications. The multi-functionality of this class of phosphor is tailored by optimising the relative concentration of the trap-levels within the large band gap ($E_g=7.4$eV). In this paper we determine the trap-levels in Dy$^{3+}$ activated nanocrystalline calcium aluminate (CaAl$_2$O$_4$: Dy$^{3+}$) phosphor by rigorous analysis of the complex TL curves by computerised-glow-curve-deconvolution (CGCD) technique. We assume the kinetics to be the general order kinetic ($1 \leq b \leq 2$). Six trap levels have been identified with a lifetime ranging from 8 hours to 10$^8$ years at room temperature. The ones with $\tau_{300}$ = 6.46×10$^5$ years, 1.02×10$^7$ years and 9.02×10$^8$ years in principle can be the candidates for TL dosimetric application.

1. Introduction

Calcium aluminate (CaAl$_2$O$_4$) doped with rare earth elements have been proposed in various applications like persistence luminescence and radiation dosimetry [1-14]. In these works, the use of thermoluminescence (TL) has been realised by one and all. Among these, Bo Liu et al., Madhukumar et al., Ziyauddin et al. studied TL of CaAl$_2$O$_4$: Dy$^{3+}$ [12-14]. In all these works the possibility of applications is speculative, with no critical analysis of TL data. In this paper, we present the electron lifetime ($\tau$) in various trap levels present in nanocrystalline CaAl$_2$O$_4$: Dy$^{3+}$. Toward this end, we performed rigorous computerised-glow-curve-deconvolution (CGCD) of the whole curve of the phosphor between 50˚C and 450˚C. The large band gap of CaAl$_2$O$_4$ ($E_g = 7.4$ eV) act as an excellent host that exhibits a broad strong peak around 420˚C. Here we would like to point out that all standard commercial Thermoluminescence dosimeter (TLD) materials have large band gaps [15].
The broad intense TL peak spread over the range 250ºC - 450ºC is expected to be stable enough for dosimetry. We investigate that aspect in a completely new way by decoding it and investigate the dose response of the most intense peak observed over the range 0.5 to 20 Gy that covers the clinical range. The data presented provide a new way to study future TL dosimetric materials in terms of lifetime of charge in the proposed dosimetric peak.

2. Experimental

2.1. Sample Preparation

CaAl$_2$O$_4$:Dy$^{3+}$ phosphors with various concentrations of Dy$^{3+}$ doping have been prepared by combustion route following the work of Fumo et al. [16, 17]. The method is ideal for preparation of nanomaterial [18]. In this process, Dy$_2$O$_3$ is dissolved into 2 ml of conc. HNO$_3$ acid to convert it into dysprosium nitrate [Dy (NO$_3$)$_3$]. Aluminium nitrate [Al(NO$_3$)$_3$.9H$_2$O], calcium nitrate [Ca(NO$_3$)$_2$.4H$_2$O], urea, and dysprosium nitrate [Dy (NO$_3$)$_3$] (thus formed) weighed in stoichiometric ratio are dissolved in distilled water. The mixture is transferred to a pre-heated muffle furnace at 500º C. The solution starts boiling and forms a viscous solution. After complete dehydration of the mixture, it starts auto combustion along with evolution of a large volume of gas. We introduce the final product to a furnace at 950 ºC for 2 hours. This technique is well known for the number of materials [17]. We have synthesized CaAl$_2$O$_4$: (x) Dy$^{3+}$, where x = 0.01, 0.05, 0.1, 0.3 and 0.5 at. %. We find that 0.1 at% of Dy$^{3+}$ have the maximum TL count. In this work, we present the dosimetric probability of this combination with various doses ranging from 0.5 to 20 Gy, a zone that is good enough for clinical dosimetry.

2.2. Characterization

The prepared samples were characterized by XRD and EDX study. It confirms that the phosphors are CaAl$_2$O$_4$: Dy$^{3+}$ nanocrystalline powder of particle size 41.16 ± 2.2 nm. XRD data confirm the formation of nanocrystalline CaAl$_2$O$_4$: Dy$^{3+}$ with no other detectable phases of calcium aluminate or any other compound.

2.3. TL data acquisition

5 mg of the sample after excitation by $^{60}$Co Radioisotope (γ radiation in Teletherapy unit Bhabhatron II, India) is used for standard reference condition. We acquire the data in a Nucleonix TL/OSL1008 reader system, the heating rate used is 5ºC/sec. The background is also recorded and is used to eliminate the unwanted signal.

2.4. TL data analysis

In this we have deconvoluted the TL curve using the program of Chung version (1.0.3) [19]. It is user friendly. The major advantage is that it enables us to investigate high temperature TL peaks that has not been possible to record in equipment. The programme gives consistent values of the trapping parameters ($E$, $s$ and $b$). The programme also enables to integrate high temperature TL peak which could be recorded completely.

3. Results and discussion

The XRD data of the CaAl$_2$O$_4$:Dy$^{3+}$ (0.1at. %) is shown in figure 1(a) along with the standard data (ICDD 00-023-1036). It confirms the formation of CaAl$_2$O$_4$ with any detectable other phases of Calcium.

| TLD          | LiF: Mg, Ti | CaF$_2$:Dy | KMgF$_3$:Ce | BeO  |
|--------------|-------------|-------------|-------------|------|
| Band Gap (eV)| CaSO$_4$:Dy | Al$_2$O$_3$:C | Li$_2$B$_4$O$_7$:Mn | C (diamond) |
|              | 9.5         | 8.7         | 8.5         | 5.5  |

Table 1. Materials accepted as TLDs & their band gap ($E_g$)
Aluminate or starting compounds. The particle size as obtained by Scherrer’s formula is found to be 41.16 ± 2.2 nm. The EDX data in figure 2(b) shows that the concentration of Dy\(^{3+}\) to be 0.11%. It confirms with an experimental input concentration of Dy\(^{3+}\) doping the synthesized.

TL curves of CaAl\(_2\)O\(_4\): Dy\(^{3+}\) (0.1at. %) excited with various doses of γ ray (0.5, 1, 3, 5, 10 and 20 Gy) are shown in figure 2. It shows the presence of distinctively separated TL peaks in zone 50ºC to 250ºC and between 250ºC to 450ºC. Because of experimental limitations it has not been possible to record the entire high temperatures zone completely. The result of CGCD of two typical doses excitation, namely 0.5 Gy and 20 Gy are shown in figure 3. The best fit TL parameters are presented in table 2. The result has shown very good consistency. It is seen that TL peaks that are stable are good enough for TL dosimetric application. The most intense peak occurs at 410.42 ± 9.86 ºC.

![Figure 1](image1.png)

**Figure 1.** (a) XRD of CaAl\(_2\)O\(_4\):Dy\(^{3+}\) after annealing at 950 ºC and standard ICDD 00-023-1036. (b) EDX Data of CaAl\(_2\)O\(_4\):Dy\(^{3+}\).

![Figure 2](image2.png)

**Figure 2.** TL Curve of CaAl\(_2\)O\(_4\):Dy\(^{3+}\) (0.1at. %) γ ray excitation of various doses of 0.5, 1, 3, 5, 10 and 20Gy
Figure 3. CGDC of TL Curve of CaAl$_2$O$_4$:Dy$^{3+}$ excitation of (a) 0.5 Gy (b) 20 Gy of γ radiation

Figure 4. DRC of CaAl$_2$O$_4$:Dy$^{3+}$ excitation of various doses of γ radiation at heating rate 5°C/sec

Table 2. Calculated TL parameters of CaAl$_2$O$_4$:Dy$^{3+}$

| Dose (Gy) | Peak | $E$ (eV) | $s$ | $b$ | $T_{max}$ °C | $I$ (Norm) | $\tau_{300}$ | FOM%    |
|-----------|------|----------|-----|-----|-------------|------------|-------------|---------|
| 0.5       | i    | 1.07     | 1.65×10$^{10}$ | 2   | 225         | 3          | 1.95×10$^{12}$ Years | 1.40    |
|           | ii   | 1.23     | 1.04×10$^{10}$ | 2   | 306         | 14         | 1.47×10$^{10}$ Years |         |
|           | iii  | 1.30     | 7.31×10$^{09}$ | 2   | 346         | 34         | 3.31×10$^{09}$ Years |         |
|           | iv   | 1.41     | 5.79×10$^{09}$ | 2   | 400         | 100        | 2.37×10$^{08}$ Years |         |
| 20        | i    | 1.05     | 2.22×10$^{10}$ | 2   | 310         | 6          | 7.64×10$^{09}$ Years |         |
|           | ii   | 1.21     | 1.01×10$^{10}$ | 2   | 350         | 28         | 6.46×10$^{08}$ Years | 0.30    |
|           | iii  | 1.28     | 1.01×10$^{09}$ | 2   | 385         | 67         | 1.02×10$^{07}$ Years |         |
|           | iv   | 1.42     | 2.88×10$^{09}$ | 2   | 426         | 100        | 9.02×10$^{06}$ Years |         |
4. Conclusion
The most intense TL peak that occurs in the region 410.42 ± 9.86 ºC is found to be ideal for TL
dosimetric application in the range 0.5 to 20Gy. The computer software used for CGCD is capable of
integrating the TL peaks, even though we could not record the whole curve.

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