

## Thermoluminescence dosimetry of rare earth doped calcium aluminate phosphors

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**Abstract.** The thermoluminescence (TL) properties of calcium aluminate ( $\text{CaAl}_2\text{O}_4$ ) doped with different rare earth ions have been studied and their suitability for radiation dosimetry applications is discussed. It is observed that monocalcium aluminate doped with cerium is a good dosimeter having linear response up to about 4 kGy of radiation doses. Dopant concentration of 0.25 mol% cerium gives maximum TL emission. The well-defined single peak observed at 295°C can be advantageously used for high temperature dosimetry applications.

**Keywords.** Photoluminescence; thermoluminescence; radiation dosimetry.

### 1. Introduction

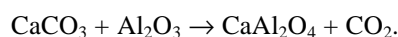
Thermoluminescent materials are used as passive dosimeters in a wide range of radiological applications. Alkaline earth aluminate ceramics are important host materials that have been prepared and studied by several researchers for luminescence applications (Matsuzawa *et al* 1996). Alkaline earth aluminate belongs to the spinel group of minerals ( $\text{MA}_2\text{O}_4$ ) (Dekkers and Woensdregt 2002) with general chemical composition,  $\text{AB}_2\text{O}_4$ , where A is a divalent atom such as  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and B is a trivalent atom such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ . As the metal ions of  $\text{AB}_2\text{O}_4$  are changed, the ionic ratios ( $A_2^+/B_3^+$ ) change and the symmetry of unit cell can change. The ideal spinel crystallizes in the cubic space group  $Fd\bar{3}m$  with 8 tetrahedral *a* sites and 16 octahedral *d* sites (Schipper *et al* 1993). The usual anions are oxygens and are located on the 32 *e* sites arranged in cubic close packed layers. The unit cell contains eight molecules of  $\text{AB}_2\text{O}_4$ . In the normal spinel structure, all the divalent cations are located on tetrahedral *a* sites, while all trivalent cations are located exclusively on octahedral *d* sites.

Calcium aluminate crystals can also exist in monoclinic as well as orthorhombic structures (Dougill 1957). Many researchers have studied  $\text{CaAl}_2\text{O}_4$  as an important constituent of cementitious compositions (Mohamed and Sharp 1997). Of late, the thrust is on its use as luminescent host. Several reports dealing with the luminescence studies of  $\text{SrAl}_2\text{O}_4$ ,  $\text{BaAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$  are available

in the literature (Jorma and Hogne 2001). However, there are very few reports dealing with the use of  $\text{CaAl}_2\text{O}_4$  as a TL material. In this paper, we report the thermoluminescent properties of calcium aluminate doped with different rare earth ions ( $\text{CaAl}_2\text{O}_4:\text{RE}$ ) to find out its suitability in dosimetry applications.

### 2. Experimental

Calcium aluminate phosphors were prepared by traditional ceramic (solid state) synthesis method. The reaction involved can be represented as



Stoichiometric amounts of  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  were weighed taking into account different concentrations of the dopants. To this mixture, the required weight of rare earth oxide was added and the resultant mixture was thoroughly mixed in a wetting medium for about 2 h. The mixture was dried in an air oven. The dry powder thus obtained was calcined at 900°C for 4 h in an electric muffle furnace. This was further heated up to 1250°C in a high temperature furnace and retained at that temperature for 7 h.

Samples containing dopants, Ce, Dy and Sm, in different concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mol% were prepared. All samples were examined by X-ray diffraction to ascertain the phase formation.

Phosphors were given a  $^{60}\text{Co}$  gamma dose of 1 Gy before recording TL spectrum. 10 mg of irradiated powder was used for TL measurements. TL measurements were carried out

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using Nucleonix make TL reader. The PM tube employed was 9924 B type. This tube has sufficient response over a wide spectral range. Glow curves were recorded with a heating rate of 4°C/s. Photoluminescence (PL) studies were carried out to study the type of trapping centres present in the crystal lattice. Hitachi (F-4000) Fluorescence Spectrophotometer was used for PL studies.

### 3. Results and discussion

The XRD pattern obtained for  $\text{CaAl}_2\text{O}_4$  phosphor prepared in this study is shown in figure 1. The spectrum matches with the data reported in JCPDS file No. 23-1036. It has a monoclinic structure with space group  $P21/c$  with cell dimensions:  $a = 8.69800$ ,  $b = 8.09200$ ,  $c = 15.20800$  and  $\alpha = 90.00$ ,  $\beta = 90.14$ ,  $\gamma = 90.00$ . Table 1 shows a comparison of  $d$  values obtained in the XRD spectrum with the standard. Figure 2 shows TL glow curves of  $\text{CaAl}_2\text{O}_4$  doped with different RE ions. The undoped sample gives no TL emission.  $\text{CaAl}_2\text{O}_4:\text{Dy}$  (0.1 mol%) shows a sharp intense peak at 110°C with a minor peak at 282°C.  $\text{CaAl}_2\text{O}_4:\text{Sm}$  (0.1 mol%) shows a major peak at 182°C with a minor peak at 276°C.  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) shows an

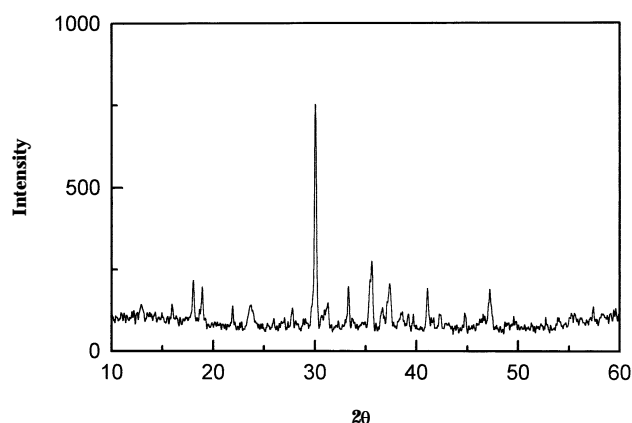


Figure 1. XRD pattern of  $\text{CaAl}_2\text{O}_4$  phosphor.

Table 1. XRD data of  $\text{CaAl}_2\text{O}_4$  (experimental and reported).

	$d_{\text{exptl}}$	$I/I_{0\text{exptl}}$	$d_{\text{JCPDS}}$	$I/I_{0\text{JCPDS}}$	$hkl$
1	5.535	24	5.530	6	012, 111
2	4.917*	20			
3	4.681	18	4.670	25	112, 112
4	4.052	10	4.040	10	020
5	3.763	13	3.710	16	211, 211
6	3.208	8	3.200	10	114, 114
7	2.973	100	2.971	100	123, 123
8	2.860	4	2.859	2	204
9	2.684	21	2.682	2	311
10	2.521	43	2.518	35	303
11	2.403	19	2.399	25	313
12	2.195	18	2.194	10	206
13	1.924	18	1.914	10	420

\*Not identified.

intense well defined peak at 295°C. It is observed that TL intensity of Ce doped phosphor is very high compared to Dy and Sm doped phosphors. The sensitivity of Ce doped phosphor is nearly thrice as that of Dy and Sm doped ones. The peak observed at 110°C for Dy doped one is not good for dosimetry applications as its fading rate will be very high. Also the major peak at 182°C observed for Sm doped phosphor is also not good enough for dosimetric applications due to its low intensity. The well-defined single peak obtained at 295°C in the case of Ce doped phosphor can be used for dosimetry applications. It is seen that 0.25 mol% of Ce gives maximum TL emission (table 2).

#### 3.1 Photoluminescence studies

The photoluminescence studies were carried out only on Ce doped phosphors since it was observed that only Ce doped phosphor satisfies the essential requirements of a good TL dosimeter. The excitation spectrum of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) scanned for emission wavelength, 350 nm, is shown in figure 3. The bands observed at 300 and 315 nm are assigned to the transitions from  $4f$  to the lowest Stark level of  $5d$  state of  $\text{Ce}^{3+}$  ions (Kutty 1990). The

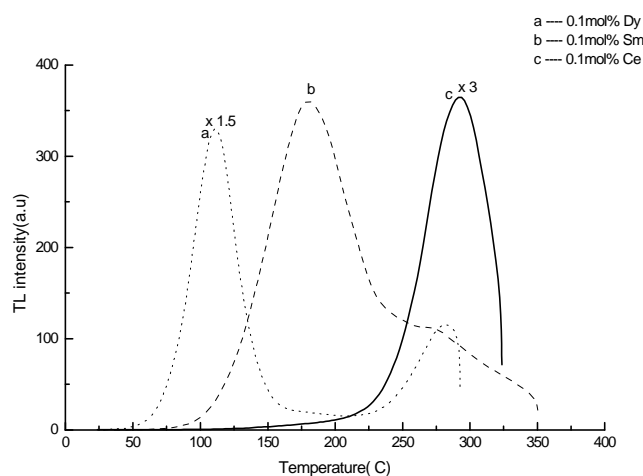


Figure 2. TL glow curves of a.  $\text{CaAl}_2\text{O}_4:\text{Dy}$ , b.  $\text{CaAl}_2\text{O}_4:\text{Sm}$  and c.  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol% each). Dose 1 kGy.

Table 2. TL intensity of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  phosphor with variation in Ce concentration.

Ce concentration (mol%)	Relative TL intensity (peak height) (peak at 295°C)
0.05	0.34
0.10	0.45
0.15	0.52
0.20	0.63
0.25	1.00
0.30	0.83
0.35	0.68
0.40	0.55
0.50	0.43

multi-peaks observed in the excitation spectrum indicate that different defect related traps are present in the crystal lattice. The defect related trapping centres could be filled by either electron transport through conduction band or by tunneling through  $5d$  states. Figure 4 shows the emission spectrum of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  obtained for an excitation wavelength, 315 nm. A broad emission band ranging from 330–350 nm together with a weak band at 467 nm is seen. The broad emission of  $\text{Ce}^{3+}$  ions is due to  $5d-4f$  transitions in nature in which the  $5d$  orbital is not well shielded from the crystal field as the  $4f$  orbital is, because the  $5d$  orbital is situated further away from  $4f$ . The luminescence of  $\text{Ce}^{3+}$  is very intense since the transitions involved are parity allowed (Claude 1984). These transitions take place from the excited states to the  ${}^2F_{5/2}$  and  ${}^2F_{7/2}$  ground states of  $\text{Ce}^{3+}$  ions.

### 3.2 Effect of radiation dose on TL intensity

Figure 5 shows TL response of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) irradiated with different doses of  $\gamma$ -radiations. The height

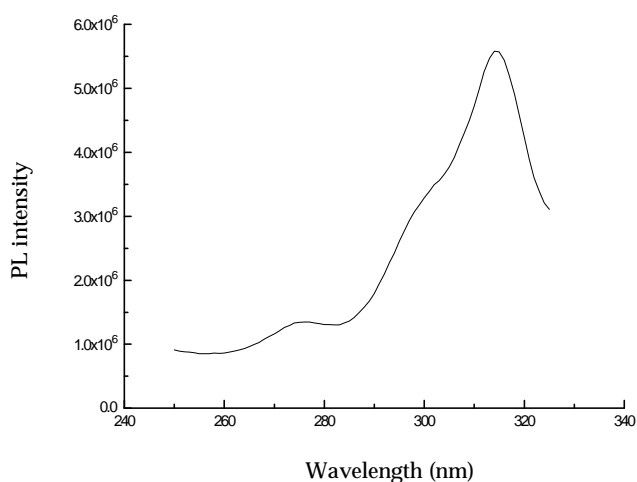


Figure 3. Excitation spectrum of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) ( $I_{\text{em}} = 350$  nm).

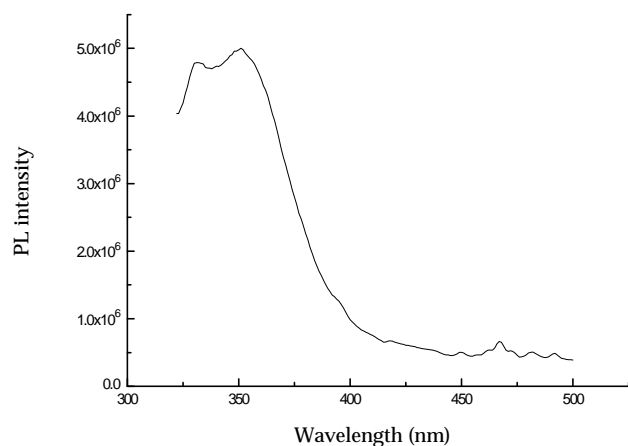


Figure 4. Emission spectrum of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) ( $I_{\text{ex}} = 315$  nm).

of 295°C peak is plotted as a function of exposure. It is seen that the TL response of the phosphor is almost linear for low doses and tending to saturate at higher doses above 4 kGy. Hence this phosphor can be used for dose measurements up to 4 kGy.

### 3.3 Fading

Figure 6 shows the variation of TL response with storage duration of irradiated  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%) phosphor. Periodic checking of TL response shows 5% fading of 295°C peak over a period of two weeks. This is well within the accepted rate of fading of standard TL phosphor (Nambi 1977; Mckeever 1985).

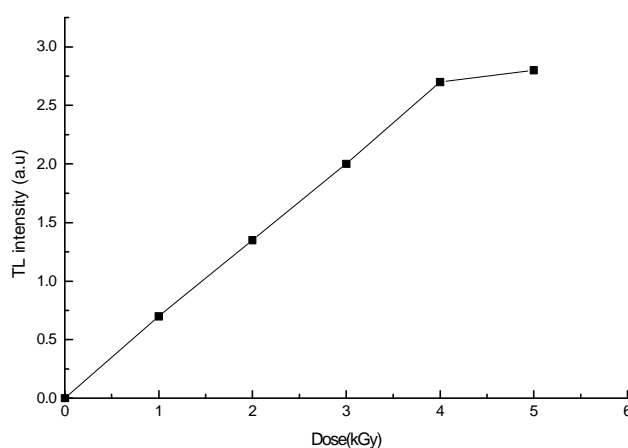


Figure 5. Dose response curve of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%).

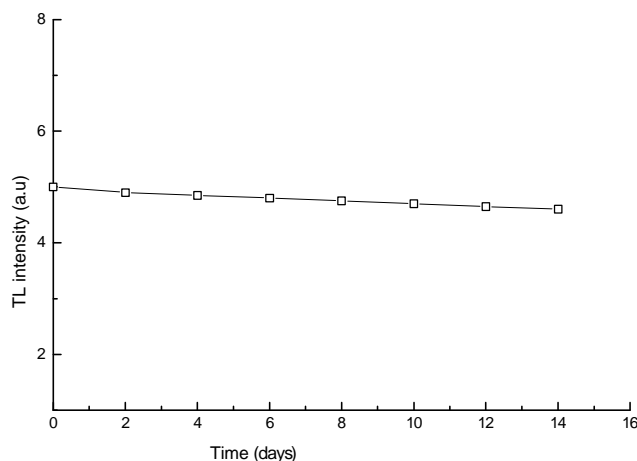


Figure 6. Fading characteristic of  $\text{CaAl}_2\text{O}_4:\text{Ce}$  (0.1 mol%).

Table 3. Comparison of TL response.

Phosphor	Most intense TL peak temperature (°C)	Relative TL intensity
$\text{CaSO}_4:\text{Dy}$	230	1
$\text{CaAl}_2\text{O}_4:\text{Ce}$	295	0.5

### 3.4 Sensitivity

Table 3 gives a comparison of TL response of  $\text{CaAl}_2\text{O}_4$ :Ce phosphor with the standard one ( $\text{CaSO}_4$ :Dy) used for radiation dosimetry applications. It is observed that the sensitivity of  $\text{CaAl}_2\text{O}_4$ :Ce phosphor is only 50% as that of  $\text{CaSO}_4$ :Dy, when both were exposed to same dose of radiation.

### 4. Conclusions

From the PL and TL studies it is confirmed that  $\text{Ce}^{3+}$  doped  $\text{CaAl}_2\text{O}_4$  is a good material for dosimetry applications. The emission centres are  $\text{Ce}^{3+}$  ions. The fading rate is very small and its TL response is linear up to radiation dose of 4 kGy. Though TL sensitivity of  $\text{Ce}^{3+}$  doped  $\text{CaAl}_2\text{O}_4$  is less when compared to the widely used  $\text{CaSO}_4$ :Dy commercial phosphor, it should be noted that the 295°C peak observed in  $\text{CaAl}_2\text{O}_4$ :Ce can be used for high temperature dosimetry applications with more advantage (TL peak of  $\text{CaSO}_4$ :Dy is at about 230°C only).

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### References

- Claude F 1984 *Luminescence—encyclopedia of inorganic chemistry* (New York: Academic Press)
- Dekkers R and Woensdrecht C F 2002 *J. Cryst. Growth* **236** 441
- Dougill M M 1957 *Nature* **180** 292
- Jorma H and Hogne J 2001 *J. Alloys Compounds* **323–324** 326
- Kutty T R N 1990 *Mater. Res. Bull.* **25** 485
- Matsuzawa T, Aokiy Y, Takeuchi N and Murayama Y 1996 *J. Electrochem. Soc.* **143** 2670
- Mckeever S W S 1985 *Thermoluminescence of solids* (Cambridge University Press)
- Mohamed B M and Sharp J H 1997 *J. Mater. Chem.* **7** 1595
- Nambi K S V 1977 *Thermoluminescence: Its understanding and applications* (Sao Paulo, Brazil: IEA Informacao)
- Schipper W J, Hamelink J J, Langeveld E M and Blasse G 1993 *J. Phys. D: Appl. Phys.* **26** 1487