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Thermally stimulated luminescence studies in combustion synthesized polycrystalline aluminum oxide

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Abstract. **Synthesis of materials by combustion technique results in homogeneous and fine crystalline product. Further, the technique became more popular since it not only saved time and energy but also was easy to process. Aluminum oxide phosphor was synthesized by using urea as fuel in combustion reaction. Photoluminescence (PL) and thermally stimulated luminescence (TSL) characteristics of γ-irradiated aluminum oxide samples were studied. A broad PL emission with a peak at ~465 nm and a pair of strong and sharp emissions with peaks at 679 and 695 nm were observed in γ-rayed samples. The PL intensity was observed to increase with increase in γ-ray dose. Two prominent and well resolved TSL glows with peaks at 210°C and 365°C were observed in all γ-irradiated Al_2O_3 samples. The TSL intensity was also found to increase with increase in γ-ray dose. The TSL glow curves indicated second order kinetics.**

Keywords. **Photoluminescence; thermoluminescence; gamma irradiation; colour centres.**

1. Introduction

Thermally stimulated luminescence (TSL), also called thermoluminescence (TL), is extensively used as a technique in dosimetry. The energy absorbed by a phosphor on being exposed to some ionizing radiation is released as light on subsequently heating it. The intensity of light emitted by the phosphor on being heated gives an idea of the concentration of defect centres caused by the interaction of ionizing radiation with matter. Further, TSL is a convenient technique to understand the charge trapping and detrapping mechanisms that result from the interaction of the radiation with the existing defects in material. However, there is no simple model or explanation for TSL mechanism because of the wide variety of processes involved. Aluminum oxide was one of the earlier materials studied for its possible application as a radiation dosemeter owing to its superior thermal and chemical stability and low effective atomic number (Rieke and Daniels 1957). Further, it is a highly sensitive luminescence dosemeter material and it has been the subject of many studies in thermo and optically stimulated luminescence. It constitutes a class of TSL phosphors with good performance, especially when doped with carbon. A good amount of work on TSL of transparent Al_2O_3 and $Al_2O_3:C$ crystals have been reported (Summers 1984; McKeever *et al* 1999; Chithambo *et al* 2002). The powder form of this phosphor has some special advantages such as good flexibility of dosimeter size, shape etc. Synthesis of oxide phosphors has been achieved by a variety of routes such as solid-state reactions, sol–gel techniques (Rao 1993), hydroxide precipitation (Kinsman *et al* 1994), hydrothermal synthesis (Veitch 1991) and combustion synthesis (Kingsley and Patil 1988; Zhang and Stangle 1994). Combustion synthesis is particularly an easy, safe and rapid production process besides energy and time savings. This quick, straightforward process can be used to produce homogeneous, high-purity, crystalline oxide ceramic powders (Kingsley and Patil 1988). The preparation of aluminum oxide by combustion process using different fuels results in different particle sizes. For example, if glycine and hydrazine are used as fuels they yield nanoparticles (Mimani and Patil 2001). The grain size affects the sensitivity, dose response and other parameters of TSL glow curves. A good compromise is to use powders with grain sizes between 75 and 200 μm (Bos 2001). In the present investigation, urea is used as fuel which yields polycrystalline aluminum oxide. The objective of our present investigation is to understand the photoluminescence (PL) and thermoluminescence behaviours of combustion synthesized polycrystalline γ-irradiated aluminum oxide.

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2. Experimental

Polycrystalline aluminum oxide was synthesized by combustion technique based on the procedure described elsewhere (Nagabhushana *et al* 2007). As synthesized aluminum oxide was grained into a fine powder using an agate mortar and 50 mg of each sample was weighed using a digital balance (Sartorius) with ± 0·1 mg accuracy. These samples were packed in black paper and were irradiated with γ-rays (^{60}Co) for the dose ranging from 1·251 to 7·527 KGy. PL studies were performed using excitation at 325 nm light from He–Cd laser (KIMMON) and Mechelle900 spectrograph in the range 200–1100 nm wavelength region. The PL setup had a cooled CCD array-based detection system. The laser light was made to incident on the sample at 45° and the luminescence light was collected using a collector assembly and transmitted to the spectrograph through optical fibre for detection and analysis. The TSL measurements were carried out at a heating rate of 5° Cs^{-1} using PC based TSL analyser system (Nucleonix Systems Pvt. Ltd., Hyderabad, India).

3. Results and discussion

Photoluminescence emission spectra of combustion synthesized pristine and γ-irradiated polycrystalline aluminum oxide are shown in figure 1. A broad and weak emission in the range 425–600 nm and a pair of sharp emissions with peaks at 679 and 695 nm are observed in both pristine as well as γ-rayed samples. The sharp emissions are commonly known as $R1$ and $R2$ (doublet) lines of Cr^{3+} impurity substituting Al site in aluminum oxide and they are assigned to a well known radiative transition $^2E \rightarrow {}^4A_2$ of substitutional Cr^{3+} ions (Toyoda *et al* 1998). When the samples are exposed to γ-rays, PL emission at 679 and 695 nm is enhanced besides a well resolved blue emission at ~ 465 nm. The ~ 465 nm emission may be attributed to F_2^+-centres (two oxygen vacancies with three electrons) (Nagabhushana *et al* 2007). Further, the intensity of R lines in pristine sample is observed to be lower when compared to that in γ-rayed ones. It is believed that the increase in emission intensity of R line might be due to re-absorption of 465 nm light into the absorption bands of the Cr^{3+} ions (McKeever *et al* 1999).

Figure 2 shows the thermostimulated luminescence glow curves of combustion synthesized aluminum oxide γ-irradiated for doses in the range 1·251–7·527 KGy. The glow curves clearly show two well resolved and well separated TSL glow peaks, one at 210°C (T_{g1}) and another at 365°C (T_{g2}). Zhang and coworkers (Zhang *et al* 2006) studied TSL and optical absorption (OA) of pure α-Al_2O_3 crystals under γ-irradiation. They reported the OA bands with peaks at 205 and 230 nm and they were attributed to F-centre and F^+-centres, respectively. Further, the TSL of 100 Gy γ-rayed samples showed a TSL glow with peak at 210°C and they attributed it to the relaxation of the F-centre electron from 3P excited state to the 1S ground state (Zhang *et al* 2006). The first TSL glow with peak at 210°C observed in the present work may be attributed to the F-centres. Kortov *et al* (2004) recorded TSL of electron irradiated Al_2O_3 in the temperature range 327–527°C. This high temperature glow peak was attributed to the presence of deep traps which are oxygen vacancies produced in the anion sublattice of aluminum oxide by ionizing radiation (Kortov *et al* 2004). In the present investigations, it is believed that F_2^+-centre is responsible for this high temperature glow peak. However, it should be mentioned that this point needs more detailed investigations using other techniques such as thermostimulated conductivity, thermoluminescence emission, electron spin

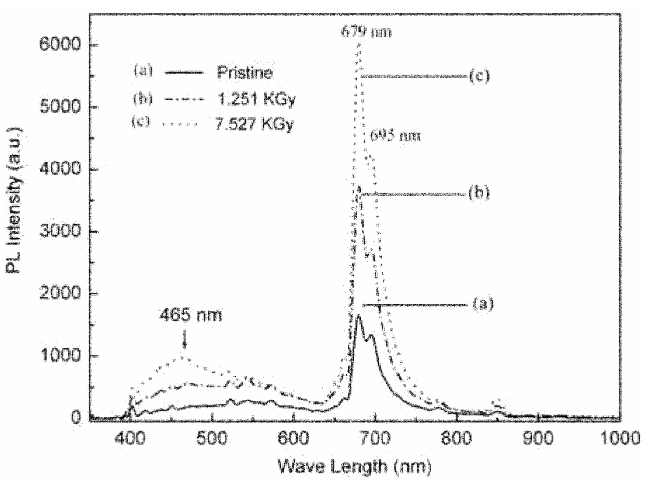

Figure 1. Photoluminescence emission (λ_{ex} = 320 nm) spectra of combustion synthesized pristine and γ-irradiated polycrystalline aluminum oxide.

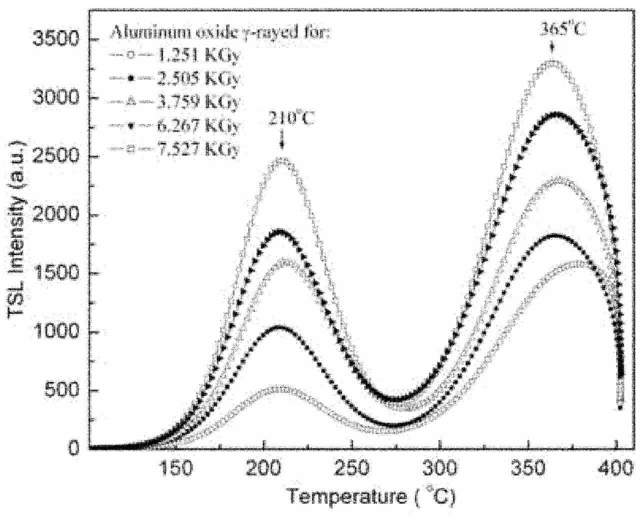

Figure 2. Thermostimulated luminescence glow curves of combustion synthesized γ-irradiated aluminum oxide (β = 5° Cs^{-1}).

resonance, photoacoustic studies/optical absorption etc in order to understand the TSL mechanism leading to generation and trapping of defect centres due to ionizing radiation and light emission in aluminum oxide during thermal stimulation.

Figure 3 shows the variation of TSL intensity with γ-ray dose in combustion synthesized aluminum oxide. It is found that the TSL intensity in combustion synthesized alumina increases linearly with increase in dose. The low temperature glow peak (T_{g1}) temperature is observed to be steady for the entire range of γ-ray dose. That is, no peak shift was observed at low temperature TSL peak (T_{g1}). But, it is observed that the high temperature TSL glow peak (T_{g2}) slightly shifts towards lower temperature side with increase in γ-ray dose as can be seen from figure 3. However, from the glow curves, it is observed that the area under the T_{g1} and T_{g2} increases linearly with increase in γ-ray dose. The shift in TSL glow peak position and width might be due to the occupancy of deep traps, since a step annealing procedure gradually shifts the peak back to the original position. The physics of changes in the peak temperature are yet to be understood, but part of the shift to low temperature at high doses may be attributed due to the kinetics of processes as suggested by Yukihara and coworkers (Yukihara *et al* 2004).

The evaluation of kinetic parameters known as trapping parameters, i.e. activation energy (E) of the traps involved in TSL emission, order of kinetics (b) and frequency factor (s) associated with the glow peaks of TSL are important aspects of TSL studies. Any complete

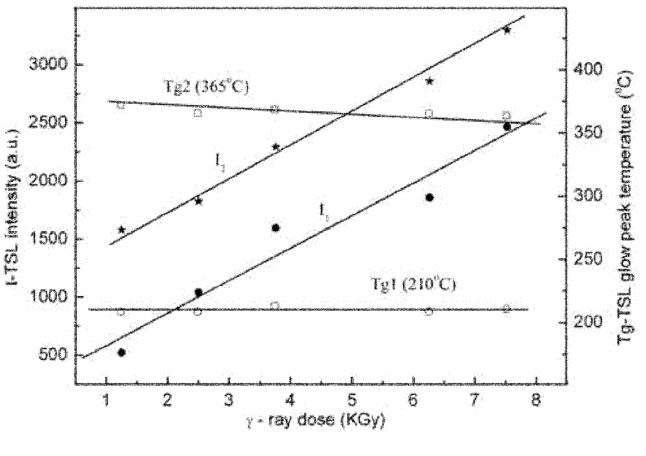

Figure 3. Variation of TSL intensity and TSL glow peak temperature with γ-ray dose in combustion synthesized aluminum oxide ($\beta = 5°\ Cs^{-1}$).

Table 1. Kinetic parameters of as prepared aluminum oxide irradiated with γ-rays for 7·527 KGy obtained by using the glow curve shape method (modified by Chen).

T_g	T_m (°C)	μ_g	b	E (eV)	S (s^{-1})
1	210	0·51	2	1·01	$7{\cdot}51 \times 10^{9}$
2	365	0·49	2	1·52	$2{\cdot}68 \times 10^{11}$

description of the TSL characteristics of TSL material requires the knowledge of these parameters. To determine the order of kinetics, the form factor (symmetry factor), μ_g, [$\mu_g = (T_2 - T_m)/(T_2 - T_1)$], which involves T_1 and T_2 are calculated where these are the temperature corresponding to the half of the maximum intensities on either side of the glow peak maximum (T_m). Theoretically, form factor which ranges between 0·42 and 0·52, is close to 0·42 for first order kinetics and 0·52 for second order kinetics (Horowitz *et al* 2001). The form factors of T_{g1} and T_{g2} glows irradiated with 7·527 KGy are found to be 0·51 and 0·49, respectively. The trap parameters are calculated using glow curve shape method (modified by Chen) and tabulated in table 1. The detailed description of calculations is discussed in our previous communication (Nagabhushana *et al* 2008). The activation energy and frequency factors are estimated to be 1·01 eV, 1·52 eV and $7{\cdot}51 \times 10^9\ s^{-1}$, $2{\cdot}68 \times 10^{11}\ s^{-1}$ for T_{g1} and T_{g2}, respectively.

4. Conclusions

Photoluminescence and thermoluminescence of polycrystalline aluminum oxide phosphor synthesized by combustion technique using urea as fuel are studied. The γ-rayed samples show a broad PL emission with peak at 465 nm and doublet Cr^{3+} emission at 679 and 694 nm are observed. The 465 nm emission is attributed to F_2^+ defect centre formed during γ-irradiation. Two well resolved TSL glows with peaks at 210°C and 365°C are observed in γ-irradiated samples. The low temperature TSL glow peak (210°C) is attributed to F-centres and the high temperature TSL glow peak (365°C) is tentatively attributed to F_2^+ defect centre. The order of kinetics for these two TSL glow peaks for 7·527 KGy γ-rayed samples are calculated to be 0·51 and 0·49, respectively which confirm the second order kinetics. The high temperature TSL peak (T_{g2}) shifts slightly towards lower temperature with increase in the doses. The TSL intensity in the present powder form of Al_2O_3 increases with increase in γ-ray dose. These studies suggested that the TSL glow peak at 210°C in combustion synthesized aluminum oxide can be considered as radiation dosimetric peak after studying the dosimetric characteristics viz. fading, annealing behaviour, energy response, reproducibility etc.

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