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TL, OSL and PL studies in Al_2O_3:Si,Ti phosphor

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Abstract

Thermoluminescence (TL) and optically stimulated luminescence (OSL) characteristics of Al_2O_3:Si,Ti phosphor have been studied. Its TL and OSL sensitivity is 1/9th and 1/120th respectively, compared to that of Al_2O_3:C commercial phosphor. Its dose vs. OSL response is linear up to 5 Gy, beyond which it shows slight supralinearity up to a dose of 3×10^3 Gy. The main TL peak at about 276 °C shows maximum emission at about 405 nm. Deconvolution of continuous-wave OSL (CW-OSL) decay curve suggests three individual CW-OSL decay components corresponding to photoionization cross-sections of 1.2×10^{-18}, 2.7×10^{-19}, 7.0×10^{-20} cm^2. For an absorbed dose of 2×10^3 Gy followed by annealing at 530 °C for 20 min and a test gamma dose of 1 Gy, the radiation-induced sensitization factor for the CW-OSL response was 2.1. This can be explained by filling of deep traps ($>$ 530 °C). The photoluminescence (PL) spectrum of Al_2O_3:Si,Ti shows emission at 410 nm for excitation at 240 nm. From PL measurements we could not detect any F and F^+ center emissions in the Al_2O_3:Si,Ti phosphor which is prepared under highly oxidizing conditions. The emission around 410 nm matches the emission reported in the literature for Ti^{4+} ions in Al_2O_3.

Keywords: Al_2O_3:Si,Ti; Optically stimulated luminescence; Photoluminescence; Thermoluminescence; Phosphor; Photoionization cross-section

1. Introduction

Al_2O_3:Si,Ti prepared by sintering in air was developed earlier by Mehta and Sengupta (1976a, 1977), and reported as a sensitive thermoluminescent material. Under the highly oxidizing conditions used in the preparation of Al_2O_3:Si,Ti, titanium is likely to be in the Ti^{4+} state (McKeever et al., 1995; Evans, 1994; Molnar et al., 2001). The phosphor in the grain size range 74–149 µm (mesh 100–200) has been found useful in radiation dosimetry (Mehta and Sengupta, 1976a). Thermoluminescence (TL) glow peaks at 50, 125, 250, 325, 475 and 625 °C with emission in blue region (420 nm) have been reported for the heating rate of 3 °C/s (Mehta and Sengupta, 1976b). Out of these, TL peak at 250 °C was observed to be most intense having a detection threshold of 0.01 mGy. Detailed TL studies on Al_2O_3:Si,Ti, such as dose vs. TL response, phototransferred thermoluminescence (PTTL), ultraviolet (UV) induced TL and radiation-induced sensitization, had been reported earlier by Mehta and Sengupta (1976a, b, 1978). The TL peaks at 250 and 475 °C are reported to exhibit radiation-induced sensitization due to the influence of the traps related to the 625 °C TL peak (Mehta and Sengupta, 1976a). McKeever (1985) states that "the mechanism of sensitization is closely related to the phenomenon of supralinearity and often the models which have been invoked to explain one can be used to explain certain features of the other." Therefore, it is worthwhile to investigate the sensitization effect in those phosphors, which show supralinearity in their dose response. Recently, Yukihara et al. (2003, 2004) reported that the TL and optically stimulated luminescence (OSL) of Al_2O_3:C have similar dose response to ionizing radiation, characterized by a linear–supralinear–saturation behavior with a decrease in the signal for doses higher than the saturation dose. They also report that high beta dose causes sensitization of the main TL peak (~177 °C) and OSL signal in Al_2O_3:C sample that was subsequently annealed at 400 °C and given a test beta dose. It was shown that the sensitization is related to filling of deep electron traps which become unstable at ~827–927 °C.

In the present investigation we report the OSL characteristics of Al_2O_3:Si,Ti along with some TL and photoluminescence (PL) studies.

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2. Experimental method

The Al_2O_3:Si,Ti phosphor was prepared according to the procedure described by Mehta and Sengupta (1976a) and McKeever et al. (1995). All the samples used in the present study contained 300 ppm Si and 10 ppm Ti. The phosphor in the grain size range 100–200 mesh was selected for the present work.

Al_2O_3:Si,Ti phosphor powder was annealed at 900 °C for 30 min and was allowed to cool to room temperature by withdrawing the sample from the furnace and placing it on an alumina brick prior to irradiation. TL and OSL measurements were carried out using the TL and OSL readers described by Seethapathy et al. (1999) and Kulkarni et al. (2005, 2007). The TL glow curves were recorded at a constant heating rate of 4 °C/s. The OSL measurements were carried out at room temperature for gamma irradiated samples using an optical excitation unit, consisting of high intensity blue light emitting diode (LED) cluster with $\lambda_p = 470$ nm, $\Delta\lambda = 20$ nm incorporated in the TL/OSL reader. The light intensity at the sample was measured to be 45 mW/cm^2 for 350 mA DC current through the LED cluster employed during measurements. The GG-435 and UG-1 optical filters were used to prevent the stimulation radiation from reaching the photomultiplier tube (PMT). The luminescence intensity was recorded using a photon counting module interfaced to the computer through an RS-232 serial interface. TL and OSL sensitivities of Al_2O_3:Si,Ti were compared with commercial α-Al_2O_3:C phosphor purchased from Landauer Inc., USA. For studying radiation-induced sensitization, Al_2O_3:Si,Ti phosphor was irradiated with a gamma dose of 2×10^3 Gy, annealed at 530 °C for 20 min, and given a test gamma dose of 1 Gy, after which a TL or OSL measurements was carried out to determine the TL/OSL sensitivity (S). The TL/OSL sensitivity of the freshly annealed sample (S_0) at a test gamma dose of 1 Gy was also determined. The sensitization factor (S/S_0) was determined for TL as well as OSL measurements. Fluorescence spectra were recorded on FP-750 Spectrofluorometer (Jasco, Japan) having red sensitive WRE-362 PMT. The slit width was kept at 5 nm each for excitation and emission windows. TL emission spectra were recorded using the TL emission spectrometer with EMI 9924 PMT with S11 response described by Sanaye et al. (2003). In this system, TL emission could be recorded in the spectral range 320–650 nm. For recording TL emission, the temperature of the sample in the heater strip was maintained 60–70 °C less than T_{max} of TL peak under study so that fading of TL signal during the recording is not appreciable.

3. Results

Fig. 1 shows TL glow curves for Al_2O_3:Si,Ti and Al_2O_3:C phosphors. For a readout cycle up to 400 °C, Al_2O_3:Si,Ti has four TL peaks at 158, 191, 276, 355 °C whereas Al_2O_3:C has a prominent TL peak at 208 °C. Fig. 2 shows normalized continuous-wave (CW)-OSL decay curves for Al_2O_3:Si,Ti and Al_2O_3:C phosphors. TL sensitivity of Al_2O_3:Si,Ti was found to be 1/12th of the commercially available Al_2O_3:C for area integration between 75 and 320 °C, whereas it was 1/9th for area integration between 75 and 390 °C. The corresponding factor was 1/19th on the basis of peak height measurements of 276 °C TL peak in Al_2O_3:Si,Ti and 208 °C TL peak in Al_2O_3:C. OSL sensitivity of Al_2O_3:Si,Ti was found to be 1/120th of the Al_2O_3:C phosphor. It may be mentioned here that these numbers are only relevant in the equipment used in these measurements and under the conditions of the measurement (e.g., emission filters, heating rate, stimulation wavelength, etc.).

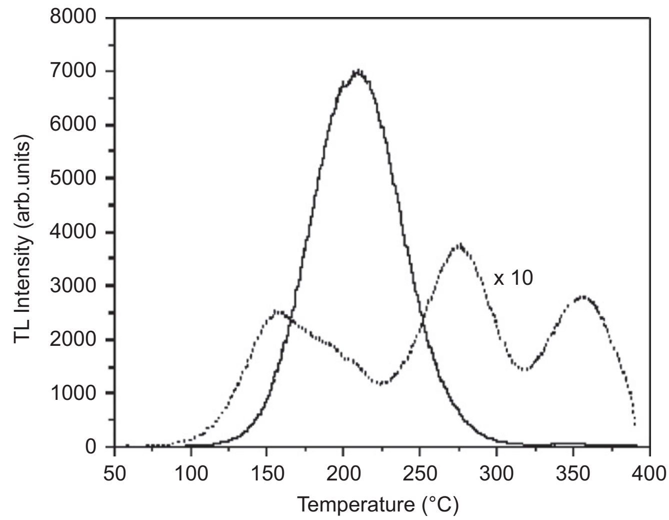

Fig. 1. TL glow curve of Al_2O_3:C (——) and Al_2O_3:Si,Ti (······) following a γ-ray dose of 0.5 Gy.

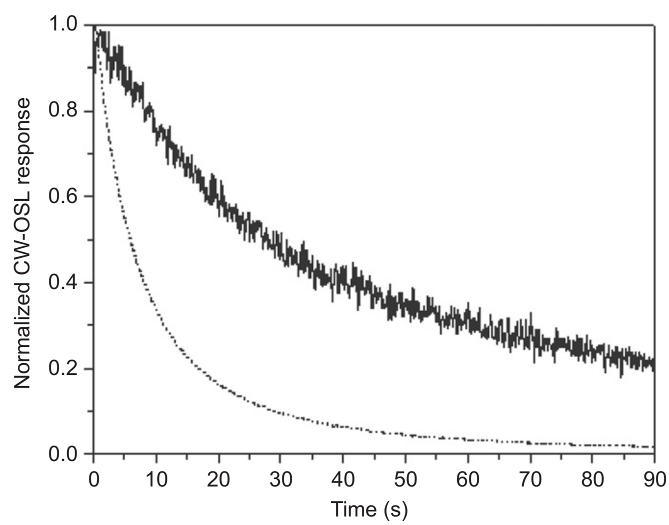

Fig. 2. CW-OSL decay curves of Al_2O_3:Si,Ti (——) and Al_2O_3:C (······) following a γ-ray dose of 0.5 Gy.

Fig. 3 shows dose vs. OSL response of Al_2O_3:Si,Ti in the dose range 0.1–10^4 Gy. It can be seen that the dose response is linear up to 5 Gy. For further increase in dose it shows slight supralinearity up to a dose of 3×10^3 Gy, beyond which it saturates.

Fig. 4 shows CW-OSL curve for Al_2O_3:Si,Ti for an absorbed dose of 20 Gy at a constant stimulation power of 20 mW/cm^2.

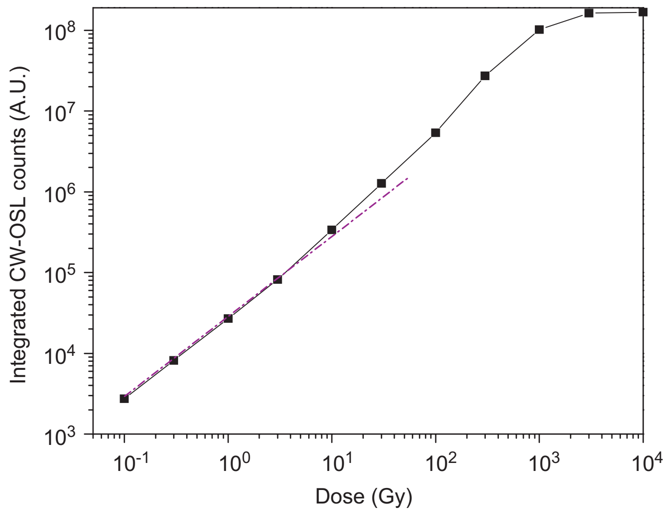

Fig. 3. CW-OSL intensity vs. dose response of Al_2O_3:Si,Ti.

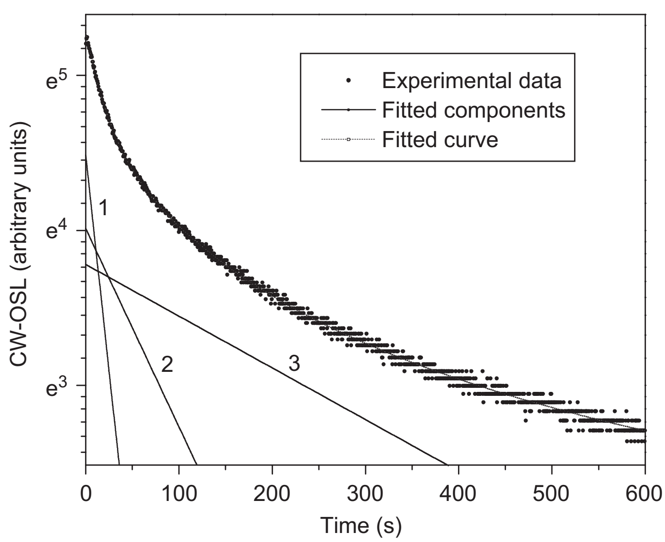

Fig. 4. CW-OSL of Al_2O_3:Si,Ti following a γ-ray dose of 20 Gy. Various components are obtained by curve fitting.

It can be seen from the results of curve fitting that the data can be described by superposition of three first-order components. The sum of the three components of the CW-OSL curve is shown by the fitted curve. The third-order fitted exponential decay curve can be represented by the following equation:

$$I_{\text{CW-OSL}} = A_1 \exp(-f_1 t) + A_2 \exp(-f_2 t) + A_3 \exp(-f_3 t), \quad (1)$$

where f_1, f_2 and f_3 are the excitation rates for the respective OSL traps having values 0.055, 0.0127 and 0.0033 s^{-1}, respectively, and A_1, A_2 and A_3 are constants having values 88.50, 55.23 and 43.81, respectively. The photoionization cross-section ($\sigma(\lambda)$) and decay constant ($\tau(\lambda)$) values of the three OSL traps, as obtained from the deconvolution of the experimental CW-OSL curve, are given in Table 1, along with the uncertainties for the evaluated values.

Table 1
Determination of photoionization cross-section for various OSL components in the CW-OSL curve

CW-OSL components	Decay constant τ (s)	Photoionization crosssection σ (cm^2)
1	18.0	1.2×10^{-18}(±2%)
2	78.0	2.7×10^{-19}(±5%)
3	299.0	7.0×10^{-20}(±8%)

Table 2
Radiation-induced sensitization factor (S/S_0) for TL and CW-OSL response of Al_2O_3:Si,Ti

S. No.	Al_2O_3:Si,Ti	S/S_0 factor
1	158 °C	2.9
2	276 °C	5.0
3	356 °C	6.6
4	CW-OSL response	2.1

Post-irradiation annealing at 530 °C; test dose = 1 Gy.

For an absorbed dose of 2×10^3 Gy followed by annealing at 530 °C, 20 min and test gamma dose of 1 Gy, radiation-induced sensitization factors for 276 and 355 °C TL peaks were 5.00 and 6.6, respectively (Table 2). For the CW-OSL after similar treatment, the radiation-induced sensitization factor was 2.1.

Figs. 5(a) and (b) show the excitation spectrum of Al_2O_3:Si,Ti for emission at 410 nm and emission spectrum for excitation at 240 nm, respectively.

Fig. 6 depicts the TL emission spectrum of Al_2O_3:Si,Ti after irradiation to 2 kGy gamma rays. The TL emission spectrum of the main TL peak at about 276 °C shows maximum emission at about 405 nm.

4. Discussion

Although the OSL sensitivity of Al_2O_3:Si,Ti is 1/120th compared to that of Al_2O_3:C, the wide dynamic range may open the possibility of using this material in high dose dosimetry, e.g., in irradiation of food products. The phosphor shows radiation-induced sensitization of 250 and 475 °C TL peaks which has been attributed to filling of deep traps (Mehta and Sengupta, 1977). The sensitized phosphor is expected to show enhanced sensitivity as well as nearly linear dose response, which could further extend its application in dosimetry.

The CW-OSL curve could be described by superposition of three first-order components. The data could be fitted satisfactorily using third-order exponential decay equation (Eq. (1)). It may be noted that on the basis of exponential nature of the isothermal decay of the TL glow peaks and no shift in peak position, Mehta and Sengupta (1977) have reported that TL peaks in the range 250–635 °C obey first-order kinetics.

For α-Al_2O_3:C crystals Akselrod et al. (1990) have reported that the F center has an emission around 420 nm when excited with 205 nm, whereas the emission of F^+ center is reported at 330 nm for excitation at 230 and 255 nm. In our PL studies, no excitation band at 205 nm was observed for emission

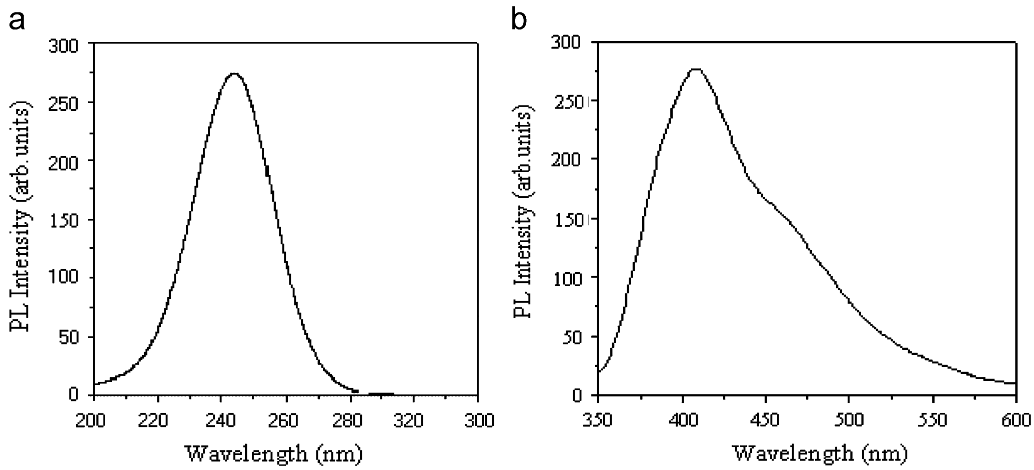

Fig. 5. Photoluminescence excitation and emission spectra of Al_2O_3:Si,Ti. (a) Excitation spectrum of Al_2O_3:Si,Ti measured at 410 nm. (b) Emission spectrum of Al_2O_3:Si,Ti for excitation at 240 nm.

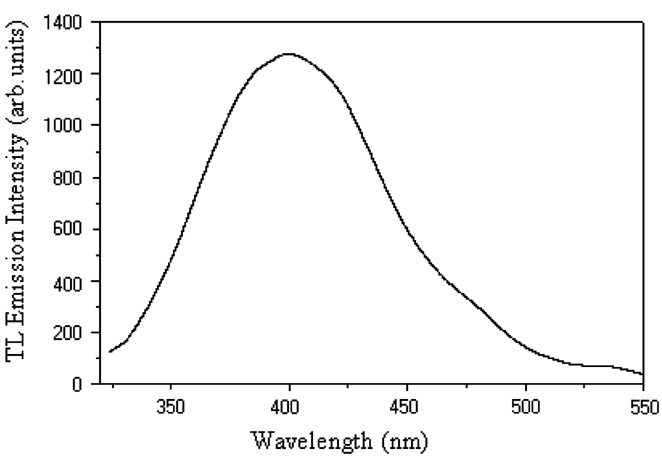

Fig. 6. TL emission spectrum of Al_2O_3:Si,Ti measured for 276 °C peak for a given dose of 2 kGy.

in the range 400–480 nm. Also no emission at 330 nm was observed for excitation at 230 and 255 nm. This rules out the presence of F and F^+ centers in as-prepared and gamma irradiated (2×10^3 Gy) samples. In this respect the Al_2O_3:Si,Ti phosphor is different from Al_2O_3:C which contains large concentrations of F and F^+ bands in as-prepared samples. We also performed PL studies to detect Ti^{3+} emission, if any, in our samples. The basic optical spectroscopy of Ti^{3+} ($3d^1$) in Al_2O_3 is well known (McClure, 1962; Powell et al., 1986). Ti^{3+} shows a broad excitation band in the green spectral region corresponding to the $^2T_2 \rightarrow {}^2E$ transition. The emission is ascribed to $^2E \rightarrow {}^2T_2$ transition and consists of a broad, Stokes-shifted band in the near infrared region with a maximum at about 740 nm upon excitation with green light (Blasse and Verweij, 1990). In our PL studies no emission in the region of 720–740 nm was observed for excitation in the range 480–550 nm in as-prepared as well as in gamma irradiated samples of Al_2O_3:Si,Ti. This ruled out the formation of Ti^{3+} during gamma irradiation. The PL emission observed at about 410 nm matches with that reported in literature for Ti^{4+} ions in Al_2O_3 (Blasse and Verweij, 1990). The TL emission spectrum also shows emission around 405 nm. Blasse and Verweij (1990) have reported that the blue emission of Al_2O_3:Ti is due to a charge-transfer transition involving Ti^{4+} ion.

5. Conclusions

The OSL sensitivity of Al_2O_3:Si,Ti is 1/120th of that observed in Al_2O_3:C. Its dose vs. OSL response is linear up to 5 Gy, beyond which it shows slight supralinearity up to 10^3 Gy. Therefore, the phosphor can be used for dosimetric applications in the dose range 0.1–10^3 Gy. The curve fitting of CW-OSL data could be described by superposition of three first-order components. On excitation with 240 nm Al_2O_3:Si,Ti gives emission at 410 nm, which matches with that reported in literature for Ti^{4+} ions in Al_2O_3.

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