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On the stability of TL traps of alumina

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Thermoluminescence (TL) of heat-treated (in the temperature range 450 to 1400° C) α-Al_2O_3 powders have been studied by X-irradiation at room temperature (27° C). The TL patterns have indicated essentially two groups of traps; one in the range 50 to 250° C and the other in the range 200 to 450° C. Apart from other thermal stability characteristics, preferential bleaching by light in the wavelength region of 540 to 630 nm has been observed only in the case of the first group of TL traps. It is concluded that the TL phenomena in α-Al_2O_3 are in general controlled by trace impurities rather than intrinsic lattice defects and the TL traps of the system may be associated with a distribution of trapped holes (O^-, O^0) stabilized by trace impurities.

1. Introduction

Fluorescence [1, 2], thermoluminescence [3–6] and colour centres [5, 7–9] in Al_2O_3 and similar oxide groups of ionic solids have been studied by many workers in the past. All these investigations, which are made mostly on commercially available α-Al_2O_3 (corundum) crystals, have been carried out either by irradiating with γ-rays from Co^{60} or by using high-energy radiation from reactors. Attempts to explain the absorption spectra (both optical [8] and ESR [10–12]) in the light of the established models of colour centres in the alkali halide group of ionic crystals [13] have not been very successful. Essentially, these investigations have concluded that additional lattice defects are not likely to be produced during irradiation, but electron transfer may take place between ions like Cr^{3+} (trace impurities), Al^{3+} and O^{2-} resulting in the formation of some trapped holes (O^-, O^0 etc.), suitably stabilized near the lattice sites or the transformed impurity ions (such as Cr^{3+} converted to Cr^{2+}) or pairs of Al-ions which are paramagnetic in nature [14, 15]. Thus these results could not suggest any definite model for the irradiation products of Al_2O_3.

The present investigation has been undertaken to study the TL traps of α-Al_2O_3 with a view to obtaining more information regarding the energy storage and stability of the traps produced by X-rays and for this purpose the specimens are subjected to various treatments such as heating at different temperatures, exposing to exciting radiation etc., as described in the following section. The results of these studies indicate that by X-irradiation essentially two groups of traps have been produced in α-Al_2O_3, namely, one occurring in the temperature range 50 to 250° C which is found to be less stable than the second occurring at high temperatures (between 200 and 450° C). From their stability and other considerations, it has become possible for us to throw some light on the electronic processes involved in the TL phenomena of this system.

2. Experimental methods

Extrapure (Sarabhai Merck Chemicals Ltd., India) anhydrous alumina powder (α-Al_2O_3) has been studied in this investigation irradiated by X-rays (using ДРОН-I, X-ray tube with Cu target operated at 30 kV, 10 mA) at room temperature (27° C); in all cases the samples are exposed to X-rays for 15 min at a distance of 4 cm from the target. Powders are heat treated at different temperatures in the range 450 to 1400° C in air in a globar furnace for periods up to 10 h by placing the material in a platinum crucible. After each heating the crucible is taken out of the furnace and the material is quenched to room temperature by blowing cold air for about 5 min. Since deformation takes place in the material, depending on

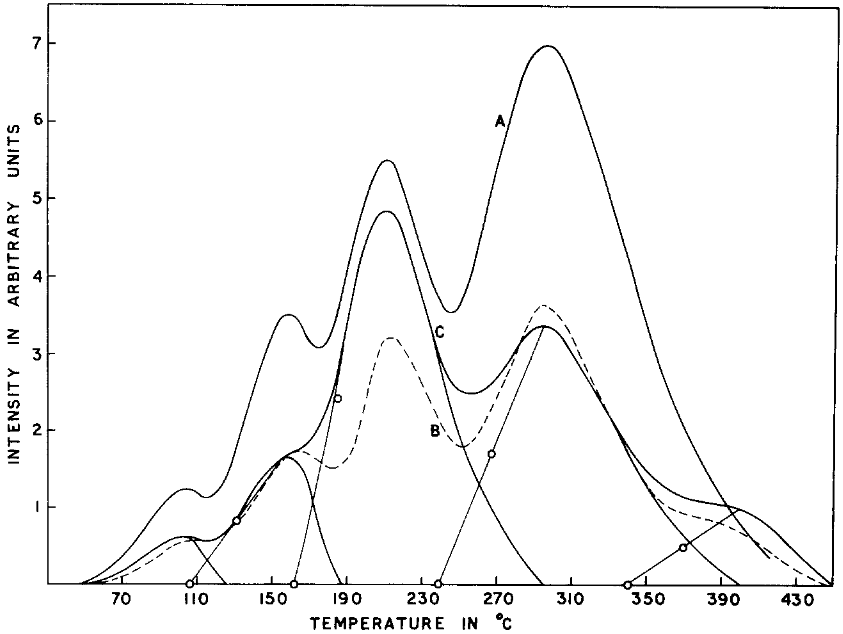

Figure 1 TL glow curves of α-Al_2O_3 samples. A, fresh; B and C, sintered at 1400° C for 2 and 10 h respectively. Curve C is resolved by using Rao's method [19].

the sintering temperature, the resulting effect on the irradiation products is expected to yield further information about the defects, and such effects can be better understood by studying the nature of the related TL traps. In view of this, the samples are purposefully sintered in the temperature range mentioned above and studied along with the untreated samples.

In all cases the powders, after being thoroughly ground to a uniform grain size (200 mesh), are packed in a brass well (0.5 cm diameter and 0.05 cm depth) and exposed to X-rays. After exposure, heating of the sample is done in a vacuum chamber ($\approx 10^{-3}$ torr) at a constant rate of $(27 \pm 1)°\,C\,min^{-1}$ and the emitted TL is detected by a photomultiplier tube (RCA 1P28); the complete TL set up has been described in our earlier paper [16]. Thermal stability and optical bleaching experiments have been carried out in the following way.

(a) By storing the irradiated sample in darkness at room temperature, the loss of TL emission with storage time is recorded at different intervals.

(b) By heating the irradiated sample to different glow peak temperatures, the effect on the residual TL has been studied.

(c) Optical bleaching has been studied initially by exposing the X-rayed sample to light from tungsten as well as hydrogen lamps. The reduction in TL is noted from these experiments and the samples are later exposed to light through different filters.

3. Results

Several commercial powders of α-Al_2O_3 obtained from different sources have been studied in this investigation by irradiating them with X-rays at room temperature. Though these materials are found to contain similar trace impurities, namely, Fe, Ni, Cr, etc., they are all found to emit, after X-irradiation, TL exhibiting glow peaks almost in the same temperature regions but the relative intensity distribution amongst the different glow peaks varies from one variety of sample to another. Thus, in the present study, Extrapure α-Al_2O_3 (Sarabhai Merck Chemicals Ltd, India) with a comparatively low impurity concentration level has been used and heat treated as described in Section 2. Taking this as the starting material several samples have been prepared by doping with impurities like Cr, Ti, V, Co, Ni, etc., and the effect of impurities on the TL emission has also been studied (these results will be presented separately).

The TL glow curve of α-Al_2O_3 powder (taken fresh from the bottle) after X-irradiation at room temperature (27° C) has indicated four well-defined glow peaks at 104, 158, 210 and 296° C (Fig. 1, curve A). Repeated cycles of X-raying and heating (up to 450° C) followed by quenching

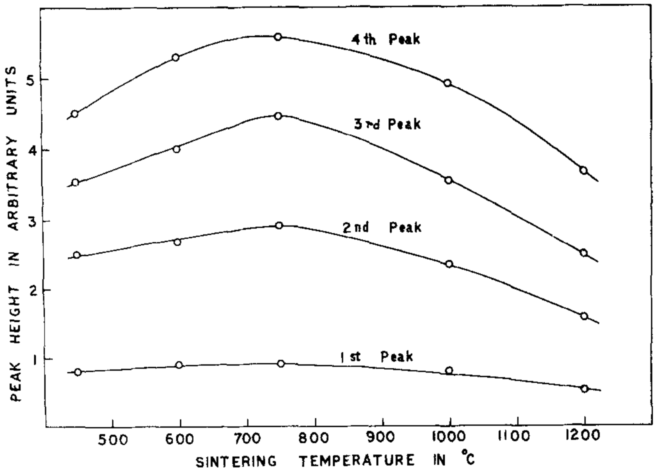

Figure 2 Relative intensities of the TL glow peaks of α-Al_2O_3 sintered at different temperatures for 2 h in each case.

has not produced any change in the peak positions nor in their relative intensities. In the case of powders sintered at and above 500° C, some changes have, however, been observed. As the sintering temperature is increased beyond 500° C, the TL output increases gradually up to 750° C, and then decreases with further increase of sintering temperature (Fig. 2). In Fig. 1, for instance, full glow curves are shown in two cases (curves B and C) for the samples sintered at 1400° C for 2 and 10 h, respectively. This figure also includes the analysis of the TL pattern (for curve C) to calculate the trapping parameters using Rao's method [19]. Prolonged heating at higher temperature produces higher TL yield but the output in no case exceeded the value obtained for the samples sintered at 750° C. Further, an additional glow peak around 400° C has been observed for the sample sintered at 1400° C.

In order to study the stability of the TL pattern and investigate the bleaching (both thermal and optical) characteristics, samples (sintered at 1400° C for 10 h) after X-irradiation are preserved in darkness at the same temperature for different periods of time, as well as subjected to different treatments as described in the caption of Fig. 3. Considering these results the TL traps of α-Al_2O_3 can be grouped as those (first group) occurring in the temperature range of 50 to 250° C and the other (second group) in the range 200 to 450° C. The two glow peaks occurring at lower temperatures, namely 104 and 158° C, in the first group, are observed to be destroyed completely with ageing (> 24 h) while the third glow peak

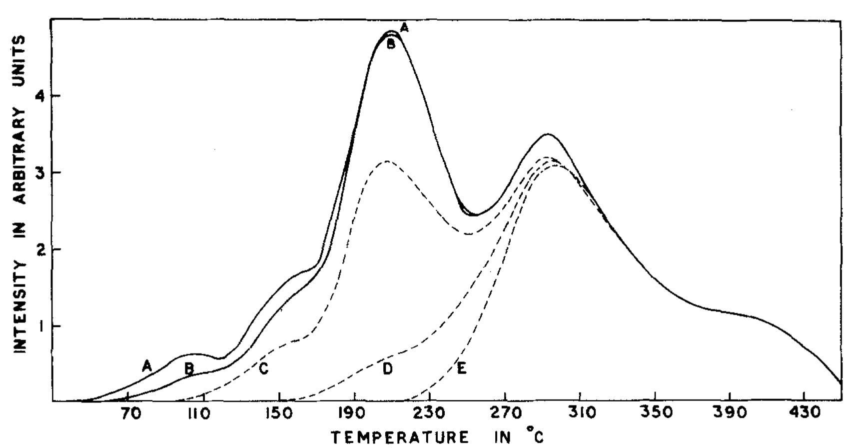

Figure 3 Bleaching characteristics of the TL glow peaks of α-Al_2O_3 sintered at 1400° C for 10 h and irradiated by X-rays (30 kV, 10 mA) for 15 min at room temperature. A, immediately after X-irradiation; B, stored in darkness at room temperature for 15 min after irradiation; C, D and E, exposed to light in the wavelength region of 540 to 630 nm at room temperature for 15, 30 and 120 min, respectively.

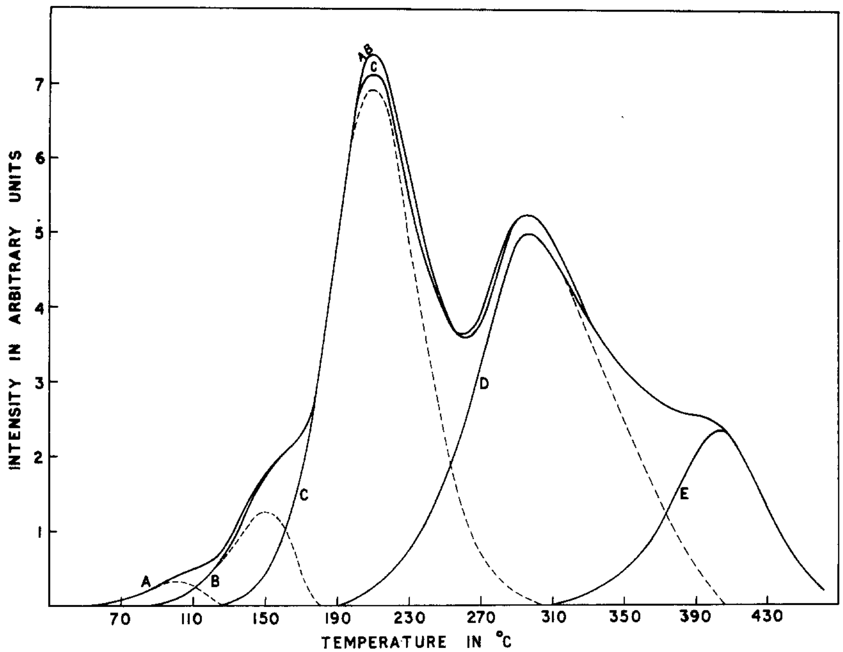

Figure 4 Partial thermal bleaching of TL glow peaks of α-Al_2O_3. Dotted portions in each case are the contribution of that peak, obtained by subtracting the contributions of the other peaks; for example in curve D the contribution of E is subtracted and so on.

(at 210° C) and the second group (at 296 and 400° C) of TL peaks are thermally more stable than the first two. Sufficient TL output is obtained in the case of samples stored even for periods of days and the pattern still exhibits the last three glow peaks. Optical bleaching has also produced similar features but at a relatively faster rate. While exposure to u.v. light has no effect, shining with visible light in the wavelength region of 540 to 630 nm (using long pass filters) produces a marked reduction in the intensities of the first three glow peaks of the TL pattern (Fig. 3, curve D). Complete removal of the first three glow peaks has been observed if the sample is optically bleached in this way for 2 h (Fig. 3, curve E).

In Fig. 4, results are presented for the partial thermal bleaching experiments, namely, removal of the glow peaks successively by heating the irradiated sample to glow peak temperatures. By adopting such thermal cleaning procedure, it has been possible not only to study the stability of the residual TL but also has enabled us to calculate the trap depths (E) and the frequency factors (S or $S'n_0$) using different methods [17–19]. It is interesting to note that the values of the trapping parameters thus obtained have compared very well with those calculated by an initial rise method [17] shown in Fig. 5; all the values are shown in Table I. Considering the stability characteristics of the two groups of TL traps and since the second group gives rise to a very stable TL output, the corresponding TL emission can be very effectively used in TL dosimetry.

TABLE I

Peak temperature (° C)	E(eV)			Frequency factor (sec^{-1})	
	1*	2†	3‡	S	$S'n_0$
400	1.60	1.44	1.57	1.62×10^{10}	
296	1.28	1.24	1.17		1.79×10^{9}
210	0.92	1.11	1.09		1.03×10^{10}
156	0.94	0.83	0.88	2.22×10^{8}	
100		0.75	0.77	8.50×10^{8}	

*By initial rise method [17].
†By Rao's method [19].
‡By Chen's formula [18] after thermal cleaning.

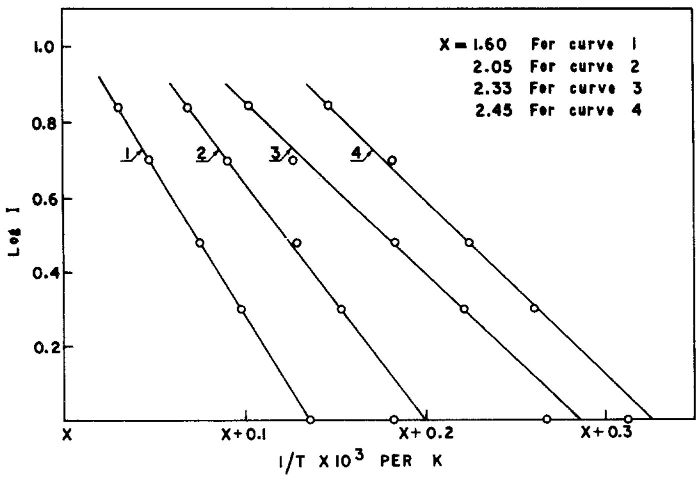

Figure 5 Analysis of the TL glow peaks (of Fig. 4) by initial rise method. (1) 400° C, (2) 296° C, (3) 210° C, and (4) 156° C peaks.

4. Discussion

Thermoluminescence (TL) emitted by irradiated crystals during the process of heating is, in general, attributed to a radiative recombination process in which, (a) a released electron may combine with a trapped hole, or (b) a released hole may destroy a trapped electron centre, or (c) released electrons and holes may combine at a luminescent centre, or (d) may involve a metastable state in the specific cases of impurities. While it becomes very difficult to elucidate the related electronic processes in every individual TL glow peak by considering the results of TL glow curves only, an attempt to explain the overall nature of the glow peak can always be made if these results are discussed in a comprehensive way along with the other features, like optical absorption, electrical conductivity, luminescence spectra and other defect-controlled structure-sensitive properties. Thus, by using the available data on α-Al_2O_3 in the literature [1–15] and the existing models for the colour centres in the alkali halide group of crystals, we have tried to explain the essential features observed in the TL exhibited by X-irradiated α-Al_2O_3, namely, (a) occurrence of two groups of TL traps with different thermal stability characteristics and (b) preferential optical bleaching of the first group of traps (occurring in the range 50 to 250° C) by light of wavelength in the region 540 to 630 nm.

It is known that, except by using very high energy radiation [15, 20, 21], it is not ordinarily possible for ionizing radiation like X-rays to produce point defects in α-Al_2O_3, since the basic crystal structure of corundum (rhombohedral) does not permit ion displacements at lower collision energies. This may possibly be the reason for not observing any significant change in the TL output after repeated cycles of X-irradiation and heating. The small increase observed in the TL output of this system with the increase of sintering temperature up to 750° C may be attributed to the additional lattice defects produced due to plastic deformation. The decrease in the output and appearance of the fifth glow peak at 400° C for samples sintered at and above 1400° C is likely to be due to the entering of trace impurities like Cr^{3+}, Fe^{3+}, etc., (otherwise present in the material as a mechanical mixture) into the lattice of α-Al_2O_3; this viewpoint is supported by our results (to be published) on the TL of impurity-doped alumina.

Results on optical absorption [5, 7–9] and ESR spectra [10–12] of corundum single crystals suggest that apart from the traps associated with the impurities present in the system, a large number of different types of trapped holes are also likely to be produced depending upon the process and nature of irradiation. The ionization produced during irradiation liberates electrons from O (anions) which are assumed to be trapped by the trace impurities like Cr^{3+}, Fe^{3+}, Ti^{4+}, etc. as well as by defect cation (Al^{3+}) sites (predominant Frenkel disorder in the cation lattice [22]). To explain the thermal stability characteristics we have tentatively considered two groups of traps. Our result, that by shining the X-irradiated α-Al_2O_3 with light of wavelength in the range 540 to 630 nm all the first group of TL peaks are removed leaving the high temperature glow peaks (occurring in the range 200 to 450° C) unaffected, suggests that the first group differs from the second in its stability and during the progress of optical bleaching the electrons excited from the electron traps destroy the related trapped holes (O^- or O^0) in close proximity. Our thermal cleaning experiments (Fig. 4), by which the TL pattern is resolved, also yielded convincing information regarding the nature of the traps (values of trap depths and involved kinetics are presented in Table I) which further adds to the viewpoint that the TL glow peaks occurring in the temperature region of 50 to 250° C are likely to be related to the trapped holes (O^- or O^o) as suggested above.

In all the cases of α-Al_2O_3 samples studied in the present investigation, the TL emission is observed to be magenta in colour. The spectral composition of the emission essentially consists of broad bands in the blue and red regions. Our preliminary results on doped samples (with Cr^{3+}, Ti^{4+} and V^{5+}) also indicate that the glow peaks occur in the same temperature regions as observed for undoped α-Al_2O_3, while, depending upon the type of impurity, one or other emission band mentioned above becomes prominent. Thus the TL phenomena in α-Al_2O_3 may be presumed to be predominantly controlled by trace impurities rather than intrinsic lattice defects. Considering the order of kinetics and the value of the trap depth, the TL traps of α-Al_2O_3 may be in general associated with a distribution of trapped holes (O^-, O^o) and the high temperature glow peaks in view of their difference in stability may be tentatively identified with deep-lying hole traps stabilized by impurities.

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