Concerning secondary thermoluminescence peaks in α-Al_2O_3:C

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Thermoluminescence characteristics of two subsidiary glow peaks, one below 100°C and the other above 300°C, have been studied for measurements between 30°C and 500°C in α-Al_2O_3:C. The thermoluminescence intensity of the lower temperature peak decreased with storage with a half-life of about 150 s. In contrast, the intensity of the higher temperature peak increased with storage towards some maximum. The peak-temperature of each of the secondary glow peaks was essentially constant with dose, whereas that of the main peak decreased with irradiation. The dose response for the three peaks was similar except for sublinear growth in the higher temperature peak at low dose values. These effects are discussed in terms of changes in the concentration of F^+ luminescence precursors brought about by competitive electron re-trapping at deep electron-traps or hole-traps. This work refines the physics and application of α-Al_2O_3:C luminescence in radiation dosimetry.

Introduction

Thermoluminescence (TL) is a sensitive technique for monitoring changes in the concentration of defects in insulators. The basis of TL is that many imperfections in materials, either impurities or intrinsic defects, can act as charge traps or luminescence sites. Ionizing radiation can transfer electrons or holes to trapping sites. The subsequent release of the trapped charge by heating at a linear rate can be recorded as a temperature-resolved set of luminescence signals. The application of thermoluminescence to radiation dosimetry is possible because, in principle, the luminescence intensity is proportional to the concentration of sites as well as to the absorbed radiation dose.

Carbon-doped aluminium oxide, α-Al_2O_3:C, commercially available as TLD-500, has become established in luminescence dosimetry. The thermoluminescence of aluminium oxide usually consists of a high-intensity peak near 200°C (referred to hereafter as the dosimetry peak), and a number of weaker-intensity secondary peaks below and above 200°C, whose relative intensity depends on the dosimeter's treatment such as irradiation or exposure to light. The application of TLD-500 in personnel dosimetry is based on the dosimetry peak only.[1]

Dosimetry-quality samples of α-Al_2O_3:C are grown in a highly reducing atmosphere in the presence of carbon to induce in the material high concentrations of oxygen vacancies, F and F^+ centres.[2] The thermoluminescence, emitted at 420 nm, depends on the recombination of electrons at F^+ centres, oxygen vacancies each with one trapped electron. The intensity of the luminescence is directly correlated with the concentration of F^+ centres.[1,3]

Because α-Al_2O_3:C is highly sensitive to thermal stimulation, simultaneous measurement of the various glow peaks to a similar level of accuracy poses an experimental problem. In γ-irradiated samples, for instance, the main peak is about 1000 times more intense than a subsidiary, lower temperature peak.[4] Previous methods used to address the problem include the simultaneous measurement of TL and thermally stimulated conductivity[3] and use of a different photomultiplier-gain for each peak.[4]

This report is concerned with the influence of irradiation and storage on thermoluminescence intensity of secondary glow peaks in α-Al_2O_3:C as well as irradiation-related changes in the associated peak temperatures. The interest in this suite of measurements is in the effects related to competitive electron re-trapping at deep traps.

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Experimental details

Experimental samples consisted of aluminium oxide disks, 5 mm in diameter and 1 mm thick (Rexon TLD Systems, Ohio). Prior to use, all samples were annealed at 800°C for 15 min in a Buehler Furnace (Buehler, Coventry, U.K.) followed by rapid cooling in air. The anneal was carried out to remove residual charge present in deep traps due to natural or laboratory irradiation.

Unless otherwise stated, all thermoluminescence measurements were made at the Scottish Universities Environmental Research Centre, Glasgow, using a semi-automatic TL reader built in-house. The luminescence was detected by a Thorn EMI B2F/RF1 photomultiplier through a Schott BG-39 filter (transmission band 340–620 FWHM), selected to coincide with TL emitted by α-Al_2O_3:C at 420 nm.

Samples were irradiated at room temperature using either a version V3 ^{90}Sr β-source Auto Irradiator (Littlemore Scientific Engineering) at 180 Gy h^{-1} or a ^{241}Am γ-source at 0.62 Gy h^{-1} as described previously.[4]

Thermoluminescence was measured immediately after irradiation, with due care being taken not to expose samples to light between irradiation and measurement in view of the propensity of the luminescence of α-Al_2O_3:C to fade with exposure to light.

Results and discussion

Glow curve structure

Figure 1 shows a thermoluminescence glow curve from α-Al_2O_3:C measured at 5°C s^{-1} over the range 20–500°C following β-irradiation to 4 Gy. The glow curve consists of two peaks, the dosimetry peak at 208°C and a subsidiary peak at 73°C. For the samples used in this study, a third peak, weaker in intensity than either of the other two, appeared with increasing dose, at about 330°C, but was more pronounced for β-doses greater than 20 Gy. In as-received, unannealed samples without laboratory irradia-

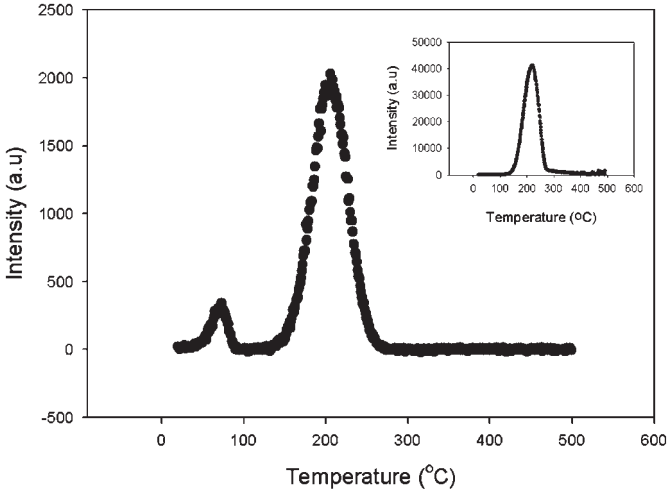

Fig. 1. A thermoluminescence glow curve measured from α-Al_2O_3:C at 5°C s^{-1} from 20–500°C following β-irradiation to 4 Gy. The inset is a glow curve from an unirradiated sample.

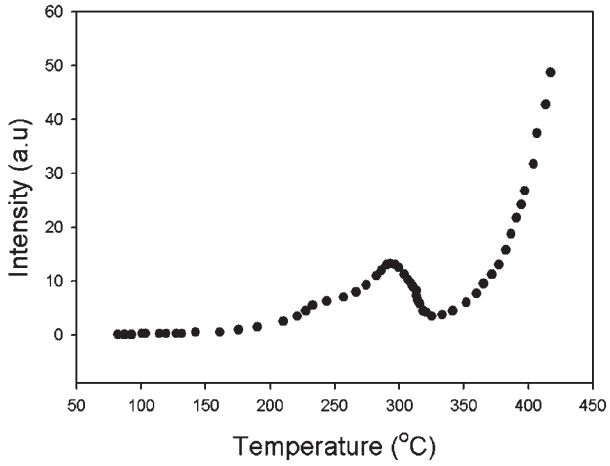

Fig. 2. A glow curve measured from a γ-irradiated sample at 0.25°C s^{-1} after an initial heating to 240°C to remove the main peak.

tion, however, only the main peak was present (inset to Fig. 1), probably induced by natural irradiation. In contrast, thermoluminescence from β-irradiated α-Al_2O_3:C at similar dose levels (2.5 Gy) consisted only of two peaks, the main peak at 160°C and a less intense peak at 290°C for heating at 0.25°C s^{-1}.[4] Some studies suggest that the main glow peak may be a composite of several overlapping peaks.[3]

The degree of overlap of peaks collocated with the main peak at its higher temperature end was assessed using a thermal cleaning routine[5] on a TL reader described previously.[4] A β-irradiated sample was heated at 0.25°C s^{-1} to 240°C to remove the main peak (at 160°C) and then reheated from room temperature to record the remaining glow curve. Figure 2 shows the glow curve after thermal cleaning, with evidence of additional overlapping peaks, the discernible ones near 230 and 290°C. In this work, peak III refers to the latter, whose peak height can be identified relatively easily. In these experiments, only the peak in γ-irradiated samples could be separated in this manner.

Dose response

Figure 3 compares the change in luminescence intensity with irradiation, the dose response, for the three glow peaks in α-Al_2O_3:C for β-irradiation up to 50 Gy. Irradiation was done *in situ* at 0.05 Gy s^{-1} and the TL measured over the range 20–500°C at 5°C s^{-1} using a RISO TL/OSL-DA-15 reader.[6] The intensity of all three peaks increased with irradiation. For the main glow curve (Fig. 3b), the increase was linear initially, grew supralinearly, then decreased above 30 Gy in broad agreement with the results of Yukihara *et al.*,[7] who observed an increase in intensity with irradiation up to about 29 Gy, followed by a decrease, or saturation, for greater irradiation doses. The changes in peak I resemble those in the main dosimetry peak. However, the intensity of peak III increased only slowly at first and gradually tended towards saturation beyond about 20 Gy. In comparison, the dose response of the main peak in γ-irradiated samples of α-Al_2O_3:C was linear at low doses (up to about 10 Gy), then successively became supralinear, underwent saturation and decreased thereafter.[4] This dose-response profile is similar to that of the main peak in β-irradiated samples as discussed above. On the other hand, the dose response of the higher temperature glow curve in γ-irradiated α-Al_2O_3:C was linear with dose and did not saturate as does peak III in β-irradiated samples.

Effects of irradiation on peak temperature

Figure 4 shows the change of peak temperature with irradiation dose in α-Al_2O_3:C for peaks I, II and III. The peak temperature for both peaks I and III was essentially constant at about 82 and 360°C, respectively, suggestive of first-order kinetics. However, the peak temperature for the dosimetry peak decreased with increasing irradiation. This feature was also observed in samples annealed between irradiation and measurement. A decrease of peak temperature with dose is indicative of non-first-order behaviour and is specifically a feature of second-order thermoluminescence. Detailed kinetic analysis by Kitis *et al.*[8] and by Kortov *et al.*[9] shows a kinetic order of 1.42 and 2, respectively, for the dosimetry peak.

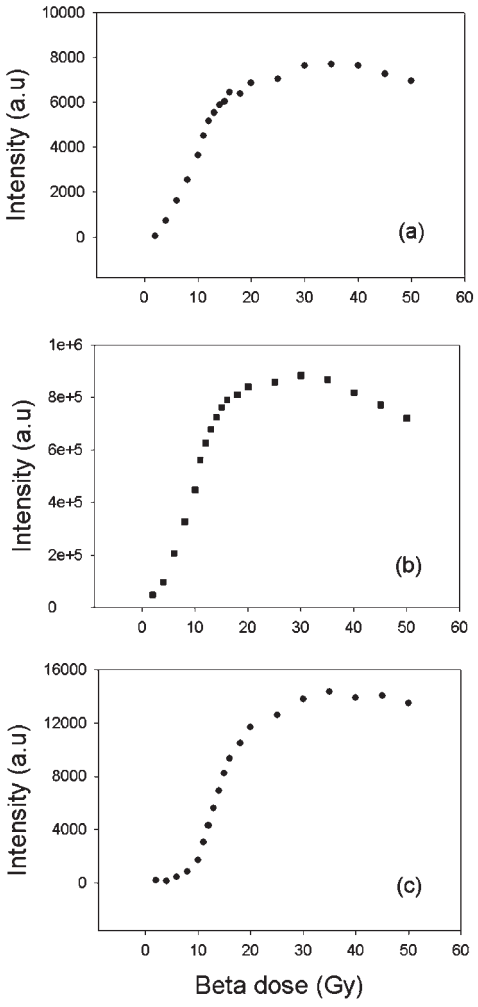

Fig. 3. A comparison of thermoluminescence dose response in the main peak (**b**), peak I (**a**) and peak III (**c**).

Fading characteristics

The effect of delay between irradiation and measurement on the TL intensity of the subsidiary glow curves, peaks I and III, was investigated to assess qualitatively the degree of competitive re-trapping at electron traps. Figure 5 shows the effect of this delay on the intensity of peak I in (a) and of peak III in (b). The intensity of peak I decreased with delay between irradiation and measurement, with a half-life of about 150 s. The decrease of intensity of peak I was accompanied by an increase in the width of the base of the main peak, suggesting enhanced electron re-trapping at the trap associated with the main peak.

The intensity of peak III increased with delay between irradiation and measurement, rapidly at first then tending to saturation thereafter. The greater intensity suggests that re-trapping was more efficient at the trap associated with the main peak than at the trap associated with the lower temperature peak I.

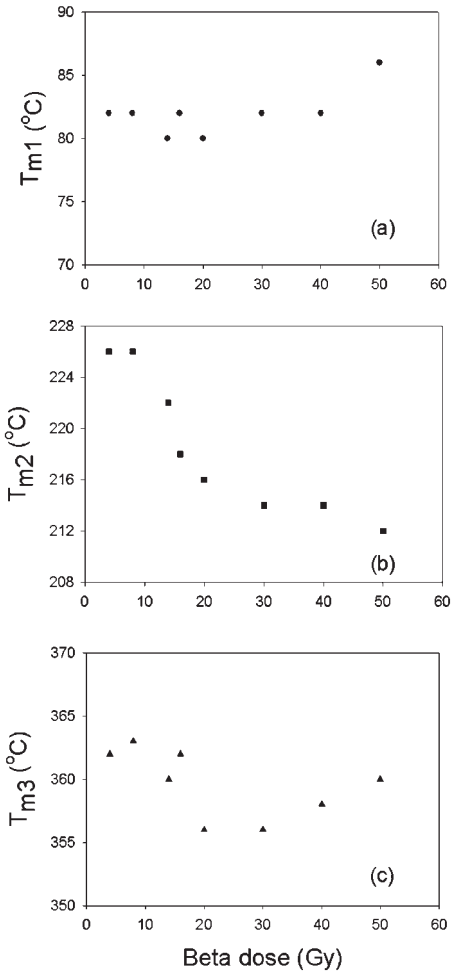

Fig. 4. The change of peak temperature with irradiation dose in α-Al_2O_3:C for peak I (**a**), the dosimetry peak (**b**) and peak III (**c**).

Model

Studies concerned with the main dosimetry peak show that the thermoluminescence of α-Al_2O_3:C is centred at 420 nm and that the main dosimetry trap is an electron trap.[1,7] The basic mechanism responsible for luminescence is the recombination of an electron with an F^+ centre, producing an excited F centre. Luminescence at 420 nm is emitted following relaxation of the electron from an excited 3P state to the 1S ground state ($F^+ + e \rightarrow F + h\nu_{420\ nm}$).[1] The F^+ luminescence precursors are produced either during crystal growth or by capture of holes by F centres. The dose response of the main peak as well as that of the secondary glow peaks may thus be understood by analysing changes in the concentration of F^+ centres brought about by the competing effects of electron capture at luminescence traps or at competitor sites identified as deep electron-traps or deep hole-traps.[7]

To account for the dose-response results of Fig. 3, we use an energy-band scheme shown in Fig. 6, based on models of Yukihara *et al.*[7] and Vinceller *et al.*[10] but with minor modifications to explain the dose response of secondary peaks. Transition 1 denotes the transfer of electrons to the conduction band as a result of ionizing radiation. The free electrons may then be captured (downward arrows) at electron traps ST, ID, or MT associated with peaks I, III, and the main dosimetry trap, respectively. Electrons from the conduction band can also be captured at deep electron-traps (DT) and at deep hole-traps (HT). The deep traps do not participate directly in luminescence emission and are thus primarily competitor traps.

At low β-irradiation, up to about 10 Gy in the linear region for peak I, the main peak and peak III in Fig. 3, the rate of production of F^+ centres by capture of holes at F centres and the conversion of F^+ to F centres by holes is approximately equal, so that there is only a negligible effect on the concentration of F^+ luminescence precursors. Competition for electrons is important when the concentration of empty deep electron-traps or filled hole-traps is large. However, as the deep electron-traps fill, more electrons become available for the luminescence process, hence the supralinear increase in luminescence intensity. At higher irradiation doses, of the order of 20–30 Gy, with deep electron-traps essentially full, electrons recombine preferentially at F^+ centres. It is presumed that owing to a number of factors including low capture cross section, saturation at deep hole-traps occurs more slowly than at deep electron-traps. Holes can therefore still be captured at deep hole-traps and the concentration of F^+ centres

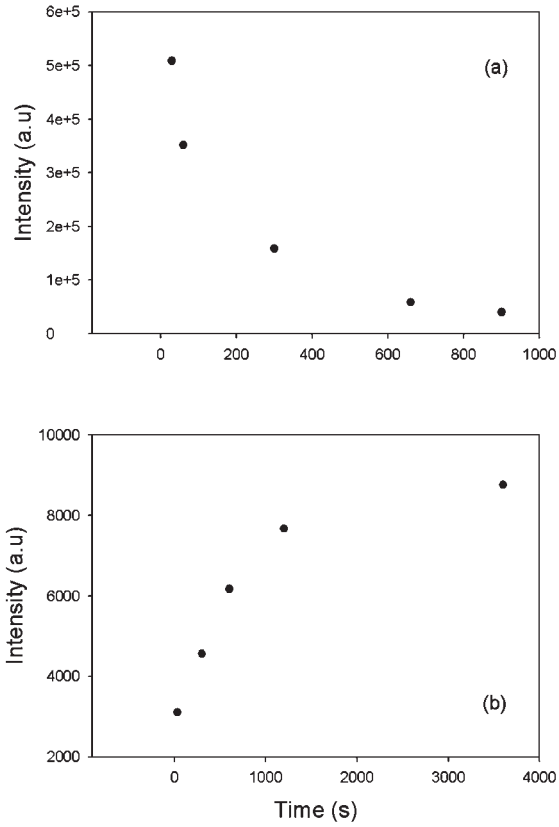

Fig. 5. The influence of delay between irradiation and measurement on peak I (**a**) and peak III (**b**).

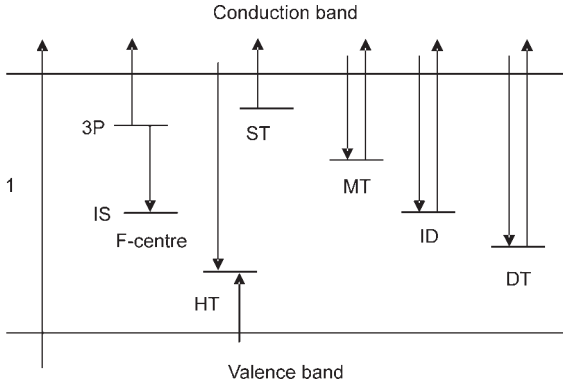

Fig. 6. An energy-band scheme showing the shallow trap (ST), dosimetry trap (MT), and intermediate energy trap (ID) associated with peak I, the main dosimetry peak, and peak III, respectively. The deep electron-trap (DT) and deep hole-trap (HT) compete for free electrons from the conduction band. Electrons are transferred to conduction band by ionization (transition 1).

must eventually decrease.[7] The overall effect is seen in Fig. 3 as the onset of saturation. In the case of peak III, the initial sublinear increase in intensity could be due to not only competitive trapping of holes at deep hole-traps rather than at F centres but also to thermal quenching of luminescence, which becomes severe at temperatures above the main dosimetry peak.[11,12]

Concluding remarks

This study refines our understanding of the physical processes responsible for luminescence in α-Al_2O_3:C, to improve its application in radiation dosimetry. Applications in dosimetry rely on accurate determination of the dependence of luminescence intensity on absorbed radiation dose, a growth curve. In principle, the intensities usually determined from either glow curve height or area are proportional to the absorbed radiation dose. However, in practice there are experimental complexities to do with changes in luminescence sites, for example F centres, brought about by the luminescence-exciting radiation. This study addresses an instance of the latter.

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