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SUPERLINEAR DOSE DEPENDENCE OF HIGH TEMPERATURE THERMOLUMINESCENCE PEAKS IN Al_2O_3:C

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We report on strong superlinearity of high temperature (300–700°C) thermoluminescence (TL) peaks in α-Al_2O_3:C powder. The main dosimetric peak at ~200°C, previously found to exhibit slight superlinearity, is now shown to yield a slope of ~1.15 on a log(intensity) vs. log(dose) curve. Higher temperature peaks at ~320, 450 and 650°C, previously reported following UV and X-ray excitation, have now been observed after beta irradiation and showed stronger superlinearity. Using a blue filter, the weak peak at ~320°C started about quadratically and the slope on the log–log scale decreased gradually from 2 to about unity at ~100 Gy. The two higher temperature peaks at ~450 and ~650°C also exhibited a strong superlinear dose dependence in this dose range, with an average slope of ~2. Roughly similar behaviour has been found when a UV filter was used. The possible explanation of the strong superlinearity is discussed.

INTRODUCTION

The thermoluminescence (TL) of Al_2O_3 samples with different dopants has been studied by several researches for nearly 50 years. Rieke and Daniels[1] were the first to report on TL from gamma-irradiated Al_2O_3. Several research groups studied the TL properties of differently doped Al_2O_3 crystals [for a review, see McKeever *et al.*[2]]. Akselrod *et al.*[3] were the first to introduce anion defective alpha-Al_2O_3:C, which became one of the leading dosimetric materials owing to its high sensitivity. The samples are grown in a highly reducing atmosphere so as to induce large concentrations of oxygen vacancies. These are observed as F- and F^+-centres, which have an important role in the TL process. Powder samples are obtained by grinding the single crystals. The main TL peak in alpha-Al_2O_3:C was reported to appear in the temperature range of 180–210°C[1–4], the maximum temperature depended mainly on the heating rate although some effect may be due to differences between bulk and powder samples and between different sources of irradiation. The emission of this peak consists of two main bands, centred at 420 and 330 nm[5]. The former is believed to originate from a recombination of an electron with an F^+-centre and the latter of a hole with an F-centre. According to Colyott *et al.*[5], in the latter case, thermally released holes may recombine with F-centres producing excited F^+-centres. Energy transfer from the F^+- to F-centres may then occur, yielding emission at both 330 and 420 nm. As an alternative, they suggest the possibility that the peak is a composite of two components, one associated with an electron trap and the other with a hole trap, with the former dominating at the low temperature side of the peak and the latter at the high temperature side.

Milman *et al.*[6] reported on higher temperature peaks in alpha-Al_2O_3. Following UV irradiation, they found TL peaks at ~180°C (the main dosimetric peak) as well as at ~300, ~460 and ~610°C while heating at 2°C s^{-1}. They report that the luminescence spectra exhibit bands characteristic of F- and F^+-centres, which, as mentioned above, are similar to the previously reported results on the main dosimetric peak. Molnár *et al.*[7] also report the same high temperature peaks, following X-ray exposure.

There is some disagreement in the literature on whether the high temperature peaks mentioned result from the same F- and F^+-centre emissions. As pointed out above, Milman *et al.*[6] suggest that the high temperature peaks exhibit bands characteristic of F- and F^+-centres. However, a later work by Akselrod *et al.*[8] shows that both emissions quench ~150–200°C. Molnár *et al.*[9] maintain that the peaks at ~300 and ~500°C include an F^+-emission at ~350 nm (as compared with the 335 nm at room temperature), while the peaks at ~180 and ~700°C are mainly blue. In fact, each of these peaks has both blue and UV components, but with different proportions. They state that the blue emission of the dosimetric peak is undoubtedly F-centre emission whereas the blue emission of the ~700°C peak may or may not be associated with the F-centre. Molnár *et al.*[9] try to reconcile these two arguments by suggesting that in the case of F^+-centres, the reason might be that the reported quenching data refer to F^+-centres created by particle irradiation. As for the

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F-centres, they state that it is believed the quenching might not reach 100% at high temperature.

In a recent paper, Yukihara *et al.*[10] studied in detail the behaviour of the main peak at ~180°C following beta irradiation. For one batch of samples studied, B1040, the dose dependence has been found to be slightly superlinear in the range of 1–50 Gy. The authors discuss the role of the F- and F^+-centres in the emission process. They also report effects of sensitisation and desensitisation, which, along with the superlinearity, are explained by competition processes associated with a deep hole trap and a deep electron trap that become unstable at 530–600 and 830–930°C, respectively. Yukihara *et al.* [10] suggest that the reactions $F+h \rightarrow F^+$ and $F^+ + e \rightarrow F$ are nearly balanced and, therefore, the concentrations of the F- and F^+-centres do not change significantly.

In the present work, the dose dependence of the higher temperature peaks, following beta excitation has been studied. The slight superlinearity of the main peak at ~200°C observed previously[10], is accompanied by a significantly stronger superlinearity of the higher temperature peaks. A crude separation between the blue and UV emissions of the high temperature TL has been performed by the use of glass filters (see below).

MATERIALS AND METHODS

The material used in this work was powder samples purchased from Landauer Inc., probably from batch B1040 (as identified by the dose dependence of the main dosimetric peak). Fresh powder samples, 3.8 mg in weight, were used in each measurement so as to avoid possible effects of sensitisation. The TL measurements were taken using a Risø TL/OSL-DA-15 automatic reader with an integrated $^{90}Sr/^{90}Y$ β source, which was used for the irradiation. The light detector was an Electron Tubes 9235QB15 photomultiplier tube. The heating rate used in all measurements was 5°C s^{-1}. For separation of the emission, a 'blue' filter, Oriel 51670, with a maximum transmission at 410 nm and a 'UV' filter, Hoya U-340, with a maximum transmission at 325 nm, were used. Preliminary measurements have been performed with a Melles Griot 03FIU123 interference filter with a maximum transmission at 326.1 nm and full width half maximum (FWHM) = 10 nm.

RESULTS

The dependence of the different peaks on the beta-excitation dose has been monitored. Figure 1 depicts the dose dependence of the dosimetric peak at ~210°C as measured through the 'blue' filter. The initial slope on the log-log scale is ~1.15, meaning a weak superlinearity as reported before[10]. The weak peak at ~320°C is also shown (the scale is ×20 in the given arbitrary units), yielding a slope of ~2 at 1 Gy, which gradually decreases to ~1 at ~100 Gy. Figure 2 shows the dose dependencies of the peaks at ~450 (open circle) and ~650°C (cross) as measured through the 'blue' filter. The dependence is rather strongly superlinear with an average slope of ~2 on the log–log scale. The slope is seen to be lower (though still >1) at the low and high ends of this dose range, and significantly >2 in the range of 5–50 Gy, meaning more than quadratic dose dependence.

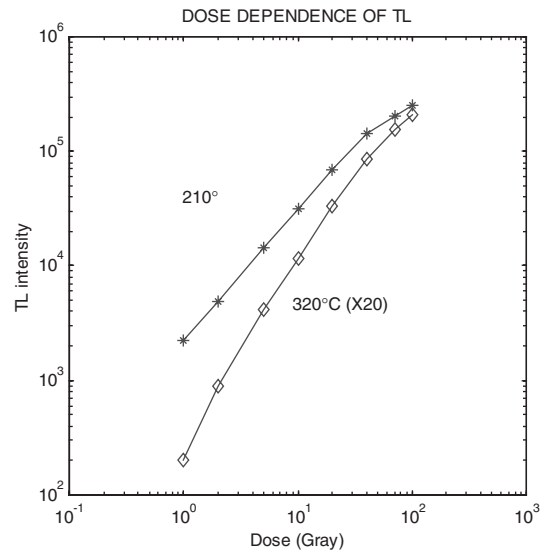

Figure 1. Beta-irradiation dose dependence of the 'dosimetric' TL peak at ~210°C (asterisk) and the 320°C peak (open diamond). The blue filter has been used for the emission.

Figures 3 and 4 depict the beta dose dependence of TL as measured through the Hoya U-340 glass UV filter. Generally speaking, the results are similar to those in Figures 1 and 2 with some differences in the details of the behaviour and the maximum temperatures. Figure 3 shows the dose dependence of the ~200°C peak (asterisk), which like its 'blue' counterpart is slightly superlinear. The ~330°C weak peak (open diamond) is somewhat more superlinear though the dependence is not identical to that of the 'blue' peak shown in Figure 1. In the results shown in Figure 4, the main difference as compared with Figure 2 is that the maxima of the third and fourth peaks occur at ~505 and ~630°C, respectively. The general appearance of the dose dependence curves of the 505 (open circle) and 630°C (cross) 'UV' peaks is rather similar to that of their 'blue' counterparts shown in Figure 2.

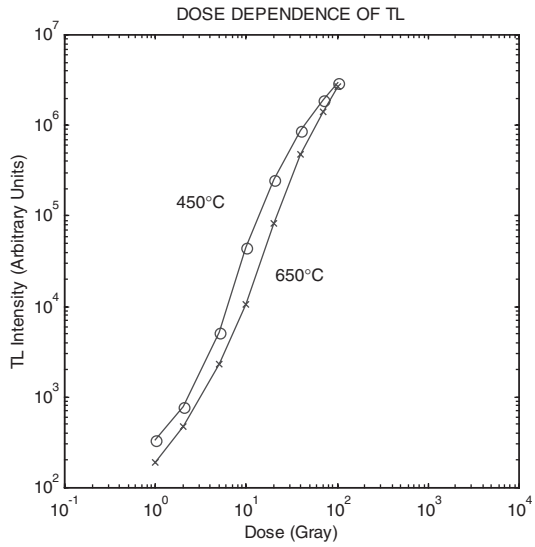

Figure 2. Beta-irradiation dose dependence of the ~450°C (cross) TL peak and the ~650°C (open circle) peak. The blue filter has been used for the emission.

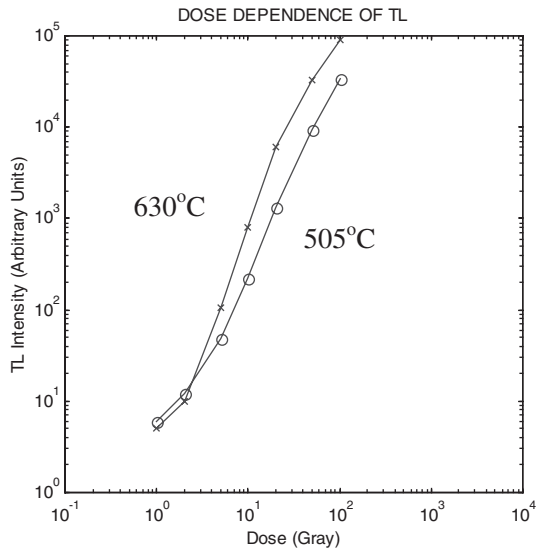

Figure 4. Beta-irradiation dose dependence of the ~505°C TL peak (open circle) and the ~630°C peak (cross); the emission was measured through the UV filter.

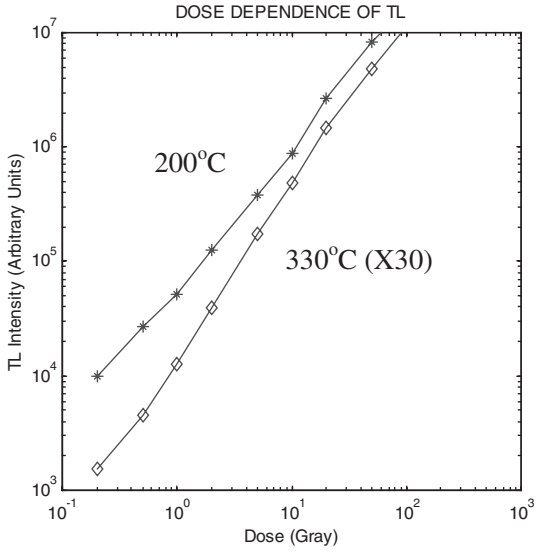

Figure 3. Beta-irradiation dose dependence of the ~200°C TL peak (asterisk) and the ~330°C peak (open diamond); the emission was measured through the UV filter.

DISCUSSION

The main new result of this work is that the high temperature TL peaks in Al_2O_3:C, previously known to be excitable by UV light and X rays, can also be excited by beta irradiation at room temperature. Furthermore, the dose dependence of these peaks is rather strongly superlinear. The blue and UV components as measured through appropriate filters behave in a slightly different manner and also occur at somewhat different temperatures, but the general dose dependence looks similar. As pointed out in the literature[11], superlinear dose dependence of TL is usually explained as the result of competition with disconnected trapping states or with radiationless centres during the excitation or during the heating stage or both. Although there is some overlap in the transmission of the two filters used, we tend to believe that following beta irradiation, the emission is due to the F+h (~330 nm) and F^++e (~420 nm) reactions as previously suggested for X-ray and UV irradiated samples[6,9] for the same peaks. As pointed out in the introduction, the concentration of the F- and F^+-centres do not change significantly neither during the excitation nor during the heating stage[10]. This seems to rule out the possibility that the strong superlinearity is due to competition during heating, since, in this situation, both the concentrations of the trapping state and the luminescence centre are dependent on the excitation dose more or less linearly, but owing to the presence of a strong competitor, the TL intensity is proportional to the product of these two concentrations. Since the relevant centres here seem to be practically dose independent, a linear dose dependence of the trapped carriers' concentration would necessarily result in a nearly linear dose dependence of the TL on the dose. One has, therefore, to resort

to an explanation based on the competition during excitation. The difficulty here is (both with respect to the present work and the previous ones[6–9]) that both the blue and UV TL components occur at nearly the same temperatures and display a similar dose dependence. The explanation, however, requires that the blue and UV emissions be related to electron and hole trapping states, each of which is accompanied by a deeper, disconnected trapping state of the same kind, which makes the superlinearity due to competition during excitation possible. At present, however, the full picture is not available. Yukihara *et al.*[1] stated while discussing the dosimetric peak at ~200°C that '...it is evident that the peak changes result from complicated, simultaneous mechanisms that may involve competition, simultaneous release of electrons and holes from overlapping energy levels of different nature...'. The additional information revealed in this work concerning the higher temperature peaks may make the full interpretation even more difficult or, possibly (hopefully), give a new clue concerning the full model.

In conclusion, the new results of the superlinear dose dependence of the blue and UV emission components of the high temperature TL peaks seem to include some important information concerning the TL mechanism of Al_2O_3:C. In a follow-up work, it is planned to repeat the dose dependence TL using interference filters in order to check whether the blue and UV emissions in the high temperature peaks are indeed related to the F- and F^+- centres or, perhaps other possibilities should be pursued. In fact, preliminary measurements with the Melles Griot 03FIU123 interference filter gave very similar results to those reported above with the 'UV' glass filter. A further work along these lines is planned although it seems to be rather difficult experimentally in particular with the low-intensity peaks at the low doses excitation range where the superlinear dose dependence is most strongly exhibited. Another interesting point to investigate is the UV and X-ray dose dependence of the high temperature peaks. These peaks were reported in the literature[6,9], but no dose dependence measurements were made.

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