

# Thermoluminescence dose response of quartz as a function of irradiation temperature

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**Abstract.** The thermoluminescence (TL) response of pure Norwegian quartz as a function of irradiation temperature ( $T_{\text{irr}}$ ) and dose has been investigated. The TL response of the (150–230 °C) and (230–350 °C) glow curve intervals shows a strong dependence on  $T_{\text{irr}}$  between 77 and 373 K† in the dose range from 54 to  $8.4 \times 10^4$  Gy. Both glow curve intervals also show temperature dependent dose response properties. The 150–230 °C interval is supralinear from the lowest dose (54 Gy). Its maximum supralinearity factor appears at  $T_{\text{irr}} = 293$  K. The 230–350 °C interval shows sublinear behaviour below  $T_{\text{irr}} = 193$  K, while at  $T_{\text{irr}} \geq 273$  K it shows the well known dose response curves. Its maximum supralinearity factor appears at  $T_{\text{irr}} = 323$  K. The linear response is extended up to 460 Gy at  $T_{\text{irr}} = 273$  K and falls to 80 Gy at  $T_{\text{irr}} = 373$  K.

## 1. Introduction

The radiation induced effects in quartz have been extensively studied for pure physics and technological purposes (Haliburton *et al* 1981, McKeever 1984). These effects are dependent on impurities concentration. Among the impurities,  $\text{Al}^{3+}$  plays an essential role, in both synthetic and natural quartz (Haliburton *et al* 1981). The  $\text{Al}^{3+}$  ion substitutes  $\text{Si}^{4+}$  thus requiring charge compensation. Such charge compensators are alkali ions ( $\text{M}^+$ ),  $\text{H}^+$  at interstitial sites, or radiation induced holes at oxygen ions (Martin 1983, Haliburton *et al* 1981). The removal of the compensators from the  $\text{Al}^{3+}$  sites, which is temperature dependent, gives rise to the creation of  $[\text{Al}_c^+]^0$  centres. For example if the irradiation temperature exceeds 200 K the alkali ions become mobile. The  $[\text{Al}_c^+]^0$  centres play an important role in the TL properties of quartz (McKeever 1985, Alonso *et al* 1983, Jani *et al* 1983b).

TL dose response curves for quartz obtained at various irradiation temperatures, are useful not only for understanding the physics of TL and the role of impurities in radiation effects, but also, for practical applications in TL dosimetry and archaeometry (Durrani *et al* 1977). A brief review of the work already performed in this area is now given.

† In the present work the irradiation temperatures will be given in K; any other temperatures in °C.

For the above room-temperature glow curve Aitken *et al* (1974) reported that the sensitivity of the 325 °C peak of quartz decreases as the  $T_{\text{irr}}$  increases from 293 to 373 K for a dose of 15 Gy, while it remains constant for a dose of 400 Gy. McKeever *et al* (1978) and Durrani *et al* (1977) observed an increase in the TL response of the (240–420 °C) integral, by a factor of 5, between the  $T_{\text{irr}}$  193 and 293 K for a dose of 50 Gy and by a factor of  $10^3$  for a dose of 6 kGy. Jani *et al* (1983b), after a set of irradiations at 77 K, 293 K and at ‘293 plus 77 K’ on synthetic and natural quartz, suggest that the  $[\text{AlO}_4]^{0-}$  hole-like centres which are created when the alkali ions are moving away from aluminium sites, participate in the TL processes in the 200–300 °C region of the glow curve. Kitis and Charalambous (1988) studied the TL response of pure Norwegian quartz and quartz extracted from pottery, in fine and coarse grains, as a function of  $T_{\text{irr}}$ . In the case of pure Norwegian quartz they found a strong dependence of the response on  $T_{\text{irr}}$  which was a function of dose.

For the below room-temperature glow curve, Malik *et al* (1981) found that the TL response of the (185–270 K) integral was decreased as  $T_{\text{irr}}$  was increased from 100 to 300 K. This result, according to McKeever *et al* (1985), can be correlated with the increase in the intensity of the (230–420 °C) integral as a function of  $T_{\text{irr}}$ , as observed by Durrani *et al* (1977) (as well as by Kitis and Charalambous 1988). The above correlation leads to the conclusion that at high enough  $T_{\text{irr}}$  alkali ions are able to move away from the aluminium sites

during irradiation giving rise to the formation of  $[Al^{3+}]$  centres, which act as recombination sites.

The TL dose response of quartz is highly supralinear (Ichikawa 1968, David *et al* 1978) under room-temperature irradiation. However, there is nothing known about  $T_{irr}$  dependent supralinearity, except the two dose response curves at  $T_{irr} = 193$  and 273 K in the dose region  $10^4$  to  $1.5 \times 10^5$  Gy (Durrani *et al* 1977).

The aim of the present work is twofold. First, to present a complete set of data on the dependence of the TL response of quartz on  $T_{irr}$ , how this is affected by dose and the results of  $T_{irr}$  on the TL dose response  $f(D)$ , as defined by Horowitz (1984). Secondly, to contribute to the research of the TL mechanism in looking for a universal behaviour of the TL response against irradiation temperature.

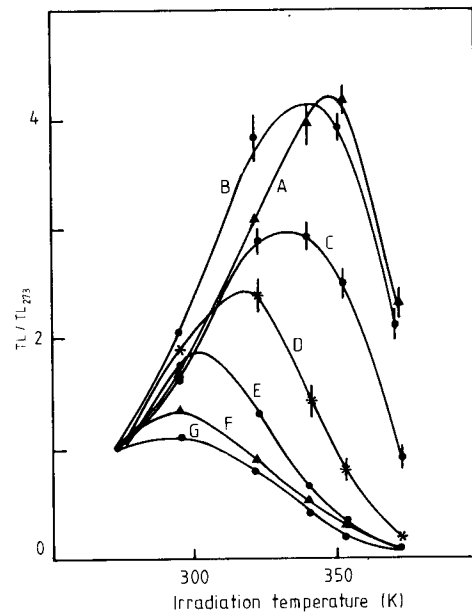
## 2. Experimental procedure

The samples studied in the present work were pure Norwegian quartz powder of dimensions 100–140  $\mu m$ . Prior to irradiation they were annealed at 500 °C, for 1 hour in air and cooled rapidly to room temperature. The irradiation temperature range was 77–373 K and the dose range 54–8400 Gy. A  $^{60}Co$  gamma-cell unit (Type 200 of Atomic Energy of Canada Ltd.) was used for all irradiations with a dose rate of 0.07 Gy  $s^{-1}$ . The irradiations at 77, 193 and 273 K were performed in Dewars containing liquid nitrogen,  $CO_2$  + alcohol and ice, respectively. For the higher  $T_{irr}$  a furnace was used whose temperature was controlled with  $\pm 2$  °C accuracy. Both Dewar and furnace were inserted in the cylindrical irradiation chamber of the gamma cell (diameter 8.9 cm and height 14 cm). The samples were left in the furnace, prior to irradiation, for 5 min to achieve the desired temperature. At the end of irradiation the samples were removed from the furnace within 20 s and cooled to room temperature. The measurements were performed with the Harshaw 2000A-B TLD reader in  $N_2$  atmosphere at a heating rate of 6.7 °C  $s^{-1}$ .

## 3. Experimental results

The glow curve of Norwegian quartz consists of a number of glow peaks. The intense glow peak at about 110 °C is not studied because of its short half-life at room temperature. There is also a well defined glow peak at about 180 °C which does not appear at  $T_{irr} = 77$  K, even if the dose exceeds 8.4 kGy. At  $T_{irr} = 193$  K this glow peak appears only for doses greater than 460 Gy, while at  $T_{irr} \geq 273$  K it appears for very low doses. For typical glow curves at various  $T_{irr}$  see Kitis and Charalambous (1988). Above 230 °C the glow curve consists of more than an unresolved glow peak.

$\ddagger f(D) = [F(D)/D]/[f(D_1)/D_1]$  where  $F(D)$  is the TL for a dose  $D$  and  $F(D_1)$  the TL at a low dose  $D_1$ .



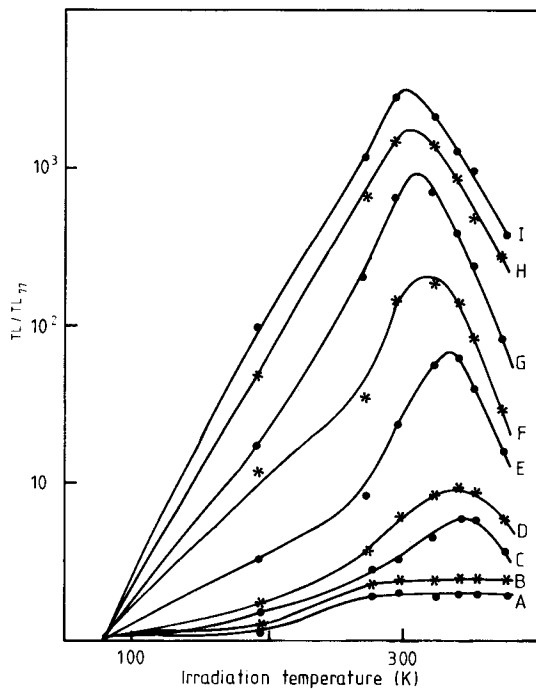
**Figure 1.** The response of the 150–230 °C glow-curve integral as function of  $T_{irr}$  for various doses. Normalisation to 273 K. Doses (in Gy) are A, 55; B, 80; C, 135; D, 465; E, 2100; F, 4200 and G, 8400.

For this reason we chose for our study well defined glow-curve intervals instead of heights at various ordinates of temperature. Namely, we chose the integrals between 150–230 °C and 230–350 °C.

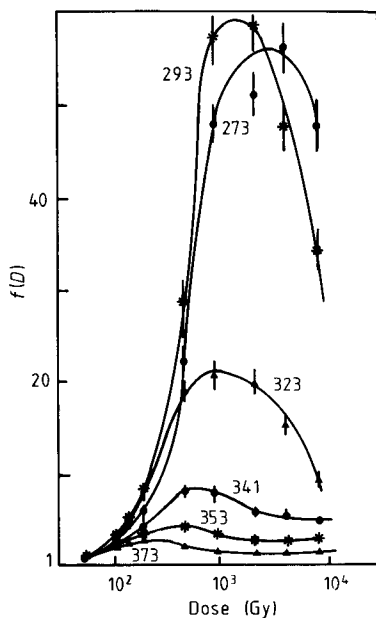
Figure 1 shows the TL response of the 150–230 °C glow curve integral as a function of  $T_{irr}$  for various doses normalised to the response at 273 K. The TL response of this integral initially increases until a maximum value is reached and then decreases rapidly. As the dose increases, this maximum value of the response shifts to lower  $T_{irr}$ , i.e. the maximum appears at 353 K for a dose of 54 Gy and at 293 K for a dose of 8.4 kGy.

In figure 2 the TL response of the 230–350 °C integral is shown, normalised to the response at 77 K. The TL response increases continuously until a maximum value is reached and then starts to decrease. As the dose increases, this maximum value increases and shifts to lower  $T_{irr}$ , i.e. the response is increased by a factor of 3 between 77 K and 293 K and is nearly independent of  $T_{irr}$  between 293 and 373 K for doses up to 80 Gy. For a dose of 110 Gy the maximum value of the response (by a factor of 6.5) is observed at  $T_{irr} = 353$  K, while for a dose of 8.4 kGy the maximum value of the response is about  $3.5 \times 10^4$  and appears a little above room temperature. However, if the TL response of this integral is normalised relative to 273 K, we can observe that (i) the behaviour of the 230–350 °C integral is quantitatively similar to that of the 150–230 °C integral (figure 1), for the above room-temperature  $T_{irr}$  range and (ii) that the main increase of the response is observed between 77 and 293 K.

In figure 3 the behaviour of the TL dose response  $f(D)$ , for the integral 150–230 °C, is shown as a function of dose for various irradiation temperatures. The peak in this region gives  $f(D) > 1$  (supralinearity), even from



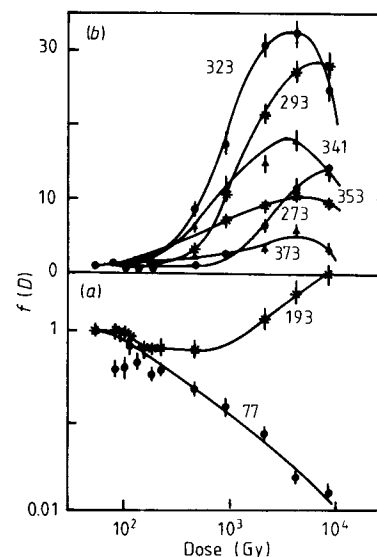
**Figure 2.** The response of the 230–350 °C glow-curve integral as function of  $T_{\text{irr}}$  for various doses. Normalisation to 77 K. Doses (in Gy) are A, 55; B, 80; C, 110; D, 190; E, 465; F, 930; G, 2100; H, 4200 and I, 8400.



**Figure 3.** TL dose response  $f(D)$  of the 150–230 °C glow-curve integral for various  $T_{\text{irr}}$  in K.

the lowest dose (54 Gy) of the present work. The variation of  $f(D)$  is strongly dependent on both dose and  $T_{\text{irr}}$ . Also,  $f(D)$  presents a maximum which shifts to lower doses as  $T_{\text{irr}}$  increases.

The TL dose response  $f(D)$  of the 230–350 °C integral has a very peculiar behaviour, which is shown in



**Figure 4.** TL dose response  $f(D)$  of the 230–350 °C glow curve integral for various  $T_{\text{irr}}$  in K.

figure 4. At  $T_{\text{irr}} = 77$  K (figure 4(a)) the behaviour is continuously sublinear,  $f(D) < 1$ . At  $T_{\text{irr}} = 193$  K the behaviour is sublinear for doses up to 460 Gy, but becomes supralinear,  $f(D) > 1$ , for higher doses. For irradiation temperature  $T_{\text{irr}} \geq 273$  K, the  $f(D)$  against dose curves consist of a linear, supralinear and a sub-linear region (figure 4(b)). As the  $T_{\text{irr}}$  increases, the maximum  $f(D)$  initially increases, takes its higher value of about 30 at 320 K and then it drops off. The dose width of the linear region also depends on  $T_{\text{irr}}$ . Namely, at  $T_{\text{irr}} = 273$  K the linear region extends up to 460 Gy, at 293 K up to 150 Gy and at higher  $T_{\text{irr}}$  up to 80 Gy.

#### 4. Discussion

There are two important points to the above results for which we would like to give explanations. First, the initial rapid increase of the TL response from the lowest  $T_{\text{irr}}$  (77 K) up to  $T_{\text{irr}}$  where the maximum response value is observed. Second, the sharp decrease of the TL response observed after the maximum as well as the shift of the sharp decrease threshold to lower  $T_{\text{irr}}$  as the dose increases.

To explain the first point we will examine the effects of irradiation temperature on the three basic elements of thermoluminescence, i.e. the moving entity, the trap and the luminescence centre. In the case of quartz most researchers suggest that the moving entity is an electron (McKeever 1985, Sibley 1988). Moreover, for the doses used in our study, the probability of defect creation by electronic processes is much greater than the probability of the other two mechanisms, elastic collision and radiolysis (Sibley 1988).

Under the effect of the irradiation temperature,  $T_{\text{irr}}$ , electrons (moving entities) from thermally unstable traps, with  $T_{\text{max}} < T_{\text{irr}}$ , are transferred to thermally stable ones with  $T_{\text{max}} > T_{\text{irr}}$ . The electrons that

are trapped by thermally unstable traps are simultaneously released, then having two possible actions. First, to recombine with holes at luminescence centres and second to be retrapped by a thermally stable trap. It is obvious that in the latter case the response of the corresponding glow peak will be enhanced. Therefore, through this electron transfer mechanism the TL response of a stable glow peak will be increased as the  $T_{\text{irr}}$  increases (figures 1 and 2).

However, the above mechanism is insufficient to explain the considerable increase of the TL response against  $T_{\text{irr}}$  for very high doses. For the latter some additional mechanism is required. For example, it is possible that under the effect of  $T_{\text{irr}}$  new traps and luminescence centres are created. However, excluding the moving entity, there are no unambiguous correlations between defects, impurities and specific glow peaks (traps and luminescence centres). A lot of work performed in this direction, indicates that the  $[\text{Al}^{3+}]^0$  centres act as recombination sites for electrons released from traps. These hole traps are created, as  $T_{\text{irr}}$  increases, from Al-M<sup>+</sup> centres when the alkali ions are moving away from aluminum sites along the open *c*-axis channels (Markes and Haliburton 1979, McKeever 1985). The alkali ions are stabilised elsewhere in the lattice acting as electron traps (Jani *et al* 1983b). Malik *et al* (1981) observed an increase in the concentration of the  $[\text{Al}_c^+]^0$  and Al-OH centres, as  $T_{\text{irr}}$  increased from 77 to 300 K, which is correlated with the decrease of thermoluminescence intensity of the 185–270 K integral. Furthermore, it has been reported by other researchers that the concentration of the Al-hole centres (Koumvakalis 1980, Markes and Haliburton 1980, Martin 1983) as well as *E'* and *E''* type centres (Jani *et al* 1983a, Bossoli *et al* 1982) increases as  $T_{\text{irr}}$  increases. Especially, Jani *et al* (1983b) directly correlated the thermoluminescence of 200–300 °C integral with Al-hole centres, because the maximum emission in this temperature range coincides reasonably well with the thermal anneal step of these centres, which occurs at 300 °C. Jani *et al* (1983b) correlated, also, the thermoluminescence below 200 °C with E type centres having annealing steps at these temperatures. However their correlation is qualitative and not quantitative. Durrani *et al* (1977), who had found similar results to ours in the  $T_{\text{irr}}$  range 77–273 K, attributed the increase of the response between 193 and 273 K at low doses to the creation of  $[\text{Al}^{3+}]$  hole trap centres. They also attributed the large increase of sensitivity at high doses to the creation of new electron traps, which are compensated by the excess of the Al-M<sup>+</sup> centres. From the compiled data presented above, the role of the Al-hole centres as recombination sites and of alkali ions as trapping sites becomes evident. On one hand, their concentration increases as  $T_{\text{irr}}$  increases. According to these conclusions we suggest that as the irradiation temperature increases the concentrations of both traps and luminescence centres increase. On the other hand the electrons from thermally unstable traps are transferred, with respect to the electron transfer mechanism

mentioned earlier, to pre-existing deeper traps as well as to the new ones created by irradiation. Therefore, since luminescence centres are available, the response of glow peaks which correspond to thermally stable traps will be increased.

Primarily it must be elucidated from the second point of the discussion that the sharp decrease of the response, (figures 1 and 2) is in excess of the decrease due to thermal decay of TL, which is expected during long exposure times at high  $T_{\text{irr}}$ . Indeed, for high doses (long irradiation times) the threshold of the sharp decrease lies at a value of  $T_{\text{irr}}$  between 300–353 K and it is questionable that glow peaks at 180 °C and above 230 °C (second integral) will be affected by these irradiation temperatures. To confirm this we need the *E* (activation energy) and *S* (frequency factor) parameters of the glow peaks existing in the studied integrals. We have not estimated the *E* and *S* parameters of the glow peaks in Norwegian quartz. So, we used the corresponding *E* and *S* as tabulated by Aitken (1985). The calculated half lives, at  $T_{\text{irr}} = 373$  K, the larger of the present work, lie between 110 hours and 180 years. These half lives must be compared with our maximum irradiation time of 46 h. From the comparison with the experimental results (figures 1 and 2), we conclude that the sharp decrease is not solely due to thermal decay during the exposure time. So, we suggest that another different mechanism must exist which is responsible for the excess to thermal decay decrease of the TL response.

A probable mechanism which can explain the sharp decrease of the response, as well as the shift of its threshold to lower  $T_{\text{irr}}$  as the dose increases (figures 1 and 2) is that a thermally unstable trap is never filled completely, but attains an equilibrium state between filling and emptying (Christodoulides *et al* 1971). This situation remains, even if the dose exceeds the saturation dose of this trap, i.e. the dose for which the trap would be in saturation if it was thermally stable. Above this saturation dose, the unstable trap traps excess electrons, which are simultaneously released. Part of them annihilate holes at luminescence centres, which under normal conditions correspond to stable ones. Therefore, the TL response of the glow peaks due to stable traps is decreased. On the other hand, as the dose becomes greater than the saturation doses of the unstable traps, the threshold of the sharp decrease shifts to lower  $T_{\text{irr}}$ .

Moreover, at very high  $T_{\text{irr}}$  (353–373 K) other effects, excluding thermal fading and the previous mentioned mechanism, contribute to the sharp decrease of the response. Such an effect is thermal quenching, which can take place at this  $T_{\text{irr}}$  region as has been observed in many phosphors and in quartz especially, by Wintle (1975). Also, at these high  $T_{\text{irr}}$  various defects which act as traps or luminescence centres become mobile and consequently they will be annealed. Obviously, all the above mentioned mechanisms could take place simultaneously, thus leading

to a sharp decrease of the response in excess of thermal fading.

In summary, it has been found that pure Norwegian quartz is very sensitive to irradiation temperature. Its response depends strongly on  $T_{\text{irr}}$  and in addition this dependence is a function of dose. It also exhibits temperature dependent supralinearity. In particular the 230–350 °C glow curve integral is sublinear below  $T_{\text{irr}} = 193$  K, while for  $T_{\text{irr}} \geq 273$  K it shows linear, supra-linear and finally sublinear behaviour. The upper dose limit of linearity varies from 460 Gy at  $T_{\text{irr}} = 273$  K to below 80 Gy at  $T_{\text{irr}} = 373$  K.

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