

## MODELLING THE PRE-DOSE EFFECT IN THERMOLUMINESCENCE

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**Abstract** — The increase of sensitivity of quartz by  $\beta$  or  $\gamma$  irradiation, followed by high temperature activation has been studied. The model previously suggested, including a reservoir through which holes get into the recombination centre, thus increasing the sensitivity to a given test dose, is now given a concrete mathematical form. Sets of simultaneous differential equations for the different stages of irradiation and heating are numerically solved sequentially so as to simulate the physical processes taking place. The dependence of the sensitivity on the excitation dose is followed, in particular at the high doses where the sensitivity approaches saturation. The assumption of exponential approach to saturation is tested, showing that, indeed, even in this complicated situation the exponential approximation is valid.

### INTRODUCTION

The sensitisation of various thermoluminescence (TL) materials by  $\beta$  or  $\gamma$  irradiation followed by an anneal at high temperature is a well-known phenomenon<sup>(1–3)</sup>. Briefly described, the sensitivity of a given sample is its TL emission in response to a given test dose. The sensitivity of the sample can be changed in such a way that in a subsequent heating, the response of the same TL peak in the same sample is different, normally larger. The main reason, discussed here, for such a change of the sensitivity is the application of a relatively large dose to the sample, followed by an anneal at a relatively high temperature. It should be mentioned that the following discussion pertains mainly to the 110°C peak in natural quartz and the results considered are utilised for the pre-dose dating technique. A typical example of the sequence of actions taken and measurements made with a sample of quartz are as follows (see e.g. Ref. 3):

- (1) The initial sensitivity  $S_0$  to a small test dose ( $\sim 0.01$  Gy) is measured by heating the sample to  $\sim 150^\circ\text{C}$  following the administration of the test-dose.
- (2) The ‘high’ dose  $N$  (of the order of  $\sim 1$  Gy), which simulates the natural dose in archaeological samples, is applied followed by an annealing at  $\sim 500^\circ\text{C}$ ; the sample is then cooled back to RT.
- (3) Another test dose of the same size is applied and the sample is heated at the same heating rate as in step 1 to  $150^\circ\text{C}$ . The occurrence of the pre-dose sensitisation effect is expressed by the response to the second test dose,  $S_N$  being larger than the

response  $S_0$  to the first due to the large irradiation followed by annealing.

The first theory explaining the pre-dose effect was given by Zimmerman<sup>(1,2)</sup>. The basic energy level scheme given by her includes one electron trapping state  $T$  and two hole states  $R$  (reservoir) and  $L$  (luminescence centre). During the excitation by  $\beta$  or  $\gamma$  rays, electrons are raised from the valence to the conduction band, which can be trapped in the trapping states  $T$  (see Figure 1). The holes go preferably to the reservoir  $R$ , however, there is a non-negligible probability of the holes going to  $L$  so that thermally freed electrons can recombine with them during the heating, which results in the emission of TL of the unsensitised material. The annealing stage, typically to  $500^\circ\text{C}$  following the application of a high dose empties all the electrons from  $T$ , yielding a rather high TL peak at  $\sim 110^\circ\text{C}$  (which may or may not be recorded). Its more important effect is to release thermally the holes from the reservoir  $R$ , which will sub-

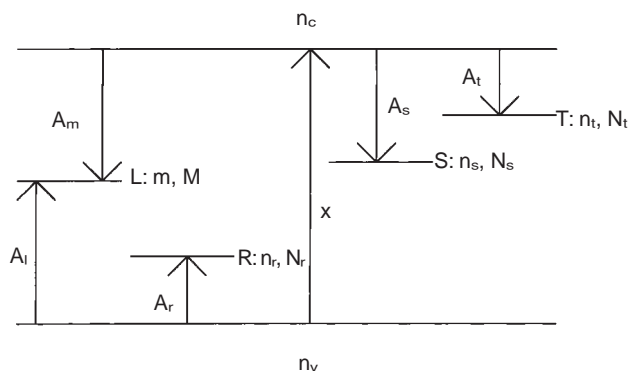


Figure 1. Energy level diagram including the electron trapping state,  $T$ , the competitor,  $S$ , the hole reservoir,  $R$ , and the luminescence centre,  $L$ .  $n_c$  and  $n_v$  are the free electron and hole concentrations respectively and  $x$  the rate of production of free electrons and holes. The transitions shown are those taking place during the excitation stage.

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sequently be trapped in the luminescence centre L. According to Zimmerman, this increase in the concentration of holes in the luminescence centre is the reason for the higher response to a subsequent test dose. In a later work, Chen<sup>(4)</sup> argued that in the framework of the model with T, R and L levels, the observation that the finally measured TL is proportional to the filling of L and, at the same time, there is a linear dependence on the size of the test dose, i.e. on the concentration of trapped electrons in T, are contradictory. Following previous concepts by Kristianpoller *et al*<sup>(5)</sup> explaining superlinearity, which indeed occurs in the 110°C peak in the unannealed quartz<sup>(6)</sup>, Chen<sup>(4)</sup> resolved the above mentioned contradiction by assuming an extra electron level which competes for electrons during the heating stage. The full energy level diagram is shown in Figure 1.

In the present work, we follow the model described, with two electron and two hole trapping states by writing the relevant simultaneous differential equations and solving them numerically for certain choices of sets of trapping parameters. The sets of equations are to be presented and solved for the different stages of 'short' irradiation (test dose) and heating (readout); 'long', high dose irradiation followed by annealing, and another 'short' irradiation and heating. This sequence can be repeated several times. Obviously the sample parameters are kept constant along such a sequence, and thus, if a certain choice of one or more parameters is required for explaining a certain feature, the same values of the parameters are to be kept along the sequence, and only the final results would show if the feature in question really behaves as expected when all the stages of the experiment have been followed. Of course, the situation is rather complicated due to the large number of parameters involved.

One other important point is to be considered. The basic pre-dose method assumed that in the relevant dose range, the dependence of the sensitivity on the dose is linear. This may not be the case in particular when a number of additional calibration doses are given to the sample following the 'natural' dose which is to be determined. Chen<sup>(4)</sup> suggested a way to extend the applicability of the method to determine the dose (and thereby the age) by assuming that the sensitivity depends on the dose exponentially, namely,

$$S = S_{\infty} (1 - e^{-D/B}) \quad (1)$$

where  $S_{\infty}$  is the saturation value of  $S$ ,  $D$  is the dose and  $B$  a constant with dose dimensions. In a recent work by Leung *et al*<sup>(7)</sup>, a regression method was developed for the evaluation of paleodose using the pre-dose technique, making use of the assumption that the approach to saturation is exponential. Using the numerical solutions in the present work, we can follow these possibilities within the framework of a comprehensive model.

## KINETIC EQUATIONS AND THEIR SOLUTIONS

The first step in following numerically the above-mentioned model is to write the equations governing the processes of excitation presented in Figure 1. The set of simultaneous differential equations (rate equations) is

$$dn_t/dt = A_t n_c (N_t - n_t) \quad (2)$$

$$dn_s/dt = A_s n_c (N_s - n_s) \quad (3)$$

$$dn_c/dt = x - A_t n_c (N_t - n_t) - A_s n_c (N_s - n_s) - A_m m n_c \quad (4)$$

$$dn_v/dt = x - A_t n_v (M - m) - A_r n_v (N_r - n_r) \quad (5)$$

$$dm/dt = A_t n_v (M - m) - A_m m n_c \quad (6)$$

$$dn_r/dt = A_r n_v (N_r - n_r) \quad (7)$$

Here,  $n_t(\text{cm}^{-3})$  and  $N_t(\text{cm}^{-3})$  are the concentrations of trapped electrons and trapping states, respectively, in the 'main' T traps;  $n_s(\text{cm}^{-3})$  and  $N_s(\text{cm}^{-3})$  are the concentrations of trapped electrons and trapping states of the competitor, respectively;  $n_r(\text{cm}^{-3})$  and  $N_r(\text{cm}^{-3})$  are the concentrations of holes in the reservoir and the trapping states in the reservoir, respectively;  $m(\text{cm}^{-3})$  and  $M(\text{cm}^{-3})$  are the concentrations of the holes and states in the luminescence centres, respectively;  $n_c(\text{cm}^{-3})$  and  $n_v(\text{cm}^{-3})$  are the concentrations of free electrons and holes, respectively;  $A_t(\text{cm}^3 \cdot \text{s}^{-1})$  and  $A_s(\text{cm}^3 \cdot \text{s}^{-1})$  are the trapping probabilities in T and S respectively;  $A_r(\text{cm}^3 \cdot \text{s}^{-1})$  and  $A_l(\text{cm}^3 \cdot \text{s}^{-1})$  are the probabilities of hole trapping in R and L, respectively; and  $A_m(\text{cm}^3 \cdot \text{s}^{-1})$  is the recombination probability of free electrons with trapped holes in the luminescence centres.  $x(\text{cm}^{-3} \cdot \text{s}^{-1})$  is the intensity (dose rate) of the excitation irradiation which produces pairs of free electrons and holes.

The set of equations has been solved by using the built-in ode23 Matlab package solver. Once this set of equations is solved for an irradiation time of  $t$  seconds, the applied dose is calculated as  $D = x t$ . Of course, the program described so far which follows the process of excitation, can be used for both the test dose and high dose simulations.

A second part of the program developed is that which simulates the heating process. In addition to the magnitudes described above with respect to Figure 1,  $E_t$  and  $s_t$ , the activation energy (eV) and frequency factor ( $\text{s}^{-1}$ ) of the electron trapping state are to be considered, as well as  $E_r$  and  $s_r$ , the activation energy and frequency factor of the reservoir. It should be noted that in the low temperature heating, up to  $\sim 150^\circ\text{C}$ , the main interest is the intensity at the maximum of the peak. Therefore the program is allowed to identify the maximum temperature and the intensity there, but the run continued up to  $\sim 150^\circ\text{C}$  so as to simulate properly the experimental conditions and the possible effect on the subsequent stages of the experiment. As explained by Aitken<sup>(8)</sup>, the quenching effect seen following 'high' excitation followed by only low temperature annealing (e.g.  $150^\circ\text{C}$ ) has to do with the recombination with holes in the

recombination centre, which causes the final concentration  $m$  following the application of the next test dose to be smaller than expected.

The rate equations governing the process taking place during heating are as follows,

$$dn_t/dt = A_t n_c (N_t - n_t) - s_t \exp(-E_t/kT) n_t \quad (8)$$

$$dn_s/dt = A_s n_c (N_s - n_s) \quad (9)$$

$$dn_c/dt = s_t n_t \exp(-E_t/kT) - A_t n_c (N_t - n_t) - A_m n_c m - A_s n_c (N_s - n_s) \quad (10)$$

$$dn_v/dt = n_r s_r \exp(-E_r/kT) - A_r n_v (N_r - n_r) - A_1 n_v (M - m) \quad (11)$$

$$dm/dt = A_1 (M - m) n_v - A_m n_c m \quad (12)$$

$$dn_r/dt = A_r n_v (N_r - n_r) - n_r s_r \exp(-E_r/kT) \quad (13)$$

The intensity of the emitted TL is assumed, as mentioned above, to be the result of recombination of free electrons with trapped holes in the centres of concentration  $M$ , thus, it is given by

$$I(T) = A_m m n_c \quad (14)$$

In the conventional way, a linear heating function is utilised, namely,  $T(t) = T_0 + \beta t$  where  $\beta$  is the (constant) heating rate and  $T_0$  the initial temperature. The parameters appearing in Equations 8–14 are the same as in Equations 2–7 since we are dealing with the same physical system. A heating rate of  $5 \text{ K.s}^{-1}$  has been used.

## THE MODEL AND NUMERICAL RESULTS

The general considerations made in the past concerning the pre-dose effect, usually took separately into consideration effects occurring during the excitation and during the heating of the sample. In this sense, the present treatment is more comprehensive, performing all the stages of the procedure, namely, low and high dose excitations as well as low and high temperature annealings, on the same sample which, in our case, is represented by the same set of trapping parameters. The experimental results to be explained by the model are as follows:

- (1) Linear dependence of the signal on the size of the test dose.
- (2) Apparently exponential approach to saturation (see Equations 1 above and 15 below) of the sensitivity with repeated additive doses. At low doses, this can be approximated as a linear dependence.
- (3) Three accompanying effects are only briefly mentioned. These are the quenching by high dose exposure<sup>(8)</sup>, the UV reversal<sup>(1)</sup> and the distinction between reservoir and centre saturations<sup>(4)</sup>. These are seen in the results of the present calculations, but will be discussed in detail elsewhere.

The number of parameters to be chosen is very large,

which may bring one to the conclusion that any behaviour can be explained. Indeed, different choices of parameters may bring about different behaviours. The main point in this respect is, however, that it was easy to choose sets of parameters that result in a good simulation of *all* the above mentioned phenomena by just keeping in mind some required relations between these parameters. The choice of sets of parameters, and the numerical qualitative results associated with one such set follow.

The basic idea behind the concept of the reservoir is that, during the irradiation, the created holes go preferably into the reservoir  $R$ . In the example discussed here, and referring to Figure 1,  $A_r = 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $A_1 = 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$  have been chosen. The  $E_r$  and  $s_r$  values are to be chosen such that heating to  $\sim 150^\circ\text{C}$  will not release any significant number of trapped holes whereas heating to  $500^\circ\text{C}$  will do so.  $E_r = 1.4 \text{ eV}$  and  $s_r = 10^{13} \text{ s}^{-1}$  have been taken. Thus, although the retrapping into  $R$  is stronger than the capture in  $L$ , most of the holes move into  $L$  during the high temperature annealing. Moreover, this choice ensures the UV reversal since, once a hole is released (at RT) by UV from  $L$  into the valence band, it will preferably go back into  $R$  rather than to  $L$ . The  $N_r$  and  $M$  capacities have been chosen to be  $10^{13} \text{ cm}^{-3}$  and  $10^{14} \text{ cm}^{-3}$ , respectively. The values of  $E_t$  and  $s_t$  should be taken so that the peak will occur at  $\sim 110^\circ\text{C}$ , i.e.  $\sim 383 \text{ K}$ . Here  $E_t = 1.0 \text{ eV}$  and  $s_t = 10^{13} \text{ s}^{-1}$  have been chosen. In order to have both a linear dependence of the signal on the test dose as well as a dependence of the measured sensitivity on the applied high dose, it has been argued by Chen<sup>(4)</sup> that a necessary condition is that the trapping into the competitor  $S$  should be faster than the recombination. Here  $A_s = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  and  $A_m = 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$  have been taken. As for the retrapping probability  $A_t$ , the results were found to be rather insensitive to changes in this parameter, and  $A_t = 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$  was chosen. The capacities of the trapping and competitor states have been taken as  $N_t = 10^{13} \text{ cm}^{-3}$  and  $N_s = 10^{12} \text{ cm}^{-3}$ , respectively. Finally, the initial values of the different functions should be set. At first sight, setting all of them to zero sounds reasonable. This indeed is the case as far as  $n_c$ ,  $n_v$ ,  $n_t$  and  $n_r$  are concerned. If one assumes a prior heating to high temperature, the choice of  $n_c(0) = n_v(0) = n_t(0) = n_r(0) = 0$  is obvious. However,  $S$  is considered to be disconnected at least as far as heating to  $500^\circ\text{C}$  (and perhaps more) is concerned. Up to this temperature,  $n_s$  is not depleted, which leaves  $n_{s_0} \neq 0$  for the next step. For the sake of neutrality, one has to assume  $m(0) = n_s(0)$  and these values may be non-zero. The importance of choosing  $m_0 \neq 0$  has to do with the linear dependence of the TL signal on the size of the test dose. As has been discussed before<sup>(5,6)</sup>, the occurrence of a strong competitor ( $S$  in the present case) may result in a superlinear dose dependence. Indeed, solving the sets of equations with the above parameters along

with  $m(0) = n_s(0) = 0$  yielded a quadratic test dose dependence. However, a choice of

$$n_s(0) = m(0) = 10^{10} \text{ cm}^{-3}$$

made the test dose dependence linear and still showed all the other experimentally observed features of sensitisation, quenching and UV reversal. The test dose was also chosen to be  $5 \times 10^8 \text{ cm}^{-3}$  and the increments of the 'large' dose 100 times larger, namely,  $5 \times 10^{10} \text{ cm}^{-3}$ . It is important to note that although the approach to saturation looks natural in such a situation, the processes leading to the final results are rather complicated both in the real samples and in the presently simulated results. One can ask whether the exponential approach to saturation is a good approximation to the numerical results. Since, both in the experimental results in quartz and in the numerical values found here,  $S_0$  is not negligibly small as compared to the sensitised values of  $S$ , it was preferable to write the approximated dose dependence of  $S$  as

$$S = S_0 + S_\infty (1 - e^{-D/B}) \quad (15)$$

rather than Equation 1. The sensitivities calculated above were fitted to this 3-parameter expression, the parameters to be determined being  $S_0$ ,  $S_\infty$  and  $B$ . The best fit for evaluating the three parameters is performed by least squares. The 'experimental' points as well as the best-fitted curve are plotted against the dose on the same graph in Figure 2.

## CONCLUSION

In this work, the model with one active trapping state, one thermally disconnected competitor trap and two hole states, namely, a radiationless reservoir and a radiative luminescence centre was studied. The relevant sets of differential equations have been numerically solved

and the experimental procedures of having a sequence of high dose increments have been simulated. This curve is best-fitted to the expression 15, and the fit looks very good.

All the experimental features previously observed in the 110°C peak in quartz, were found here as a result of these calculations, when the 'appropriate' set of parameters was chosen. Finding such a set of parameters turned out to be rather easy when the qualitative considerations mentioned in the literature concerning specific features were taken into consideration. These experimental features include the linear dependence of the signal on the size of the test dose, the approach to saturation, the UV reversal and the radiation quenching effect.

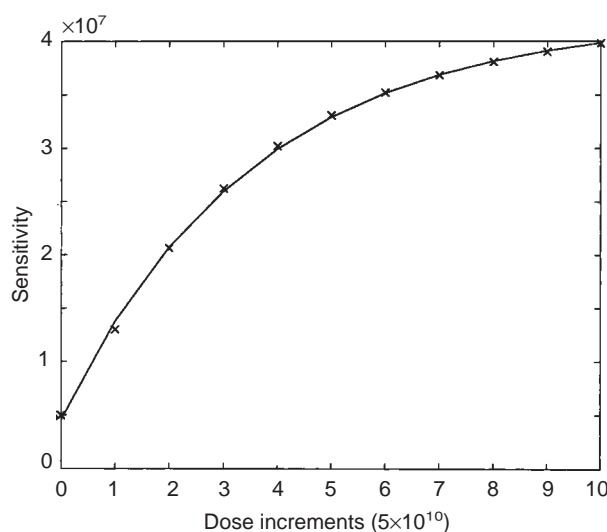


Figure 2. Simulated sensitivity as a function of the number of increments of high dose ( $\times$ ). The full curve is the best fitted exponential function. The relevant parameters are given in the text.

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