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THEORETICAL ACCOUNT OF THE SENSITIZATION AND DE-SENSITIZATION IN QUARTZ

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Abstract—A model is presented which can explain previously published experimental results of sensitization and de-sensitization of the 460 nm emission in the 110°C TL peak in synthetic quartz. The simple model presented includes one kind of recombination center and two kinds of trapping states, one directly related to the TL peak and the other which acts as a competitor. Once a set of parameters is chosen, the set of simultaneous differential equations is numerically solved for the three stages of the experiment, namely, excitation, relaxation and heating in each cycle. Following the experimental procedure, such repeated cycles are performed starting from either low or high initial sensitivity. For a given repeated "test dose", the sensitivity approaches the same equilibrium level, starting from either low or high values, both in the experiments and simulated results. This agreement between the experimental and numerical results adds credibility to the competing trap model of sensitization. As opposed to the conventional pre-dose effect of the 380 nm emission, the occurrence of the hole reservoir is not required for the model.

1. INTRODUCTION

THE INCREASE in sensitivity of thermoluminescent materials as a result of irradiation followed by high temperature annealing, has been seen in different materials. In particular, this effect has been observed in the 110°C peak in which β or γ irradiations of, say, 1 Gy, followed by heating to $\sim 500^\circ\text{C}$ increased the sensitivity substantially, in some samples by more than an order of magnitude. The effect was first discovered by Fleming and Thompson (1970), and a model explaining it was given by Zimmerman (1971). It is to be noted that in these measurements, only the 380 nm component of the emission was measured; thus, the described results are specific to this near-UV emission.

The model by Zimmerman basically consists of one electron trapping state which thermally releases electrons at around 110°C, and two hole centers. One of these, termed the reservoir, is assumed to be rather close to the valence band, and has a high cross-section for capturing free holes, as compared to the other center. During the irradiation, the holes are favorably captured by the reservoir. During the heating stage, they are thermally released into the valence band, and are transferred into the other (recombination) center, thus increasing the sensitivity to a test dose administered following the annealing. Zimmerman (1971) also reported a reduction of the sensitivity following UV illumination of the sensitized sample. This de-sensitization was reversible in the sense that re-heating to $\sim 500^\circ\text{C}$ restored the high sensitivity. The explanation of this effect was that the UV light

released holes from the luminescence center, which preferably go back to the reservoir.

Chen (1979) pointed out a difficulty in this model, arguing that if this were the situation, the initial concentration m_0 of holes in centers would be the dominating factor, which means that $m_0 < n_0$, where n_0 is the initial concentration of electrons in traps. Further measurements showed that, for a given filling of holes in centers, the measured TL was proportional to the size of the test dose which implies that $n_0 < m_0$. The only way out was to accept a model, previously suggested by Kristianpoller *et al.* (1974) for explaining superlinearity, which assumes the existence of a competitor due to which the measured intensity depends on $n_0 m_0$ rather than on $\min(n_0, m_0)$.

Several investigators studied different aspects of the pre-dose effect and its applications (see e.g. Aitken and Murray, 1976; Bailiff, 1985; McKeever *et al.*, 1985; Yang and McKeever, 1988, 1990). In another work, Chen *et al.* (1988) reported a very strong superlinearity of the 110°C peak in synthetic quartz, and explained it semi-quantitatively using the above mentioned competitor model by Kristianpoller *et al.* (1974). The emission studied in this work was ~ 460 nm. A more detailed theoretical account has recently been given by Chen and Fogel (1993).

The same synthetic powder samples were the subject of a work by Chen *et al.* (1991) which studied the changes of sensitivity of the ~ 460 nm emission as measured using a 9558QB photomultiplier with an optical filter. The results are reproduced in Fig. 1. Sensitization and de-sensitization

of the 110°C peak were measured by cycles of β irradiation followed by annealing. With a pristine powder sample, cycles of, say, 8 Gy applied test dose, followed by heating to 300°C caused an increase in the sensitivity up to an equilibrium level as seen in curve (b₁). Similar results are seen in (a₁) and (c₁), but with 4 Gy and 12 Gy test doses, respectively. If, however, the same sets of cycles are performed on a previously sensitized sample by, say, an initial β dose of 100 Gy followed by heating to 300°C, the repeated test dose application plus 300°C annealing caused a decrease in the sensitivity. Here, the sensitivity went down to equilibrium values (a₂, b₂, c₂) rather close to those reached by the sensitization curves with the same repeated test doses.

In the present work, the same kind of results are numerically simulated, using a simple energy level model with one kind of recombination center, one active trapping state, and one kind of competing trap.

2. THE MODEL

The energy scheme is shown in Fig. 2. The two trapping states are N_1 and N_2 (denoting also the total concentrations of the two trapping states) with instantaneous occupancies of n_1 (m⁻³) and n_2 (m⁻³). E_1 and E_2 are the activation energies (eV), s_1 and s_2 (s⁻¹) are the frequency factors, and A_{n1} , A_{n2} (m³ s⁻¹) are

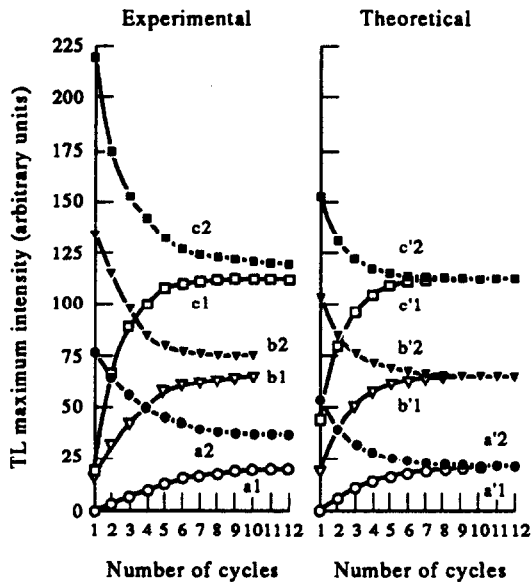


FIG. 1. Experimental results (left) and numerical results (right) of sensitization and de-sensitization of the 460 nm, 110°C TL peak in synthetic quartz. Curves a₁, b₁ and c₁ show the growth curves of TL with a 4, 8 and 12 Gy test dose cycle, respectively. a₂, b₂ and c₂ give the de-sensitization curves for the same cycles, after initial strong sensitization of 100 Gy followed by 300°C annealing. The theoretical results on the right-hand side simulate the same situation using the model described in Fig. 2, using the parameters mentioned in the text, and numerical solution of the appropriate differential equations.

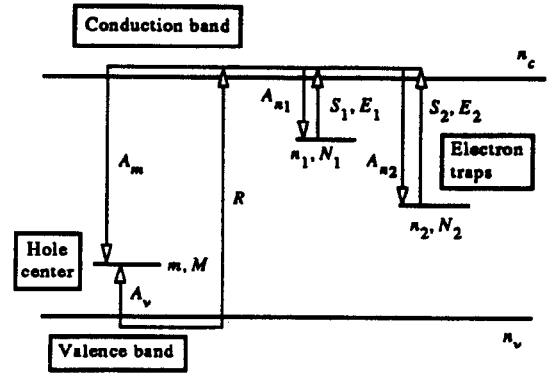


FIG. 2. Energy level scheme of the given model. Two electron trapping states are shown with concentrations N_1 , N_2 and occupancies n_1 , n_2 , respectively. The frequency factors are s_1 , s_2 ; the activation energies E_1 , E_2 and the retrapping probabilities A_{n1} , A_{n2} , respectively. n_c and n_v are the concentrations of electrons in the conduction band and holes in the valence band, respectively. R is the rate of electron-hole production, proportional to the dose rate. M and m are the total concentration and occupancy of hole centers. A_c and A_m are the trapping and recombination probabilities of holes from the valence and electrons from the conduction band, respectively, into the recombination center.

the retrapping probabilities. n_c and n_v (m⁻³) are the concentrations of electrons in the conduction band and holes in the valence band, respectively. R is the rate of production of electron-hole pairs (m⁻³ s⁻¹), proportional to the dose rate. A_m and A_v are the recombination probabilities of electrons and holes, respectively, into the hole centers and M and m (m⁻³) are, respectively, the hole center concentration and occupancy. The differential equations governing the process during the excitation phase are:

$$dn_1/dt = A_{n1}n_c(N_1 - n_1) - s_1n_1 \exp(-E_1/kT) \quad (1)$$

$$dn_2/dt = A_{n2}n_c(N_2 - n_2) - s_2n_2 \exp(-E_2/kT) \quad (2)$$

$$-dm/dt = A_mmn_c - A_vn_v(M - m) \quad (3)$$

$$dn_v/dt = R - A_vn_v(M - m) \quad (4)$$

$$dn_c/dt + dn_1/dt + dn_2/dt = dn_v/dt + dm/dt. \quad (5)$$

A relaxation period is being simulated in which the temperature of the sample is kept constant for a certain period of time after the excitation has stopped ($R = 0$). During this time, n_c and n_v decay down to negligible values. The final concentrations reached at this stage serve as initial values for the heating phase (readout). A constant heating rate is assumed, $T = T_0 + \beta t$; the hole center is assumed to be far enough from the valence band so that in this stage $n_v = dn_v/dt = 0$, and, of course, $R = 0$. The emitted light is assumed to be proportional to the rate of recombination, so that equation (3) changes in the final stage into

$$I = -dm/dt = A_mmn_c. \quad (3')$$

3. NUMERICAL RESULTS

The parameters chosen for the numerical calculations were $E_1 = 0.9$ eV; $E_2 = 1.4$ eV; $s_1 = s_2 = 10^{12}$ s⁻¹; $A_v = A_m = 2 \times 10^{-20}$ m³ s⁻¹; $N_1 = 1.99 \times 10^{20}$ m⁻³; $N_2 = 10^{18}$ m⁻³; $M = 2 \times 10^{20}$ m⁻³; $\beta = 1^\circ\text{Cs}^{-1}$; $A_{n1} = A_{n2} = 10^{-20}$ m³ s⁻¹; $R = 10^{18}$ m³ s⁻¹ in (a'); $R = 2 \times 10^{18}$ m³ s⁻¹ in (b'); $R = 3 \times 10^{18}$ m³ s⁻¹ in (c').

The simultaneous differential equations were solved using conventional algorithms (see e.g. Chen and Fogel, 1993). The results shown on the right-hand side of Fig. 1 are of the maximum intensity of the 110°C peak as a function of the number of preceding cycles of "test dose" applications plus heating to ~300°C. At least qualitatively, the numerical results resemble the experimental ones for the three values of R taken. In each case, the TL yield reached the same equilibrium level starting from either low or high sensitivity. The final level reached was slightly more than linearly dependent on the dose rate R , again, similar to the experimental results.

4. CONCLUSION

A model of competing trapping states, previously successful in explaining the very strong superlinearity of the ~460 nm emission (as measured with a 9558QB PM tube, through a combination of a 2A Kodak Wratten filter which cuts out wavelengths below 400 nm, and a Corning 4-72 glass filter which suppresses black body radiation) in the ~110°C TL peak in unannealed synthetic quartz, has now been used to account for more recent results of sensitization and de-sensitization of the same peak. It is to be noted that the effects of superlinearity and sensitization are intrinsically connected. One way of stating that superlinearity occurs at a given range of doses, is to say that once a unit of dose has been imparted, the sensitivity of the sample to the next unit is higher. The effect discussed here is, however, more complicated since the stage of heating takes place between two consecutive excitations. It is encouraging, nevertheless, to see that exactly the same energy level model results in a behavior which agrees so well with the experiments.

We would like to note that both the experimental and theoretical curves are given in arbitrary units (see Fig. 1). One adjustable parameter has been set so that the equilibrium response in (c₁) and (c'₁) is the same. The results in curves (a) and (b) are seen to be similar though not identical with those in (a') and (b'). The reasons for this are, probably, that more elements are influencing the experimental results on one hand, and that the choice of parameters is not unique, and it stands to reason that another choice might have been even more successful. Bearing these reservations in mind, the agreement between experimental and theoretical results is surprisingly good. This adds, of course, credibility to the model of competition during heating for explaining superlinearity. In fact, in the same way as in the previous work (Chen and Fogel,

1993), the competitor has been asserted here, and its role taken into account both in the excitation and readout phases, which gives a more comprehensive account of the physical situation.

It should be reiterated that in this model, the reservoir, essential in the explanation of the pre-dose effect of the 380 nm emission, plays no role here. The UV reversal of sensitization, which strengthens the reservoir model there, should be checked experimentally in the 460 nm emission peaks. Also, cycles of the present kind can be attempted with the 380 nm emission. It can be predicted with some caution, that the two effects are unique each to its respective emission range; the main reason for this is that the two effects are seen at the same kind of sample, but at two different dose ranges. The important common factor in the two models is, however, the central part played by the competitor.

Although these results are specific to synthetic quartz, to some extent, similar effects may occur in archaeological and geological samples, which may explain some undesirable occurrences in these materials. The effect may look like an irreproducibility of the results, and it may be detrimental in the laboratory calibration of dating. Also, understanding this effect may help in improving the accuracy of the pre-dose dating method.

REFERENCES

- Aitken M. J. and Murray A. S. (1976) The pre-dose technique; radiation quenching. The Edinburgh symposium on archaeometry and archaeological prospection. Extended Abstracts (London: HMSO).
- Bailiff I. K. (1985) Pre-dose and inclusion dating: a comparison using iron age and early medieval pottery. *Nucl. Tracks* **10**, 771-777.
- Chen R. (1979) Saturation of sensitization of the 110°C TL peak in quartz and its potential application in the pre-dose technique. *European PACT J.* **3**, 325-335.
- Chen R., Abu-Rayya M. and Kristianpoller N. (1991) Sensitization of thermoluminescence in synthetic quartz—heat treatment and radiation effects. *J. Luminescence* **48**, 833-837.
- Chen R. and Fogel G. (1993) Superlinearity in thermoluminescence revisited. *Radiat. Prot. Dosim.* **47**, 23-26.
- Chen R., Yang X. H. and McKeever S. W. S. (1988) The strongly superlinear dose dependence of thermoluminescence in synthetic quartz. *J. Phys. D: Appl. Phys.* **21**, 1452-1457.
- Fleming S. J. and Thompson J. (1970) Quartz as a heat resistant dosimeter. *Health Phys.* **18**, 567-578.
- Kristianpoller N., Chen R. and Israeli M. (1974) Dose dependence of thermoluminescence peaks. *J. Phys. D: Appl. Phys.* **7**, 1063-1072.
- McKeever S. W. S., Chen C. Y. and Halliburton L. E. (1985) Point defects and the pre-dose effect in natural quartz. *Nucl. Tracks* **10**, 489-495.
- Yang X. H. and McKeever S. W. S. (1988) Characterization of the pre-dose effect using ESR and TL. *Nucl. Tracks* **14**, 75-79.
- Yang X. H. and McKeever S. W. S. (1990) The pre-dose effect in crystalline quartz. *J. Phys. D: Appl. Phys.* **23**, 237-244.
- Zimmerman J. (1971) The radiation induced increase of the 100°C TL sensitivity of fired quartz. *J. Phys. C: Sol. St. Phys.* **4**, 3265-3276.