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# MODELS FOR THE SENSITIZATION OF THERMOLUMINESCENCE IN SILICA FIBRES

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**Abstract**—Several models have been suggested for the sensitization effect, which is the enhancement of the TL sensitivity following irradiation and thermal annealing The main models are reviewed here, as well as methods by which the appropriate model for the case under study may be established Some of these methods are demonstrated in relation with a sensitization effect which was recently found in Ge–$SiO_2$ Nd optical fibres Initially the TL emission spectrum consisted of a major blue band and a weaker green band The sensitization effect was much stronger for the green band, and for high doses it exceeded the blue one It is argued that the sensitization is compatible with the Zimmerman–Chen model which is based on the transfer of electronic charge carriers and a "competition during heating"

## 1. INTRODUCTION

THE SENSITIZATION of thermoluminescence, also termed the pre-dose effect, is the change of sensitivity of a sample to a given test dose, resulting from its exposure to a prior irradiation followed by a thermal annealing The effect was first observed by Cameron (1964) in LiF and later by Aitken's group in quartz [see e g Fleming (1968) and Aitken (1979)] This group studied in detail the sensitization of the 110°C peak in natural quartz (crystalline $SiO_2$) and developed the pre-dose technique for dating pottery based on this effect

Several models have been suggested for the sensitization effect in various materials The purpose of this work is to review the main models and the techniques by which the right model for the case under study may be established Some of these techniques are demonstrated in relation to a sensitization effect which was recently found in silica optical fibres

## 2. MODELS FOR THE SENSITIZATION

### 2 1 *Zimmerman's "reservoir" model*

Zimmerman (1971) suggested that the sensitization of the 110°C peak in quartz, which had been attributed to the recombination of thermally released electrons with hole centres, is due to the occurrence of a "reservoir" centre, *R*, in which holes accumulated during the irradiation *R* is characterized by a high probability for capturing holes, and is too deep to release holes in the temperature range studied by the TL However, when the crystal is heated to ~500°C, the holes in *R* are thermally released into the valence band, and are eventually trapped in the recombination centres More holes are thus available now and a subsequent irradiation of the sample by a "test dose" reveals an increase of sensitivity

### 2 2 *The Zimmerman–Chen model—"competition-during-heating"*

Chen (1979) discussed the inconsistency of the fact that, on one hand, in Zimmerman's model the measured TL depended on the concentration of holes in the recombination centres, and on the other hand, the 110°C peak was found to be linear with the test dose He resolved this by postulating, in addition to the defects assumed by Zimmerman, another trap, $T_c$, which competes for charge carriers during the heating stage (see Fig 1) The filling of this trap should be hardly dependent on the excitation dose while the transition into it should be more probable than both recombination and retrapping (see also Chen and Kirsh (1981), pp 200–203)

### 2 3 *Ion migration models*

The sensitization might involve the migration of ions which becomes feasible due to the irradiation and heating This ionic migration may produce new defect complexes which act as traps or recombination

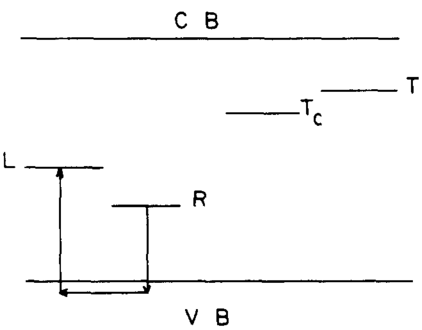


FIG 1 Energy levels involved in the sensitization of TL in quartz according to the Zimmerman–Chen model *L*—a hole luminescence centre, *R*—a hole reservoir, *T*—an electron trap, $T_c$—another trap which competes for electrons during the heating stage

centres Halperin *et al* (1986) found that the irradiation of synthetic quartz at a low temperature (15–77 K) followed by a thermal annealing at 200 K, and a second irradiation at the low temperature, caused the appearance of a new TL peak at 190 K They found that the first irradiation and the subsequent heating caused the migration of Li ions along *c*-axis channels from $AlO_4$ to $SiO_4$ sites, and formed new electron traps According to Yang and McKeever (1990) the movement of $H^+$ ions may be the actual cause for the sensitization of the 110 C peak in quartz, rather than the transfer of holes from a reservoir

2 4 *The removal of a competing trap*

Sensitization may also be caused by eliminating the trap which acts as a "competitor-during-heating" in the Zimmerman–Chen model described above Once the competitor has been removed all charges released from traps will find their way to recombination centres and thus the TL per unit dose will increase Chen *et al* (1988) explained by this model the increase of the 110 C peak following firing to 950 C

## 3 METHODS BY WHICH THE RIGHT MODEL MAY BE ESTABLISHED

Several types of measurements can be performed in order to study the sensitization effect and find out which of the models might be appropriate for the specific case under study

(1) The spectral structure of the TL is important information which can cast light on the recombination centres and on competition processes (Townsend and Kirsh 1989)

(2) By evaluating the kinetic parameters (activation energy frequency factor and order of reaction) of the various TL peaks the traps from which the charge carriers are thermally released can be characterized or even identified with known defects It is advantageous to perform the kinetic analysis on monochromatic TL curves rather than on the curve of the total light intensity Thus concurrent recombination processes which produce different spectral bands are distinguishable (Kirsh 1988)

(3) The curve of the TL intensity vs the annealing temperature (thermal activation curve) may cast light on the processes involved An Arrhenius type dependence $[I \sim \exp(-E/kT)]$ may occur whether the sensitization stems from the transfer of electronic charges or from ionic motion In the first case the activation energy $F$ characterizes the depth of the reservoir below the conduction or valence band In the second case it represents the energy required for the hopping of the ion between two adjacent unit cells In some samples of quartz the sensitization of the 110 C peak was found to obey the Arrhenius law with activation energies of 1 34–1 55 eV (Fleming, 1979) Yang and McKeever (1990) found that the activation curve of this peak was sample dependent Halperin *et al* (1986) found for the 190 K peak in quartz, a peak-shaped activation curve centred at 220 K

(4) The dose dependence of the sample before and after the treatment should be checked Chen *et al* (1988) showed that the competition-during-heating mechanism, which may be involved in the sensitization, may also cause a strong superlinear dose dependence Thus, dose dependence which is superlinear before the sensitization and linear after it may indicate that model D is the most probable candidate

(5) The dependence of the effect on the pre-dose and the test-dose is significant Discussing the pre-dose dating, Chen (1979) showed what one can expect for the Zimmerman–Chen model in cases where the reservoir and/or the centre are close to saturation or far from saturation (see also Chen and Kirsh (1981) pp 304–308)

(6) If an exposure to near UV light eliminates the sensitization it corroborates the electronic-charge-carriers models, since it is unlikely that the UV can restore the distribution of ionic defects Zimmerman (1971) found that UV light in the range 250–320 nm reduced the sensitivity of the 110 C peak and could bring it to the original value A subsequent heating to ~500°C (with no further irradiation) recovered the high sensitivity Her explanation was that the UV light released holes from the recombination centre to the valence band, from which they fall preferably (at room temperature) back into the reservoir

(7) Auxiliary methods such as ESR or optical absorption measurements are very useful for the study of the defects formed or destroyed during the sensitization ESR was essential in identifying the defects involved in the sensitization of both the 190 K peak of quartz (Jani *et al* 1986 Halperin *et al* 1986) and the 110 C peak (McKeever *et al* 1985 Yang and McKeever, 1990)

## 4 A TEST CASE—THE SENSITIZATION OF SILICA OPTICAL FIBRES

As an example for the application of some of the techniques mentioned above we shall now describe the study of a sensitization effect in optical fibres of silica (amorphous $SiO_2$) containing Ge and Nd The effect was discovered by Ellis *et al* (1989) Some of the results were published elsewhere (Ellis *et al* 1989 Kirsh *et al* 1989) and will be summarized here briefly

4 1 *Experimental*

Optical fibres of a germano-silicate core (4 mole % $GeO_2$) containing 450 ppm $Nd^{3+}$ and an estimated 2 ppm of $OH^-$ were used The fibres were X-irradiated at RT and then heated at a rate of 20 K $min^{-1}$ up to 450 C The TL spectrum was scanned in the range 300–800 nm by a Bausch and Lomb grating monochromator coupled to a stepping motor The readings were corrected for the wavelength sensitivity of the monochromator and photomultiplier (EMI 9659QA)

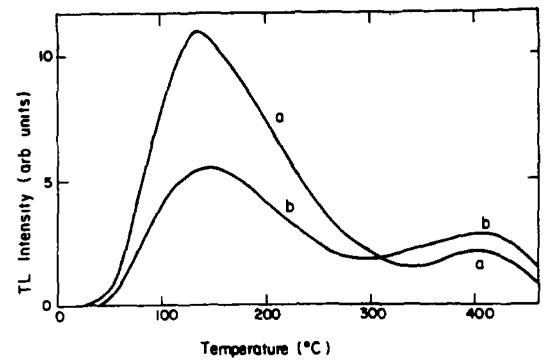


FIG 2 "Monochromatic" TL curves recorded at 400 nm (a) and 520 nm (b), following a pre-dose of 1 2 kGy and a test-dose of 1 2 kGy

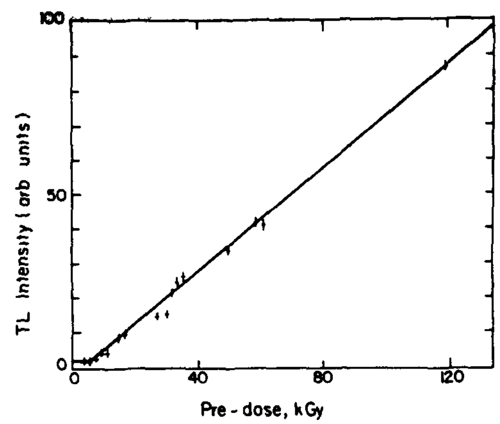


FIG 4 The intensity of the 520 nm band as a function of the pre-dose, for a test-dose of 18 Gy After a small region of a constant signal the growth is linear In the series of measurements described here the irradiation was by a $\beta$ source However, X-irradiation gave similar results (after Ellis *et al*, 1989)

4 2 *Results*

4 2 1 *Spectral analysis* The TL curve consisted of two broad peaks at 140 and 410°C, as shown in Fig 2 Over all this temperature range the emission spectrum was the same Initially the spectrum consisted of a major blue band at 400 nm, and a weaker green band centred at about 520 nm, as shown in Fig 3(a) The intensity of both bands increased due to the combined effect of irradiation at RT, and several minutes of thermal annealing above 320°C This is demonstrated in Fig 3(b) For both bands the sensitivity to a given test-dose grew with the increasing pre-dose However, the green band grew much faster, and for high pre-doses it exceeded the blue one

4 2 2 *Kinetic analysis* By applying the initial-rise method and a best-fit programme for kinetic analysis, it was found that the broad TL curve could be described as composed of five overlapping peaks (Kirsh *et al*, 1989) The main peak which occurred at about 150°C represented a distribution of activation energies between 0 94 and 1 35 eV The other peaks occurred at 90°C (0 86 eV), 340°C (1 45 eV), 375°C (1 68 eV) and 418°C (1 72 eV) All of them were of the second order and the frequency factors were between 1 2 and $6 \times 10^{10}\,s^{-1}$ The important result is that both the 400 and 520 nm bands could be described by the same set of activation energies, indicating that the blue and green bands involve the same system of traps

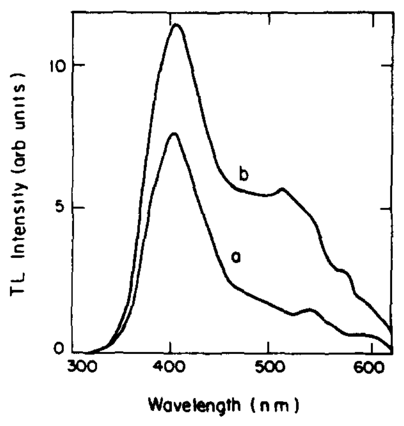


FIG 3 Emission spectra of the TL at 130°C (a) Following a test-dose of 1 2 kGy (no pre-dose), (b) following a pre-dose of 1 2 kGy and a test-dose of 1 2 kGy The annealing temperature was 450°C

4 2 3 *Activation curve* The intensity of the green band was found to depend on the annealing temperature according to an Arrhenius law, with an activation energy of 0 52 eV (Ellis *et al*, 1989)

4 2 4 *Dose dependence* Ellis *et al* (1989) found that both bands grew with the pre-dose However, the green band depended linearly on the pre-dose, after a small range of a constant signal, as shown in Fig 4 The growth of the blue band with the pre-dose was sub-linear There was no difference whether the pre-dose was given in one shot, or in parts separated by heatings The dependence of both bands on the test dose was found to be linear

## 5. DISCUSSION

There is evidence that above RT the TL in $SiO_2$ involves electron traps and hole recombination centres (McKeever, 1984) In the following we shall try to match the results described above with the Zimmerman–Chen model, by assuming two recombination centres which we shall designate $L_B$ and $L_G$, for the blue and green bands respectively According to this model $L_B$ is readily filled with holes during the irradition, while $L_G$ is filled mainly during the heating stage, through the depletion of a reservoir $R$, which has a high probability of capturing holes during the irradiation

In recent measurements we found that the blue band has a Gaussian shape when described as a function of the photon energy The Gaussian is centred at 3 08 $\pm$ 0 01 eV and its half-width is ~0 29 eV (Kirsh *et al*, 1991) Guzzi *et al* (1987) ascribed a similar Gaussian emission band at 3 1 eV to the $O_2^-$ molecular ion (a pair of a lattice oxygen and an interstitional one) which is an intrinsic hole centre in $SiO_2$ Skuja and Trukhin (1989) disagreed with this conclusion and suggested that the 3 1 band is related to Ge impurity Measurements in our laboratory (Ellis *et al*, 1989) are in favour of Guzzi's model, since the band at 400 nm was the major feature in the luminescence of a wide variety of doped and undoped silica fibres, indicating that the luminescent centre is an intrinsic defect We therefore suggest to identify $L_B$ with $O_2^-$

As for $L_G$, in a previous work it was suggested that this is a hole centre in which a Nd ion is incorporated (Kirsh *et al*, 1989) We gave several justifications for that suggestion Firstly, in previous measurements only Nd-doped fibres were found to exhibit this band (Ellis *et al*, 1989) Secondly, the valence of Nd is usually + 3, and it should form a hole trap if it enters the lattice substitutionally for Si An important hole centre in natural quartz is associated with $Al^{3+}$, and the recombination of electrons with the $Al^{3+}$–$h^+$ centre produces an emission band at 470 nm (McKeever *et al*, 1985) One can expect the recombination of electrons with a similar $Nd^{3+}$–$h^+$ centre to produce a similar emission band

Recent measurements (Kirsh *et al*, 1991) gave further support to this supposition We found that several small peaks, which are superimposed on the 520 nm band, can be identified with lines in the emission spectrum of $Nd^{3+}$ These lines are possibly due to the excitation of the $Nd^{3+}$ ion as a secondary effect of the $e^-$–$h^+$ recombination

The reservoir, $R$, and the competitor trap, $T_c$, should have high probabilities for capturing holes (during the irradiation) and electrons (during the heating) respectively They are probably rather common intrinsic defects It is known that broken Si–O bonds are readily created by ionizing radiation and are also present in as-grown samples, especially silica (Stapelbroek *et al* 1976, Greaves, 1978, Lucovsky, 1979, 1980) The resulting dangling oxygen bonds and empty Si orbitals are potential hole and electron traps, respectively, and are plausible candidates for $R$ and $T_c$ Indeed, a $Nd^{3+}$ which substitutes a $Si^{4+}$ ion should result in a free oxygen bond This is compatible with the fact that the green band is sensitized more strongly than the blue band, which implies that $R$ is near $L_G$

Other electron traps, from which electrons are thermally released to give the observed TL, may include $Ge^{4+}$ in various environments (to account for the distribution of activation energies) as well as oxygen vacancies ($E'$ centres) Although Ge is tetravalent, like Si, its higher electron affinity makes it an efficient electron trap (McKeever *et al*, 1985) Oxygen vacancies, which appear in quartz only after particle irradiation, have been observed in as-grown silica (Levy, 1960, Nelson and Crawford, 1960)

This model for the sensitization of TL in Ge–silica $Nd^{3+}$ fibres is obviously a tentative one Several points, such as the significance of the activation energy of 0 52 eV, which was found for the dependence of the sensitization on the annealing temperature, are not yet clear An alternative model, which involves the migration of ions and the production of new complexes, may also be considered There is some evidence that originally only few of the Nd ions in silica substitute $Si^{4+}$ ions while most of them exist in clusters (Arai, 1986) Thus, the sensitization might involve the diffusion of $Nd^{3+}$ and their entering into $Si^{4+}$ sites, where they can act as hole centres

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