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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

THE EFFECT OF THERMAL ANNEALING ON LUMINESCENCE CENTRES IN Ge–SILICA FIBRES

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The radioluminescence spectrum of Ge–silica fibres doped with Nd is found to change by the effect of pre-irradiation and thermal annealing. Originally the spectrum consists of a gaussian band centred near 3.1 eV (400 nm). Following the irradiation and heating an additional asymmetric band appears near 2.4 eV (520 nm). On top of this band there is a line spectrum, which can be ascribed to internal transitions of the Nd^{3+}. On the basis of the spectroscopic data and previous results of thermoluminescence measurements, a model is suggested for the luminescence and the effect of the thermal annealing. The blue and green bands are ascribed to an O_2^- molecular ion and a hole centre near the Nd^{3+} ion, respectively.

It was found recently by Ellis *et al.* [1] that the combined effect of irradiation and thermal annealing changes the emission spectrum of thermoluminescence (TL) in Ge–silica fibres doped with Nd. Following X or β irradiation, the fibre showed a broad TL peak at about 175°. Initially the emission spectrum consisted mainly of a blue band near 400 nm. However, prior irradiations followed by thermal annealing above 320° generated a green emission band at about 520 nm. The intensity of both bands grew with the accumulated dose of the prior irradiations. It was shown that because of this effect the fibre can be used as a rereadable dosimeter of radiation.

In a previous work [2] we performed a kinetic analysis of the TL. We found that the TL curves at 400 and 520 nm consisted of 5 overlapping peaks and could be described by the same set of kinetic parameters. It was con-

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cluded that the blue and green bands involve the thermal release of charge carriers from the same set of traps, and their recombination with two distinct luminescence centres.

In this work we studied the combined effect of pre-irradiation and thermal annealing on the radioluminescence (RL) of the samples (i.e. the luminescence emitted during X-irradiation) and on the phosphorescence (PP) which is the long-time decay of the luminescence after the termination of the irradiation.

Experimental

The samples were optical fibres of silica (amorphous SiO_2) which contained Ge (4 mole %) and Nd^{3+} (450 ppm). The fibres were kept in the vacuum and irradiated at room temperature for periods of 1-40 minutes, by a tungsten target X-ray tube which provided 30 Gy/min. The emission spectrum was continuously scanned by a Bausch and Lomb grating monochromator coupled to a stepping motor. The readings were later corrected for the spectral response of the monochromator and photomultiplier (EMI 9659QA).

Results

The emission spectra of the RL before and after the thermal annealing are described in Figs 1 and 2. The unit of the y-axis represents a photomultiplier current which corresponds approximately to $5 \cdot 10^6$ photons emitted by the sample per second, after estimating the efficiency of the collection optics, monochromator and photomultiplier. The x-axis represents the energy of the photons in eV rather than the wavelength, since this representation reveals the gaussian shape of certain bands. All the graphs in Figs 1-3 are normalized to the same sample mass.

The RL spectrum of an unannealed sample is shown in Fig. 1 at the beginning of the irradiation (a) and after 40 minutes of a continuous irradiation (b). Two prominent features appear in both spectra: a gaussian band centered at 3.08±0.01 eV (402 nm) with a half-width of 0.29 eV, and an asymmetric band centered near 2.4 eV (517 nm) which seems to be structured. The intensity of both bands was found to increase with the accumulated dose.

When the irradiated sample was annealed above 320° for several minutes and then recooled to room temperature, the intensity of its initial RL emission was found to increase both in the 3.1 eV and the 2.4 eV bands. However, the 2.4 eV band grew faster with the dose of the pre-irradiation (the pre-dose). Figure 2*a* depicts the initial RL emission of the sample after an irradiation of 40 minutes and annealing at 450°. The 3.1 eV band increased compared to the Fig. 1*a* by a factor of ~2 and the 2.4 eV band by a factor of 7. The structure of the 2.4 eV band is now more apparent, with several peaks, or sub-bands, superimposed on the broad band between 2.1 and 3.3 eV. Figure 2*b* shows the RL spectrum after an irradiation of 40 minutes (in addition to a pre-irradiation of 40 minutes). Comparison with 2*a* shows that the 3.1 eV band increases during the irradiation, while the 2.4 eV band decreases. This bahavior is markedly different from that of the untreated sample, in which the intensity of both bands increases during the irradiation (Fig. 1).

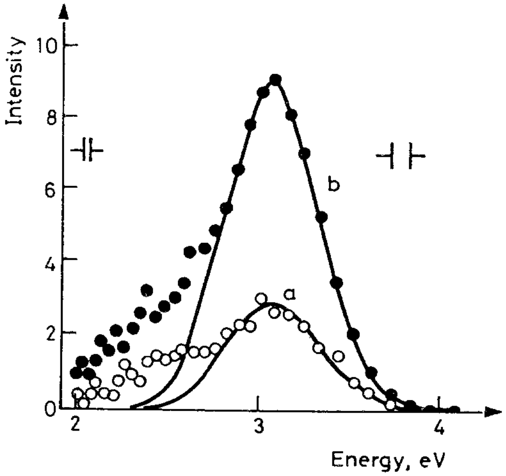

Fig. 1 The RL spectrum of an unannealed sample. (a) At the beginning of the irradiation. (b) After 40 minutes of a continuous irradiation (an absorbed dose of 1200 Gy). The points represent experimental results while the line describes the optimization of a gaussian function to the data

The emission spectrum of the thermoluminescence (TL) is shown in Fig. 3*a* for an unannealed sample, following an irradiation of 30 minutes. Figure 3*b* refers to the same sample after an irradiation of 30 minutes, heating to 450° and an additional irradiation of 30 minutes at room temperature. The TL was recorded using a heating rate of 20 deg/min. Similarly to the

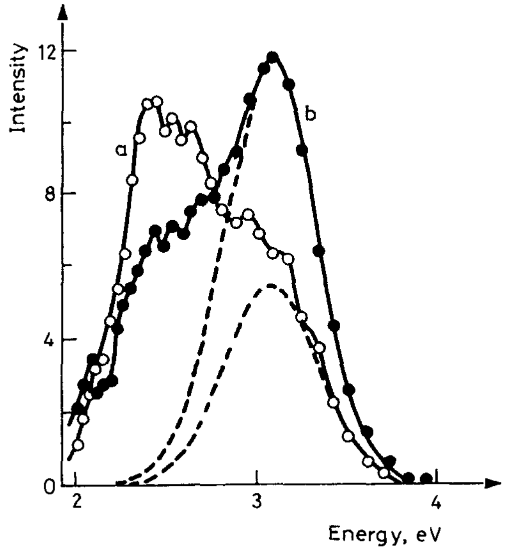

Fig. 2 RL emission spectra after an irradiation of 40 minutes (1200 Gy) and annealing at 450°C. (a) At the beginning of the second irradiation. (b) After 40 minutes. The solid line which departs from the gaussian was drawn to connect the experimental points

RL, the TL emission spectra consist of the 2.4 eV and 3.1 eV bands, and both becomes more intense with the increasing pre-dose. The 2.4 eV band however grows faster and for higher pre-doses it exceeds the 3.1 eV band. The dependence of both bands on the dose of the second irradiation was found to be linear. The PP emission spectrum was very similar to that of the TL. The PP decay at room temperature followed a t^{-x} law with $x \approx 0.6$, indicating some kind of non-uniform distribution of traps [3].

Discussion

We have previously found [2] that the TL of the fibres at the blue (3.1 eV) and green (2.4 eV) bands could be described by the same set of kinetic parameters. Each of the TL curves was found to consist of a main peak which showed a distribution of activation energies between 0.94 and 1.35 eV, and four minor peaks with the activation energies of 0.86, 1.45, 1.68 and 1.72 eV. All the peaks were of the second order and their frequency factors were between $1.2 \cdot 10^{10}$ and $6 \cdot 10^{10}$ sec^{-1}. On the basis of these findings, and the evidence that above room temperature the TL in SiO_2 involves electron traps and hole luminescence centres [4-7], the following model was suggested for the TL of the fibres. The irradiation creates hole centres which are thermally stable, and electron centres which release electrons upon the subsequent heating. The blue emission is produced when the released electrons recombine with hole centres which we designate L_B, while the green emission is caused by the recombination of electrons with another type of hole centres, labeled L_G.

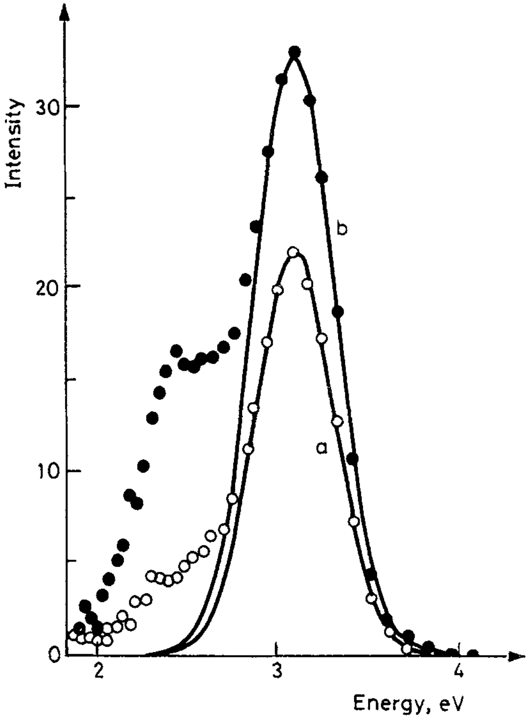

Fig. 3 TL emission spectra at 140°C. (a) Following an irradiation of 30 minutes (900 Gy). (b) Following an irradiation of 30 minutes, heating to 450°C and an additional irradiation of 30 minutes at room temperature

We previously explained the increase in the TL sensitivity of the fibres [2] by a model which had been suggested by Zimmerman [8]. The model assumes that in addition to L_B and L_G there is another hole trap or 'reservoir', R. This trap is characterized by a high probability for capturing holes and is too deep to release holes in the temperature range studied by the TL. The pre–irradiation fills R with holes. During the thermal annealing these holes are released into the valence band and trapped preferably in L_G. A TL measurement which follows a subsequent irradiation of the sample by a test dose, reveals an enhancement of the green band, because more holes are now trapped in L_G.

Since the emission spectrum of the RL is similar to that of the TL, one can assume that the same model applies here as well. The X-irradiation produces electron-hole (e^--h^+) pairs but has little effect on the concentration of ionic defects such as L_B and L_G. Some of the electrons and holes recombine immediately, while others are trapped in various traps. Recombinations of electrons with holes trapped at L_B and L_G produce the observed RL emission bands. Let N_i denote the concentration of the i trap, and n_i – the concentration of the filled traps ($i = B, G$). It can usually be assumed [9] that the trapping rate is proportional to the concentration of empty traps N_i–n_i, while the recombination rate at the traps is proportional to n_i. If n_B and n_G are small at the beginning of the irradiation, they should grow with time and increase the RL intensity, as observed by us (Fig. 1a,b). A saturation is expected after some time, since as n_i increases, the trapping rate decreases. The increase of the RL and TL intensity as function of the pre–dose can be explained by Zimmerman's model mentioned above. The decrease of the 2.4 eV band with time in the RL of the irradiated–and–heated sample (Fig. 2b) indicates that after the transfer of holes from R to L_G, n_G is so large that recombination exceeds trapping.

Identification of the luminescence centres L_B and L_G with known defects may be suggested by comparing the spectral structure of the 3.1 and 2.4 eV bands with published data. Guzzi *et al.* [10] ascribed a 3.1 eV gaussian band in silica to the O_2^- molecular ion (a pair of a lattice oxygen and an interstitional one) which is an intrinsic defect in SiO_2. Skuja and Trukhin [11] later disagreed with this conclusion and suggested that the 3.1 eV band is related to Ge impurity. Measurements in our laboratory have shown [1] that this band is the major feature in the TL and RL of a variety of doped and undoped silica fibres. It supports Guzzi's model since the luminescent centre involved seems to be an intrinsic defect. Thus we identify L_B with the O_2^- defect.

As for L_G, in the previous work [2] we attributed the 2.4 eV band to the recombination of electrons with a Nd^{3+}-h^+ center (a hole adjacent to the Nd^{3+} ion). We gave several justifications for that model. The RL spectra measured in the present work lend further support to this suggestion. The fine structure of the 2.4 eV band can be identified with lines in the emission spectrum of Nd^{3+}. The peaks at 2.08, 2.40 and 2.55 eV match the transitions $^4G_{9/2} \rightarrow {}^4I_{13/2}, {}^4I_{11/2}, {}^4I_{9/2}$. The peaks near 2.65, 2.95, 3.15 and 3.30 eV correspond to the transitions $^4D_{3/2} \rightarrow {}^4I_{15/2}, {}^4I_{13/2}, {}^4I_{11/2}, {}^4I_{9/2}$. (The stat, $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ and $^4I_{15/2}$, are the lowest in the energy diagram of Nd^{3+} and their centres are at about 150, 2060, 4040 and 6020 cm^{-1} $G_{9/2}$ (G) and $^4D_{3/2}$ (L) which were found to luminescence in $LaCl_3$ are located at about 20800 and 27700 cm^{-1} respectively [12]). These lines might be due to the excitation of the Nd^{3+} ion, as a secondary effect of the recombination of an electron with the hole trapped at L_G.

Potential electron traps in our samples are Ge^{4+} ions in various environments and O^{2-} vacancies. Ge is expected to substitute Si in the SiO_2 lattice, but its higher electron affinity makes it an efficient electron trap, with or without charge compensator [13]. O^{2-} vacancies (*E'* centres) appear in quartz only after particle irradiation, but were found in as grown silica [14, 15].

The hole trap *R*, which shows high efficiency in capturing holes, is probably a common intrinsic defect. The fact that the 2.4 eV band is affected by the irradiation–and–heating treatment more strongly than the 3.1 eV band, implies that *R* is formed preferably near the L_G site. A broken oxygen bond is a plausible candidate for *R*, since Nd^{3+} which substitutes a Si^{4+} ion should result in a free oxygen bond. It should be mentioned that ruptured Si – O bonds are readily created by ionizing radiation and are also presented in as grown material, especially silica [16-19].

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Zusammenfassung — Das Radiolumineszenzspektrum von mit Nd versetzten Ge-Siliziumoxidfasern ändert sich durch den Einfluß von vorheriger Bestrahlung und thermischem Tempern. Ursprünglich besteht das Spektrum aus einer Gaußschen Bande mit dem Mittelpunkt bei etwa 3.1 eV (400 nm). Nach Bestrahlung und Erhitzen zeigt sich in der Nähe von 2.4 eV (520 nm) eine zusätzliche, asymmetrische Bande. An der Spitze dieser Bande befindet sich ein Linienspektrum, was internen Übergängen von Nd^{3+} zugeschrieben werden kann. Auf der Grundlage der spektroskopischen Angaben und vorangehender Resultate aus Thermolumineszenzuntersuchungen wurde für die Lumineszenz und den Einfluß des thermischen Temperns ein Modell entwickelt. Blaue bzw. grüne Banden werden O_2^- Molekülionen bzw. Leerstellenzentren in der Nähe von Nd^{3+}-Ionen zugeschrieben.