Phototransferred thermoluminescence and phosphorescence related to phototransfer in annealed synthetic quartz

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Abstract. Phototransferred thermoluminescence and phosphorescence related to phototransfer in synthetic quartz is reported. The glow curve shows a number of unstable electron traps only one of which is involved in phototransfer. Kinetic analysis of both types of phototransferred signal gives an activation energy of ~ 0.55 eV for this electron trap. The PTTL intensity goes through a peak with illumination time and this is ascribed to the relative concentration of phototransferred electrons and, holes at a recombination centre. On the other hand, the dose dependence of the phototransferred thermoluminescence is superlinear.

1. Introduction

Quartz is a common natural mineral used in retrospective dosimetry using luminescence based methods [1]. Luminescence is typically emitted from previously irradiated insulators as a result of optical or thermal stimulation [2]. The ionizing radiation creates free electrons some of which get localized at pre-existing point defects termed electron traps. Thermoluminescence (TL) is observed when an irradiated material is heated at a controlled rate. The signal appears as a set of peaks known as a glow curve. Each peak is associated with an electron trap.

When an irradiated material is partially heated to remove lower temperature peaks, it is found that exposing the same material to light of certain wavelengths reproduces these peaks. This phenomenon, otherwise called phototransferred thermoluminescence (PTTL), is observed in natural and synthetic quartz [3–5]. The general principle of PTTL is that electrons are moved, by light, from thermally inaccessible traps (otherwise called deep traps) to unstable shallow traps.

The study of PTTL in this report was augmented by use of phosphorescence. This is the decay of thermoluminescence as a function of time at a constant temperature. Isothermal decay curves from phosphorescence can be analysed using various kinetics methods to determine parameters such as activation energy associated with the TL process.

This report is concerned with features of PTTL and, phosphorescence resulting from phototransfer in annealed synthetic quartz. In particular, we report the dependence of the PTTL on illumination time, and the influence of dose on the phototransferred phosphorescence as well as kinetic analysis of the phosphorescence. To the best of our knowledge kinetic analysis of phototransferred phosphorescence in synthetic quartz has never been reported.

2. Experimental details

Synthetic quartz of grain size 90-500 μm (Sawyer Research Products, Ohio, USA) was used. A few milligrams of sample was placed on stainless steel discs of 1 mm thickness and 10 mm diameter. Luminescence was measured using a RISØ TL/OSL-DA-20 Luminescence Reader. Samples were irradiated using an inbuilt ^{90}Sr/^{90}Y beta source at a dose rate of 0.1 Gy/s. Luminescence was detected by an EMI9235QB photomultiplier tube through a 7.5 mm thick Hoya U-340 filter (transmission band 280-390 nm). All TL measurements were made in a nitrogen atmosphere to avoid spurious luminescence from air and to improve thermal contact between the sample disc and the heater plate. Samples were annealed at 500^{o}C for 10 minutes before use in order to remove any residual signal. The quartz is subject to the pre-dose effect and the heating also improved its sensitivity by way of thermal activation [6].

3. Results

3.1. General features

Figure 1 shows a glow curve obtained following heating to 500^{o}C at 1^{o}C/s after irradiation to 100 Gy. The plot shows six peaks at 76, 104, 170, 210, 285 and 340^{o}C labelled as I to VI, respectively.

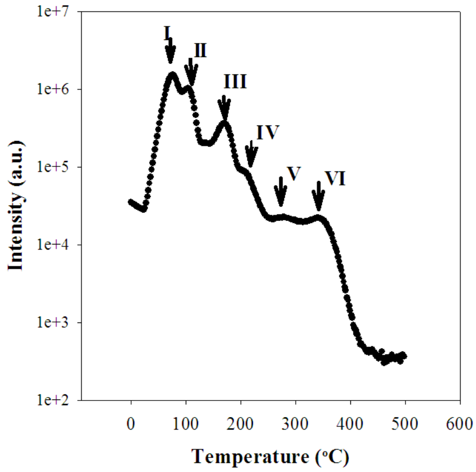

Figure 1. A glow curve measured at 1^{o}C/s following irradiation to 100 Gy.

3.2. Phototransferred thermoluminescence

PTTL was produced in a number of steps. The sample was first irradiated to 100 Gy and then preheated to 200^{o}C in order to empty the shallow traps at 76, 104 and 170^{o}C. These three peaks were removed to ease the search for phototransferred signal. The sample was thereafter exposed to 470 nm blue LED light for 20 s to cause the transfer of electrons from deep to the shallow traps. Finally, the sample was heated to 500^{o}C at 1^{o}C/s to obtain the complete glow curve.

Figure 2 shows the glow curve obtained after phototransfer. The phototransferred peak is seen at 76^{o}C, the position of the original peak I. Peaks II and III were not reproduced by phototransfer.

To observe the effect of illumination time on the PTTL, similar experiments were conducted except that the sample was illuminated for durations between 1 and 1000 seconds each time. Figure 3 shows the change of peak intensity with illumination time. The intensity of the photransferred peak increases with time up to 20 seconds and decreases thereafter to some stable value. The solid line through data will be explained later in the text.

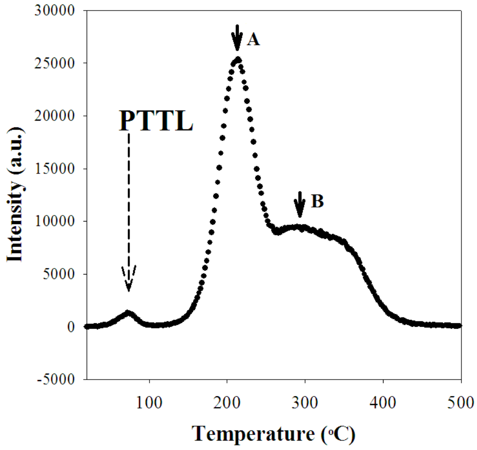

Figure 2. A TL glow curve after phototransfer. The arrow indicates the phototransferred peak. The other peaks A and B, are peaks resulting from the residual TL signal in the sample.

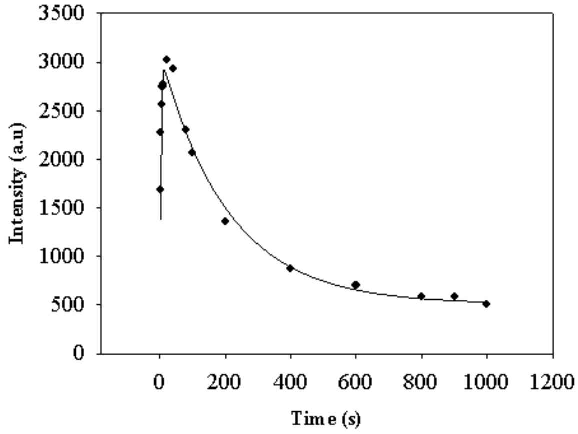

Figure 3. Variation of PTTL intensity with illumination time.

3.3. Phosphorescence

Since shallow traps are unstable, the expected loss of charge at ambient temperature may be monitored and analysed using phosphorescence. Here, the sample was beta irradiated to a certain dose and the phototransfer induced as before. The phosphorescence related to phototransfer was then measured at various temperatures between 52 and 60^{o}C. These temperatures correspond to the rising edge of peak I and measurements were made for doses between 100-500 Gy.

Figure 4 shows a phosphorescence decay curve measured at 55^{o}C following a dose of 200 Gy. The time dependence of the phosphorescence intensity $I(t)$ is exponential, that is,

$$I(t) = I_o \exp(-p\,t) \tag{1}$$

where I_o is initial intensity and p is the decay constant given by

$$p = s \exp(-E\,/kT) \tag{2}$$

where E is the activation energy, s the frequency factor, k Boltzmann's constant and T the measurement temperature [2]. Equation (1) implies that the phosphorescence follows first order kinetics. The linear form of the semi-logarithmic plot of $I(t)$ and t (figure 4, inset) suggests that this is indeed the case. The decay constant p, which is just the slope in a semi-logarithmic plot of $I(t)$ against t, provides a means to calculate the activation energy E of the associated electron trap. As can be deduced from equation 2, if values of p are obtained at different temperatures, the value of E can be found from a plot of p against t on a semi-log scale.

Figure 5 shows a plot of $\ln(p)$ against $1/kT$ corresponding to 200 Gy. These measurements were made for doses from 100-500 Gy. The mean activation energy was 0.55±0.04 eV. The mean frequency factor was 6×10^6 s^{-1}. The kinetic parameters E and s for the phototransferred peak were also evaluated using the various heating rates method [2] where the peak temperature T_m depends on heating rate β as

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{E}{sk}\right) \tag{3}$$

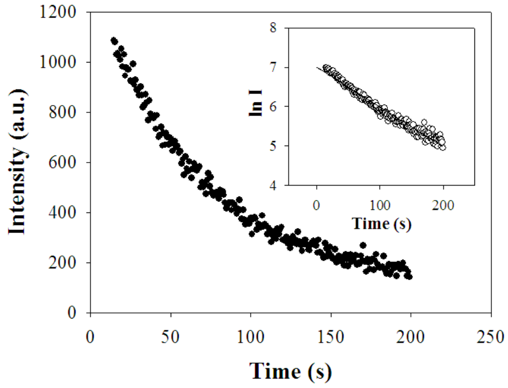

Figure 4. Phosphorescence measured at 55^{o}C following a 200 Gy dose. The inset shows a semi-log plot of the intensity against time.

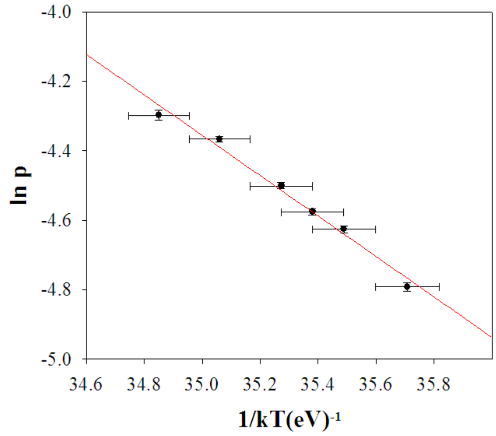

Figure 5. The relationship between ln (p) and $1/kT$ for phosphorescence.

Figure 6 shows $\ln(T_m^2/\beta)$ against $1/kT_m$ for heating rates from 0.1 to 5^{o}C/s. The activation energy E, worked out from the slope of best fit was 0.56±0.04 eV and frequency factor s was $4{\times}10^6$ s^{-1}. These values are consistent with those obtained from figure 5 for phosphorescence related to phototransfer. The reasons for the anomalous low values for s are under consideration. The quartz studied here sometimes shows a weak peak collocated with the main one [7]. The

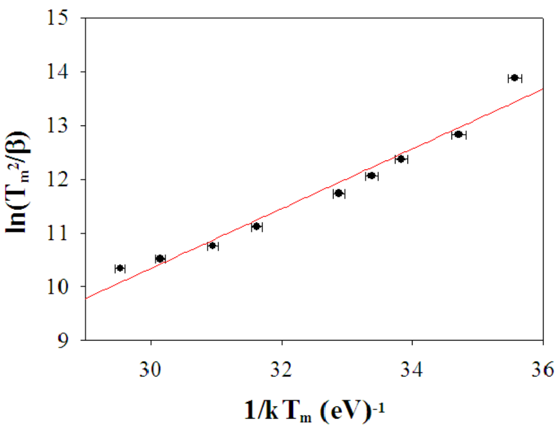

Figure 6. Application of the variable heating rate method on the PTTL.

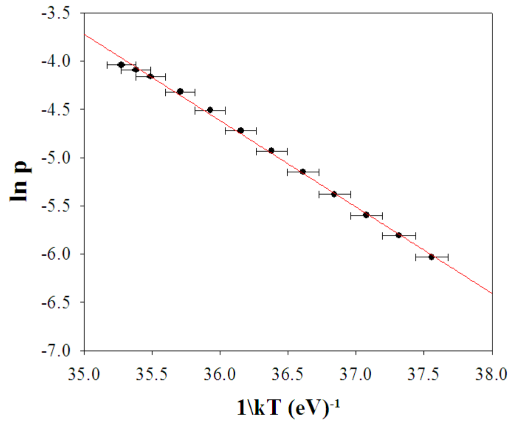

Figure 7. The plot is ln p against $1/kT$ for original TL.

activation energy of this secondary peak was determined as 0.53±0.01 eV using the area method of Chithambo [7]. The consistency of E values from figures 5 and 6 and ref. [7] suggest that this is the peak that is phototransferred. To verify this assumption, measurements of phosphorescence were made on a separate sample, preheated to remove peak I. The activation energy of the next peak in the series was determined using the temperature dependence of phosphorescence (figure 7) as 0.89±0.01 eV and its s as $10{\times}10^{11}$ s^{-1}.These values indeed differ from those of peak I.

3.4. *Dose response of photransferred phosphorescence*

The dependence of the phosphorescence intensity on irradiation dose was studied for doses between 5 and 500 Gy. Measurements were made at an arbitrarily chosen temperature of 56^{o}C. Intensities were determined as areas under each phosphorescence decay curve.

Figure 8 shows the growth curve where the intensity changes with dose D as

$$S(D) = aD^2 + bD + c \tag{4}$$

where $S(D)$ is the analytical form of the intensity and a (in Gy^{-2}), b (in Gy^{-1}), c (in arbitrary units) are constants. The non-linear dose response of figure 8, was quantified using the superlinearity index $g(D)$ which gives a measure of the change in slope of the growth curve and is given by

$$g(D) = \left[\frac{DS''(D)}{S'(D)}\right] + 1 \tag{5}$$

where $S'(D)$ and $S''(D)$ are respectively the first and second derivatives of $S(D)$ [6]. A value of $g(D) > 1$ indicates superlinearity, $g(D) = 1$ linearity and $g(D) < 1$ signifies sublinearity. The inset to figure 8, a plot of $g(D)$ against D where $g(D) > 1$ despite the dose shows that the dose response is superlinear.

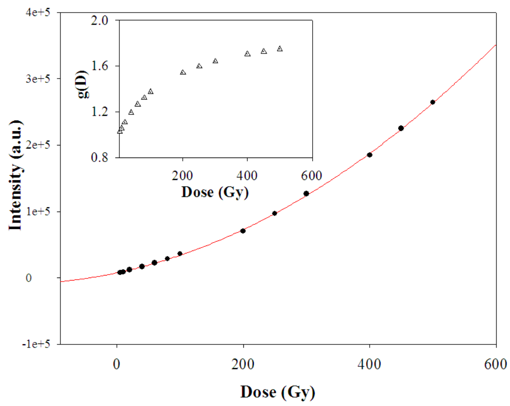

Figure 8. The phototransfered phosphorescence growth curve at 56^{o}C. The inset shows the superlinearity.

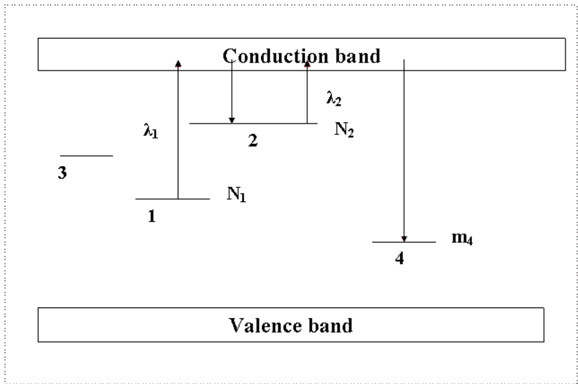

Figure 9. Energy band diagram to explain PTTL.

4. Discussion

The change of PTTL intensity with illumination (figure 3) can be explained with reference to the energy band diagram of figure 9. Some electrons optically excited out of the deep trap (level 1), with electron concentration N_1 at a rate λ_1, are retrapped, via the conduction band, at the shallow trap (level 2). The concentration of electrons in the shallow trap at the end of the illumination is N_2. Intermediate energy electron traps not involved in phototransfer are shown as level 3. Phototransferred luminescence is produced when electrons from the shallow trap recombine with holes at the recombination centre (level 4). The holes, as electrons at traps, are produced following irradiation. For short illumination, the number of electrons moved from the deep to the shallow trap is less than the concentration of holes m_4 at the recombination centre. Assuming that the resultant thermoluminescence intensity is proportional to N_2, the PTTL intensity would be expected to increase with N_2 as long as $N_2 < m_4$. At extended illumination, the number N_2 may exceed m_4 and so the PTTL intensity will tend to decrease to some constant value with time as long as $m_4 \neq 0$. This qualitatively explains the result in figure 3.

The charge movement between the deep and shallow trap may alternatively be expressed as

$$dN_1/dt = -\lambda_1 N_1 \tag{6}$$

$$dN_2/dt = -\lambda_2 N_2 + \alpha \lambda_1 N_1 \tag{7}$$

where λ_2 is the rate of optical transfer of charge out of the shallow traps [3]. The general solution of coupled equations 6 and 7 is

$$N_2(t) = A(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{8}$$

where A is a constant. Assuming that the PTTL intensity I is proportional to N_2, the data in figure 3 can be described as $I \propto (e^{-\lambda_1 t} - e^{-\lambda_2 t})$. The solid line through data in figure 3 is the best fit of an equation of the form $(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + d$ where d is an experimental offset. This simple model assumes no retrapping into the deep or shallow traps, but as evident, satisfactorily describes the data.

Concerning the dose response (figure 8), $N_2 < m_4$ for any dose. The superlinear response occurs due to the increase in phototransferred electrons and so does PTTL with dose.

5. Summary

Synthetic quartz has a number of shallow electron traps one of which was reproduced by phototransfer. The PTTL of this trap goes through a peak with illumination time. This is due to the relative concentrations of the photransferred electrons and, holes at the recombination centre. The unstable nature of the shallow trap is illustrated by the presence of phosphorescence emitted even at ambient temperature. The activation energy of this trap was calculated as 0.55±0.04 eV by kinetic analysis of phosphorescence and verified by the variable heating rate method as 0.56±0.04 eV. The PTTL intensity depends on irradiation and its increase with dose is superlinear.

Acknowledgments

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