

Luminescence lifetime components in quartz: Influence of irradiation and annealing

M.L. Chithambo* and F.O. Ogundare

* Rhodes Univ, Dept Phys & Elect, ZA-6140 Grahamstown, Eastern Cape South Africa

Abstract

Pulsed optically stimulated luminescence measured from quartz under certain combinations of annealing and measurement temperature can be resolved into multiple lifetime components. We have studied the influence on these lifetime components of annealing temperature up to 900 °C, beta irradiation dose as high as 1700 Gy, and temperature of stimulation up to 200 °C. Although the time-resolved spectra from which the lifetimes are determined may be measured without heating between irradiation and measurement, a necessary protocol in steady-state optical stimulation applications, studies reported in this paper have been augmented with investigations on the effect of temperature and duration of preheating on the principal and secondary lifetimes. Luminescence spectra for measurements up to 200 Gy consist of a single lifetime but two components occur thereafter, both are independent of radiation dose. The principal lifetime of $\approx 35 \mu\text{s}$ is not affected by temperature of anneal whereas the secondary lifetime increases from 9 to 18 μs when the annealing temperature is changed from 600 to 900 °C. The dependence of both the principal and secondary luminescence lifetimes on measurement temperature can be explained by thermal quenching of the associated luminescence. However, the influence of irradiation, preheating, and annealing on the lifetimes can be explained with reference to an energy band scheme in which the primary mechanism in the processes leading up to luminescence emission is the change in concentration of holes at various luminescence centres caused by annealing.

1. Introduction

Natural quartz is the material of choice for retrospective dosimetry applications using optically or thermally stimulated luminescence (Bøtter-Jensen et al., 2003). The amount of optically stimulated luminescence (OSL) from quartz increases significantly if the quartz is heated close to or above its first phase inversion point of 573 °C before use (Bøtter-Jensen et al., 1995). Similar annealing-induced enhancement in sensitivity of thermoluminescence (TL) from quartz was attributed to changes caused by the annealing in the physical processes leading up to the emission of luminescence as well as to improved recombination probability at the luminescence centres ([Bøtter-Jensen et al., 2003] and [Zimmerman, 1971]). Notions of annealing causing changes at luminescence centres were supported by differences between TL emission bands of heated and unheated quartz (Bøtter-Jensen et al., 1995).

Thermally induced sensitivity change in quartz OSL was studied further by Galloway (2002) using pulsed optical stimulation. The latter produces time-resolved spectra which can be resolved into individual components each with a discrete mean lifetime. The luminescence lifetime denotes the delay between stimulation and emission of luminescence and comprises the time to evict an electron from a trap, transit time through the conduction band, and the lifetime of the excited state at the luminescence centre (Chithambo and Galloway, 2001). In most cases, the luminescence lifetime is dominated by the intra-luminescence centre lifetime ([Chithambo and Galloway, 2001] and [Clark et al., 1997]). Since the lifetimes are closely linked with transitions at luminescence centres, their use can facilitate investigation of processes leading to emission of OSL. One of the propositions by Galloway (2002), related to changes in TL emission bands noted earlier (Bøtter-Jensen et al., 1995), was that changes in sensitivity could be properly explained on the basis of several charge transfer mechanisms including transfer of holes from a non-radiative to radiative centres, a feature that also affected luminescence lifetimes. Galloway (2002) noted that time-resolved spectra measured at certain temperatures from annealed quartz could be deconvolved into multiple lifetimes. The existence of such multiple lifetimes was further evidence that emission of luminescence in quartz might indeed involve several luminescence centres whose relative dominance depends on several factors including annealing and measurement temperature. Chithambo and Ogundare (2007) reported preliminary measurements of the characteristics of the lifetime components in sedimentary quartz. Chithambo et al. (2008) made a similar study on quartz from an archaeological site in Brazil.

The aim of this paper is to further explore the dynamics of luminescence emission in quartz by using features of its lifetime components. To this end, investigations are reported on the effect on lifetime components of duration and temperature of annealing between 500 and 900 °C, radiation dose up to 1700 Gy, and duration and temperature of preheating as well as stimulation temperature.

2. Experimental details

Time-resolved luminescence was measured using the pulsing system described previously ([Chithambo and Galloway, 2000a] and [Galloway, 2002]). Luminescence was stimulated at a pulse width of 11 μs using a set of 470 nm blue light-emitting diodes (Nichia NSPB-500) and detected in the spectral window 340–380 nm by an EMI 9635QA photomultiplier through Schott BG39 and UG11 filters. Prior to use, samples (BDH Ltd, UK) were annealed in a furnace at various temperatures up to 900 $^{\circ}\text{C}$, rapidly cooled in air afterwards, and then beta irradiated at 1.43 Gy min^{-1} using a ^{90}Sr beta source. Except for tests on the influence of preheating on lifetimes, time-resolved spectra were measured without heating between irradiation and measurement, a procedure used in continuous optical stimulation to minimize phosphorescence usually present soon after irradiation. The preheating could be omitted because in pulsed optical stimulation, the phosphorescence is not correlated in time with the light pulse ([Chithambo and Galloway, 2000a] and [Galloway, 2002]). Unless otherwise specified, luminescence was stimulated at room temperature, $\approx 25^{\circ}\text{C}$.

Lifetimes were evaluated from the part of each time-resolved spectrum after the light pulse by fitting exponential functions of the form $f(t) = \sum A_i \exp(-t/\tau_i) + B$ where τ_i is the lifetime of the i th component, A_i is a scaling factor, t is time, and B a constant added for background. The uncertainty $\Delta\tau$ in the lifetime is associated with the scatter in data points in the time-resolved spectrum used to evaluate the lifetime. Exponential functions are used on the basis that when luminescence is stimulated from an electron-trap with an initial electron population A using a short light pulse of duration t_1 , and where the probabilities of stimulation and decay are, respectively, s and λ , the rate $I(t)$ of luminescence emission after stimulation is

$$(1) \\ I(t) = sA[\exp(\lambda t_1) - 1] \exp(-\lambda t),$$

an exponential decay after the end of stimulation at $t = t_1$ where $\tau = 1/\lambda$ (Chithambo, 2007a). Luminescence lifetimes can also be extracted from the portion of the time-resolved spectrum during stimulation where the corresponding expression is $I(t) = sA[1 - \exp(-\lambda t)]$ (Chithambo, 2007a). These analytical methods are based on a simple model consisting of one electron-trap and one type of luminescence centre with emission involving electron transition through the conduction band as in the discussions of OSL by McKeever and Chen (1997) and Chen and Leung (2002). However, in typical time-resolved optical stimulation, the stimulating light pulse is brief and consequently, the reduction in trapped charge due to optical stimulation in that time is negligible and as a result retrapping is also assumed to be negligible ([Chithambo, 2007a] and [Chithambo, 2007b]). Chithambo and Galloway (2000b) made preliminary but qualitative considerations concerning the influence of retrapping on pulsed-luminescence from quartz. In more detailed studies, Chithambo and Galloway (2001) showed that the concurrent temperature dependence of lifetimes and luminescence intensity determined from the same spectra could be properly explained on the basis of the Mott–Seitz model of thermal quenching and assumption of negligible retrapping. The influence of retrapping on pulsed-OSL growth curves was discussed by Chen and Leung (2002) whose theoretical model predicted superlinear dose dependence if retrapping was dominant. However, experimental investigations of obvious non-negligible retrapping in pulsed-OSL from quartz remain outstanding. This paper is therefore based on the assumption of negligible retrapping as before (e.g. [Chithambo and Galloway, 2001] and [Galloway, 2002]).

The theoretical bases of mathematical methods for analysis of time-resolved luminescence spectra, including non-first order alternatives, have otherwise been described in greater detail by Chithambo (2007a) and compared with experimental and computer-simulated results (Chithambo, 2007b).

Fig. 1 shows an example of a time-resolved spectrum from quartz. The heavy line through data points is the best fit of a sum of two exponentials giving lifetime components of value $34.2 \pm 0.4 \mu\text{s}$ and $9.6 \pm 1.1 \mu\text{s}$. Henceforth, the terms ‘principal lifetime’ and ‘secondary lifetime’ will be used to describe, respectively, the longer and the shorter of the resultant lifetimes for analysis using a sum of two exponential functions. The notation for these lifetime components will follow.

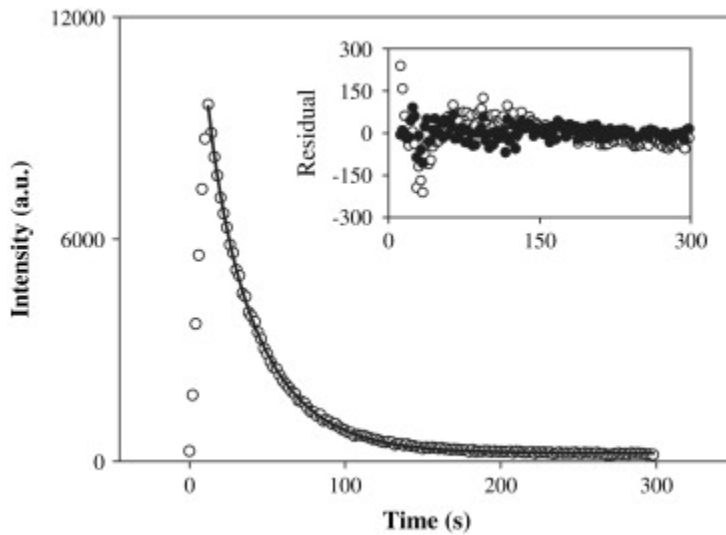


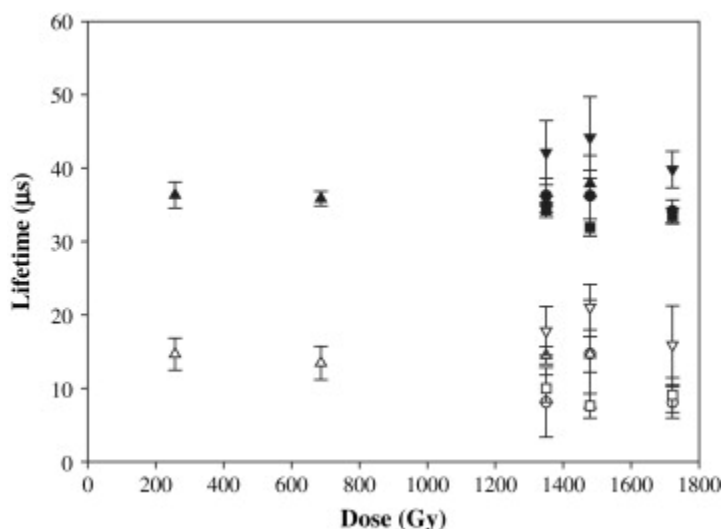
Fig. 1. A time-resolved spectrum from quartz annealed at 800 °C then dosed to 1350 Gy before stimulation. The residuals (inset) show the need for a sum of two exponentials (solid symbols) rather than a single exponential (open symbols) to better describe the data after the light pulse.

Time-resolved spectra discussed in this paper should not be confused with decay curves produced in continuous optical stimulation. A decay curve displays the change of luminescence intensity with duration of stimulation whereas a time-resolved spectrum displays the delay between stimulation and luminescence emission ([Chithambo and Galloway, 2000a] and [Chithambo and Galloway, 2000b]).

3. Results and discussion

3.1. Influence of irradiation on lifetime components

The influence of irradiation on lifetimes was investigated on five sets of quartz each annealed for 1 h at 500, 600, 700, 800 and 900 °C. Fig. 2 shows the relationship between both the principal and secondary lifetimes and beta dose between about 250 and 1720 Gy for all except the quartz annealed at 500 °C. Only one lifetime independent of dose could be obtained from the latter whereas two components could be found from all else if irradiated to greater than 200 Gy. The principal and secondary lifetimes, corresponding to a given annealing temperature, are also independent of dose. However, the values of the lifetime are not identical at all temperatures. The average value of the principal lifetime for quartz annealed at 600, 700, 800 and 900 °C is about 36, 33, 36 and 46 μs respectively whereas the secondary lifetimes for the same temperatures are 10, 9, 14 and 21 μs respectively.



is increased from 600 to 900 °C. The dotted line through the secondary lifetime data points in Fig. 4 is only a visual guide.

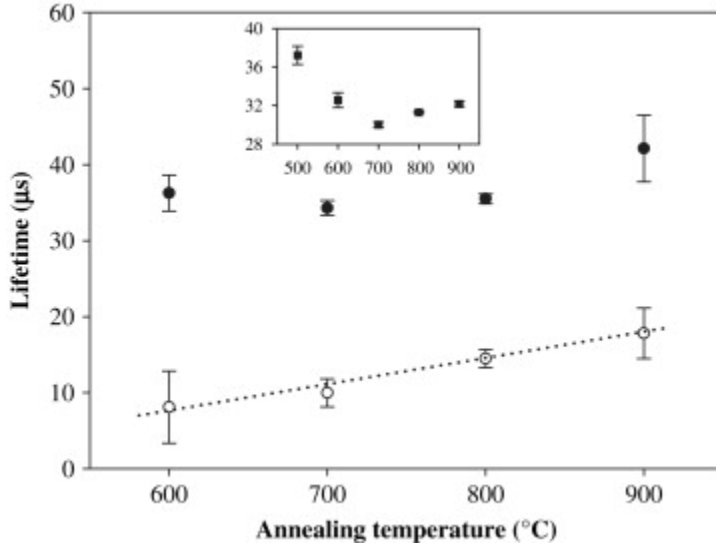


Fig. 4. The influence of annealing temperature on the principal (solid circles) and secondary lifetimes (open circles). Data from single exponential analysis is shown in the inset for comparison.

The inset to Fig. 4 shows the corresponding change of the lifetime determined from single exponential analysis for annealing between 500 and 900 °C. The inset has been included to help explain the effect of annealing on lifetime components τ_L and τ_S in the main graph. Where the lifetime is independent of annealing below 500 °C but decreases continually thereafter e.g ([Galloway, 2002] and [Chithambo et al., 2008]), the behaviour is interpreted as reflecting a change in importance of luminescence emission from L_H to L_L centres since the transfer of holes from L_H to L_L centres becomes more efficient with increase in annealing temperature. In this case ([Galloway, 2002] and [Chithambo et al., 2008]), the change in lifetime with annealing temperature from the higher value τ_H to the lower one τ_L is modelled as

(2)

$$\tau(T) = \tau_L + (\tau_H - \tau_L) / [1 + C \exp(-W/kT)]$$

where C is a constant, k is Boltzmann's constant, T is the absolute temperature and W is the activation energy of the non-radiative luminescence centre (R in Fig. 3) above the valence band. Equation (2) applies for lifetimes evaluated using a single exponential and is valid in cases where the lifetimes are dominated by contributions from τ_H initially and then τ_L later as the annealing temperature increases.

It should be noted that although annealing causes a transfer of holes between luminescence centres, it is the relative dominance of a particular centre that defines the lifetime. As pointed out in Section 3.1, the lifetime components τ_L and τ_S should become important as the annealing temperature increases beyond 500 °C. The principle lifetime (τ_L), with value $35.4 \pm 1.3 \mu\text{s}$ for samples annealed at and below 800 °C, can be compared to $33.3 \pm 0.8 \mu\text{s}$ determined for τ_L by Galloway (2002). Now, since lifetimes from single exponentials (Fig. 4, inset) should resemble the possible combined trend of the principal (τ_L) and secondary lifetimes (τ_S), reasons that account for the former should also explain the latter. This notion is used below to explain τ_L and τ_S in Fig. 4.

In order to account for the increase in the secondary lifetimes (τ_S) with annealing, it is reasonable to assume that at these temperatures there is sufficient thermal energy to release electrons from the deep trap DT (see Fig. 3) as well as significant release of holes from L_S centres. Some of the holes may then repopulate L_L and L_H centres. The repopulation is similar to the preferential capture of holes by some other than other centres in the description of thermal sensitization (Bøtter-Jensen et al., 1995). Thus as the temperature increases, the number of holes lost from L_S centres through electron recombination to produce luminescence, and through transfer to other centres exceeds the number transferred to this centre by annealing. The contribution of luminescence from L_S centres to the total signal will then tend to decrease and that from the acceptor L_L centre increases. Thus the gradual increase in the secondary lifetime τ_S from about 9 to 18 μs between 600 and 900 °C is consistent with increasing dominance of the centre L_L in the measured luminescence. A similar explanation was used (Ogundare and Chithambo, 2007) to account for an increase in lifetime (one component) with annealing temperature.

The influence of the duration of annealing on both the principal (τ_L) and secondary lifetimes (τ_S) was examined in samples annealed at 800 °C for 10, 30 and 60 min and was found to be negligible.

3.3. Lifetimes and preheating temperature

Fig. 5 shows the influence of preheating temperature on principal (τ_L , solid circles) and secondary lifetimes (τ_S , open circles; inset) for samples annealed at 800 °C for 10 min, irradiated to 257 Gy, then preheated at 120, 160 and 220 °C for 5 min prior to measurement at 25 °C. In each case, the lifetime for an unheated sample, considered as preheated at 25 °C, is included for comparison. The principal lifetime increases from $34.2 \pm 1.3 \mu\text{s}$ to $42.4 \pm 3.1 \mu\text{s}$ when the preheating temperature is increased to 220 °C, the maximum used in the tests. On the other hand, the effect of preheating on the secondary lifetimes is minimal. The results of Fig. 5 can be understood as showing that preheating reverses somewhat the effect of annealing in that in this case holes are transferred from L_L to L_H centres, increasing the influence of the latter in the signal, as is evident in the systematic increase of the principal lifetime τ_L with temperature of preheat. In good agreement with this work, Galloway (2002) found that lifetimes from preheated samples were consistently greater than those from unpreheated ones. The feature was also accounted for as evidence of hole release from L_L to L_H traps induced by preheating. Note that although the non-radiative centre R is an additional route for hole recapture, analyses of sensitivity changes (Galloway, 2002) suggested that holes released from L_L centres are not recaptured at the non-radiative centre R to any significant extent. This conclusion, relevant in this discussion, is also consistent with thermal sensitization models (e.g [Bøtter-Jensen et al., 1995] and [Zimmerman, 1971]) that although hole retrapping can occur at R centres at ambient temperatures, it does not at high temperatures. Lastly, the effect of the duration of preheating on the lifetimes, for preheating at 220 °C for 1, 5 and 10 min, was negligible.

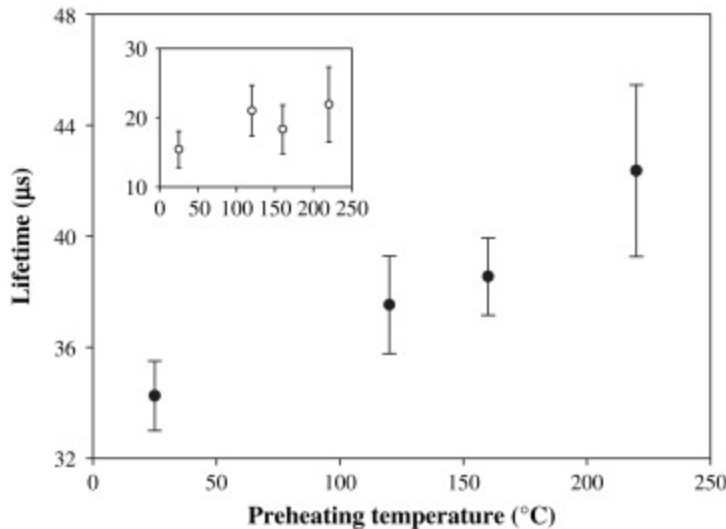


Fig. 5. Principal (solid circles) and secondary lifetimes (open circles) against preheating temperature.

3.4. Measurement temperature and lifetime components

The effect on lifetimes of measurement temperature up to 200 °C was examined in samples annealed for 1 h at 800 °C (Fig. 6), 700 °C and 900 °C; and for 30 min at 800 °C one of which was preheated at 220 °C for 1 min (inset, Fig. 6). A 1350 Gy dose was used to enable measurement of multiple lifetimes and the sequence of measurements up to 200 °C. The longer lifetimes are comparable below 100 °C but decrease thereafter up to 200 °C (Fig. 6, main graph). The change for the shorter lifetime (Fig. 6, main graph) is qualitatively similar. It can be deduced from Sections 3.2 and 3.3 that the initial value of the lifetime in each case in Fig. 6 is determined by the annealing or preheating temperature before stimulation. The temperature dependence of a lifetime, as exemplified in Fig. 6, is independent of the order in which the stimulation temperature is changed, low to high or vice-versa ([Chithambo and Galloway, 2001] and [Galloway, 2002]) and as such manifests the exclusive influence of temperature on the lifetime. This, as explored below, provides a means to identify and quantify physical processes of the lifetime in a way not readily possible using the discrete band model of Fig. 3.

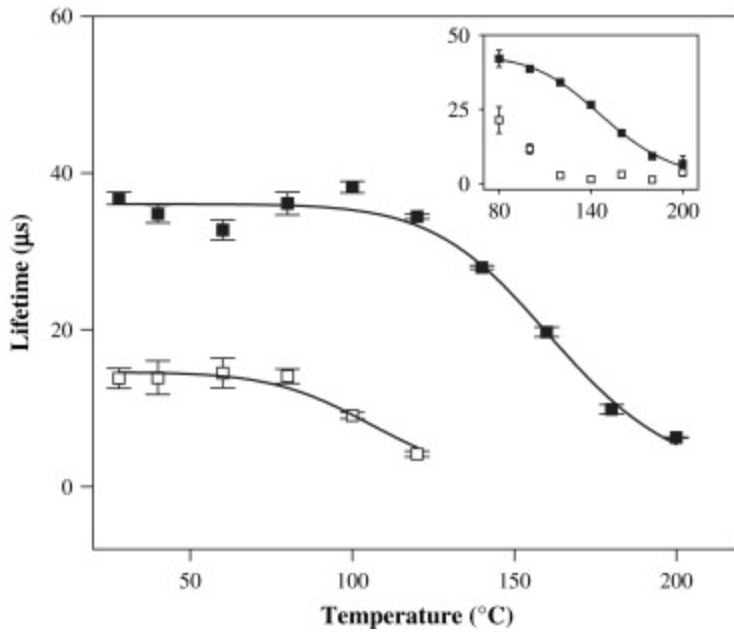


Fig. 6. Temperature dependence of lifetimes for samples annealed at 800 °C for 60 min, and for 30 min then preheated at 220 °C for 1 min (inset).

The temperature dependence of lifetimes in Fig. 6 is evidence of thermal quenching of the associated luminescence and varies as $\tau(T) = \tau_{\text{rad}} / [1 + C \exp(-\Delta E/kT)]$ where T is the absolute temperature, τ_{rad} is the radiative lifetime at 0 K, ΔE is the activation energy for thermal quenching, k is Boltzmann's constant and the constant C (also in Eq. (2) is equal to $\nu\tau_{\text{rad}}$ where ν is the frequency factor for the non-radiative process (Chithambo, 2007b). The solid lines through data points are the best fit of $\tau(T)$. Table 1 shows $\Delta E = 0.84 \pm 0.01$ eV for the principal lifetime τ_L and 0.72 ± 0.02 eV for τ_S . For comparison, ΔE linked to specific centres in other studies were 0.84 ± 0.01 eV for τ_S (Chithambo et al., 2008) and 0.79 ± 0.15 eV for τ_L (Galloway, 2002).

Table 1.

Thermal quenching activation energy associated with lifetime components.

Temperature of anneal (°C)	Duration of anneal (min)	ΔE (eV)		
		τ_H	τ_L	τ_S
700	60	–	0.84 ± 0.01	0.70 ± 0.04
800	60	–	0.85 ± 0.01	0.75 ± 0.01
900	60	–	0.84 ± 0.01	0.72 ± 0.02
800	30	–	0.84 ± 0.01	0.72 ± 0.01
800	30	0.64 ± 0.04^a	–	–

^a Preheated at 220 °C for 1 min.

Although this work was not concerned with the lifetime τ_H associated with centre L_H (see Fig. 3), measurements were made to determine ΔE corresponding to τ_H and for this, samples were preheated. The preheating was done to exploit the conclusion that preheating transfers holes from L_L to L_H centres increasing the contribution of the latter in the luminescence (Section 3.3). Although the longer lifetime would still nominally be τ_L , its associated ΔE should be expected to tend towards that for τ_H due to the increased influence of centre L_H brought about by preheating. It is instructive to recall (Section 3.1, paragraph 2) that τ_H is usually dominant in quartz annealed below 600 °C ([Chithambo et al., 2007] and [Galloway, 2002]). Fig. 6 (inset) shows, for the preheated sample, lifetimes for which $\Delta E = 0.64 \pm 0.04$ eV

for the longer component. This can be compared to 0.60 eV for quartz annealed at 600 °C and preheated at 125 °C for 5 s (McKeever et al., 1997) or 0.63 ± 0.07 eV for a sample annealed at 500 °C and preheated at 220 °C for 5 min (Chithambo and Galloway, 2001). Finally, the factor ν for lifetimes τ_L and τ_S was found to be of the order of $2 \times 10^{14} \text{ s}^{-1}$ consistent with the Debye vibration frequency $10^{12}\text{--}10^{14} \text{ s}^{-1}$ (McKeever and Chen, 1997).

Table 1 lists values of the activation energy ΔE associated with three separate lifetimes τ_H , τ_L and τ_S . The ΔE values are thus for thermal quenching at each of the luminescence centres L_H , L_L and L_S . These luminescence centres, which are shown as discrete energy levels in Fig. 3 would, in the Mott–Seitz configurational coordinate model (Bøtter-Jensen et al., 2003), be separate excited states of a luminescence centre with the non-radiative centre R of Fig. 3 as the ground state (see also Galloway, 2002). Since the activation energy for thermal quenching ΔE is the energy required for a radiationless transition between a specific centre and the ground state, its value should differ for three separate excited states. The set of ΔE values 0.64 eV, 0.72 eV and 0.84 eV determined for centres L_H , L_L and L_S respectively is consistent with this interpretation.

4. Conclusion

Time-resolved luminescence from quartz can be de-convolved into multiple lifetime components. We have studied the influence on the lifetime components of annealing between 600 and 900 °C, irradiation, measurement and preheating temperature. The principal lifetime of value about 35 μs is independent of annealing temperature whereas the secondary lifetime increases from 9 to 18 μs between 600 and 900 °C. The dependence of both lifetime components on measurement temperature can be explained by thermal quenching effect on the associated luminescence. On the other hand, effects due to irradiation, preheating, and annealing can be accounted for with reference to an energy band model in which a key feature is the change in concentration of holes at luminescence centres caused by annealing.

References

- Bøtter-Jensen, L., Agersnap Larsen, N., Mejdahl, V., Poolton, N.R.J., Morris, M.F., McKeever, S.W.S., 1995. Luminescence sensitivity changes in quartz as a result of annealing. *Radiat. Meas.* 24, 535–541.
- Bøtter-Jensen, L., McKeever, S.W.S., Wintle, A.G., 2003. *Optically Stimulated Luminescence Dosimetry*. Elsevier, Amsterdam.
- Chen, R., Leung, P.L., 2002. The decay of OSL signals as stretched-exponential functions. *Radiat. Meas.* 37, 519–526.
- Chithambo, M.L., 2007a. The analysis of time-resolved optically stimulated luminescence. I: theoretical considerations. *J. Phys. D.: Appl. Phys.* 40, 1874–1879.
- Chithambo, M.L., 2007b. The analysis of time-resolved optically stimulated luminescence: II. Computer simulations and experimental results. *J. Phys. D: Appl. Phys.* 40, 1880–1889.
- Chithambo, M.L., Galloway, R.B., 2000a. A pulsed light emitting diode system for stimulation of luminescence. *Meas. Sci. Technol.* 11, 418–424.
- Chithambo, M.L., Galloway, R.B., 2000b. Temperature dependence of luminescence time-resolved spectra from quartz. *Radiat. Meas.* 32, 627–632.
- Chithambo, M.L., Galloway, R.B., 2001. On the slow component of luminescence stimulated from quartz by pulsed blue light emitting diodes. *Nucl. Instrum. Methods B* 183, 358–368.
- Chithambo, M.L., Ogundare, F.O., 2007. Relative features of the principal and secondary luminescence lifetimes in quartz. *Phys. Stat. Sol. C* 4, 914–917.
- Chithambo, M.L., Ogundare, F.O., Feathers, J., 2008. Principal and secondary luminescence lifetime components. *Radiat. Meas.* 43, 1–4.
- Chithambo, M.L., Preusser, F., Ramseyer, K., Ogundare, F.O., 2007. Time-resolved

luminescence of low sensitivity quartz from crystalline rocks. *Radiat. Meas.* 42, 205–212.

Clark, R.J., Bailiff, I.K., Tooley, M.J., 1997. A preliminary study of time-resolved luminescence in some feldspars. *Radiat. Meas.* 27, 211–220.

Galloway, R.B., 2002. Luminescence lifetimes in quartz: dependence on annealing temperature prior to beta irradiation. *Radiat. Meas.* 35, 67–77.

McKeever, S.W.S., Chen, R., 1997. Luminescence models. *Radiat. Meas.* 27, 625–661.

McKeever, S.W.S., Botter-Jensen, L., Agersnap Larsen, N., Duller, G.A.T., 1997. Temperature dependence of OSL decay curves: experimental and theoretical aspects. *Radiat. Meas.* 27, 161–170.

Ogundare, F.O., Chithambo, M.L., 2007. Time resolved luminescence of quartz from Nigeria. *Optical Mater.* 29, 1844–1851.

Zimmerman, J., 1971. The radiation induced increase of the 110 °C TL sensitivity of fired quartz. *J. Phys. C* 4, 3265–3276.