On the correlation between annealing and variabilities in pulsed-luminescence from quartz

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Abstract

Properties of luminescence lifetimes in quartz related to annealing between 500 and 900ºC have been investigated. The luminescence was pulse-stimulated at 470 nm from sets of granular quartz annealed at 500, 600, 700, 800, and 900ºC. The lifetimes decrease with annealing temperature from about 42 to 33μs when the annealing temperature is increased from 500 to 900ºC. Luminescence lifetimes are most sensitive to duration of annealing at 600ºC, decreasing from 40.2 ± 0.7 μs by as much as 7 μs when the duration of annealing is changed from 10 to 60 min. However, at 800–900ºC lifetimes are essentially independent of annealing temperature at about 33μs. Increasing the exciting beta dose causes an increase in the lifetimes of the stimulated luminescence in the sample annealed at 800ºC but not in those annealed at either 500 or 600ºC. The temperature-resolved distribution of luminescence lifetimes is affected by thermal quenching of luminescence. These features may be accounted for with reference to two principal luminescence centres involved in the luminescence emission process.

Keywords: Luminescence lifetimes; Quartz; Pulsed LEDs

PACS classification codes: 78.47.+p

1. Introduction

The thermal history of quartz has a profound effect on its luminescence and the physical processes leading to the emission of the luminescence. These effects are seen as a strong dependence of the optically and thermally stimulated luminescence on annealing temperature or temperature during stimulation (Botter-Jensen et al., 1995 and Poolton et al., 2000) as well as an annealing-temperature dependent variation in luminescence lifetimes (Chithambo, 2002 and Galloway, 2002).

Studies of dynamics of luminescence in quartz using time-resolved optical stimulation, a technique introduced by Sanderson and Clark (1994) on feldspar but later applied to studies on quartz by Bailiff (2000) as well as by Chithambo and Galloway (2000), show that besides annealing temperature, additional factors affecting lifetimes include combinations of annealing temperature and temperature during measurement (Galloway, 2002), duration of annealing which affects the temperature-resolved distribution of lifetimes (Chithambo, 2002) as well as pre-measurement optical bleaching of some luminescence following irradiation (Chithambo, 2003a). The said experiments (Chithambo, 2002, Chithambo, 2003a and Galloway, 2002), concerned with annealing-related changes in lifetimes, were conducted using stimulation by pulsed 525 nm green light. In a subsequent study (Chithambo, 2003b), the influence of annealing and bleaching was investigated in the same quartz but with pulsed 470 nm stimulation. It was observed here that, depending on annealing temperature, systematic differences appeared between lifetimes measured promptly after irradiation and those preceded by partial bleaching of the luminescence.

This paper reports further investigations of features of luminescence lifetimes from annealed quartz stimulated using pulsed 470 nm blue light. Factors studied are the influence on lifetimes of annealing temperature, duration of annealing, irradiation and temperature during stimulation.

2. Experimental details

Samples used were 90–500µm 'acid-washed' granular quartz (BDH Ltd, UK). Sets of the samples were annealed at 500, 600, 700, 800 and 900ºC for 10, 30 and 60 min. The primary aim of the annealing was to obtain material for comparative analyses rather than to enhance luminescence emission, a consequence of annealing (Botter-Jensen et al., 1995 and Galloway, 2002). The same quartz was used in previous experiments (Chithambo, 2002 and Galloway, 2002).

Time-resolved luminescence spectra were measured at a dwell time of 2 µs over a dynamic range of 300 µs using the pulsing system of Chithambo and Galloway (2000) slightly modified to use a multichannel scaler instead of the combination of time-to-pulse height- and digital-to-analogue converters. The ORTEC MCS-plus multichannel scaler was used to simultaneously trigger light-emitting-diodes as well as initiate a data recording sweep. Once such a sweep is started, the scaler acquires photon counts sequentially in its channels, advancing with negligible dead-time through the selected channels, 150 in this case. The signal during stimulation is made up of a build-up of luminescence and scattered luminescence stimulating light. After the pulse, the luminescence decays away over photomultiplier noise only. Each time-resolved luminescence spectrum, a distribution of cumulative photon counts against time, was acquired over typically 100 000 sweeps.

A set of four 470 nm blue LEDs (Nichia NSPB-500) each operated at 11 µs pulse-width were used to stimulate luminescence from samples. The luminescence was detected between 340–380 nm by an EMI 9635QA photomultiplier through a combination of Schott BG39 and UG11 filters.

Luminescence lifetimes τ were calculated by fitting exponential functions of the form $L(t) = A\ \exp[-(t - t_1/\tau] + B$ to the spectrum after the pulse $L(t)$, where t, t_1, A and B are the time, pulse-width, scaling parameter, and background, respectively. The curvefitting was based on the Marquardt–Levenberg algorithm, and was done using the software SigmaPlot (SPSS Inc, USA). The optically stimulated luminescence was measured simultaneously with phosphorescence since the latter does not affect luminescence lifetimes (Galloway, 2002). Except for dose dependence tests, measurements were made on samples irradiated to 64 Gy at 1.43 Gy/min using a ^{90}Sr beta source.

3. Results

3.1. Influence of annealing temperature on lifetimes

Fig. 1 shows luminescence lifetimes measured at 25ºC as a function of annealing temperature. The comparison is made for samples heated for 10 min at 500, 600, 700, 800 and 900ºC. The lifetimes decrease with annealing temperature from 41.8 ± 0.3 µs at 500ºC down to 32.8 ± 0.2 µs at 800ºC and 33.6 ± 0.2 µs at 900ºC. On the other hand, below 500ºC, the lifetime measured from an unannealed sample was about 37 µs. A pattern of change in lifetimes similar to that of Fig. 1 was observed in the same quartz under 525 nm stimulation (Galloway, 2002) with lifetimes decreasing from about 41.5 to 31.5 µs when the annealing temperature was increased from 500^{c} to 1000ºC.

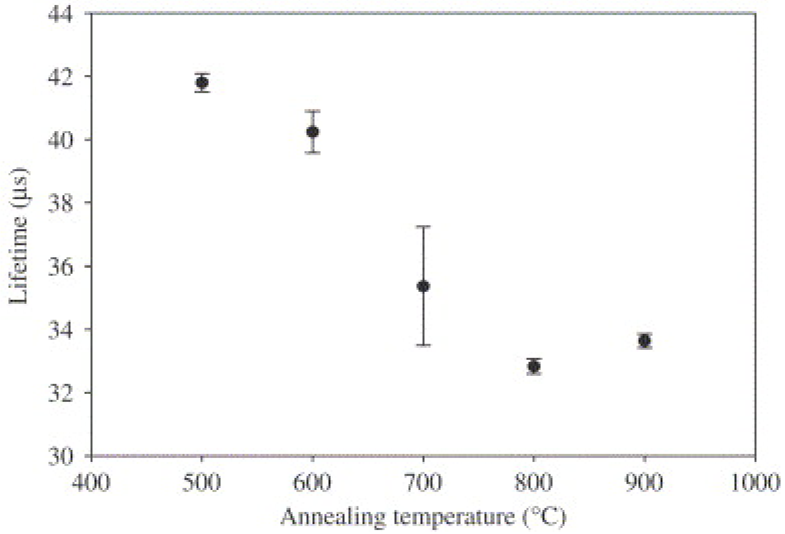

Fig. 1. The change of luminescence lifetimes with annealing temperature for measurements made at 25ºC. Samples were beta irradiated to 64 Gy.

3.2. Dependence of lifetimes on the duration of annealing

The effect of duration of annealing on lifetimes is shown in Fig. 2 for samples annealed at 500, 600, 700, 800 and 900ºC for 10, 30 and 60 min. All lifetimes were measured at 25ºC. Luminescence lifetimes for samples annealed at 500ºC undergo a small but noticeable reduction from 41.8 ± 0.3 to 38.6 ± 0.7 µs when the duration of annealing is increased from 10 min to 1 h. This change in lifetimes is greater for samples annealed at 600ºC, a temperature close to the first phase inversion point of quartz at 573ºC. In this case, the lifetimes decrease by as much as 7 µs from 40.2 ± 0.7 µs to 33.1 ± 0.7 µs when the duration of annealing is changed from 10 min to 1 h. The change for annealing at 700ºC is somewhat similar to that for 600ºC, although at about 3 µs between 10 and 60 min, smaller in magnitude. However, the lifetimes for samples annealed at 800 and 900ºC are essentially independent of duration of annealing at about 33 µs. In similar investigations but using stimulation at 525 nm, Galloway (2002) found that lifetimes at 600ºC decreased approximately exponentially from about 41 to 31 µs between 500–1000ºC whereas at 900ºC, lifetimes were not affected by duration of annealing.

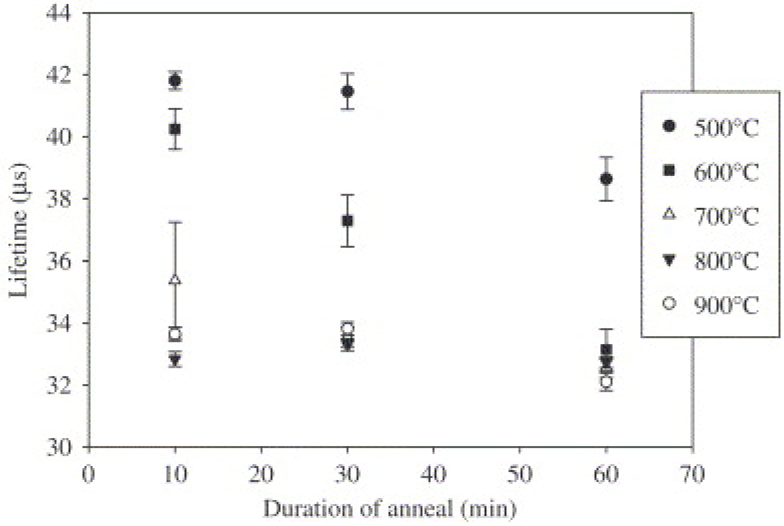

Fig. 2. The influence of duration of annealing on lifetimes at 25ºC for samples annealed for 10, 30 and 60 min at 500, 600, 700, 800 and 900ºC.

3.3. Influence of beta dose on luminescence lifetimes

Fig. 3 compares the dependence on beta dose of lifetimes obtained at 25ºC from samples annealed for 10 min at 500, 600 and 800ºC. Luminescence lifetimes in samples annealed at 500 and 600ºC are independent of beta dose at about 41 µs. The results for the 500ºC sample are consistent with lifetimes measured in the slow component of the same quartz which are also not influenced by beta dose (Chithambo and Galloway, 2001).

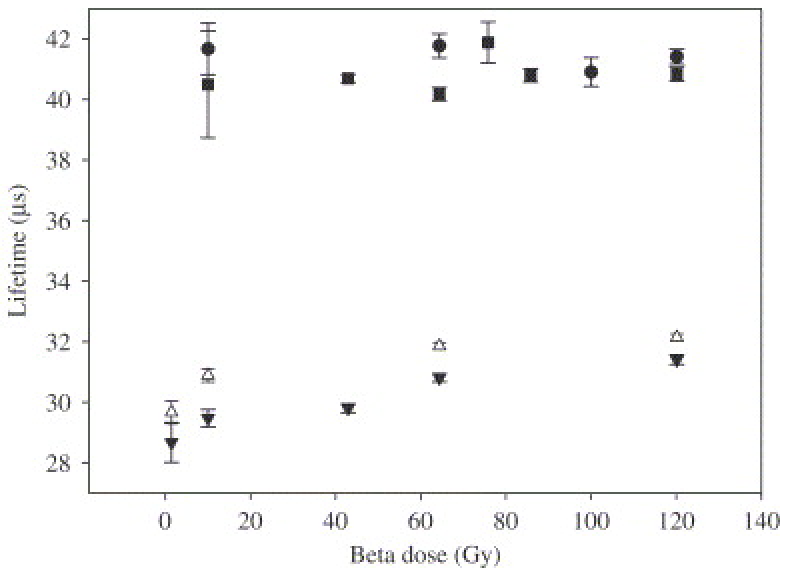

Fig. 3. Luminescence lifetimes corresponding to beta irradiation for samples annealed for 10 min at 500ºC (circles), 600ºC (squares), and 800ºC (solid downward triangle). Additional results for the quartz annealed at 800ºC for 1 h (open triangle) are included for comparison.

Considering the quartz annealed at 800ºC, it is found that lifetimes increase gradually with beta dose from 28.7 ± 0.7 μs at 1 Gy to 31.4 ± 0.2 μs for irradiation to 120 Gy. This pattern of change is reproduced by an alternative sample annealed at 800ºC but for 1 h. For the latter, lifetimes change from 29.7 ± 0.4 μs at 1 Gy to 32.1 ± 0.1 μs at 120 Gy.

3.4. Lifetimes and temperature during measurement

Fig. 4 shows the change of lifetimes with measurement temperature between 25 and 200ºC for quartz annealed at 500 and 600ºC. Samples were annealed for either 30 min, or 10 min (insets to Figs. 4(a) and (b)).). The temperature dependence of lifetimes for samples annealed at 500ºC appears to be independent of the duration of annealing. In both cases, lifetimes decrease similarly with temperature from 25 to 200ºC although only slowly up to 100ºC and more rapidly thereafter. In Fig. 4(b) for the 600ºC quartz, the rate of decrease of lifetimes is greater for the sample annealed for 30 min than for the one annealed for 10 min.

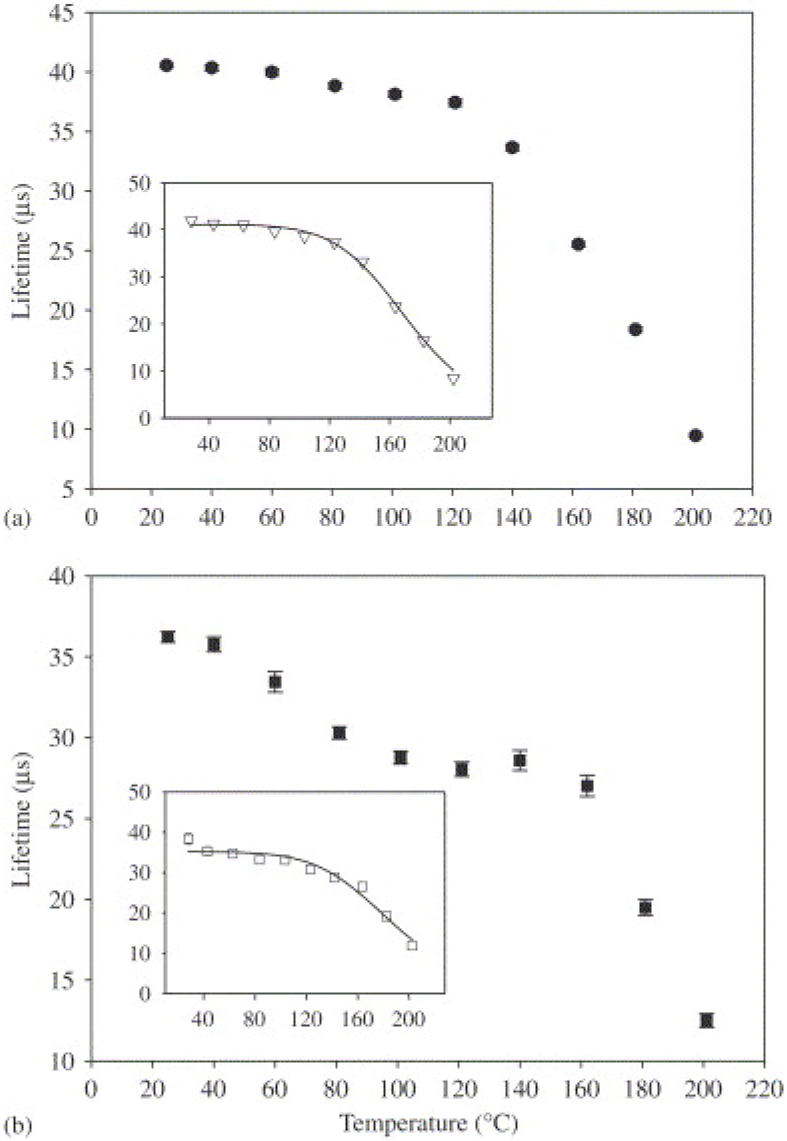

Fig. 4. The change of luminescence lifetimes with measurement temperature in quartz annealed at 500ºC for 30 min (a) 500ºC for 10 min (inset to (a)) 600ºC for 30 min (b) and at 600ºC for 10 min (inset to (b)).

4. Discussion

The change of luminescence lifetimes with measurement temperature as shown in Fig. 4 is due to increased thermal effect on lifetimes and thermal quenching on the associated luminescence (Bailiff, 2000 and Chithambo and Galloway, 2001). The temperature-dependence of lifetimes $\tau(T)$, particularly for samples annealed at 500ºC, and at 600ºC for 10 min (inset to Fig. 4(b)) is well described by the usual equation $\tau(T)=\tau_{\mathrm{rad}}/(1+C\exp(-\Delta E/kT))$, where τ_{rad} is the radiative lifetime at absolute zero of temperature, ΔE is the activation energy of thermal quenching, k is Boltzmann's constant, T is absolute temperature in K and C is a constant. In the selected examples of Fig. 4, the values of activation energy were calculated as 0.73±0.04, 0.76±0.04 and 0.73 ± 0.07 eV, respectively for samples annealed at 500ºC for 10 and 30 min, and at 600ºC for 10 min. The lifetimes for the quartz annealed at 500ºC are consistent with previous calculations (Chithambo, 2003b and Galloway, 2002). However, the distribution of lifetimes for the sample annealed at 600ºC for 30 min cannot be accurately described by the thermal quenching equation cited above.

The non-monotonic decrease of lifetimes of Fig. 4(b) for the quartz annealed at 600ºC for 30 min is similar to that reported for quartz annealed at 800 and 900ºC (Chithambo, 2002 and Galloway, 2002). The lifetime measured after these annealing temperatures is thought to consist of two components τ_H and $\tau_L$with one becoming dominant depending on measurement temperature (Galloway, 2002). The lifetimes are associated with luminescence emitted from luminescence centres L_H and L_L additional to the non-radiative centre as in the band model of Botter-Jensen et al. (1995). In this modification, annealing can transfer holes from L_H to L_L. In the sample annealed at 600ºC for 30 min, each of the lifetimes τ_H and τ_L have probably different temperature-dependent characteristics so that the combination does not simply vary as $\tau(T)=\tau_{rad}/(1+C\exp(-\Delta E/kT))$ from 20 to 200ºC. In addition, there is a possible further transfer of holes to centre L_L during measurement causing a rapid decrease of lifetimes overall.

The increase of lifetimes with dose for the sample annealed at 900ºC for 10 min can be explained by the increase in lifetime from τ_L to τ_H because of the preferential trapping of holes at the L_H centre of holes produced during irradiation (Galloway, 2002). On the other hand, that the lifetime is constant with dose for samples annealed at 500 and 600ºC means that the L_H centre in these cases is not sufficiently depleted prior to irradiation and measurement thus maintaining τ_H as the dominant lifetime component.

Luminescence lifetimes are most sensitive to duration of annealing at 600ºC and least at 800–900ºC. This behaviour is consistent with the supposition that the transfer of holes from the L_H to L_L centres becomes more efficient with increase in annealing temperature (Galloway, 2002) and at 900ºC in this work, with increase in duration of annealing. This explains the decrease in lifetimes from about 40μs (τ_H) to about 33 μs (τ_L) at 600ºC or the predominance of τ_L, of the order of 33 μs, at 800–900ºC.

It is interesting to note that Bailiff (2000) reported a lifetime of about 40 μs from synthetic quartz and 33μs from granular quartz. In light of the present results, the differences in those lifetimes may now be attributed to differing thermal history between the two quartzes. Indeed, Chithambo (2004) found that lifetimes in synthetic quartz are also affected by annealing.

5. Conclusion

The correlation between annealing and changes in luminescence lifetimes has been studied in quartz annealed between 500 and 900ºC.

Luminescence lifetimes decrease from about 42 to 33 μs when the annealing temperature is increased from 500 to 900ºC. The lifetimes also decrease with duration of annealing but mostly so in the quartz annealed at 600ºC. When the annealing temperature is increased to 800–900ºC, it is found that lifetimes are essentially independent of annealing temperature at about 33 μs. However, lifetimes at 900ºC increase with beta dose whereas those from samples heated to 500–600ºC are not influenced by magnitude of beta irradiation up to 120 Gy investigated.

The distribution of luminescence lifetimes with measurement temperature is affected by thermal quenching of luminescence with an activation energy of about 0.73 eV. However, this distribution may also be influenced by duration of annealing in the sample annealed at 600ºC for 30 min. As such, the temperature dependence of lifetimes in the latter cannot be properly accounted for by thermal quenching of luminescence alone.

Properties of lifetimes related to annealing, measurement temperature and irradiation can be explained by the relative dominance of two principal luminescence centres involved in the luminescence emission process (Galloway, 2002). Further work is required to better understand the influence of annealing on the dependence of lifetimes on measurement temperature.

Acknowledgements

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