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Luminescence lifetimes in natural quartz annealed beyond its second phase inversion temperature

M.L. Chithambo

Department of Physics and Electronics, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

HIGHLIGHTS

- Luminescence lifetimes in natural quartz annealed beyond its second phase inversion temperature is reported.
- Lifetimes increase with dose, annealing between 800 and 1000 °C, and preheating.
- Lifetimes under stimulation temperature are affected by direction of heating.
- Changes are accounted for in terms of hole-transfer luminescence centres.

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ABSTRACT

The influence of annealing, irradiation dose, preheating and measurement temperature on luminescence lifetimes has been studied in quartz annealed at 1000 °C. The measurements were supplemented by studies on quartz annealed at 900 and 800 °C. Lifetimes increase with dose as well as with temperature and duration of annealing between 800 and 1000 °C. Preheating produces the same effect. The changes are accounted for in terms of hole-transfer from the non-radiative luminescence centre to and between radiative centres. The influence of measurement temperature on lifetimes depends on whether the stimulation is carried out from ambient to 200 °C or otherwise. This result is unlike that in quartz annealed at or below 500 °C where lifetimes are independent of the direction of heating. In particular, lifetimes decrease monotonically when measurements are made from 20 to 200 °C but not when recorded from 200 to 20 °C. The latter produces a pattern resembling that in quartz annealed up to 500 °C. The results are concluded as evidence of thermal effects on separate luminescence centres. In support of this, different values of the activation energy for thermal quenching were found for each supposed luminescence centre. The change of the corresponding luminescence intensity with temperature is also qualitatively consistent with this notion.

1. Introduction

The use of natural quartz for retrospective dosimetry using optically or thermally stimulated luminescence is well documented (Preusser et al., 2009). When the quartz is annealed beyond its first phase inversion temperature of 573 °C, its sensitivity to optical stimulation, monitored as the amount of signal per unit irradiation dose, is significantly enhanced (Bøtter-Jensen et al., 1995; Galloway, 2002). It is now known that changes in luminescence intensity brought about by annealing are accompanied by corresponding ones in luminescence lifetimes in natural quartz (Galloway, 2002; Chithambo and Ogundare, 2009) as well as in synthetic quartz (Chithambo et al., 2011). The lifetimes, determined from time-resolved luminescence spectra, denote the delay between stimulation and emission of luminescence, and are also associated with transitions at luminescence centres. Thus they are a means to study physical processes of luminescence.

A key observation concerned with the use of time-resolved spectra was that changes in lifetimes that accompany sensitivity variations are caused by transfer of holes to and between particular luminescence centres by annealing (Galloway, 2002; Chithambo et al., 2008a; Chithambo and Ogundare, 2009). In a related study combining use of luminescence and positron lifetimes (Chithambo et al., 2011), it was determined that irradiation did not change the defect concentration and annealing did not produce new defects in quartz further isolating hole transfer as a consequence of annealing.

The proposition that change in importance of certain

E-mail address: m.chithambo@ru.ac.za.

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luminescence centres due to annealing is responsible for differences in lifetimes has been tested in other ways. For example, lifetimes from natural quartz from crystalline rocks with known thermal-provenance (used in lieu of annealing) including quartz of sedimentary, plutonic, volcanic, hydrothermal and metamorphic origin differ (Chithambo et al., 2007) consistent with the notion of annealing causing changes in relative dominance of different luminescence centres. In addition, Pagonis et al. (2011) reported an analytical model, involving two luminescence centers and a hole reservoir, which is consistent with the empirical models previously described by Galloway (2002) and by Chithambo and Ogundare (2009). In their work, Pagonis et al. (2014) combined modelling and radioluminescence and showed that annealing beyond 500 °C not only affects lifetimes but also causes changes in the emission wavelength as might be expected of different luminescence centres.

In general, the nature and value of luminescence lifetimes in quartz depends not only on annealing but on the combination of irradiation dose, annealing and measurement temperature (Chithambo and Ogundare, 2009). Thus for example, in quartz annealed up to 500 °C, only one lifetime of value ~40 μs is found irrespective of irradiation dose. On the other hand, time-resolved spectra from quartz annealed at 600–700 °C are suggestive of the presence of multiple lifetime components but with values too similar to properly distinguish one from the other (e.g. Galloway, 2002). In comparison, a principal lifetime of value ~35 μs and secondary ones of about 14 μs become manifest in quartz annealed at 800 °C when irradiated to very high (>1000 Gy) doses (Chithambo and Ogundare, 2009).

Luminescence lifetimes have been used as a means to study physical processes of luminescence emission in quartz by utilising their dependence on various parameters including measurement temperature, duration of optical stimulation, irradiation dose or by way of the dynamic throughput (Chithambo, 2007a,b; Chithambo and Ogundare, 2009; Galloway, 2002). Experimental studies have been complemented by development of relevant theory (Chithambo, 2007a), mathematical modelling (Pagonis et al., 2014) and other techniques for monitoring point-defects such as positron annihilation spectroscopy (Chithambo et al., 2011) or radioluminescence (Pagonis et al., 2014). These studies have mostly been concerned with unannealed quartz or material annealed at 500 or 600 °C, that is, near its first phase inversion temperature of 573 °C (Chithambo and Galloway, 2001; Galloway, 2002) or indeed with quartz annealed at 800 °C (Chithambo and Ogundare, 2009). There has never been a systematic study of lifetime components in quartz annealed beyond the second phase inversion temperature of 867 °C and this is the subject of this report.

The impetus for this work comes from the peculiar response of lifetimes to annealing. Whereas lifetimes are independent of annealing up to 500 °C but decrease thereafter, the change is not strictly monotonic since a slight increase in lifetimes with annealing temperature is evident between 800 and 1000 °C (e.g. Galloway, 2002). Thus far, theories on lifetimes have been developed with reference to and tested on quartz annealed at temperatures below its second phase inversion temperature. The said empirical or computational theories did not address the cited reverse behaviour in lifetimes between 800 and 1000 °C. It should be noted that our mention of phase inversion temperatures is as reference points and for emphasis and should not be misunderstood to mean that this report purports to discuss differential scanning calorimetry or measurement of phase transitions.

The primary aim of this work therefore is to study luminescence lifetimes in quartz annealed at 1000 °C, that is, well beyond its second phase transition temperature and to assess any thermal effects, such as quenching, on the associated luminescence. Supplementary measurements were made on quartz annealed at 900 and 800 °C. In particular, we investigated the influence of irradiation, annealing, preheating and stimulation temperature on lifetimes.

2. Experimental details

Samples used were commercially available (BDH Ltd, UK) 'acid-washed' granular quartz of grain size 90–500 μm. The quartz was annealed in a furnace at 1000 °C for 10, 30 and 60 min, cooled in air thereafter and then beta irradiated at a dose rate of 0.10 Gy s^{-1} using a ^{90}Sr beta source. Complementary measurements were made on samples annealed at 900 and 800 °C. The quartz, which has been used previously (Chithambo and Galloway, 2001; Chithambo and Ogundare, 2009; Galloway, 1993, 2002; Pagonis et al., 2014) has negligible feldspar content according to infrared stimulation of dosed aliquots (Chithambo and Galloway, 2001; Galloway, 1993) and is used without further chemical treatment.

Time-resolved luminescence was measured using a light-emitting-diode (LED) based pulsing system (Chithambo, 2011). In the arrangement, an ORTEC MCS-plus multichannel scaler is used to trigger a set of 470 nm blue LEDs (Nichia NSPB-500) while simultaneously processing luminescence photon counts from an EMI 9635QA photomultiplier to produce time-resolved luminescence spectra. As described previously (Chithambo and Galloway, 2001; Chithambo, 2007b), the mean light intensity at sample was determined to be 0.60 mW cm^{-2} for four blue LEDs using a calibrated PIN diode (Ealing Electro-Optics).

Luminescence was stimulated at a pulse width of 11 μs and detected in the spectral window 340–380 nm through a combination of Schott BG39 and UG11 filters. Each spectrum was obtained using 100000 sweeps, at a dwell time of 2 μs and a dynamic range of 300 μs. The stimulation temperature was controlled by an AO500 sample heater (MBE-Komponenten GmbH, Germany) in which the sample stage is a ceramic direct-current driven thin-film heater plate. Except for measurements 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 used to stimulate the luminescence (Galloway, 2002).

Lifetimes were evaluated from the portion of each time-resolved spectrum after the pulse by fitting functions of the form

$$f(t) = A\exp(-t/\tau) + B, \quad (1)$$

where τ is the lifetime, A is a scaling factor, t is time, and B a constant added to account for the background. The uncertainty $\Delta\tau$ in the lifetime corresponds to the scatter in data points in the time-resolved spectrum used to evaluate the lifetime. The mathematical basis of analytical techniques for time-resolved spectra have been described by Chithambo (2007a, b). In addition, Pagonis et al. (2011) reported a kinetic model for time-resolved spectra which quantitatively reproduces the model of Chithambo (2007a,b).

3. Results and discussion

3.1. Influence of irradiation on lifetimes

The influence of irradiation on lifetimes was investigated in quartz annealed at 1000 and 900 °C. A set of three samples was prepared for each temperature. Fig. 1 shows the dependence of lifetimes on dose for quartz annealed at 1000 °C (Fig. 1a) and at