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Quartz OSL emission spectra and the role of [AlO$_4$]$^\circ$ recombination centres

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ABSTRACT

Synthetic crystalline quartz, with known concentrations of Al and alkali ions was used in this study. The wavelength-resolved OSL spectra were measured after different periods of optical stimulation, and more than one emission band were detected. A composite peak centred at 380 nm is seen; this is similar to the emission band for the 110 °C TL peak, that has been associated with the [AlO$_4$]$^\circ$ recombination centres. A direct correspondence between OSL signal intensity and the alkali ion concentration was observed; the signal intensity in bulk crystalline “swept out” quartz, i.e. quartz submitted to electro-diffusion, was found to be much lower than that from the ‘unswept’ quartz. These data suggest that alkali ions play an important role in the OSL phenomenon. Based on the data presented here and the existing TL studies it is inferred that OSL and the 110 °C and 325 °C TL peaks share a common recombination centre. This emission is assigned to electron recombination at Al centres with a trapped hole, [AlO$_4$]$^\circ$. A preliminary phenomenological model of TL and OSL is proposed, which is based on a spatial association between the OSL and the 110 °C TL trap.

1. Introduction

Since its first proposal as a dating technique (Huntley et al., 1985), it appeared clear that optically stimulated luminescence (OSL) is not simply due to charge eviction from traps with consequent luminescence recombination, analogous to thermoluminescence (TL), but in most cases it results from more complex mechanisms.

Specifically in quartz, one of the most studied materials for dating applications, it was soon clarified that a strong correlation exists between OSL and the TL peaks at 110 °C and 325 °C (heating rate 15 $^\circ$C s^{-1}). Furthermore these peaks are known to be interrelated through optical stimulation, the so-called PTTL (photo transferred thermoluminescence). For example, optical exposure decreases the intensity of the 325 °C peak and at the same time induces the 110 °C peak (Kaylor et al., 1995).

Even though very little is known about the defects responsible for OSL, the complex phenomenology of the OSL recombination has been extensively studied allowing the development of well defined procedures that give reliable results with good repeatability. These procedures take into account the inter-relation between traps sensitive to optical or thermal stimulation, the so-called optical and thermal traps, respectively. It has been shown that OSL dating of quartz extracted from sediments or pottery must be carried out at a temperature around 125 °C to avoid interference with the thermal trap responsible for the 110 °C TL peak and that preheating is necessary, 10 s at 200–300 °C being currently used.

Both blue and red emissions are known to occur in quartz, the most studied band being at 380 nm. This luminescence emission is very often found in quartz, not only in TL above RT, but also in the 190 K TL glow peak (Martini et al., 2000), in the low temperature RL (Halperin and Sukov, 1993) and in CL (Alonso et al., 1983). The intensity of this emission increases in the pre-dose procedure (Yang and McKeever, 1990); this effect has been related to the enhancement in the concentration of [AlO$_4$]$^\circ$ centres caused by specific high temperature heat treatments (Martini et al., 1995).

In contrast to TL and RL, the emission bands for quartz OSL have not been studied extensively; its main OSL emission is reported at 365 nm (Huntley et al., 1991) or at 380 nm (Stoneham and Stokes, 1991). Although the role of the “Al centres” has been suggested earlier, the defects responsible for trapping and recombination have not been unambiguously identified. In fact Al is always present in quartz, both natural and synthetic, as a substitutional ion for Si and it is charge compensated by alkali or hydrogen ions or by a trapped hole, giving rise to [AlO$_4$/M$^+$]$^\circ$, [AlO$_4$/H$^+$]$^\circ$ and [AlO$_4$]$^\circ$, respectively (Malik et al., 1981). By specific electro-diffusion treatments (“sweeping”) it is possible to modify the concentration of alkali ions in quartz and correlations between these ions and the luminescence properties can be investigated (Martini et al., 1987). While a number of results have been presented with regards to the

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role of alkali ions in the TL of quartz, little is known about their role in OSL.

In this paper we present new measurements of the OSL emission wavelengths. A comparison between unswept and swept quartz crystals confirms that alkali ions participate in the OSL mechanism and that the intensity of emission is strongly increased by heat treatments in both kinds of samples. Finally a trapping-recombination model of TL and OSL is proposed.

2. Materials and methods

Synthetic quartz crystals, both as-grown and hydrogen swept, "Premium Quality" (Sawyer Research Products, Eastlake, Ohio) were used. The Al content was ~10 ppm; the concentrations of alkali ions were approximately 1–3 ppm and 0.1 ppm in the as-grown and H-swept respectively. Samples were cut in the form of discs, 10 mm diameter and 1 mm thickness.

OSL measurements were carried out at 125 °C after preheating at 220 °C, using an automated Risø TL/OSL system, and with an excitation wavelength of 470 nm. Samples were irradiated using a 1.48 GBq ^{90}Sr-^{90}Y beta source (dose rate 0.1 mGy s^{-1}). Wavelength-resolved OSL measurements were performed at room temperature (RT) using a system designed and built by our laboratory: the excitation waveband was defined by a 470 nm (FWHM, 10 nm) interference coupled to a 100 W tungsten lamp. The detection system was a CCD (Jobin-Yvon Spectrum One 3000) coupled to a monochromator operating in the 210–780 nm range. The data were corrected for the spectral response of the detection system.

3. Results and discussion

3.1. The 380 nm emission in quartz

We measured the OSL spectrum of unswept quartz, which is shown in Fig. 1. The OSL intensity of the swept crystals was not strong enough to perform wavelength resolved analysis. The spectrum of Fig. 1 is evidently composite, the main emission being at around 380 nm.

In order to understand if the different spectral components are reduced by light at the same rate, i.e. if the spectrum shape changes with the duration of optical stimulation, the OSL emission spectra were measured at different time intervals during the optical stimulation. An artificial irradiation (50 Gy), followed by a 5 s pause, was given to the sample and the spectra were collected sequentially during the following 40 s integration intervals. By denoting the end of irradiation at 0 s, the first and second spectra were obtained in the time intervals 5–45 and 45–85 s during the optical stimulation, respectively. The third spectrum was recorded during 85–125 s, following switching off the light; the purpose of this measurement was to obtain a phosphorescence emission spectra. Finally, the stimulation light was switched on again and the fourth and the fifth spectra were collected in the time intervals 125–165 s and 165–205 s, respectively. These spectra are presented in the in Fig. 2a. In Fig. 2b only the spectra collected during light stimulation are shown; these are normalized for an easier comparison of shapes. The intensity of the iso-thermal phosphorescence is much lower, compared to the intensity of the OSL and is, therefore, not reported in Fig. 2b. The data in Fig. 2b suggest that different components decay at different rates during the light emission. Specifically, a longer decay time characterizes the component at lower energy. This change in the shape of the emission spectra may imply that the recombination band for TL and OSL may be slightly different (assuming a contribution from the decay of the 110 °C TL peak at RT). It could also imply that the slow OSL components may use a different band than the fast/medium OSL components (Jain et al., 2003). This point will be further studied when our spectrometer is modified to allow measurements at different temperatures.

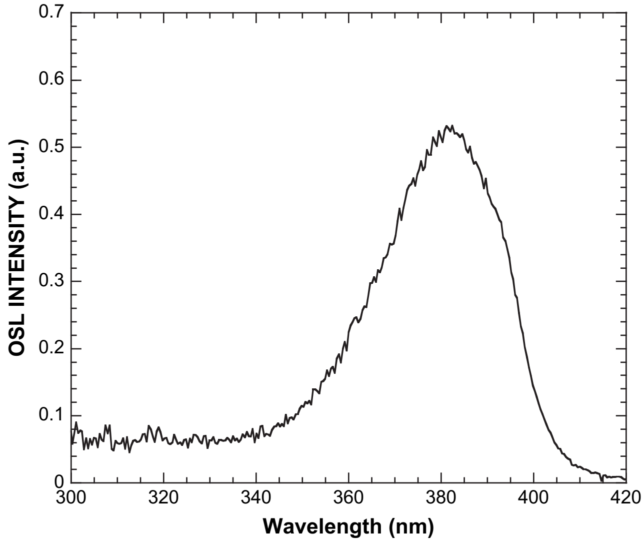

Fig. 1. Synthetic quartz crystals, "Premium Quality" Sawyer (Al 10 ppm; alkali ions 1–3 ppm); disc, 10 mm diameter and 1 mm thickness (Dose: 50 Gy; RT, no preheating, integration time = 40 s).

3.2. Role of alkali ions and the $[AlO_4]^{\circ}$ recombination centre in quartz luminescence

An inter-relation between the 110 °C TL peak and the OSL of quartz has been widely acknowledged (Wintle and Murray, 1997). It has been well established that both OSL and 110 °C TL trap do not arise from the same electron centres. For example, heating across the 110 °C TL peak induces an OSL signal (recuperation; Murray and Wintle, 1998), while optical stimulation gives rise to an increment in the 110 °C TL peak (photo transferred TL or PTTL; Murray and Wintle, 1998). However, most researchers agree on the involvement of the same recombination centres for these two processes (Chen et al., 2000). The strongest experimental evidences for this commonality are a) emission in the same wavelength band during OSL and 110 °C TL and b) a simultaneous increase in the sensitivity of the two signals due to prior heating. A further support for the former comes from the results reported here in Figs. 1 and 2.

There is wide agreement on the correctness of the Zimmerman (1971) model of the so-called pre-dose effect in quartz. This model proposes that the enhancement of sensitivity of the 110 °C TL peak is due to an increase in the availability of recombination centres. If OSL and 110 °C TL recombine at the same centres, it would imply that both these phenomena are subjected to the pre-dose effect in the same manner: in fact Stoneham and Stokes (1991) reported on this expected increase in the OSL and TL sensitivity after irradiation and heating. Similarly, in analogy with TL, it is expected that an increase in the OSL emission is seen as a consequence of preheat (Bøtter-Jensen et al., 1995); note that this is not the same as the pre-dose effect. Alkali ions are expected to play an important role in these sensitivity changes. Many defect dynamics in quartz are related to the presence of alkali ions: for example, the pre-dose effect is seen only in unswept crystals (Martini et al., 1987). The role of alkali ions also appears to be relevant in the formation of intrinsic defects, for example, both E′ and E″ centres are created only in unswept quartz (Jani et al., 1983; Bossoli et al., 1982). Schilles et al. (2001) propose that luminescence in quartz is sensitized by the removal of oxygen vacancy E1′ centres.

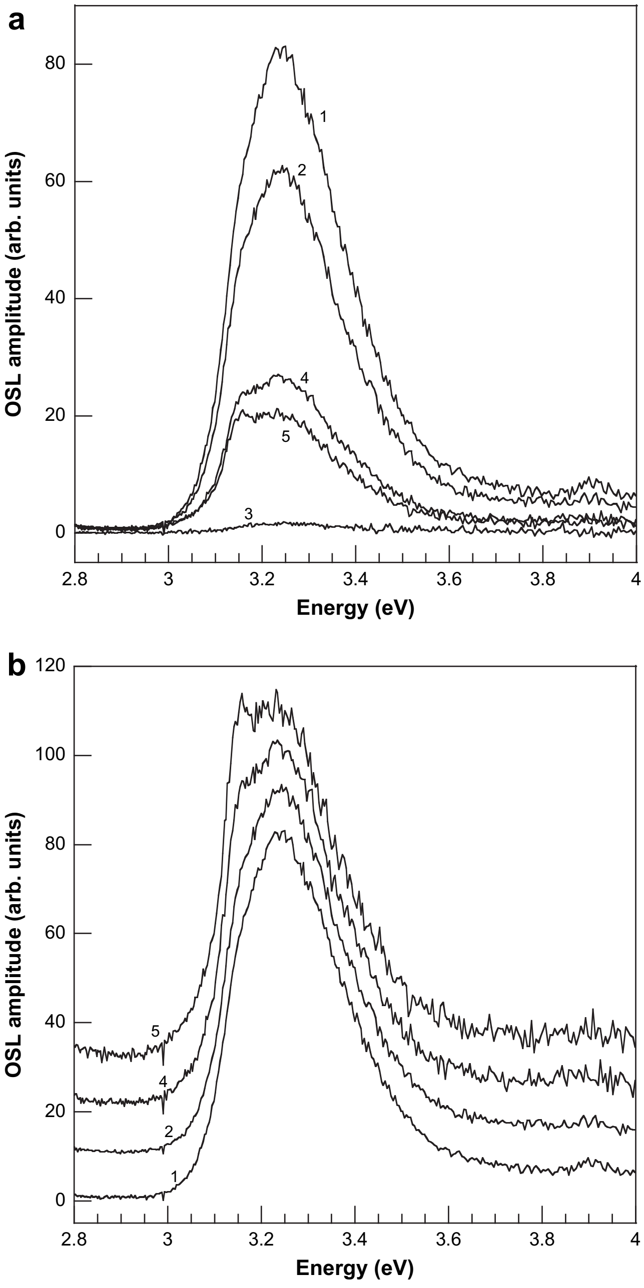

Fig. 2. (a) OSL emission spectra of synthetic quartz "Premium Quality" Sawyer (Al 10 ppm; alkali ions 1–3 ppm); disc diameter 10 mm and thickness 1 mm. The spectra were collected sequentially in the indicated time intervals after a single irradiation (Dose: 50 Gy, no preheating, integration time 40 s). 1) From 5 to 45 s under optical stimulation, 2) from 45 to 85 s under optical stimulation, 3) from 85 to 125 s without optical stimulation, 4) from 125 to 165 s under optical stimulation, 5) from 165 to 205 s under optical stimulation. (b) Same spectra as in Fig. 2a, normalized and shifted for a better comparison. Spectrum 3 measured without optical stimulation is not reported.

In Fig. 3 we present the effect of heat treatment (16 h at 1000 °C) on the OSL curves of our synthetic quartz samples. This heat treatment results in almost one order of magnitude increase for the unswept quartz and two orders of magnitude increase for the swept quartz. Note that the OSL intensity of the swept quartz is always much lower than that of the unswept quartz. These data confirm that alkali ions play an important role in OSL sensitivity change in quartz, as has earlier been recognized by Itoh et al. (2002) and by Martini and Galli (2007).

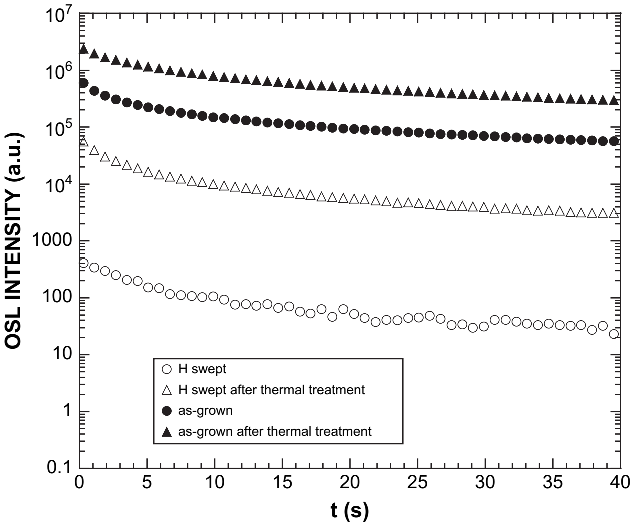

Fig. 3. Synthetic quartz crystals, both as-grown and hydrogen swept, "Premium Quality"(Sawyer Research Products, Eastlake, Ohio). Al content was around 10 ppm; the concentrations of alkali ions were approximately 1–3 ppm and 0.1 ppm in the as-grown and H-swept respectively. Samples were cut in the form of discs, 10 mm diameter and 1 mm thickness. (Dose: 50 Gy measured at 125 °C with preheating 10 s at 220 °C). Thermal treatment consists of 16 h at 1000 °C.

On the basis of the results presented here, together with experimental evidence already published, a few conclusions can be put forth in order to propose a phenomenological model of OSL recombination, strictly related to the 110 °C TL peak in quartz. In Fig. 4 a schematic representation of the model is presented. The model contains an optical trap (OT) and a thermal trap (TT); both these are electron traps and give rise to the OSL signal and 110 °C TL peak, respectively. Their de-trapping gives the same kind of recombination at $[AlO_4]^\circ$, with a 380 nm emission and they are inter-related by optical or thermal excitation which cause electron transfer across one another. These charge transfer processes give rise to the well known optically induced increase in the 110 °C TL peak (Bailey et al., 1997) and the "recuperation" effect (Aitken and Smith, 1988).

Note that a conduction band mediated charge transfer across the two levels is not necessary in this model. However, the recombination itself is routed through the conduction band. Thus, the model is not inconsistent with the published data on the invariance of the thermally stimulated conductivity (TSC), despite a simultaneous increase in TL, as observed in the pre-dose effect (Castiglioni et al., 1994), and with the first-order kinetic behaviour of the 110 °C TL peak. The invariance of TSC with a simultaneous increase in TL can be explained by an increase in the available recombination centres possibly due to the diffusion of the alkali ions. It must be pointed out that the proposed model is speculative and further measurements are necessary to support or modify it.

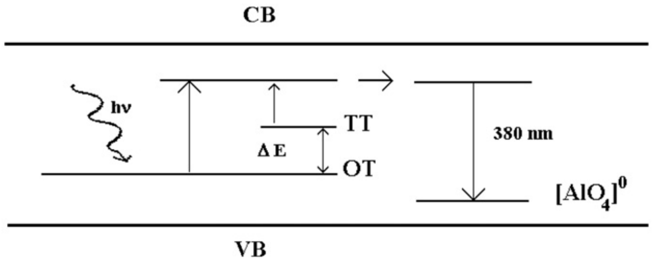

Fig. 4. Schematic diagram of the proposed model. TT Thermal Trap, OT Optical Trap.

4. Conclusion

A phenomenological model is proposed to account for the experimental evidence that relates the OSL and 110 °C TL emissions in quartz. This model relies on the inter-relationship between OSL and TL signals and on the commonality of their characteristic emission at a broad wavelength band centred at ∼380 nm. It has been shown here that this luminescence emission arises from electron recombination at $[AlO_4]^\circ$ hole traps; a direct correspondence between Al concentration and the OSL signal intensity is observed. The exact role of alkali ions in causing luminescence sensitivity changes, and linking of the emission spectral components to different OSL and TL components is yet to be investigated. Further work is also necessary to understand the exact role of the conduction band in the luminescence processes in quartz.

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