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Full Length Article

The composite nature of the thermoluminescence UV emission of quartz

Mauro Fasoli [a,b,*], Marco Martini [a,b]

[a] Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via R. Cozzi 55, I-20125 Milano, Italy
[b] INFN, Sezione di Milano Bicocca, Piazza della Scienza 1, I-20126 Milano, Italy

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ABSTRACT

The radioluminescence (RL) spectra of three types of quartz have been compared to those obtained from wavelength resolved thermally stimulated luminescence (TSL) measurements. A detailed numerical deconvolution into Gaussian components allowed to identify which of the bands are involved in either types of luminescence processes. The blue "A band" at 2.51 eV was confirmed to dominate both RL and TSL spectra in samples exposed to prolonged irradiation. The UV emission of the 110 °C TSL peak was found to be composite. Analogously to what previously reported for RL spectra, an annealing at 500 °C for 10 min induced a strong enhancement of the "C band" at 3.42 eV. This effect was particularly evident in natural and pre-irradiated quartz. A second intense UV component, the "M band" at 3.7 eV, was found to contribute to both TSL and RL spectra of samples annealed at 1000 °C for 10 min. A further broad UV emission seems to be involved only in RL emission but not in the TSL one.

1. Introduction

The luminescence properties of quartz are currently exploited in its use as a natural dosimeter [1]. It is well known that both natural and synthetic irradiated quartz emit light under stimulation, the best known of these phenomena being thermally stimulated luminescence, or thermoluminescence, TSL, and optically stimulated luminescence, OSL.

A great number of papers has been published on the most common uses of quartz in specific dosimetric applications: archaeological dating [2] and sediment studies [3]. Quartz is also fundamental for the possibility of recording unexpected irradiation due to nuclear accident [4] and in building dating [5].

The response of quartz to the exposure to ionizing radiation evidently depends on the presence of electronic traps and of luminescence centers, which in turn are related to the various defects present in the material.

Many defects of quartz are known, either of intrinsic origin or impurity related [1], the most studied being the family of oxygen vacancies and the centers related to the presence of substitutional Aluminum ions. The most often reported defect related to oxygen vacancy is the E'_1 center, while various Al centers are known, because Al ions in quartz involve an extra charge, in order to compensate the difference of valence between Aluminum and Silicon.

These mentioned defects are likely to be related, directly or indirectly, to the luminescence emissions of quartz. However, a sound description of the relationships between defects and luminescence properties is still lacking.

Three main emissions are known to be present in quartz, in the red at around 620 nm, in the blue, around 470 nm, and in the UV at 340–380 nm. These emissions have been detected in many types of luminescence, in TSL, OSL and Radioluminescence, RL. Specifically this latter technique, RL, allowed to find out that the blue and the UV emissions are in fact composite. Two independent contributions have been found in the blue, at 2.51 eV (so called A band, 490 nm) and at 2.79 eV (B band, 440 nm) [6]. Analogously, at least two emissions have been detected in the UV region at 3.42 eV (C band, 360 nm) and at about 3.7 eV (M band, 330 nm) [7]. Despite an unambiguous connection between specific defects and emission bands has not yet been found, the effect of irradiation and/or heating treatments on the intensity of some of these bands was well described in our previous investigations relying on RL technique [6–8]. In particular, three different treatments allowed to selectively enhance different RL bands emissions. In fact, a prolonged irradiation produced an intense A band (at 2.51 eV), whereas an annealing at 500 °C for 10 min induced a strong UV emission at 3.42 eV, the C band. This effect turned out to be particularly pronounced if, before heating, the sample was imparted a few hundred Gy dose. Finally, if quartz is annealed at 1000 °C for

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[*] Corresponding author at: Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via R. Cozzi 55, I-20125 Milano, Italy. Tel.: +39 02 6448 5178; fax: +39 02 6448 5400.
E-mail address: mauro.fasoli@mater.unimib.it (M. Fasoli).

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10 min a further UV emission, the M band (at 3.7 eV) was detected in RL spectra [9].

Similar treatments have been already described in the literature. For example, the procedure inducing the C band (irradiation followed by a heat treatment up to 500 °C) is similar to what is known as "pre-dose effect" in quartz [10], which has already been reported to strongly enhance the UV emission [8]. However, a thermal treatment alone has been demonstrated to enhance the UV emission, in a procedure clearly different from the pre-dose effect [11,12]. By the results presented in this paper we aim at verifying whether the just mentioned RL bands detected in the blue and in the UV regions, induced by these heat treatments, are detected also in the TSL spectra. This is particularly important for the UV region because so far only one band, generally reported at 365–380 nm, has been considered as the TSL emission in the high energy range. The presence of two UV emissions could possibly account for the differences present in the literature in the reported effects after irradiation and heat treatments.

Moreover, as a corollary, this investigation aims at the important result to confirm the RL technique as a reliable tool for the investigation of the recombination centers involved in TSL emissions, as already recently proposed [6,13]. Since the excitation with ionizing radiation is not selective, in general, we could expect to detect more emissions in RL spectra than in TSL ones. In fact, most of the TSL glow peaks in quartz are known to be due to electrons being released from a trap and thus only the emission from recombination centers having trapped a hole can be observed. At variance, in RL any type of luminescence center (including excitons and both hole and electron recombination centers) can be observed. In RL it is then to be considered the possible presence of some emissions not involved in the TSL mechanism. On the other hand, if the RL and TSL spectra turn out to be composed of the same emissions, then RL can be employed (with the advantage of higher signal to noise ratio) for the investigation of TSL luminescence centers.

2. Experimental

Three single crystals of different types of quartz were considered in our investigation: a natural colorless (hyaline), a natural smoky and a synthetic quartz (Sawyer Premium Quality). The crystals were crushed, grinded, and sieved to select grains 100–200 μm in diameter. The powders were divided into three batches and each one underwent different irradiation and/or annealing in order to selectively enhance one of the luminescence bands, as described in detail in the following section. The annealing was performed in air by putting the powders inside a fused quartz crucible into a preheated oven for 10 min. The crucible was then removed from the oven and let cool to room temperature.

The powder was fixed to steel discs (10 mm in diameter) using silicon oil. The radio-luminescence (RL) measurements were carried out at room temperature (RT) using a home-made apparatus featuring, as detection system, a back illuminated UV-enhanced charge coupled device (CCD) (Jobin–Yvon Spectrum One 3000) coupled to a spectrograph operating in the 200–1100 nm range (Jobin–Yvon Triax 180). RL excitation was obtained by X-rays irradiation, through a Be window, using a Philips 2274 X-ray tube, with Tungsten target, operated at 20 kV. During each measurement, lasting 30 s, the sample was given a dose of 10 ± 2 Gy, where the uncertainty is related to the dose calibration rather than to its repeatability that was quite good (1%). Wavelength resolved thermally stimulated measurements (WR-TSL) were carried out using a home-made equipment. The heater section was custom designed and fabricated by Tecna s.r.l. and the heating rate was 1 °C/s. The detection system was a back illuminated UV-enhanced charge coupled device (CCD) (Jobin–Yvon Symphony) coupled to a spectrograph operating in the 200–1100 nm range (Jobin–Yvon μ-HR). The time between the end of the irradiation and the start of the TSL measurements was 300 ± 5 s. We took this precaution to avoid possible spectral differences due to the emptying of traps unstable at RT, specifically the 110 °C peak whose decay time is in the order of hours. All the RL and TSL spectra (with the exception of the contour plots) were corrected for the spectral response of the detection systems and were deconvolved into Gaussian components using the least squares method with the Levenberg–Marquardt algorithm (OriginPro 9.0) and minimizing the χ^2 value. For the numerical fitting process, we relied on the results obtained in our previous investigations where the spectral parameters of each luminescence emission were determined. Specifically, the energy and the full width at half maximum (FWHM) of each component was fixed to the values reported in Table 1 of Ref. [7]. The only free parameter, for each component, was therefore the band intensity. For convenience, Table 1 shows the energy and FWHM of each Gaussian component considered in the numerical fit.

Table 1
Spectral parameters of the emission bands considered during the Gaussian deconvolution of the spectra.

Band	*E* (eV)	$\sim\lambda_{\max}$ (nm)	FWHM (eV)
O	1.92	635	0.39
A	2.51	490	0.46
B	2.79	440	0.46
X	3.06	395	0.89
C	3.42	360	0.58
M	3.73	330	0.45
D	3.93	315	0.49

3. Results

Relying on our previous investigations [9], we have treated quartz samples so to selectively enhance three different RL bands. Specifically, the A band (2.51 eV) by exposing an untreated sample to prolonged X-ray irradiation, the C band (3.42 eV) by heating an irradiated sample up to 500 °C, and the M band (3.7 eV) by annealing quartz at 1000 °C. We have then performed a wavelength resolved TSL measurement, and compared the collected spectra to the RL ones.

3.1. Effect of prolonged X-ray irradiation (A band, 2.51 eV)

The RL intensity of the band centered at 2.51 eV, in the blue region, was found to progressively increase under X-ray irradiation [9]. In order to verify whether the same emission is detected also in TSL spectra, a WR-TSL measurement was carried out on untreated samples after a sequence of 40 RL measurements which accumulated 400 Gy of X-ray dose. Fig. 1a shows the TSL contour plot obtained for the natural colorless sample. Over the entire investigated temperature range, the spectrum of the detected glow peaks is dominated by a blue emission. Two TSL peaks are clearly detected around 80 °C and 210 °C, respectively. The former is the so called 110 °C peak which is shifted to lower temperature because of the lower heating rate. We believe that the peak around 210 °C is the same one already reported by Woda et al. (see Ref. [14] and references therein). The spectra of both TSL peaks were obtained by integrating over the 50–110 °C and 140–240 °C temperature range, respectively and Fig. 1b reports the normalized spectra plotted vs the energy expressed in eV (green and blue lines). Notice that the double band emission observed for the TSL