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Radioluminescence of synthetic and natural quartz

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ABSTRACT

The effect of X-ray irradiation and thermal treatments on the radio-luminescence emission spectrum of both a natural pegmatitic quartz and a synthetic one was investigated. All the emission spectra could be deconvolved into the same set of five Gaussian components. Among the identified RL bands, a blue emission at 2.53 eV (480 nm) is enhanced under X-ray irradiation. A strong correlation with the sensitization of the so called "110 °C" TSL peak (in our measurements seen at lower temperature due to the lower heating rate) was proved, suggesting that the recombination centers associated with the 2.53 eV band are produced under X-ray irradiation and are involved in both RL and TSL luminescence mechanisms. When each irradiation was followed by heating up to 500 °C a strong sensitization of the RL band emitting at 3.44 eV and of the 110 °C TSL peak were observed. A perfect correlation between the RL and TSL emissions suggests that the recombination centers involved in the RL and TSL emissions are the same.

1. Introduction

Both natural and synthetic quartz are known to emit light under different stimulations. In particular, the delayed properties of luminescence emissions have been widely studied, also considering their applications in the field of dosimetry, allowing to date sediments and ancient ceramics as well as to carry out retrospective dosimetry (Preusser et al., 2009). Despite the wide use of quartz in such applications and the even more diffused use as an electronic oscillator, little is known relatively to the defects responsible for the various luminescence emissions. A number of studies reported on the main emission bands, which are known to be in three wavelength regions, namely in the red, at around 640 nm, in the blue around 470 nm and in the UV region, at 360–380 nm. It must be noted that the listed emissions (UV, blue and red) are probably composite, which would explain why each of them is often reported at different wavelengths. They have been detected under different stimulations: in the Optically Stimulated Luminescence (OSL), in Thermoluminescence (TSL), under stimulation by X-ray or other ionizing radiations, radioluminescence (RL) (Krbetschek et al., 1997 and references therein). Well defined relationships between the mentioned luminescence emissions and specific defects in quartz are still lacking, but a number of assignments has been put forth. Two types of defects have to be considered in quartz: the intrinsic centers related to Silicon or Oxygen vacancies and the so called "Al centers" which, despite their impurity nature, are considered as ubiquitous in quartz. A number of correlations between Al centers and luminescence emissions was proposed since 1981 by (Halliburton et al., 1981). Apparently most quartz emissions can be related to Al centers and some models have been recently proposed (Itoh et al., 2002; Martini et al., 2009). A role of Oxygen vacancies, *E*′ centers, has been also proposed, as non-radiative centers competing in the luminescence emission (Poolton et al., 2000; Schilles et al., 2001)

With the aim of contributing to the understanding of the luminescence dynamics in quartz, we have studied the radio-luminescence emissions of natural and synthetic quartzes, finding the same emission bands in the two types of quartz and a very good agreement between RL and TSL emissions. The possibility of understanding the specific role of the various defect centers could come from the comparison of luminescence spectra with measurements obtained using different techniques, like ESR.

2. Materials and methods

The investigation was carried out on two different types of quartz referred to, in the text, as K-2-00 and G0. K-2-00 crystal is

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a pegmatitic quartz from the Black Hills, South Dakota formed in the last pegmatitic stage ($T < 300\,^\circ$C). G0 is a synthetic quartz sample studied in this work, was manufactured by the French GEMMA Quartz & Crystal Company, by hydrothermal growth. The quartz originated from two pure Z-zone Y-bars with a 16×16 mm^2 squared section. Both the natural and synthetic samples were crushed and sieved to select grains of 100–200 μm in diameter.

The radio-luminescence (RL) measurements were carried out at room temperature (RT) using a home-made apparatus featuring, as detection system, a charge coupled device (CCD) (Jobin-Yvon Spectrum One 3000) coupled to a spectrograph operating in the 200–1100 nm range (Jobin-Yvon Triax 180). The data were corrected for the spectral response of the detection system.

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 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%). RL spectra were de-convoluted into Gaussian components using the least squares method with the Levenberg–Marquardt algorithm (Origin 8.0).

TSL measurements after room temperature (RT) X-ray were performed from RT up to 500 °C with a linear heating rate of 1 °C/s using a home-made system. The total emitted light was filtered by a BG12 glass (band pass 340–480 nm ca.) and detected as a function of temperature using an EMI 9635 QB photomultiplier tube operating in photon counting mode.

3. Results

RL measurements were performed on both natural and synthetic quartz: 40 consecutive spectra were collected in order to monitor the stability of the RL emission under prolonged irradiation. A dose of approximately 10 Gy was imparted to the sample during the acquisition of each RL spectrum. In Fig. 1(a and b) some of the RL spectra obtained for the natural and synthetic quartz, respectively, are shown as a function of energy.

The first RL spectrum of K-2-00 quartz shows a broad unstructured emission ranging from 1.5 to 4.5 eV approximately with the maximum close to 4.0 eV. The main effect of the irradiation is the increase of a band in the blue region close to 2.5 eV, at variance, the region around 4 eV is not affected. A minor enhancement of the RL emission in the intermediate region, between 3 and 4 eV, is also observed. The RL spectrum of synthetic quartz is similar to that of the natural one. Again, the maximum of the emission is at 4.0 eV, however the band close to 2.5 eV is already evident in the first measure. Apart from a slight increase of the band close to 2.5 eV, the prolonged irradiation has no effect at all on the RL spectra of G0 quartz.

All the RL spectra were deconvolved into Gaussian components using the Levenberg–Marquardt algorithm. The fit was performed using five bands whose energy E and width (FWHM) values were set to the values reported in Table 1 and allowed to vary of ± 0.01 eV. As an example, Fig. 2(a and b) reports the deconvolution obtained for the last RL spectra of the sequence for the natural and synthetic quartz respectively. The Gaussian fits are in very good agreement with the experimental curves. Only in the energy region ranging from 3.0 to 3.5 eV the fits are not fully satisfactory. This could be a clue of the presence of a sixth band. Preliminary RL measurements at low temperature, indeed, indicate the presence of a band close to 3.2 eV and a more detailed investigation is in progress. However, since no other clear evidence of its existence was found, it was not added to the deconvolution in this study.

The Gaussian deconvolution allowed to identify the band at 2.53 eV (480 nm) as the one being most affected by the irradiation. In fact, during the sequence of 40 measurements, its intensity increases of 2 orders of magnitude. These results confirm those previously obtained on a set of bulk synthetic quartzes (Martini et al., 2012).

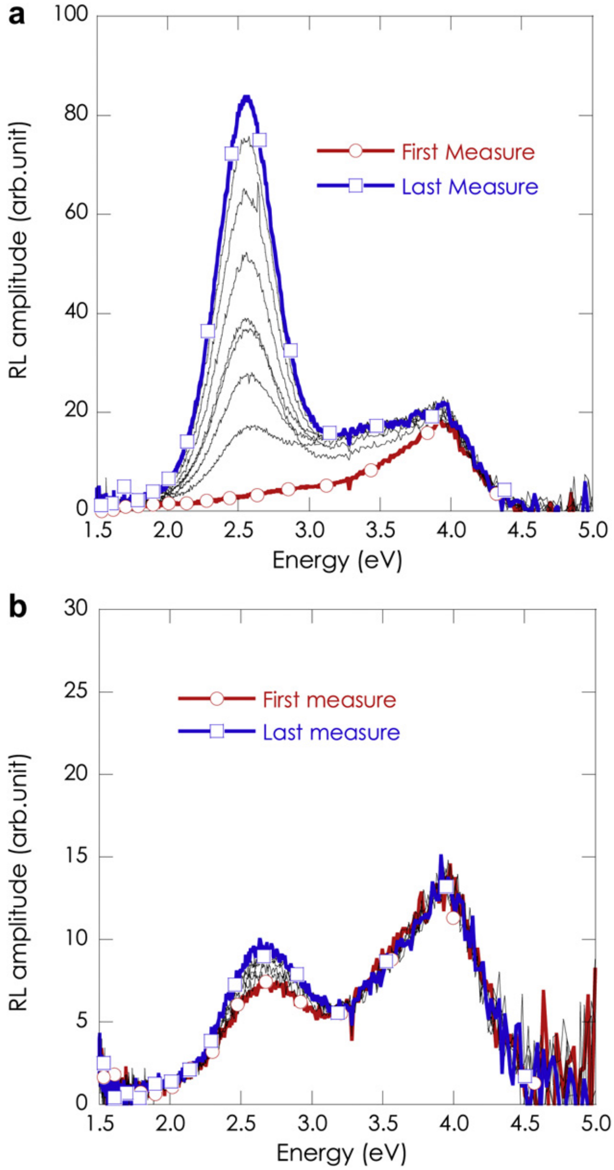

Fig. 1. Sequence of 40 RL emission spectra of K-2-00 (a) and G0 (b) quartz collected under continuous X-ray irradiation. For better readability only some of the spectra are shown.

The 2.53 eV band detected in RL is compatible with the so called blue emission at 470 nm which is known to be related to one of the recombination centers involved in the TSL process. In particular the blue emission can be observed in the recombination of the 110 °C peak (Martini et al., 1995). In order to verify whether the 2.53 eV RL

Table 1
Wavelength, energy and width (full width at half maximum) values of the detected emission bands.

Wavelength (nm)	Energy (eV)	FWHM (eV)
620	1.95	0.48
480	2.53	0.46
440	2.80	0.46
360	3.44	0.58
310	3.94	0.49

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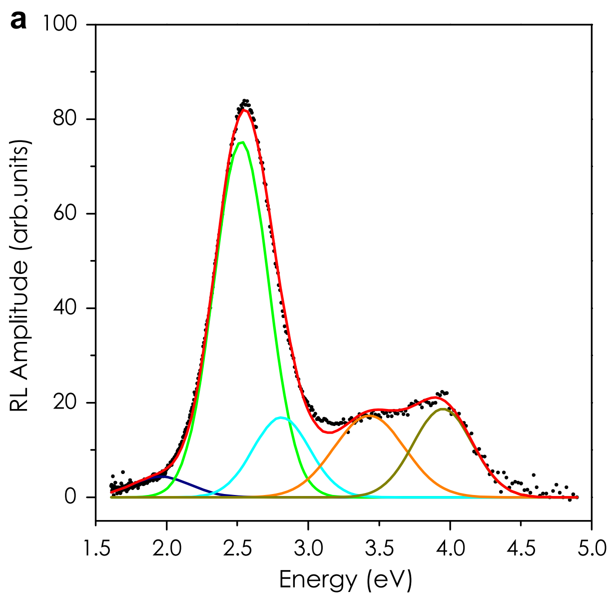

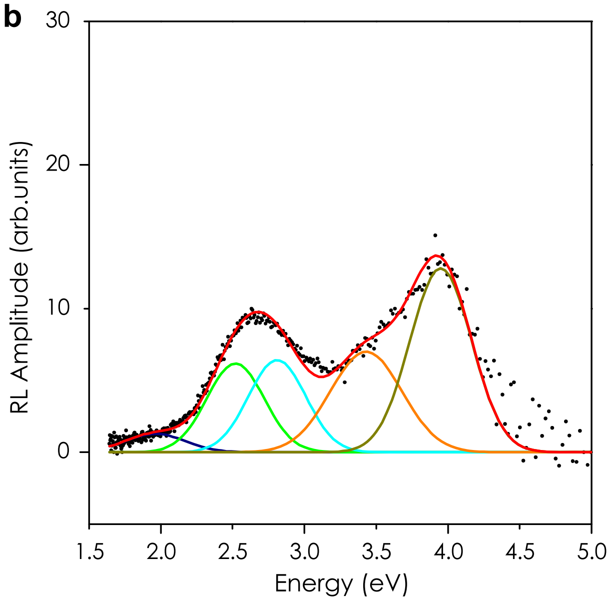

Fig. 2. Deconvolution into Gaussian components of the RL emission spectra for K-2-00 (a) and G0 (b) quartz.

bands is indeed the same blue emission detected in TSL, a specific sequence of measures was carried out allowing to check a possible correlation between the 2.53 eV RL band and the 110 °C TSL peak. The sequence consisted in the following steps:

Step 1: Heating up to 150 °C, to empty the 110 °C TSL peak.
Step 2: RL measurement, imparting 20 Gy which is used as a test dose for the following TSL measurement. The intensity of the 2.53 eV RL emission is evaluated from this spectrum.
Step 3: TSL measurement up to 150 °C, to evaluate the intensity of the 110 °C peak.
Step 4: X-ray dose of 200 Gy, to increase the 2.53 eV RL band intensity.
Step 5: Steps from 1 to 4 were repeated three times.

The results are reported in Fig. 3 were the intensity of the 110 °C TSL peak and of the 2.53 eV RL band are plotted normalized to the final value which is the one less affected by the experimental error. A perfect correlation between TSL and RL data is observed for the natural quartz. The agreement for the synthetic quartz is less evident probably because of the higher experimental error due to the much lower signal intensity.

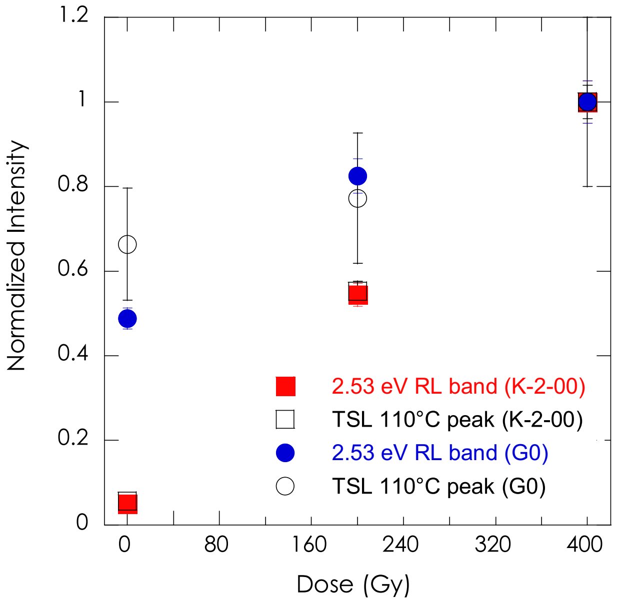

Fig. 3. Dose response curve of the 2.53 eV RL band (filled markers) and of the 110 °C TSL peak (open markers) for K-2-00 (squares) and G0 (circles) quartz. The data were normalized to the final value.

Besides the effect of the irradiation alone, we considered the effect of irradiation followed by heating. In the literature the effect of thermal treatments on the fired quartz is well documented, especially for the 110 °C TSL peak (Zimmerman, 1971). In fact, this peak is known to sensitize after a cycle of irradiation and heating up to 500 °C. The effect of a similar treatment on the RL spectra was investigated on K-2-00 and G0 quartzes with the aim of monitoring the main five bands intensities. The experimental procedure consisted in the following steps:

Step 1: Heating up to 150 °C, to empty the 110 °C TSL peak.
Step 2: RL measurement, imparting 20 Gy which is used as a test dose for the following TSL measurement. The intensity of the 3.44 eV RL emission is evaluated from this spectrum.
Step 3: TSL measurement up to 500 °C, to evaluate the intensity of the 110 °C peak and to thermally activate such a peak.
Step 4: Steps from 2 to 3 were repeated ten times.

Figs. 4 and 5 show the obtained RL spectra and TSL glow curves, respectively. The main effect of the treatment is the enhancement of the 3.44 eV RL band which becomes the dominant emission after the first few cycles. A similar effect is observed for the intensity of the 110 °C TSL peak. It is important to notice that such a peak is detected at 80 °C because of the lower heating rate (1 °C/s instead of 20 °C/s).

The 110 °C TSL peak sensitization from the first to the last measurements is approximately 3 orders of magnitude, confirming results described in the literature. Moreover, other TSL peaks are also detected at higher temperature of the glow curves, specifically, a shoulder in the 100–200 °C range and a broad composite structure from 200 to 400 °C. The intensity of all these peaks is also affected by the treatment although, in this case, the enhancement turned out to be only a factor 10–20 during the treatment. This

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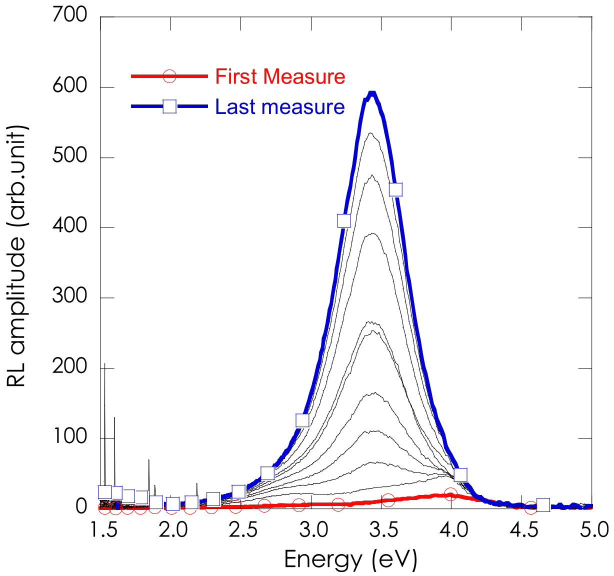

Fig. 4. Sequence of RL emission spectra of natural quartz K-2-00 obtained during X-ray irradiation (each imparting a dose of 20 Gy) followed by a heating up to 500 °C (see text).

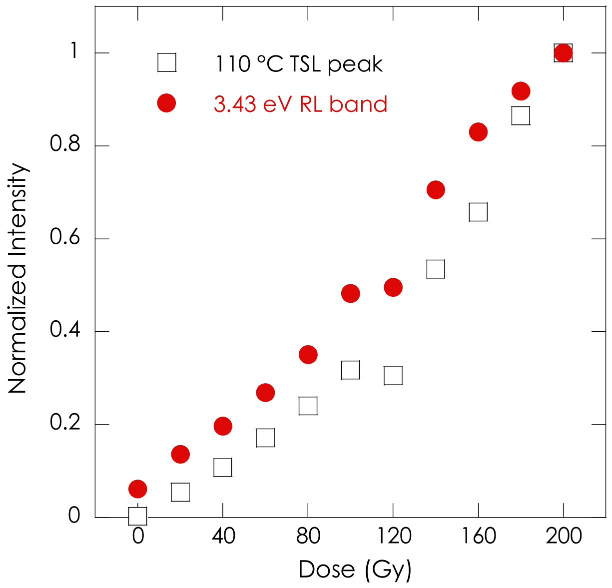

Fig. 6. Dose response curve of the 3.43 eV RL emission band and of the 110 °C TSL peak for K-2-00 quartz. The data are plotted normalized to the final value.

sensitization of the higher temperature peaks was already observed for doses in the range of hundreds kGy by Guzzo et al. (2009) but it still requires a more detailed investigation.

The sensitivity of the 110 °C TSL peak was evaluated by integrating the glow curves in the 25–120 °C temperature range while the intensity of the 3.44 eV RL emission was obtained from a Gaussian deconvolution of the spectra. A strong correlation between these emissions is evidenced in Fig. 6 where their intensity is plot as a function of the accumulated dose after normalization to the value of the final measure.

Finally the same sample used in the previous treatment was exposed to a prolonged X-ray irradiation: a sequence of RL measurements identical to the one used for Fig. 1 was performed. The RL spectra collected are reported in Fig. 7. X-ray irradiation promotes the enhancement of the blue emission at 2.54 eV; at variance, the UV emission at 3.44 eV decreases until it a reaches a minimum value at which it becomes stable. The measurements carried out on the synthetic quartz G0 showed the same dynamics of the RL bands and 110 °C TSL peak intensities observed in the natural sample.

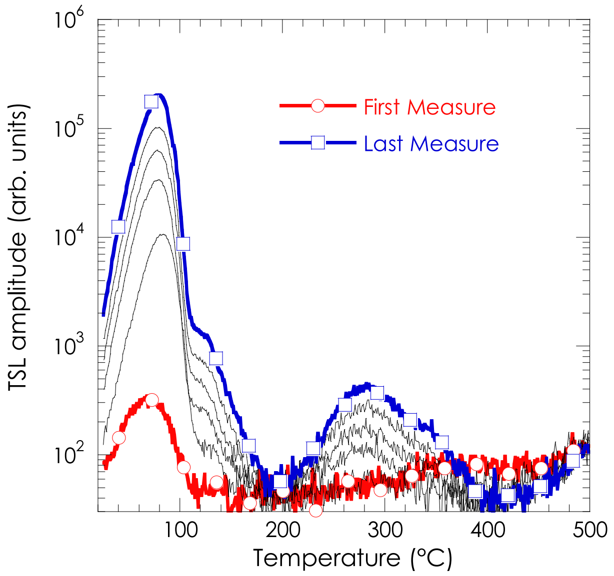

Fig. 5. Sequence of TSL glow curves of natural quartz K-2-00 obtained after X-ray irradiation (each imparting a dose of 20 Gy) (see text).

4. Discussion

The results of measurements of RL emissions evidence a number of very interesting features that shed some lights on the already known properties of luminescence emissions in quartz. The first important result is relative to the great similarities between RL spectra of synthetic and natural quartz. Even if at first sight the RL spectra of Fig. 1(a and b) appear rather different, it is evident that

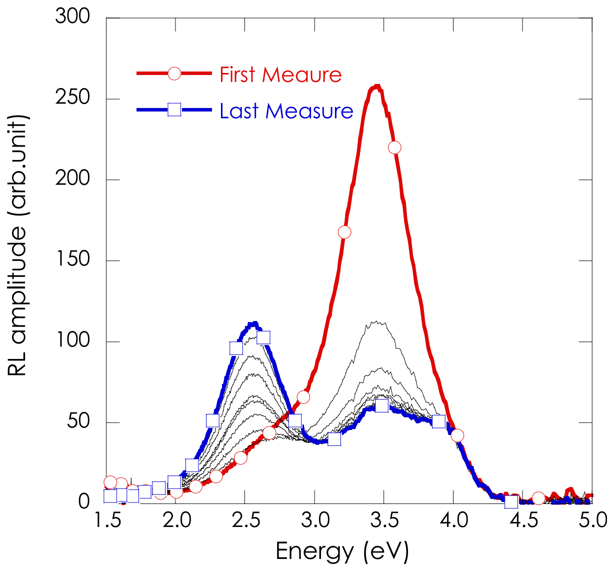

Fig. 7. Sequence of 40 RL emission spectra of K-2-00 quartz collected under continuous X-ray irradiation. This sample was previously treated with a series of irradiation followed by heat treatment up to 500 °C (see Figs. 5 and 6). For better readability only some of the spectra are shown.

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they can be deconvolved into the same components (see Figs. 4 and 5) that were evidenced in a recent paper of ours (Martini et al., 2012) relative to the RL of synthetic quartz. Looking at Fig. 1(a and b), however, a different behavior appears when the effect of irradiation is taken into account: the increase of the intensity of the band at 2.53 eV is much higher in the natural quartz with respect to the synthetic one. The relative increase of the 2.53 eV band observed in Fig. 1b is apparently lower than that shown in Fig. 3 obtained from the numerical deconvolution. This is due to the composite nature of the blue emission which is composed by a second band at 2.81 eV. In an analogous experiment carried out, in a previous study, on the same synthetic quartz, no change in the RL spectrum was detected after irradiation (Martini et al., 2012). However, it should be pointed out that the measurements were performed on a bulk sample, at variance, in this work the same material was in powder form.

An important result of the present work is the strong increase of the 3.44 eV band after a series of irradiations followed by heat treatment up to 500 °C. It is very interesting to notice that this increase is in very good agreement with the growth of intensity of the so called “110 °C” TSL peak (see Fig. 6). The dynamics of the 110 °C TSL peak and of the 3.44 eV RL band observed in this study is similar to what is already known in the “pre-dose” effect in quartz, i.e. the strong increase of sensitivity of the 110 °C TSL peak following irradiation and heating (Zimmerman, 1971). Although the doses involved in the pre-dose in dosimetric applications are much lower than the ones we used in the present work, it is interesting to notice that our RL emission band peaking at 3.44 eV (360 nm) is consistent with the 380 nm TSL emission already reported in the literature (Martini et al., 1995). The discrepancy between the two emissions can be ascribed either to the spectral correction (critical in the UV region) or to the possible composite nature of the band. A strong correlation between the RL 3.44 eV band and the 110 °C TSL peak was evidenced (see Fig. 6). This result shows that some of the recombination centers involved in the RL and TSL emissions are the same.

The effect of irradiation on quartz samples previously submitted to a sequence of irradiation-heating partly confirms the growth of the 2.53 eV band, but evidences also a decrease of the 3.44 eV band. At this stage, it is rather difficult to propose assignments to the detected emission bands, but a few features are rather clear: the growth of the 2.53 eV band under irradiation is independent from the presence of other emission bands, even if its growth is enhanced when the 3.44 eV band has been previously produced by an irradiation-heating sequence. Our results are in agreement with proposed assignment of the 3.44 eV band to the Al-hole center $[AlO_4]^0$, (Martini et al. 1995), but only measurements carried on using different techniques like ESR could possibly confirm this assignment.

5. Conclusions

Looking at the radio-luminescence (RL) emissions at RT of a natural and a synthetic quartzes of different origin, the spectra could be de-convoluted into the same emission bands. Among the identified RL bands, a blue emission at 2.53 eV (480 nm) is enhanced under X-ray irradiation. A strong correlation with the sensitization of the so called “110 °C” TSL peak (in our measurements seen at lower temperature due to the lower heating rate) was proved, suggesting that the recombination centers associated with the 2.53 eV band are produced under X-ray irradiation and are involved in both RL and TSL luminescence mechanisms.

As expected, an irradiation followed by a heating up to 500 °C, causes a strong sensitization of the 110 °C TSL peak whose sensitivity was found to be correlated to the RL band emitting at 3.44 eV (360 nm). We can conclude that electrons coming from the 110 °C peak can recombine both on 480 and on 360 nm recombination centers when they are available.

Acknowledgments

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