

Characterization through cathodoluminescence and thermoluminescence of α -SiO₂ single crystals before and after γ -radiation treatments : contribution to the evaluation of the influence of defects on the frequency-shifts

P. Guibert*, R. Chapoulie*, S. Dubernet*, A. Largeteau**, G. Demazeau**

*-IRAMat. UMR 5060 CNRS –Université Michel de Montaigne - BORDEAUX 3
CRP2A, Maison de l'Archéologie, Esplanade des Antilles 33607 PESSAC Cedex (France)
Email : guibert@u-bordeaux3.fr

** - ICMCB, CNRS, Université Bordeaux 1, site de l'ENSCP, 87, avenue du Dr. A. Schweitzer, 33608 Pessac cedex (France)
Email : largeteau@icmcb-bordeaux.crs.fr

Abstract— The fiability and performances of quartz resonators are –in particular-dependent on point defects including chemical impurities either in substitution for the Si sites or in interstitial positions in the α -SiO₂ lattice.

Such a research work is devoted to cathodoluminescence (CL) and thermoluminescence (TL) studies, before and after γ -radiation treatments, on different single crystals of α -SiO₂ [one being natural and four from hydrothermal processes].

Cathodoluminescence and thermoluminescence were selected as characterization techniques due to their complementarities concerning in particular their abilities to the detection of point defects (mainly impurities and ion vacancies) by their luminescence emission.

I. INTRODUCTION

The objective of this study is to understand the role of impurities and associated defects in quartz single crystal before and after γ -radiation treatments in correlation with the frequency-shifts observed in the space inside the satellite.

This study concerns the detection and the characterization of defects in quartz material by using three techniques which are Cathodoluminescence, Thermoluminescence and Raman. We have investigated five different kinds of quartz material: 4 being prepared through a hydrothermal crystal growth process (S2, S3, S4, S5) and one from natural origin (S1). All samples analyzed are high quality optical polished discs (9 mm in diameter, 0.45 mm thick)

The measurements are made before irradiation and after irradiation. Three irradiations doses are applied: 100krad, 1Mrad and 10Mrad.

II. CATHODOLUMINESCENCE

A. Measurement

The equipment is composed of a SEM linked to a cathodoluminescence spectrometer detector that analyses the luminescence signals while the electron beam interacts with the sample.



Figure 1: Cathodoluminescence equipment

B. Results and discussion

Figure 2 shows the CL spectrum before γ -radiation. This curve shows three principal domains dependent on the defects existing in the samples:

- The peak 1 (390-395nm) is generally attributed to the defect Aluminium center associated to a

monovalent charge compensator ion $[AlO_4/M^{+}]^0$ with $M^{+}=Li^{+}, Na^{+}$ or H^{+} [1, 2, 3, 4]

- The peak 2 (450-460nm) is associated to the radiative recombination of STE (*self-trapped exciton*), ($e^{-} - h^{+}$) created by the radiation [3, 5] and associated to a E' center (oxygen vacancy having trapped an electron) and/or to a peroxide radical or to a NBOHC (*Non Bridging Oxygen Hole Center*).
- The peak 3 (630nm) is associated to a NBOHC centre initiated by the defect $\equiv Si-OH$ [6]

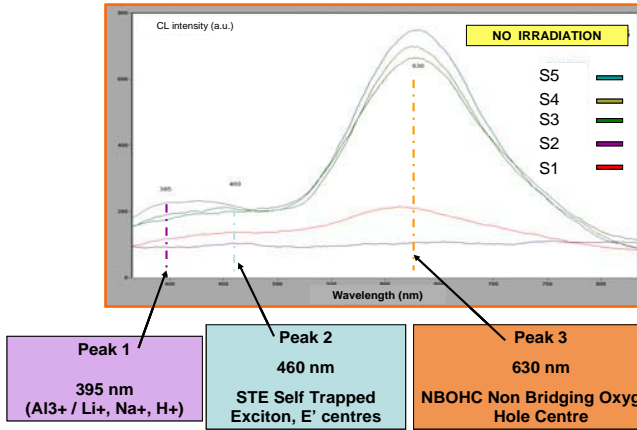


Figure 2: CL spectra before γ -irradiation

Figures 3 to 5 show spectra of quartz samples after γ -radiation. The same cathodoluminescence emitters as in non irradiated samples can be observed.

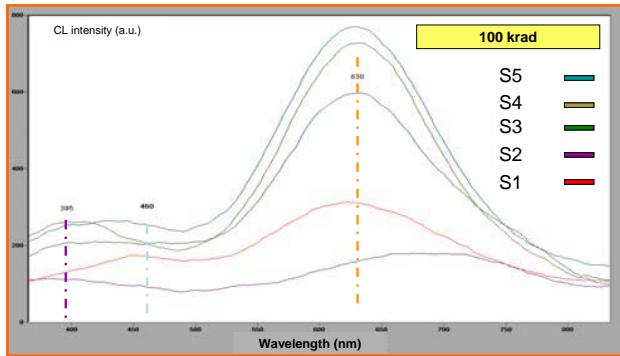


Figure 3: CL spectra after γ -irradiation (100krad)

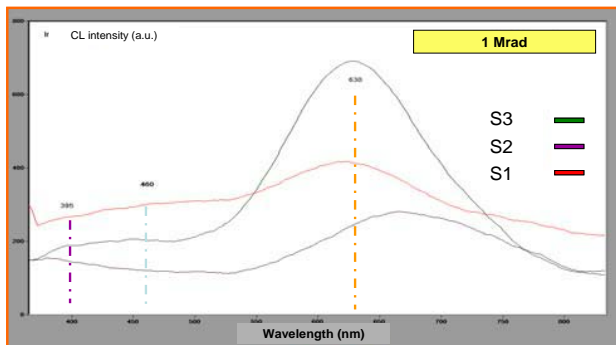


Figure 4: CL spectra after γ -irradiation (1Mrad)

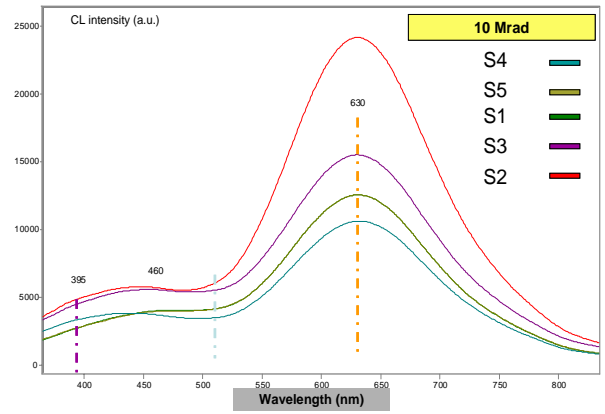


Figure 5: CL spectra after γ -irradiation (10Mrad)

III. THERMOLUMINESCENCE

A. Measurement

The equipment is composed by a laboratory built automatic TL recorder including: (A) heating finger, (B) Photo multiplier EMI 9813QKA, (C) ^{90}Sr - ^{90}Y beta source, (D) 24 position sample holder.

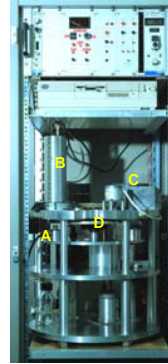


Figure 6: Thermoluminescence equipment built in the IRAMAT-CRP2A.

All TL experiments were performed using the following parameters: spectral window from 350 to 450 nm by UV blue Schott BG12 optical filters, heating from room temperature to 500°C at a rate of 2°C/s in nitrogen atmosphere.

B. Results and discussion

The figure 7 gives the TL curves of quartz discs recorded immediately after heating and β -irradiation by a low dose (10Gy, i.e. 1krad), due to the TL characterization.

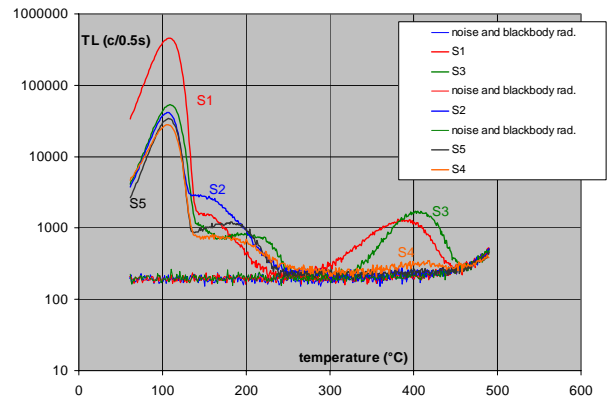


Figure 7: TL-response to a low dose β -irradiation (10Gy) of non pre-irradiated quartz

All curves exhibit low temperature (short life time at RT) signals. The 110°C TL peak is generally related to the recombination of a trapped electron with a trapped hole by an Al centre [7]. Note the order of magnitude in intensity between natural (S1) quartz and synthetic ones, all latter being ten times less sensitive than the former, meaning a low level of Al impurities in synthetic quartz.

According to the standard models of TL [8], high temperature components are the result of thermal recombination processes of charges from deep (high activation energy) traps. Besides our principle concern in this study, those traps are so stable that they are used in thermoluminescence dating of natural quartz crystals that were heated millennia ago. They are detected in S1, S3 and S4 quartz only. These high temperature signals could be correlated to the cumulative shifts of frequency of oscillators. Note that the absence of UV-blue TL in some samples does not mean that those quartz do not reveal any deep trap, they are only not observable by the technique used.

Figure 8 gives the TL curves of highly γ -irradiated quartz samples that have been given a 1kGy (100krad) gamma dose some weeks before heating.

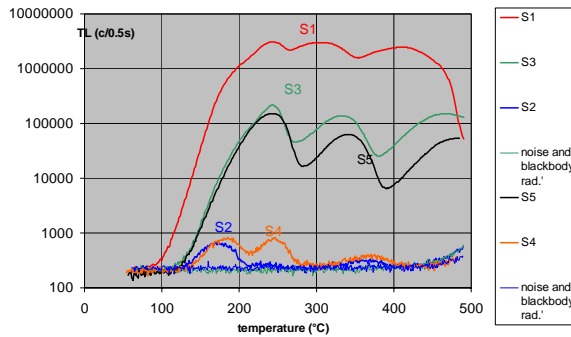


Figure 8: Response to a high dose from γ -irradiation (1kGy)

In all samples, short life time signals are erased. Mid and long term stable signals only remain. Note the orders of magnitude in intensity between natural (S1) quartz and synthetic ones for the high temperature components. Especially, S2 and S4 exhibit a very low TL intensity, the behaviour of which is still to be interpreted. The same TL patterns were encountered with the higher dosed samples (10 and 100kGy) the curves of which are not displayed here.

IV. RAMAN

A. Measurement - Results and discussion

The HeNe laser on the Renishaw 2000 system employed produces an emission light at 15803cm^{-1} (633 nm) for a power 1.3 mW on sample, with a beam diameter of ca. 1-2 μm .

The analyses are made at ambient temperature in the range $100\text{--}4000\text{ cm}^{-1}$. This spectral region is divided into two parts: Range A ($100\text{--}1200\text{cm}^{-1}$) to determine the main vibrations of quartz and Range B ($1000\text{--}4000\text{cm}^{-1}$) to show vibrations of OH groups.

All samples are oriented during the measurement in order to compare the spectra according to the crystallographic structure.

The measurements do not show significant differences between quartz samples S1, S2, S3, S4 and S5, and whatever the irradiation state.

The crystallographic structure of quartz due to the strong Si-O bonds is not modified by the γ -radiation and it appears no modifications of OH groups before and after radiation.

V. CONCLUSION

A. Cathodoluminescence

Using CL two different important emissions can be observed: a weak broad emission between 330 and 500 nm (peaking at 395 and 460 nm) so-called blue domain, and a large important one in the domain 500 to 800 nm (peaking at 630 nm) called red domain. Roughly, two different behaviours have been detected for the $\alpha\text{-SiO}_2$ single crystals before γ -radiation treatment: single crystals (S1 and S2) characterized by a weak luminescence in the red domain and the other single crystals with a strong luminescence still in the red domain with a comparable intensity. After radiation treatment (100krad and 1Mrad), the weak and broad blue band is not modified, but concerning the large red band, the intensity of luminescence seems not so modified for the single crystals (S2, S3, S4, S5) but, progressively with the increase of the γ -radiation dose, the intensity of the cathodoluminescence characterizing S1 and S2 is improved.

B. Thermoluminescence

The TL behaviour of the five $\alpha\text{-SiO}_2$ single crystals was investigated. The experimental used conditions allowed us to detect luminescence within the 350-450 nm spectral window, while heating from room temperature to 500°C at a rate of 2°C/s. TL is able to detect radiative recombination of charges that were previously trapped by irradiation into centres formed by point defects and their close environment. Immediately after a low dose irradiation (1krad) given to non irradiated samples, three different domains of luminescence can be observed: (1) at 110°C common for all single crystals, (2) 180-220°C and (3) 380-420°C the peak temperature and intensity of which depend on the type of crystals. After high gamma dose treatments (100krad and more) and a several week delay at room temperature, the remaining mid and long term trapped charges give recombination signals that are localized in the same temperature regions, (2) and (3) as low dosed samples but intensities varie according to the origin of the $\alpha\text{-SiO}_2$ single crystals and their crystal growth process.

C. Raman

The Raman spectra does not show any modifications between the different single crystals before and after γ -radiation treatments.

ACKNOWLEDGMENT

CNES (French space agency) started at the end of 2004 a R&D study taking into account quartz material and oscillator. French experts in quartz material (GEMMA, ICMCB, IRAMAT-CRP2A, LCEP, LPMC), in quartz resonator (RAKON, LCEP), in quartz oscillator (RAKON, LCEP, LPMO) and in radiation (CPO, LSI, ONERA) have been gathered to determine and understand the mechanisms responsible for the radiation sensitivity of material, resonator and oscillator, and to correlate them in order to reduce their susceptibilities.

REFERENCES

- [1] Alonso P.J., Halliburton L.E., Kohnke E.E. & Bossoli R.B. (1983) – X-ray induced luminescence in crystalline SiO₂. *Journal of Applied Physics*, **54**, 5369-5375.
- [2] Luff B.J. & Townsend P.D. (1990) – Cathodoluminescence of synthetic quartz. *Journal of Physics: Condensed Matter*, **2**, 8089-8097.
- [3] Stevens Kalceff M.A. & Phillips M.R. (1995) – Cathodoluminescence microcharacterization of the defect structure of quartz. *Physical Review B*, **52**, 3122-3134.
- [4] Gorton N.T., Walker G. & Burley S.D. (1996) – Experimental analysis of the composite blue cathodoluminescence emission in quartz. *Journal of Luminescence*, **72-74**, 669-671.
- [5] Hayes W. (1990) – The structure of the self-trapped excitons in quartz. *Review of Solid State Sciences*, **4**, 543-546.
- [6] Stevens Kalceff M.A., Phillips M.R., Moon A.R. & Kalceff W. (2000) – Cathodoluminescence Microcharacterization of Silicon Dioxide Polymorphs. In: Pagel M., Barbin V., Blanc P. & Ohnenstetter D. (eds) *Cathodoluminescence in Geosciences*. Springer, Berlin Heidelberg New York Tokyo, Chap. 8, 193-224.
- [7] Tajika Y., Hashimoto T., (2006) - Correlation of blue-thermoluminescence (BTL) properties with some impurities in synthetic quartz, *Radiation Measurements*, **41**, 809-812.
- [8] McKeever S. W. S., Chen R., (1997) - Luminescence models, *Radiation Measurements*, **27**, 5/6, 625-661.