

# Acoustic losses in quartz and their links with InfraRed measurements

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**Abstract**— The performances of quartz resonators and sensors are often limited by various defects existing in the crystal, whatever the origin of the quartz is (natural or cultured). So, before manufacturing high-quality quartz devices, it is essential to perform a systematic study of the as-grown material which will allow a prediction of the behaviour of the device. Among point defects, the most common is the OH related growth defect. It is Infrared active and it can be modified by treatments such as thermal annealing, sweeping or irradiation.

Kats carried out a classical study of hydrogen in both natural and synthetic quartz [1]. Particularly, he pointed out 4 stretching-mode infrared bands “growth-defects” including hydrogen, increasing with crystal growth-rate and decreasing when the sample is irradiated. After Kats, several authors (Lias, Chakraborty, Paterson, Bahadur...) worked on different methods to determine the OH content.

Finally, numerous researchers (Fraser and Dodd in 1966, Rudd and Houghthon in 1966, Sawyer in 1972 and 1983, Toyo in 1976...) have shown that the electrical quality factor “Q” is closely dependant on the hydrogen content in quartz. As this Q-factor does not depend only on the material quality, it has been necessary to define the resonator as nearly as possible to an ideal device, ideally designed and manufactured.

To avoid these difficulties also linked to the measurement principle of the spectrometer (“double beam” or “with Fourier transform”), we present here new measurements on SC-cut resonators working on their 10 MHz 3rd overtone. They are built in GEMMA quartz samples following a very precise manufacturing process. Furthermore, they have been extracted from various generations of cultured quartz and have also been submitted to different treatments.

## I. INTRODUCTION

Since more than 50 years, the production of synthetic quartz significantly increased, to become still today the second

material the most used after Silicon, in all electronic applications.

The first commercial process for quartz growth was developed in 1956, based on the hydrothermal growth principle. The crystal growth quality depends on several parameters such as:

- solvent and nutrient (i.e. lascas),
- mineralizer and seeds,
- temperature, temperature gradient and pressure.

We have here to notice the main role played by the temperature gradient which is responsible for the transport of the matter from the lascas to the seeds (upwards in the autoclave). Here, matter means atoms constituting the matrix of quartz, but also chemical impurities coming from the lascas and the solvent, including the strongest “poison”: Hydrogen.

Following the growth rate, and so the temperature gradient, the level of impurities can be largely lower than in the lascas. So, the control of the growth conditions can allow to get pure quartz stones (decreasing the growth rate and so the  $\Delta T$  to reach thermodynamic equilibrium). Nevertheless, for state-of-the-art applications, it is necessary to check in details the quartz crystal quality.

If 3500 tons of synthetic quartz are produced in the world each year [2], just a few of them are used for precise time and frequency applications. Evaluated at 3 to 5 hundreds tons produced by a few suppliers in the USA, Europe (Russia included) or Japan, this quartz is characterized by a quasi perfect crystalline arrangement (with a very low level of dislocations) and a level of impurities even lower (largely lower than 1 ppm weight for the best ones). Among this handle of suppliers, GEMMA produces 2.5 tons of quartz every year.

This quality of quartz is now the most adapted for the most critical and demanding applications in terms of frequency generation (synchronisation of communication networks, space applications, very precise localisation, measuring

equipments, generation of the short term stability for atomic clocks...).

Even if numerous efforts have been achieved to obtain pure quartz crystal, these materials have to be refined of their alkali defects by sweeping. Furthermore, studies have been realized in laboratories (especially by HIRST in England, the ICMCB in France in collaboration with GEMMA, RADEC...) to improve the quality either by selecting pure lascas (made of ultra pure silica or of part of Z-zones of synthetic quartz blocks) or by modifying growth conditions (use of higher pressures) allowing not only to limit insertion of impurities but also to limit the alkali concentration due to the increase of the nutrient's solubility with pressure.

So, to qualify finely this kind of crystals, we have to define new techniques or to modify (and so optimize) the process of the old ones.

## II. MEASUREMENTS TECHNIQUES

To evaluate the quality of some crystals grown by GEMMA, we have worked on samples issued from blocks belonging to different growth generations. We will call Ci and Cis (with i being equal to 2, 3 or 4), the bars belonging to the ith generation (the letter "s" joint to Ci means that the bar has been swept):

- the C2 bar is issued from a block whose seed was cut in a big stone which was grown starting using natural seed,
- the C3 bar was cut in a block belonging to the following generation,
- at least, C4 comes immediately after.

Usually, to compare the quality of these crystals, we use different techniques and particularly the **IR spectrometry method** which is an important tool for the investigation of the OH-related defects. Usually, the IR spectrum of quartz shows a broad absorption band in the region of 3  $\mu\text{m}$ . This large band is superimposed with several sharp bands. If the nature and the structure of the defects correlated with this absorption band is not yet well understood, the authors agree to say that the responsible defects are OH related.

From the IR spectrum drawn at ambient temperature, we can give an **extinction coefficient**  $\alpha_{3500}$  (expressed in  $\text{cm}^{-1}$ ) which has been established for commercial purpose and is representative of the hydrogen content. It could be determined using data which give an  $\alpha_{3500}$  equal to 1  $\text{cm}^{-1}$  for 4800 ppm relative to silicon content [3] (it means 240  $\mu\text{g/g}$ , the ratio between ppmw and ppma being equal to 20).

Another important tool to define the quality of the quartz crystal is the impurities content measurement. Usually, the used method is the **Inductively Coupled Plasma - Mass Spectrometry** which requires complicated dissolution methods with solvents containing traces of impurities polluting the solution and often requiring a distillation. So the presented results are obtained by another technique: the GDMS.

**High Resolution Glow Discharge Mass Spectrometry (GDMS)** is an extremely powerful technique for the analysis of all trace and ultra-trace elemental constituents of inorganic materials. Samples are analyzed in solid form and so do not require the laborious and complicated dissolution methods inherent to techniques such as ICP-MS. In addition, GDMS does not suffer from the extreme matrix dependence of most other elemental analysis techniques, minimizing the need for matrix matching standards.

The principle of this technique involves the atomization of a solid sample by sputtering in a low-pressure DC plasma. The sputtered atoms are then ionized in the plasma and extracted into the mass analyzer for separation and detection. We have worked with SHIVA-Tech, from EGA group, to develop this technique. Our first results are presented below.

At least and as usually, the **X-rays topographies** allow us to count the dislocations which can facilitate the transport of impurities and are responsible for the creation of etch channels when they are numerous.

## III. RESULTS

### A. Infrared spectrometry:

Here below (Fig. 1), we indicate 2 ways for the presentation of the IR spectra:

1. transmission level vs wavelength  $\nu$  ( $\% - \text{cm}^{-1}$ )
2.  $\alpha_n = (1/d) \times \text{Log}_{10}(T_{3800} / T_n)$  where d is a thickness expressed in cm.

These spectra have been obtained at the  $\text{N}_2$  liquid temperature on Y-cut samples whose the thickness is of about 5 mm. On the right curves, we can read an  $\alpha$ -value at 3500  $\text{cm}^{-1}$  which is much more higher than expected for a quartz of such a quality. It is only due to the fact that the measurements quantifying the quality of the quartz crystal have to be made at ambient temperature. Indeed, the measurement conditions are not the same following temperature (due particularly to the presence of a low temperature cell).

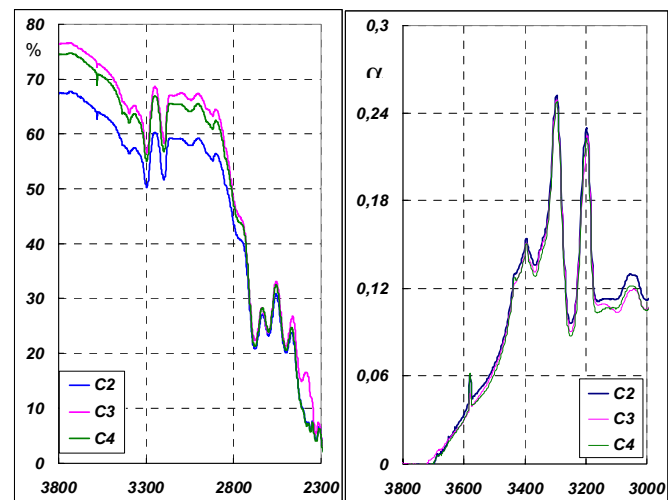
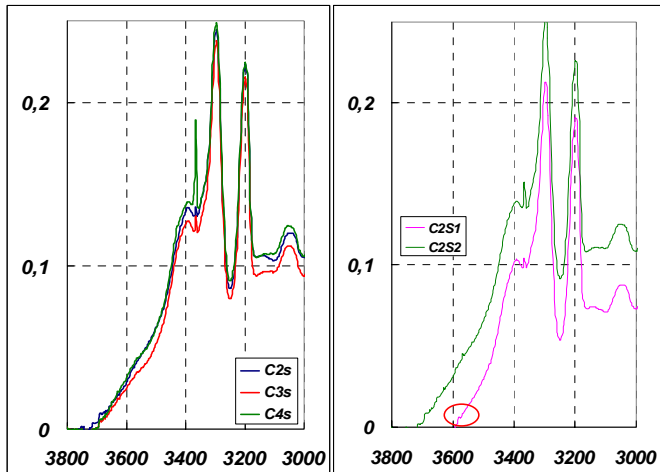


Figure 1. IR spectra of C2, C3 and C4 samples obtained in transmission at  $\text{N}_2$  liquid temperature.

On the following Fig. 2, the presented curves are the results of the Infrared spectroscopy of other thick samples issued from the swept bars called C2s, C3s et C4s. All the “s” bands (s1 to s4) have disappeared and the height of “e<sub>2</sub>” band increases with the number of generation.

*The result of a sweeping process (see Fig. 2b) performed at high temperature (about 500°C) and under high DC field of a few hundreds of V/cm is that alkali ions are replaced by holes or protons depending on sweeping environment (air or vacuum):*

- Sweeping quartz in air dissociates Al-alkali and forms Al-OH-
- Sweeping quartz under vacuum produces Al-hole, in addition to the Al-OH-



Figures 2a and 2b: the same IR spectra for swept samples (to the left) and samples from C2 swept under vacuum (S1) and “in air” (S2).

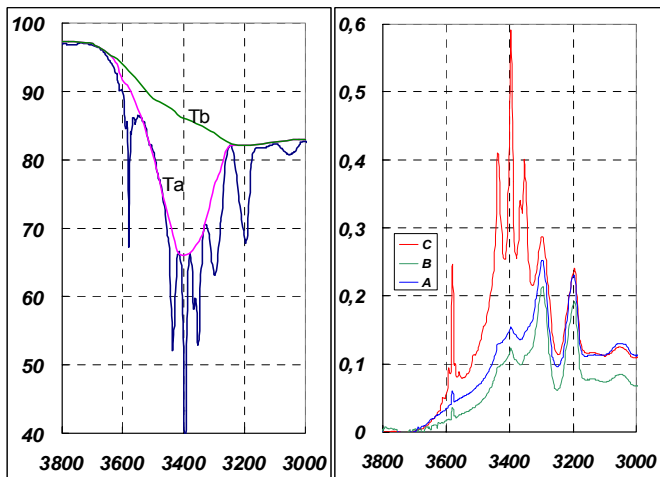


Figure 3: IR spectrum of a “bad” quality quartz and definition of the broad band surface in between Ta and Tb

The previous figure (Fig. 3) is an example of “bad” quality quartz for which the  $\alpha$ -value, measured at 3500 cm<sup>-1</sup>, is equal to 0.164 cm<sup>-1</sup>. This value, translated in hydrogen content, gives 40 µg/g of H (i.e. 40 ppmw).

A SIMS analysis, realized by Cascade belonging to the EAG group, gives, at 1 µm of the surface, a value of 0.75 µg/g of Hydrogen or 15 ppma H.

And finally, the Paterson formula [4] using the evaluation of the surface of the broad band delimited by Ta and Tb gives also a few tens of µg/g.

Just with this example, we see that the measurement of the Hydrogen content in a quartz sample is not yet well defined. As studied in [5], few practical methods based on the study of the IR spectrum exist to determine the hydrogen and hydroxyl content in quartz crystals, but the obtained results are not really in agreement. So, we will continue to exploit the SIMS analysis...

The  $\alpha$ -values measured on samples issued from the 3 generations of quartz, swept or not are presented on the following table (Table 1). As recommended in the standards, the measurements have been performed at ambient temperature.

Table 1.  $\alpha$ -values of our samples, swept or not.

in 10 <sup>-2</sup> cm <sup>-1</sup>	C2	C3	C4	C2s	C3s	C4s
$\alpha_{3500}$	1.95	2.25	2.20	1.87	1.95	1.70

### B. X-rays topographies:

These X-rays topographies (Fig.4), realized on AT-cut samples of about 1 mm thick, show that the level of dislocations is low and increases from C2 to C4.It doubles from C2 / C3 (# 30 / cm<sup>2</sup>) to C4.

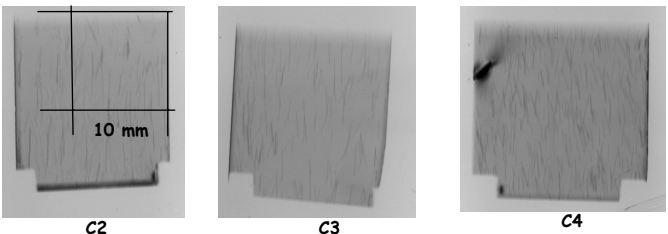


Figure 4. X-rays topographies on AT-cut samples from C2, C3 and C4, measured on the (2-1.0) reticular plane.

### C. Chemical impurities content:

The following table (Table 2) shows that the level of impurities is less than 1 ppm weight and does not increase with the growth generation number. It seems to depend only on impurities of the lascas. These measurements have been realized by GDMS after comparison with results obtained by ICP-AES spectrometry. In the case of very low impurities content, the comparison between different techniques is not easy because we cannot work on the same sample, some of the techniques being destructive.

#### IV. CONCLUSION

It remains many things to do:

- on one hand, it is necessary to continue to work on the various analyses ( $\alpha$ -value measurement, confirmation of the GDMS results by new ICP-MS analyses or by Second Ion Mass Spectrometry...),

- on the other hand, we have to define more precisely the design of the SC-cut resonators to reach the maximum value (or suppose value such) which is close to 1.4 million for the C-mode, 3rd overtone working at 10 MHz. After that, it will be necessary to establish a study program based on a numerous number of resonators in each series.

#### D. Motional parameters of resonators measurements:

The first results presented below do not allow us to have an idea of the influence of the growth generation on the quality factor of the resonant frequency of the C-mode 3rd overtone of a SC-cut resonator. Each resonator is working at 10 MHz, and 3 resonators at least have been prepared from each bar.

	Rm ( $\Omega$ )	Q (* $10^6$ )
from C2	78.5	1.28
from C3	80	1.25
from C4	76	1.30

Nevertheless, we are in agreement with the formula of Brice, reported by Sawyer in [6], which links the Q-factor of a resonator working at 5 MHz (as indicated in the standards) to the  $\alpha_{3410}$  value. Indeed, for the 3 samples C2, C3 and C4 the  $\alpha$ -value measured at  $3410 \text{ cm}^{-1}$  is  $0.07 \text{ cm}^{-1} \pm 0.001$  and the expected value of Q is:

$$2.41 \pm 0.03 \times 10^6$$

which, if we admit that it is possible to maintain the Q.f product from 5 to 10 MHz, becomes 1.2 million at 10MHz.

So, if we see here a good agreement with "old" expressions valuable for electronic grade quartz, it seems nevertheless necessary to define a new calibration formula, linking H content and Q-factor of a SC-cut resonator working at 10MHz.

It is at this price that we will be able to manufacture a quartz material even purer than that we have...

#### ACKNOWLEDGMENT

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