Crystal Quality of LGT samples: Influence on BAW resonators

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Abstract— **Materials of the Langasite family are promising to design high quality bulk acoustic waves resonators. But, as for quartz crystal, LGS and LGT "boules" exist with different quality grades (not yet normalized) [1, 2]. So, to analyze the quality of a given crystal, we have used the same tools allowing the characterization of the quartz crystal: essentially the IR / visible / UV spectrometry coupled to chemical analyzes of impurities content. These experiments and analyzes are performed on LGS and LGT samples coming from different suppliers (in USA, Russia, Japan or France).**

After that, LGT crystals have been processed into Y-cut plano-convex resonators working at 10 MHz on its 5th overtone. We have observed that these resonators present better results than those of SC-cut quartz resonators (particularly on their Q.f product). But, unlike quartz crystals, the asymptotic approximation of the analytical model of Tiersten allowing optimizing the geometrical parameters for good energy trapping is not verified. If it is possible, for quartz resonators, to maintain the Q.f product constant in the range [1 MHz, 1 GHz], it is not the same case for LGT ones.

Nevertheless, we have obtained LGT resonators, manufactured in a best quality crystal sample, with a Q-factor of about 1.8 million on their 10 MHz 5th overtones, measured at working temperatures for which we do not observed activity dips.

I. INTRODUCTION

In a frame of a study ordered by the DGA (depending on the French MOD), we are studying the potentialities of the crystals belonging to the Langasite family to use it in the time-frequency field. In other terms, we try to understand if these crystals can replace quartz to build high quality BAW resonators to insert it in Ultra Stable Oscillators. So, we have to answer many questions concerning the presented items:

- Is the quality of the crystal satisfactory?
- Are we able to design such resonators with the help of the analytical model of Tiersten?
- Is our manufacturing process suitable?
- Will the obtained results on our 10MHz resonators be excellent in all their properties?

We are aware that numerous papers have been published establishing the potentialities of crystals belonging to the LGS family, but the attractive Q.f product [3], exhibited particularly by LGT resonators is not enough to say that this material can be used in USO for time-frequency applications.

So, here, we present the work made in our laboratory through the comparison between the performances of the Y-cut LGT resonator to these of the SC-cut quartz one.

II. MATERIAL QUALITY MEASUREMENTS

A. InfraRed spectrometry

First of all, we have studied the material, by the means of the IR and NIR spectrometry, performed with a Fourier Transform spectrometer. We used a LiF detector to explore a larger range than for quartz. Indeed, usually, in quartz, we study just the absorptions in the range [3000, 3800 cm^{-1}] linked principally to the presence of Hydrogen.

On the Figure 1, we present 5 spectra of different LGS crystals. We note two sharp absorption bands, one of them being superposed to a more or less light large band in the range 3000 to 3400 cm^{-1}: it is at 3413 cm^{-1}. As for quartz, it is probably linked to the presence of hydroxyl groups, the hydrogen being present in the atmosphere of the Czochralski machine during the pulling process.

The other one appears at 5400 cm^{-1} and seems linked to the defects responsible of the color.

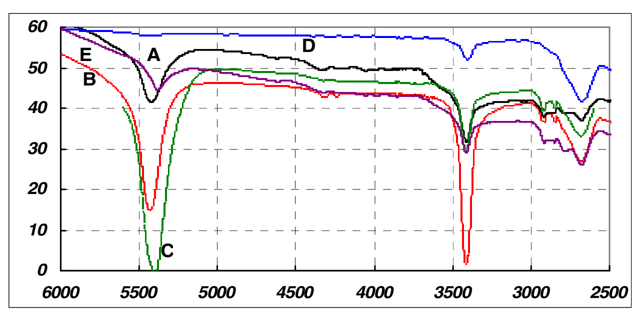

Figure 1. IR spectra of different LGS samples (% absorption vs cm^{-1})

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At each sample, we decide to affect an absorption coefficient (which is generally called α) corresponding to the depth of the sharp absorption band visible at 3413 cm^{-1}. The Beer-Lambert formula applied on the 5 samples gives the results presented in the Table 1, assuming that the absorption at 3800 cm^{-1} is only affected by the thickness of the sample. We must say that this classification is only valuable on our samples which are 5 mm thick Y-cut plates with polished faces. Indeed, the inhomogeneity of certain as-grown "boules" does not permit to affect only one value to the entire block of crystal. Nevertheless, it is always possible to standardize this measurement as it has been made for quartz through international standards, knowing that the deeper is the absorption band, the higher is α and the darker is the color.

TABLE I. ABSORPTION COEFFICIENTS OF DIFFERENT LGS SAMPLES

	LGS samples				
	A	B	C	D	E
α(3413 cm^{-1})	0.346	0.377	0.280	0.035	0.141

In the figure 2, we show 2 different spectra of LGT samples, from FOMOS named A (which is colored in yellow green), and from the University of Central Florida (made by Dr Klemenz last year). This last sample is transparent.

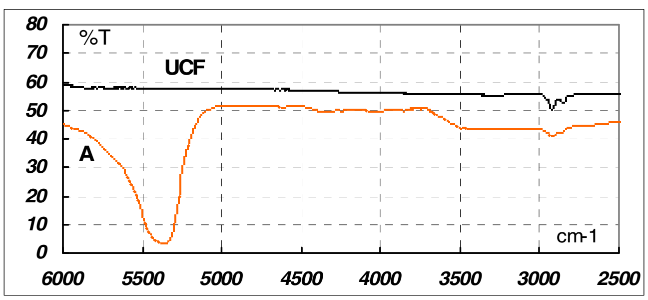

Figure 2. IR spectra of 2 different LGT samples (% absorption vs cm^{-1})

B. *UV / Visible spectrometry*

On the same Y-cut samples than previously, we have realized UV / visible spectra which show high transmittance in the wavelength region from 400 to 2400 nm (like quartz). In the short wavelength region, the transmittance of the LGS or LGT crystal is related to its color. The colorless LGT has the shortest absorption edge, at about 250 nm, unlike quartz for which the cut-off wavelength is about 180 nm.

We have to note that the samples extracted from the yellow / green colored LGT crystal become orange on their surfaces when they stay without protection on our desk. This demonstrates that the color is probably due to oxidation, the oxygen atoms entering the vacancies of the crystal.

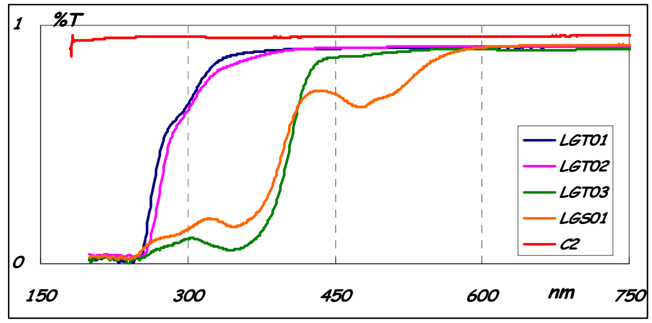

Figure 3. UV / visible spectra of different LGS and LGT samples (% absorption vs nm)

C. *Chemical analyses*

As for the qualification of quartz crystal quality, we try here to measure the level of chemical impurities trapped in the crystal during the growth. These quantities expressed in ppm weight, have been tentatively measured by 2 methods: The first one, called ICP-AES spectrometry, is not easy, due to the first necessary step to mineralize the stone. Indeed, one should not carry new impurities coming from the solvents. But, nevertheless, with this method, we can obtain the level of each constituent of the crystal itself. So, it is also possible to appreciate the stochiometry of the melt and, possibly, the composition changes during pulling. Indeed, some defects can appear in the growth crystal when the starting melt composition is not adjusted to the congruent composition [1].

TABLE II. COMPOSITION OF LGS AND LGT CRYSTALS

Mean values on 3 samples	Majors in LGS (%)			Majors in LGT (%)		
	La	Ga	Si	La	Ga	Ta
Theoretical	40.96	34.26	2.76	37.39	34.40	8.11
Expe	40.2	34.2	2.29	36.7	34.0	7.3

To analyze the trace impurities, we prefer the second method which is made on the bulk: it is called Glow Discharge Mass Spectrometry (GDMS). But it is not really efficient for micro-traces as in the best quartz crystals.

Our first results obtained with this method are presented in the table III. They concern firstly our LGT samples for which we see that the level of impurities is about the same than in electronic grade quartz crystal, except, of course, for the Silicon which is high, due probably to the insolent present in the pulling machine.

The last line of this table shows that the amount of the "classical" impurities measured in one LGS sample are much lower than in the other LGT ones. This demonstrates just that the precursors used by FOMOS are purer than those used by the UCF'lab.

TABLE III. GDMS RESULTS ON TRACES (MEAN VALUES OF 3 SAMPLES)

ppm wt	Al	Ca	Fe	Ti	Na	K	B	Si
LGT FOMOS	11	10.5	1.0	0.6	0.7	0.25	0.12	**60**
LGT UCF	40.2	34.2	2.29	5.5	0.4	0.3	0.3	**100**
LGS FOMOS	4	4	0.8	0.4	1.1	2	-	-

III. MANUFACTURING PROCESS

A. Resonator design

In applying the same analytical procedure than for quartz and developed by Harry Tiersten [4], we have calculated the dispersion constants (called M_n and P_n) and the radius of curvature for LGT resonators, working at 10MHz, providing residual amplitude at the edge. We obtain the results presented here (Table IV), giving an optimum radius of curvature (Rc) of about 500 mm for a diameter of 13.2 mm, instead of 250 mm to well trap the vibration of the C-mode of the SC-cut quartz resonator.

TABLE IV. CALCULATION OF THE DISPERSION CONSTANTS AND RADIUS OF CURVATURE FOR QUARTZ AND LGT CRYSTALS

In Gpa	M_n	P_n	Mean Rc
C 300 quartz	54	63	**250**
C500 LGT	100	47	**500**

So, in Table V, we summarized our first results, also presented in [5], on different resonators, working at 10 MHz, made in each crystal with the same design. We can note that our results are far from the “state-of-the-art” [3] due, at that time, to our bad knowledge of the manufacturing process and also to the quality of the material... But, the process and the design are exactly the same for all the home-made resonators. Nevertheless, we note that the Q.f product is clearly linked to the material quality, estimated by our absorption coefficient.

TABLE V. EXPERIMENTAL RESULTS

	Quartz 3rd Ov FEMTO	LGT State-of-art	LGT 5th Ov	LGS 5th Ov	LGS 5th Ov	LGS 5th Ov
Sample		-	**UCF**	**A**	**B**	**C**
Q ($x10^5$)	**13**	**29**	**9**	**1.5**	**0.8**	**2**
α	-	-	-	0.346	0.377	0.280

B. Contouring optimized for resonators working at 10MHz

Our observations on the previous resonators show that the vibration mode is not enough trapped. Indeed, as shown in the table above, the best value of the radius of curvature to well trap the 5th overtone, working at 10MHz, with a diameter of about 10 mm (corresponding to the *bva* design, including bridges between dormant and active parts), is close to 100 mm (see Fig. 4) and to 115 mm if the diameter is equal to 13.2 mm. For a best value of the Q.f product, we have to work at higher frequencies or with a greater diameter...

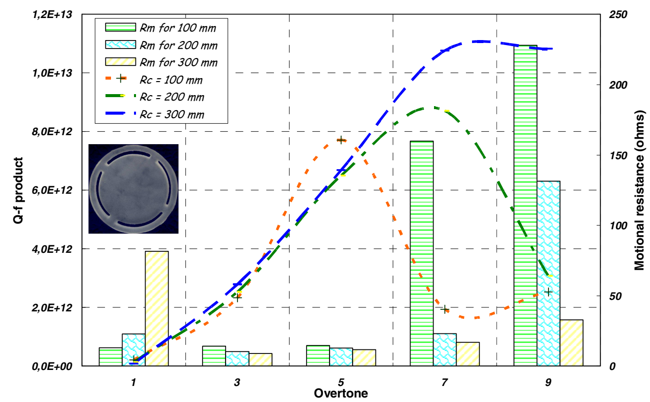

Figure 4. Q and Rm for different contourings (extracted from [5])

Here too, the quality of the material and the good definition of the mechanical process have not been taken into account, so the absolute value of the Q-factor is also far from the state-of-the-art.

Furthermore, we observe that the Q.f product is not constant from one overtone to another instead of on the SC-cut quartz resonator on its first overtones.

C. Frequency-temperature curve

On the Figure 5, we have drawn the frequency-temperature curve comparing to this of the C-mode of the SC-cut quartz resonator. We observe the quasi-parabolic shape of this curve which will be a disadvantage to adjust finely the temperature of the oven to this of the Turn Over Point of the resonator in its oscillator.

We note also that we have to modify slightly the Theta value (to -1°) to adjust the TOP at about 80°C. Indeed, the TOP of the Y-cut resonator (defined by Theta = 0°) is close to 60-65 °C.

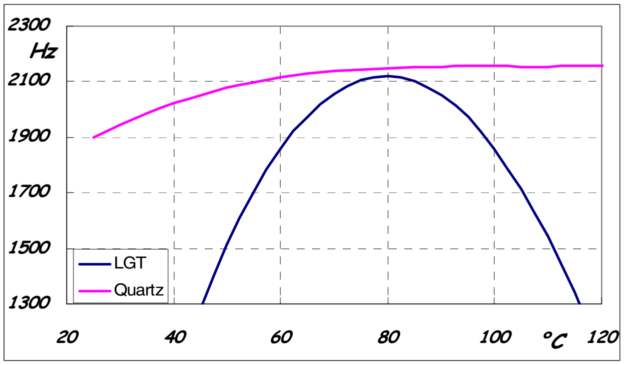

Figure 5. Frequency shift (Hz) versus Temperature (°C)

D. Mechanical process

Our final goal was to develop a satisfying machining method to manufacture high Q-factor resonator. With an empirical way, we have evaluated significant parameters of machining about sawing, lapping and polishing.

- The last step of lapping is made with alumina grains size higher than 5µm to avoid the phenomena of work hardening,
- For the polishing step, we use a machining process entirely with dry diamond powder wet by unionized water.

We check the quality of our process at each step in measuring the roughness of the surface and the quality of the resonant frequency.

The details of our procedure have been exposed in [5] and some considerations about chemical etching to anneal the stresses induced by each step of the mechanical process are presented in [6].

IV. Our Best Results

Finally, we present here our best results, obtained on a lot of LGT resonators, which are not, to day for us, easily reproducible. The best Q-factor obtained on the 10MHz 5^{th} overtone is close to 2.4 million, at ambient temperature. Unfortunately, this value decreases strongly with the temperature, to 1.8 million at the temperature of the Turn Over Point.

Furthermore, we have observed some activity dips at low temperature (see Fig. 6). We think that it is due to the very small radius of curvature. An higher value shall induce this phenomenon to lower temperatures (down to zero), outside the working range. But, for that, we have also to increase the diameter…

TABLE VI. Results on 2 Y-cut LGT and 1 SC-cut quartz resonators

		LGT01	LGT02	SC-cut
F(5^{th} Ov.) @ TOP (Hz)		9,999,960	9,999,980	9,999,985
@ 25°C	Q (x10^6)	**2.4**	**2.1**	**1.3**
	R_m (Ω)	11.5	12.5	80
@ TOP	Q (x10^6)	**1.8**	**1.6**	**1.3**
	R_m (Ω)	19	20	80
TOP (°C)		77.8	77.4	78
@ TOP	3^{rd} Ov. F R_m Q	6,002,960 17 Ω .9	6,002,905 18 Ω .78	-
@ TOP	7^{th} Ov. F R_m Q	13,983,410 45 Ω 1.3	13,983,480 43 Ω 1.2	-

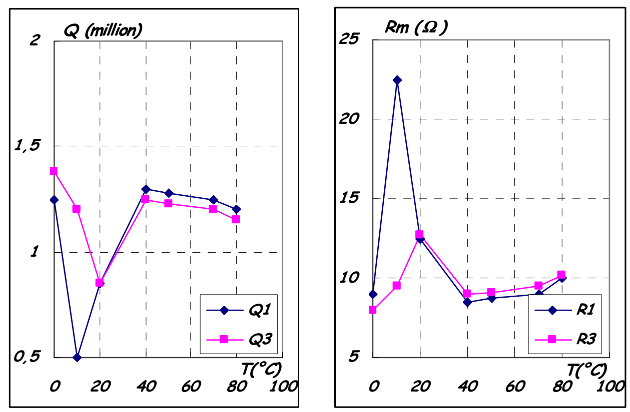

Figure 6. Examples of activity dips at 10°C for the first one and 20°C for the other

In the Table below, we indicate the frequencies of the first anharmonics, so called spurious frequencies, which are due to the way selected to trap the vibrating energy.

TABLE VII. Anharmonic modes and amplitude-frequency effect

	SC-cut 3^{rd} Ov quartz	Y-cut 5^{th} Ov. LGT
C-mode	10 MHz	10MHz
1^{st} anharm (MHz)	10,0130	10,0101
2^{d} anharm (MHz)	10,0142	10,0148
Rc (mm)	230	100
TOP	80°C	80°C
Amplitude-freq effect (in Δf/f / µW)	**1.3 * 10^{-9}**	**-0.38 * 10^{-9}**

We have also measured the value of the amplitude frequency effect which translates the frequency shift induced by variation of amplitude on the resonator. It is about four times lower than on the C-mode of the SC-cut quartz resonator. In agreement with [7, 8], we can suppose that the short-term stability of the LGT resonator will be better than this of SC-cut quartz resonator.

In 2002, we have presented (in [9]) some results concerning the frequency shift induced by forces applied on the edge of the resonator, which can be due to the clips of the mounting structure. Indeed, the knowledge of the force-frequency effect is essential to design ultrastable resonators, but also pressure sensors.

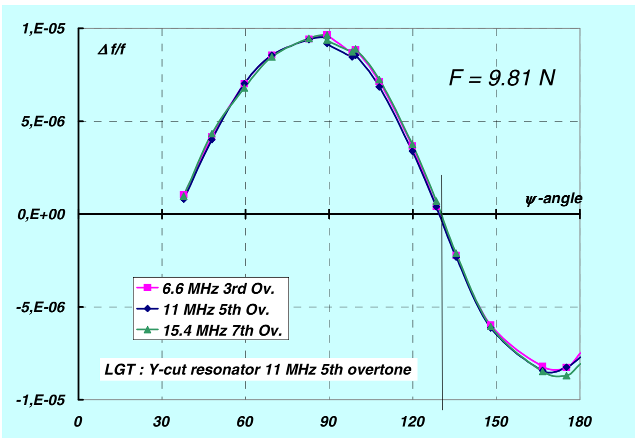

Figure 7. Frequency shift due to in-plane forces on LGT resonator

Here too, the Ratajski coefficient (depending upon the crystalline orientation and the mode of vibration) is largely lower than in quartz as prouved by the values presented below:

TABLE VIII. MAX VALUES OF $K_f(\Psi)$ FOR DIFFERENT RESONATORS

Max value	Ψ	K_f (in 10^{-15} m.s/N)
Y-cut LGS	90	0.8
Y-cut LGT	90	5.4
AT-cut quartz	0	22
SC-cut quartz	43	12

CONCLUSION

We have shown that, as for quartz crystal, LGS and LGT crystals exist with different quality grades. We have demonstrated it on various materials by two different ways: quality factor measurements on Y-cut resonators and IR / visible / UV absorption comparative spectra. Stability and quality of material are not yet guaranteed by all suppliers...

Today, LGT material from some suppliers seems more adapted and more promising to realize ultra-stable oscillators. Moreover, for resonators built in the best material, we have optimized the energy trapping of the vibrating mode (5th overtone) on two different designs ("*standard*" and *bva*) with a practical method.

But, we have some improvements to do on the manufacturing process of the 10 MHz LGT resonators:

- **annealing at higher temperatures in tacking into account the quality of the atmosphere to realize this process (vacuum or under residual pressure of Oxygen),**
- **cleaning procedure,**
- **alternative chemical etching with lapping and polishing process…**

Nevertheless, as presented in this symposium [10], we have obtained very promising values for short term and long term stability.

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REFERENCES

[1] C. Klemenz et al., "Defect structure on Langasite-type crystals: a challenge for applications," Proc. IEEE International Frequency Control Symposium, pp. 301-306, 2002.

[2] D.S. Shah, C. Klemenz, "Adaptative control system for Czochralski growth of larger diameter Langasite-type crystals" Proc. IEEE International Frequency Control Symposium, pp. 196-199, 2006.

[3] R.C. Smythe et al. "Langasite, Langanite and Langatate Bulk-Wave Y-cut Resonators", IEEE Trans. on Ultrasonics, Ferroelectrics and Frequency Control, vol. 47, n° 2, pp. 355-360, mar. 2000.

[4] D.S. Steven and H.F. Tiersten "An analysis of doubly rotated quartz resonators utilizing essentially thickness modes with transverse variation", J. Acoust. Soc.Am., vol 79, pp.1811-1826, 1986.

[5] J. Imbaud et al. "Investigations on LGS and LGT crystals to realize BAW resonators" IEEE Trans. on Ultrasonics, Ferroelectrics and Frequency Control, vol. 55, n° 11, pp. 2384-2391, nov. 2008.

[6] A. Assoud et al. "Chemical controlled dissolution of LGS samples : comparison with quartz and $GaPO_4$ », Proc. IEEE International Frequency Control Symposium, pp. 724-728, 2007.

[7] R.J. Besson et al. "Phase noise limitation due to amplitude frequency effects in state-of-the-art quartz oscillators", 50th Ann. Freq. Cont. Symposium, pp. 839, 843, 1996.

[8] Y. Kim "Amplitude-frequency effects on Y-cut Langanite and Langatate", Proc. IEEE International Frequency Control Symposium, pp. 631-636, 2003.

[9] J.J. Boy et al. "Theoretical and experimental studies of the force-frequency effect in BAW LGS and LGT resonators", Proc. IEEE International Frequency Control Symposium, pp. 223-226, 2002.

[10] J. Imbaud et al. "Measurements of ultra-stable Langatate crystal resonators", this symposium.