

# NEW INVESTIGATIONS ON THE LGT CRYSTAL INTENDED FOR TIME AND FREQUENCY APPLICATIONS

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## ABSTRACT:

Materials of the langasite family are of current interest for both Bulk Acoustic Wave and Surface Acoustic Wave devices. In particular, they could be promising solutions to Frequency and Time applications due to their  $Q.f$  product, two to three times higher than for the quartz crystal [1]. We have shown that this encouraging result is strongly linked to the crystal quality [2] and to the post thermal treatment which has been submitted the device. Among the numerous crystals belonging to the LGS family, LGT seems more interesting because of the best combination of quality of growth and material parameters [3, 4].

To qualify the LGT crystal, we have investigated different samples by means of the Infrared spectrometry (IR), the Dielectric Relaxation Spectroscopy (DRS) and the Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), this last one dealing with the nature and the amount of the chemical impurities.

Furthermore, we have investigated the inhomogeneity of our samples coming from different suppliers by measuring their optical rotary power and their coefficients of gyration  $\alpha$  at different wavelengths. The experimental results show that:

- the composition influences this coefficient  $\alpha$  following
$$\alpha(LGS) < \alpha(LGT) < \alpha(SiO_2)$$
- it does not seem significantly influenced by the growth atmosphere and the annealing,
- all analyzed samples are right-handed.

## I. INTRODUCTION:

In the frame of a program supported by the french DGA, we continue to investigate the crystal quality for crystals belonging to the LGS family and used for TF applications.

For that, last year, we bought 2 “boules” of LGT to Krystal Engineering, newly installed in Titusville (in Florida) and managed by Dr C. Klemenzenz.

They are grown in the Z-direction and their dimensions are a little bit more than 2 inches in diameter for more than 170 mm in length. The cylindrical section of the boule is about 140 mm long and it is almost homogeneous along Z.

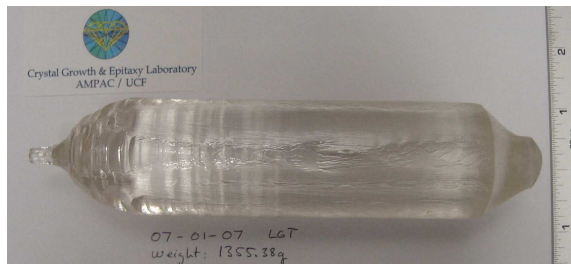


Fig. 1 and Fig. 2: “boule” of LGT as-received and after cutting

To analyse each boule, we have planned to cut each one in slices with different thicknesses as shown in the previous figures. The 2 x 5 thinner slices of 3 mm thick are perpendicular to the growth axis and dedicated to the analysis of the optical heterogeneity, as the thickest one is used to build Y-cut samples and resonators.

In [1, 2], we have proved that the quality of some LGT crystal shall be satisfactory for very high Q resonators working at 10 MHz. Furthermore, we have supposed that certain well defined treatments (as annealing, for example) can improve this quality and its influence on the behaviour of the resonant frequency.

So, to classify LGT crystals, in this paper, we recall first some results extracted from Infra Red spectra, then we continue with Dielectric Relaxation Spectrometry measurements and with very precise ICP-MS quantification to determine the atomic levels of different impurities known to be in ultra traces in the lattice of the crystal.

At least, we present measurements of the optical activity of this crystalline structure to read its unavoidable inhomogeneity (linked particularly to the seed).

## II. IR, UV AND VISIBLE SPECTROMETRY:

Presented already last year, we show in Fig. 3, 4 and 5 the Infra-Red, Ultra-Violet and visible spectra of LGS and LGT Y-cut samples. The Y-faces are polished and separated of about 5 mm. In the IR domain, the transparent samples do not present even small absorption bands and so, we are not able to define an absorption coefficient named  $\alpha$  like in quartz or in the more or less coloured LGS samples (as suggested in the Fig. 3). In the visible domain only, we can observe differences. Indeed, in this 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. So we have to find another way to qualify the crystal quality.

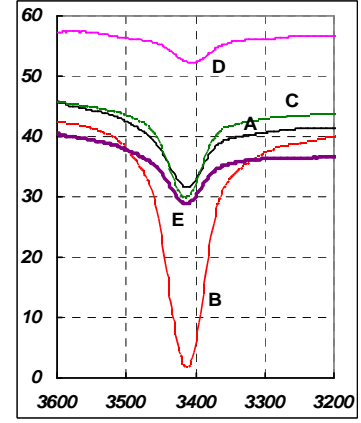


Fig.3: sharp absorption bands on different LGS crystal samples

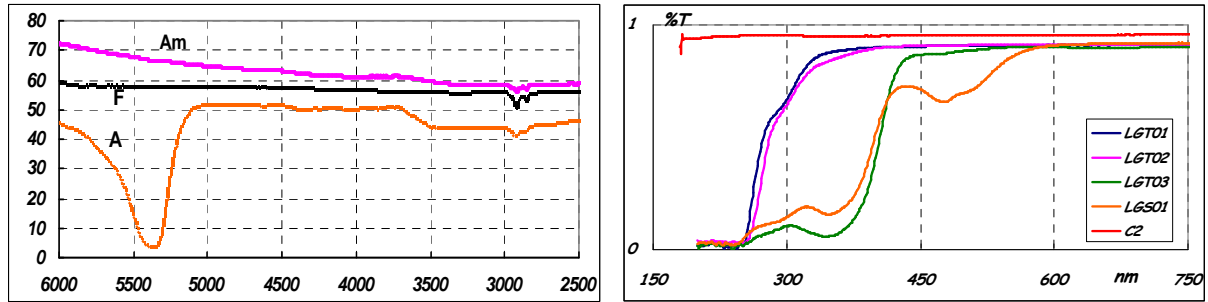


Fig. 4 (left): IR spectra of different LGT samples

Fig.5 (right): UV / visible spectra for different LGT samples, compared to quartz one.

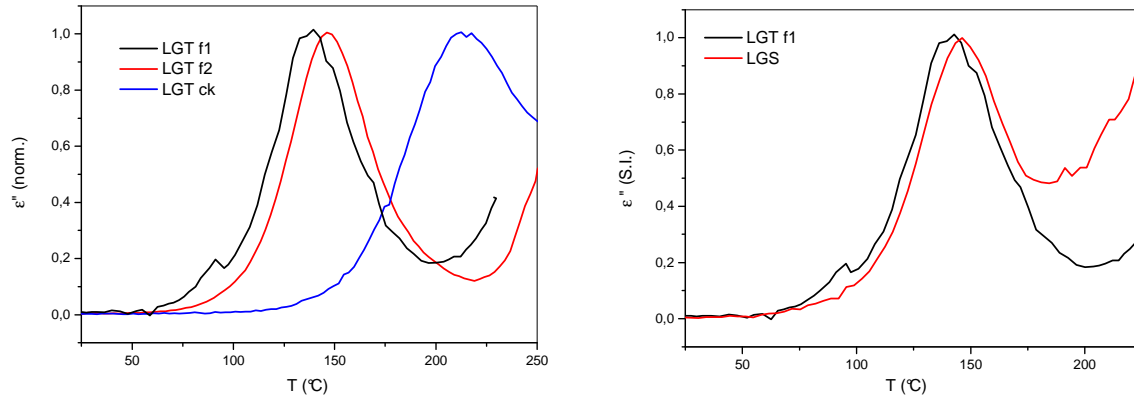
## III. COMPLEX IMPEDANCE SPECTROMETRY:

The CIS has proved that is a powerful tool for studying charges dynamics in solid, particularly in quartz crystal [5, 8]. The dielectric response can be regarded as arising from the dipolar reorientation associated to electric charges hops within short distances. The dielectric relaxation phenomenon is then ascribed to charges hopping above the potential barrier, separating 2 neighbouring positions which are energetically equivalent. In quartz materials, dielectric loss arises from chemical defects  $M^+$  hops, between two neighbouring positions. According to the elementary microscopic process, the potential barrier  $\Delta E$  to be passed over can be calculated from the relaxation time  $\tau$  that characterized the hopping mechanism, via the following relationship:

$$\tau = \tau_0 \exp \left[ \frac{\Delta E}{kT} \right]$$

where,  $k$  is the Boltzmann's constant,  $T$  represents the temperature and the pre-exponential factor  $\tau_0$  is the inverse of the oscillation frequency  $\nu_0$  of a charge carrier trapped in its site. In the following,  $\tau_0$  is assumed to be constant ( $\tau_0 = 10^{-13}$  s) [9]. The potential barrier  $\Delta E$  is then assigned to the  $M^+$  de-trapping energy, i.e. to the energy required for the  $M^+$  reorientation, without any migration from one site to another.

The complex permittivity was recorded with a NOVOCONTROL ALPHA dielectric analyser. Blocking electrodes were inserted between the sample and the metallic electrodes of the analyser, in order to transform the dc conductivity contribution of the sample into a dielectric loss peak. The temperature evolution of the dielectric loss  $\epsilon''(T)$  was measured at fixed frequency (0.02 Hz) and under a constant heating rate of 0.5 °C/min, for temperatures ranging from 25°C to 250°C.

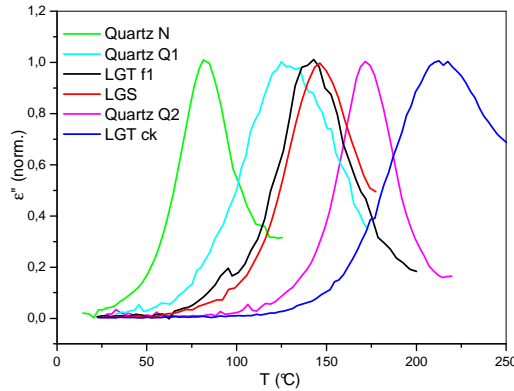


**Fig. 6 and 7: CIS of LGT samples**  
(LGTf1 and LGTf2 are extracted from coloured samples, whereas LGTck is uncoloured)

The Fig. 6 illustrates the  $\epsilon''(T)$  evolution for 3 different LGT materials. The increase of  $\epsilon''(T)$  at high temperature corresponds to the so-called Maxwell-Wagner Sillar effect, resulting from the accumulation of the ionic charges at the blocking electrodes and sample interfaces. It does not correspond to the dipolar response of the solid and is consequently not discussed in the following.

So, the dielectric response of f1 and f2 are similar and both centred near 140 – 145 °C. On the opposite, the dielectric loss peak of the LGTck (from Krystal Engineering) is shift towards higher temperature (near 215°C). So this material seems the most stable, in term of dielectric properties, since it exhibits the charge carriers having the highest trapping energy  $\Delta E$ , as indicated in the table 1.

The Fig. 7 shows the comparison between coloured LGT and LGS materials. The space charges response excepted, both  $\epsilon''(T)$  peaks are superposed. This suggests that the charge carriers are similar and exhibit the same relaxation energy.



**Fig. 8: dielectric responses of LGT, LGS and quartz crystals**

**Table 1: trapping energy  $\Delta E$  of numerous crystals (comparison with different quartz)**

	T @ $\epsilon''_{\max}$ ( $\pm 5^\circ\text{C}$ )	$\Delta E$ (eV) ( $\pm 0.02\text{eV}$ )
LGT f1	140	1.14
LGT f2	145	1.15
<b>LGT ck</b>	<b>215</b>	<b>1.34</b>
LGS	145	1.15
Gemma Quartz (Q1)	130	1.11
Sawyer Quartz (Q2)	170	1.22
Natural Quartz (N)	80	0.97

Finally, the Fig. 8 and the table 1 compare the dielectric responses of LGT and LGS crystals with quartz materials from different sources, including natural one. And the following energy sequence can be established:

$$\Delta E_{\text{Nat quartz}} < \Delta E_{\text{Synt quartz Q1}} \approx \Delta E_{\text{LGTf1}} \approx \Delta E_{\text{LGS}} < \Delta E_{\text{Synt quartz Q2}} < \Delta E_{\text{LGTck}}$$

The key point deals with the dielectric behaviour of the “LGTck” material, whose the dielectric losses peak appears at much higher temperature than the one of the best synthetic quartz: It seems very promising...

#### IV. ICP-MS ANALYZES: CHEMICAL IMPURITIES

The main impurities incorporated in the crystal during pooling process have been quantified by Inductively Coupled Plasma Mass spectrometry (ICP/MS) and by Glow Discharge Mass Spectrometry (GDMS).

GD/MS analyses allow surface measurements of different chemical species. ICP/MS gives the concentration of an element in the entire sample. This last technique needs the sample to be solubilised before analyses. The preparation

procedure is composed of three steps: cleaning, digestion and analysis. Samples have first been cleaned in a 50 % nitric acid and 10 % hydrofluoric acid solution in an ultrasonic bath during 10 minutes and then rinsed into an ultra-pure water bath. Digestion of the samples has been operated in a mix of hydrofluoric acid 60 % and nitric acid 70% for LGS samples and in a solution of hydrochloric acid 32% for LGT samples. All samples have been digested at 70°C during 10 days. Analysis was performed with an ICPMS 7500ce from Agilent technologies (Tokyo, Japan), equipped with on-line octopole collision/reaction cell. Isotopes  $^7\text{Li}$ ,  $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{28}\text{Si}$ ,  $^{39}\text{K}$ ,  $^{42}\text{Ca}$ ,  $^{47}\text{Ti}$ ,  $^{56}\text{Fe}$ ,  $^{57}\text{Fe}$ ,  $^{72}\text{Ge}$ ,  $^{103}\text{Rh}$ ,  $^{140}\text{Ce}$ ,  $^{167}\text{Er}$ ,  $^{191}\text{Ir}$ ,  $^{194}\text{Pt}$  were monitored. The measured concentrations for these elements in the four analysed crystals are listed in table 2. Results obtained by both techniques are presented..

**Table 2: analyses of chemical impurities present in the lattice of different LGS and LGT crystals (expressed in ppm weight)**

In ppmw	Al	Ca	Ti	Fe	Ge	Mg	Li	Na	K	Pt	Rh	Ir	Ce	Er	Si
<b>ICP/MS measurements:</b>															
<b>LGSf1</b>	9.7	31	63	5	1	1.5	-	9.2	-	0.8	-	55	11	-	<b>9000</b>
<b>LGSf2</b>	32	-	54	5.2	3	0.1	0.1	-	5	0.4	-	30	9	-	<b>29000</b>
<b>LGTf1</b>	<b>1.4</b>	<b>4</b>	<b>0.1</b>	<b>0.3</b>	-	<b>0.4</b>	-	-	<b>19</b>	<b>0.4</b>	-	<b>320</b>	<b>35</b>	-	<b>7</b>
<b>LGTck</b>	9	35	3.4	0.4	-	0.14	-	3.2	<b>7.5</b>	-	-	520	<b>11</b>	-	22
<b>GDMS measurements:</b>															
<b>LGTf1</b>	<b>17</b>	<b>8.8</b>	<b>1</b>	<b>1.2</b>	-	-	-	<b>1.</b>	<b>0.6</b>	-	-	?	?	?	<b>50</b>
<b>LGTck</b>	25	4	6	1.3	-	-	-	0.4	<b>0.3</b>	-	-	?	?	?	80

∴ : < Limit of Detection

? : not measured

LGSf1 and LGSf2 are issued from 2 different coloured samples (they were more or less orange/yellow) and LGTf1, grown by FOMOS, is slightly coloured in green. We recall that LGTck is coming from KE.

The first outstanding result is the high amount of Ir atoms in each sample and more especially in LGT crystals. A high level of atoms of Cerium in the samples has to be noticed also. This element does not come from outside the lattice because a cleaning procedure has been performed before analysis (see above).

At least, the Li level is, on the contrary, really negligible in all samples. For Na, the conclusion must be more nuanced... So, it is difficult today to affect the dielectric losses observed previously to a responsible clearly defined, except eventually the Iridium.

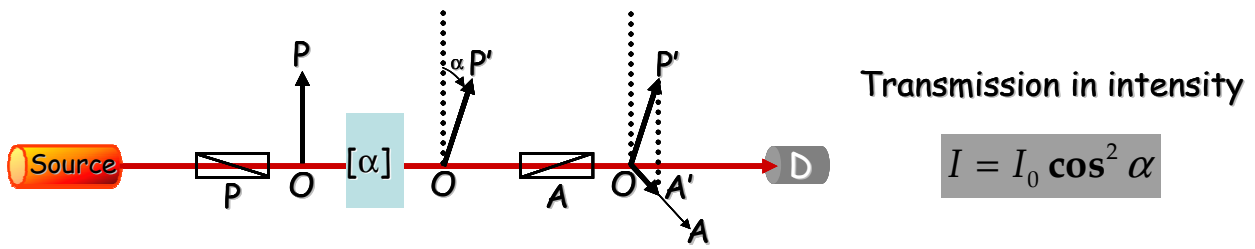
As the colour, orange/red for LGS and green/yellow for LGT (which changes to orange simply if staying long time at the atmosphere of the room), it can be affected partially by the presence of several atoms like Titanium, Iron, Aluminum... as it is observed in sapphire.

New analyses, preferably after treatments (as annealing performed at different temperatures under different atmospheres) can help us to obtain answers. They are in progress.

## V. MEASUREMENTS OF THE COEFFICIENT OF GYRATION:

At least, we have studied the optical activity of this kind of crystals, to compare to the quartz crystal for which few similar analyses have been made.

We expected that the measure of the rotary power of the light can be used to appreciate in one hand the inhomogeneity of a Z-cut blank (like our slices presented at the beginning) and mostly the role of a particular annealing. It can be observed only in the direction of the optical axis. So our set up is presented here:



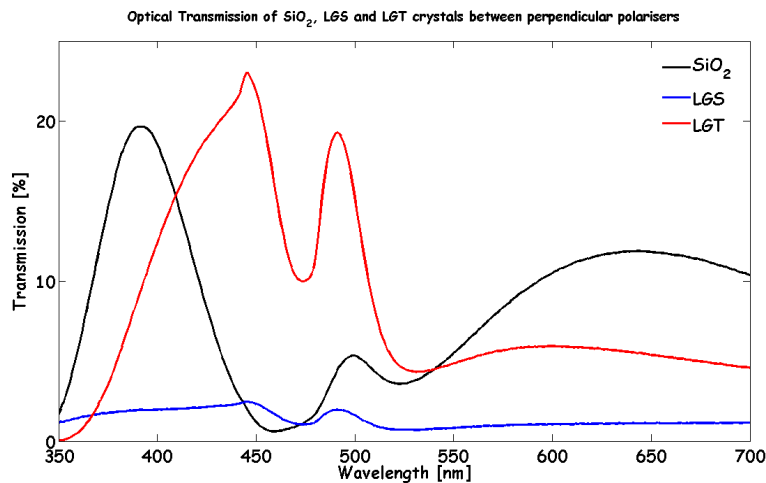
$\alpha$  is the rotation induced by the studied crystal, located between 2 crossed polarizers. After the sample, the OP' vibration has turned of  $\alpha$  degrees. But after the A polariser, we have just OA', which is the projection of OP' on OA. Furthermore, the intensity detected by the detector D is proportional to the squared value of OA'. So, to qualify our samples, we have used the 2 Biot laws:

First law:  $\alpha = [\alpha] e$       Second law:  $[\alpha] = \frac{A}{\lambda^2}$

and we obtain the graphs of the Fig. 10 for which:

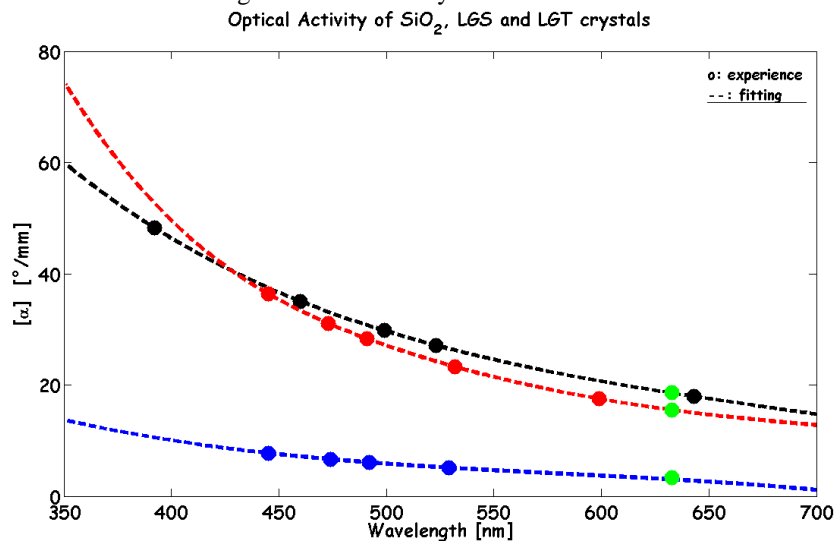
$$\alpha(\text{LGS}) < \alpha(\text{LGT}) < \alpha(\text{quartz})$$

the composition influencing the optical activity of the material.



**Fig. 9: optical transmission of various crystals measured between perpendicular polarizers.**

The values presented in the next graph are extracted from the first one (see Fig. 9), in which we have drawn the percentage of transmission versus wavelength for the same crystals.



**Fig. 10: Optical activity of quartz and LGx crystals.**

We note that we have obtained same values than these observed by various authors using crystalline quartz for rotating the polarisation in photonic applications, for which it is essential to work with very pure crystal, without optical defects readable by this kind of experiments...

In contrary, on X- or Y-cut samples, we observe interferences due to the rotary power and the properties of birefringency.

## VI. CONCLUSION:

We have performed a lot of experiments, but we have not obtained very clear conclusions. The chemical analyses are very interesting and seem sufficient, but we have to tentatively modified the structure of the defects present in the bulk to understand what kind of them can affect the quality of the component that we have to realize in the crystal.

At least, we have observed that the composition can affect the optical rotary power of the crystal, but not sufficiently to observe modifications dues to annealing.

## VII. ACKNOWLEDGEMENT:

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