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Influence of the growth and annealing atmosphere on the electrical conductivity of LTG crystals

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ABSTRACT

We present the electrical conductivity measurements of $La_3Ga_{5.5}Ta_{0.5}O_{14}$ (LGT) crystals grown by Czochralski (Cz) technique in Ir crucibles and N_2 atmosphere containing few percent of O_2. In addition, we have studied the effect of thermal annealing on the stability and the thermal conductivity. The electrical conductivity depends on the stoichiometry, the inhomogeneous impurities levels, the growth atmosphere and the post-growth annealing conditions. Furthermore, we recorded the UV–Vis transmission spectra of the LGT samples and we note that the less resistive LGT samples have an edge of the intrinsic absorption at the highest wavelengths.

1. Introduction

Owing to its high acoustic quality, its high piezoelectric coefficients and thermal stability, $La_3Ga_{5.5}Ta_{0.5}O_{14}$ (LGT) Langatate is a promising piezoelectric crystal for acoustic devices developed in the time and frequency domain and particularly for ultra-stable resonators (Bulk Acoustic Waves resonators) and high temperature wireless sensors. However, these applications require homogenous material with reproducible and performed properties.

In fact, during the growth by Czochralski process and post-growth heat treatment defects are created in LGT crystal, which limits its potential use. Point defects, arising of the growth and post-growth conditions, can react as ionic and electronic charge carriers and generate conductive losses particularly at high temperatures.

The presence of point defects significantly affects the physical and chemical properties. They can be revealed by chemical, optical and/or electrical analytical methods. In this paper, we present the characterization of the point defects and the electrical resistivity measurement of LGT crystals.

2. Experimental

2.1. The samples

As presented previously [1,2], we have selected different LGT ingots grown under different conditions. For comparison, we selected LGS sample as standard. Details of the growth conditions, thermal annealing treatment and color are indicated in Table 1 which concerns 3 different sources: CI (France), CK (USA) and FO (Russia).

2.2. Chemical analysis of LGT crystals

2.2.1. Electron Probe Micro-Analysis EPMA: major contents analysis

We have analyzed LGT samples by Electron Probe Micro-Analysis (EPMA) and we determined their atomic compositions. This microanalysis is performed on small polished samples (a few hundred square microns) having a thickness of about fifty microns. They are then bonded on resin or metal support. Each measurement corresponds to the average of a few tens of scans.

2.2.2. Femtosecond laser ablation ICP-MS (analysis of traces and ultra-traces of impurities)

All measurements were carried out on a DRC2 quadrupole ICPMS (Perkin Elmer) instrument coupled to an Alfamet

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Table 1
Growth and post-growth treatment (annealing) conditions of LGT samples and LGS sample.

Sample reference	Growth axis	Growth atmosphere	Annealing conditions	Color
CI3	X	N_2	Air, 1320 °C, 24 h	Heterogeneous light orange
CI6ba	X	N_2	Before annealing	colorless
CI6aa	X	N_2	N_2, 1400 °C, 24 h (presence of few O_2)	Heterogeneous light orange
FO	X	Ar+1% O_2	Air, 1250 °C, several days	Bright orange
CK	Z	N_2	Not annealed	colorless
LGS	X	Ar+1% O_2	Air, 1250 °C, several days	Bright orange

ba: before annealing and aa:after annealing.

femtosecond laser ablation system (Nexeya SA, Canejan, France). This laser machine is fitted with a diode-pumped Yb:KGW crystal laser source (HP1, Amplitudes Systèmes, Pessac, France) delivering 360-fs pulses at 1030 nm. The laser beam is focused with a 25-mm objective providing 15 μm diameter spot size. Further details of a previous similar model of this laser ablation system are described elsewhere [3,4]. The final ablated zone is of 500 μm × 500 μm in 50 s. Each LGT was ablated 10 times under these conditions.

Measuring conditions were adjusted for maximum sensitivity, stability and plasma robustness using a transparent glass certified reference material (NIST 612) [5].

Trace metals concentrations were determined after calibration of the fs LA/ICPMS coupling using certified glass reference material (NIST 612 and NIST 610).

2.3. UV–vis and IR spectroscopic analyses

The presence of defects significantly affects the optical properties, which can be revealed by optical transmission spectra.

The transmission spectra of LGT samples with plane and parallel polished surfaces (thickness 4–5 mm) were recorded in the wavelength range from 200 to 800 nm on a Lambda 900 UV–VIS spectrophotometer and in the range 7000 to 2000 cm^{-1} with a Magna 750 FT-IR spectrophotometer.

2.4. Electrical resistivity measurements

To calculate the electrical resistivity (ρ), Eq. (1), we measured the current intensity (I) crossing the sample at a voltage (U) of 50 V using a pico-ampere meter. The shape of LGT samples are disks of 14 mm diameter and 0.5 mm thick (e), with gold electrodes deposited (S) on the two polished faces (ϕ = 9 mm).

$$\rho(\Omega\cdot m) = U/I\cdot S/e \quad (1)$$

3. Results and discussion

3.1. Charge carriers

LGT single crystals are generally grown by Czochralski method. The properties of this material and specificities of the growth process induce defects.

The LGT layered structure with four distinct cation sites allows incorporation of substituent and/or interstitial metal ions impurities. This result is confirmed by ICP-MS analyses (Table 2).

LGT is an incongruent material [6]. Stoichiometry derivations of the melt composition generate chemical inhomogeneity in the LGT crystal which are generally compensated by the formation of either cation or anion vacancies ($V_{\ddot{o}}$, V_{La}''' …). So, we analyzed the LGT samples by EPMA to determine their chemical compositions (Table 3).

Table 2
Impurities levels in LGT analyzed by Fs Laser Ablation ICP-MS coupling (in ppm weight).

Sample	Na	Mg	Al	Ti	Cr	Fe	Ni	Cu	Zr	Sn	Ce	Pr	Gd	Ir
CI6ba	17	1	59	14	1	13	<0.1	4	8	<0.1	16	1	170	<0.1
CI6aa	59	3	165	10	1	14	10	1	8	19	16	1	171	<0.01
FO	81	9	139	25	2	40	1	1	4	22	17	2	176	1

Impurities levels in LGT analyzed by Fs Laser Ablation ICP-MS coupling (in ppm weight).
Note: The high value of Gd content can be due to interferences with other atoms.

Table 3
Stoichiometry of LGT samples analysis by EPMA.

Sample	Cationic % x/(Ga + Ta + La)	x = Ga	x = La	x = Ta
	Stoichiometry	61.1	33.3	5.6
CI6ba	average	63.2	31.4	5.4
CI6aa	average	63.4	31.4	5.2
CI3	average	63.0	31.6	5.4
CK	average	63.1	31.6	5.3
FO	average	63.2	31.7	5.1

These point defects can react as ionic ($V_{\ddot{o}}$ - V_{La}''' - Fe_i''' …) and electronic (é, h·) charge carriers. Eq. (2) describes the bulk electrical conductivity.

$$\sigma = \sum iC_i q_i \mu_i, \quad (2)$$

where C_i, q_i and μ_i are the concentration, the charge and the mobility of the *i* charge carrier, respectively.

3.1.1. Metal ions impurities

From the results of fs LA-ICP-MS analysis, presented in Table 2, we note that LGT crystals are contaminated by impurities from raw materials oxides such as lanthanides (Ce, Gd …) coming from La_2O_3 and transition metals (Fe, Ti …) from Ta_2O_5. These impurities occupy interstitial sites $Ti_i''''$and/or substitute lattice atoms Fe_{Ta}''.

Comparing the concentration of Fe and Ti in LGT FO and LGT CI6aa samples, the intensity of the color increases with the concentrations of Fe and Ti. We deduce that these impurities can contribute in LGT crystal color.

The variation of the impurities concentrations between the 2 samples CI6ba cut from un-annealed LGT ingot and CI6aa cut from the same LGT ingot after annealing, is due to inhomogeneous distribution of impurities.

After annealing, colorless LGT (CI6ba) became orange (CI6aa). We deduce that annealing modifies the valence state of Fe and Ti impurities and then also the crystal color.

3.1.2. Composition of LGT samples studied by EPMA

In the $La_3Ga_{5.5}Ta_{0.5}O_{14}$ structure, $La_3(Ga_{0.5}Ta_{0.5})$ (1)Ga_3 (2)Ga_2 (3)O_{14}, the La^{3+} cations occupy the dodecahedral sites and Ga^{3+} occupy three positions: octahedral Ga (1), which is partially

Table 4
LGT Electrical resistivity measurements.

Sample	Growth atmosphere	Annealing atmosphere	I (nA)	ρ (GΩ.cm)	Eg (eV)
CI6ba	N_2	unannealed	5.12	93.6	4,84
CK	N_2	unannealed	4.55	83.3	4,59
LGS	Ar + O_2	air	5.33	64.2	3,54
FO	Ar + O_2	air	5.39	45.3	3,26

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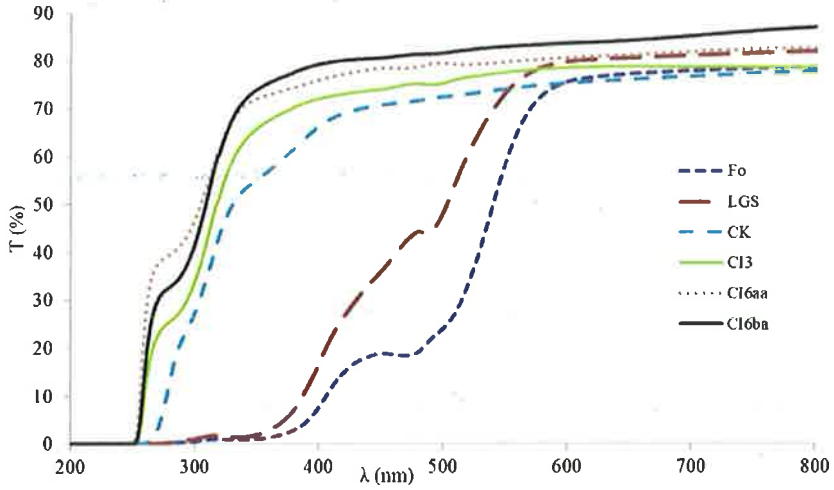

Fig. 1. UV–Vis transmission spectra of LGT samples.

occupied by Ta^{5+}, tetrahedral Ga (2) and trigonal–pyramidal Ga (3).

Comparing with the stoichiometric composition of LGT ($La_3Ga_{5.5}Ta_{0.5}O_{14}$), the Ga content of the grown LGT crystals is higher while the Ta content is lower (Table 3). So, concerning the occupancy of the octahedral sites, we conclude that the Ga:Ta ratio is higher than 1, which indicates the presence of $GaTa''$ defect in LGT crystal structure.

To conserve the electroneutrality, other point defects will be formed such as oxygen vacancies as presented in the quasi-chemical Eq. (3).

$$Ga_2O_3 \rightarrow 2\,Ga_{Ta}'' + 2\ddot{V}_O + 3O_O \quad (3)$$

The EPMA analysis of LGT crystals showed Lanthanum deficiency which leads us to suggest the existence of the hypothetical structure: $La_3Ga_6O_{27/2}$. The LGT structure $La_3Ga_{5.5}Ta_{0.5}O_{27/2+1/2}$ can be written as $La_{3\,(1\text{-}1/27)}(Ga_{5.5}Ta_{0.5})_{(1\text{-}1/27)}O_{27/2}$, knowing that $1/(1+1/27) \approx 1\text{-}1/27$. We deduce that LGT is obtained by a partial substitution of Ga by Ta in the octahedral sites of the $La_3Ga_6O_{27/2}$ structure. So,the substitution of one cation by another with higher valence $Ta_{Ga}^{\cdot\cdot}$ generates cationic vacancies as presented in the quasi-chemical Eq. (4).

$$3\,Ta_2O_5 \leftrightarrow 6Ta_{Ga}^{\cdot\cdot} + 4V_{La}''' + 15\,O_O \quad (4)$$

3.2. Electrical resistivity

Electrical resistivity measurements (Table 4), demonstrate that LGT crystal quality differs from sample to sample depending on the growth and thermal annealing conditions. LGT (CI) is twice more resistive than LGT (FO). Indeed, point defects, such as impurity, atoms vacancy, and atoms into interstitial position, add new energy levels in the band gap energy which induce higher bulk electrical conductivity.

In Ref. [7], the authors have calculated the band gap of defect-free LGT crystal at 5.279 eV. We determined the gap energy from the edge of the intrinsic absorption in UV–Vis transmission spectra (Fig. 1). Indeed, the less resistive LGT (FO) and LGS samples have an edge of the intrinsic absorption at higher wavelengths at $\lambda = 350$–380 nm compared with those of LGT (CI6ba) and CK at $\lambda = 250$–270 nm.

3.3. Influence of the growth and annealing atmosphere

The presence of oxygen in the growth atmosphere increases the bulk electrical conductivity by the creation of charge carriers (Table 4) [8–10].

After air annealing, colorless LGT crystals become orange colored. It is due to the change of impurities valence state: for example, Fe^{2+} is oxidized into Fe^{3+}.

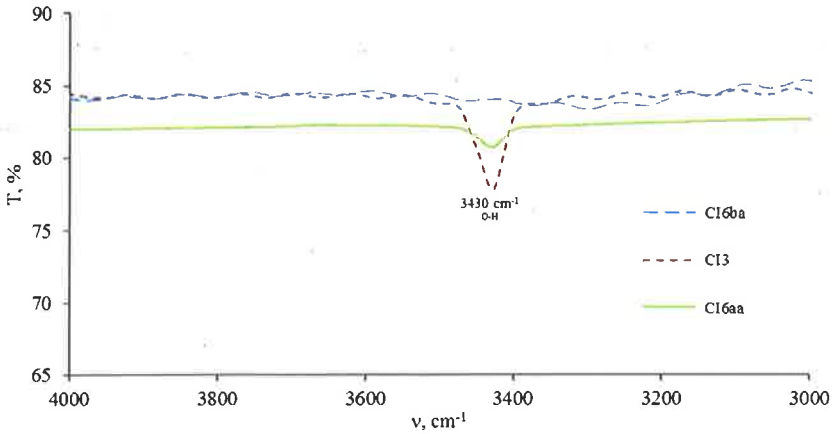

Fig. 2. IR transmission spectra of LGT samples.

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According to IR transmission spectra of LGT samples Fig. 2, annealing under Oxygen induces OH defect as described in the quasi-chemical Eq. (5).

$$\begin{aligned} &\tfrac{1}{2}\,O_2+\ddot{V}_O+2e' \leftrightarrow O_O \\ &O_O+H^{\cdot} \leftrightarrow OH^{\cdot} \end{aligned} \qquad (5)$$

4. Conclusion

In this work, we have shown that the physical properties of the LGT crystals strongly depend on the growth conditions and thermal annealing. They can affect the stability of a given resonance frequency of Ultra Stable Resonators used in the frequency and time domain. We have observed that LGT samples grown and annealed in atmosphere containing Oxygen present higher electrical conductivity which is also affected by impurities levels.

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