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journal homepage: www.elsevier.com/locate/optmatLGT ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) langatate bulk crystal grown from the melt by Czochralski technique and characterizationB. Boutahraoui^{a,d}, A. Nehari^a, J. Boy^b, X. Vacheret^b, M. Allani^b, H. Cabane^c, M. Dumortier^c, M. Derbal^d, K. Lebbou^{a,*}^a Institut Lumière Matière, UMR5306 Université Lyon1-CNRS, Université de Lyon, Lyon, 69622, Villeurbanne Cedex, France^b FEMTO-ST Institute, UFC, CNRS, ENSMM, UTBM, 25000, Besançon, France^c Cristal Innov – Université Lyon1, 73800, Sainte-Hélène du Lac, France^d Université Blida1, BP 270 route de Soumâa, Blida, Algeria

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ABSTRACT

$\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGT) langatate crystals were grown along Z-axis by Czochralski technique in argon and mixed argon with 0.1% O_2 atmosphere. The coloration and the performance of langatate crystals were strongly connected to the starting chemical composition, the gas atmosphere and the growth parameters. Any deviation from the optimal LGT generate macroscopic defects such cracks and grains boundary causing a deterioration of the crystals performance.

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1. Introduction

Piezoelectric materials play an increasingly important role in electronic applications. Among these materials lanthanum gallium tantalate (langatate) $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ (LGT), belonging to langasite family. This compound is reported as none congruent material, but it is not strong decomposition or phase transition corresponding to crystallographic structure change causing cracks and grain boundary [1]. Quite often the study of the solidified material inside crucible shows the presence of LaGaO_3 phase and LGT crystallized as secondary phases. So the LGT has a peritectic relation to LaGaO_3 phase [1]. But these problems are also connected to Ga_2O_3 oxide composition in LGT phase which can be change because of Ga_2O_3 losses during the growth process causing composition fluctuation in the La_2O_3 – Ga_2O_3 – Ta_2O_5 ternary phase diagram and evolution of the $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ composition in the ternary equilibrium diagram causing the apparition of secondary phase such LaGaO_3 . Such problem can be limited if the composition can be controlled through growing LGT crystal in Argon/ O_2 gas atmosphere which

minimize the Ga_2O_3 volatility and stabilize the growth process. The crystal structure of langasite (LGS) belongs to the structure type of calcium gallium germinate, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ with the space group P321, consistent with the crystal class 32 to which quartz also belongs. LGT may be the most suitable material for high temperature applications because its impedance is larger than that of LGS by an order of magnitude [2]. Compared to quartz, possesses several quite desired properties the highest density (6.149 g/cm³), dielectric permittivity ($\epsilon_{11}/\epsilon_0 = 19.9$, $\epsilon_{33}/\epsilon_0 = 77.2$) and offers low acoustic velocities [3], and the two most important of the desired properties are higher electromechanical coupling factor will allow wider bandwidth which is 3 times that of quartz [4], and lower acoustic loss or higher Q value which is about twice that of quartz. In addition, langatate has the same temperature compensation property as quartz [5] and its piezoelectric constants are about three times larger than those of quartz. One of the most important advantages of these crystals is that they will not undergo phase transitions up to its melting point (1510°C). Surface acoustic wave (SAW) and bulk acoustic wave (BAW) devices, using piezoelectric crystals such as LGT, have the capability to provide the desired high temperature sensors for temperature, pressure, strain, and gas species measurement. These application areas require materials to

* Corresponding author.

E-mail address: kheirreddine.lebbou@univ-lyon1.fr (K. Lebbou).

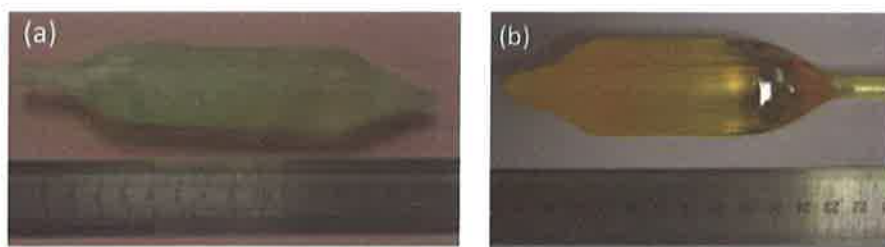


Fig. 1. LGT bulk single crystals: (a) grown under Ar atmosphere (b) grown under Ar + 0,1% O₂ atmosphere.

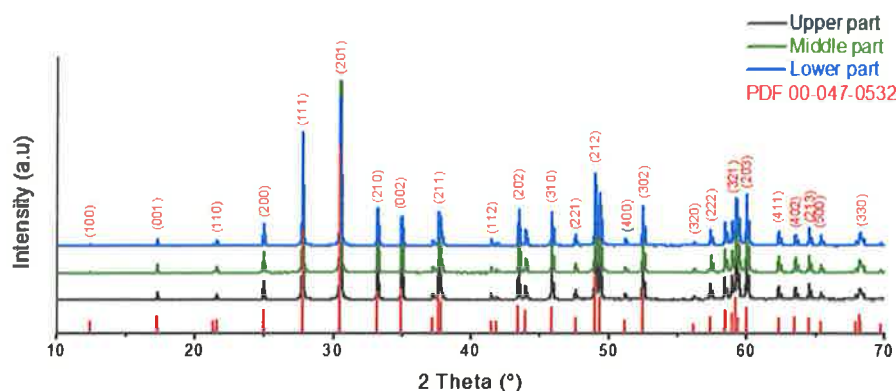


Fig. 2. Room temperature XRD patterns of different parts (top, middle, end) of the LGT crystals grown in argon-O₂ (0.1%) atmosphere.

Table 1

Lattice parameters at different position of the LGT crystal.

Crystal position	a (Å)	c (Å)
Top	8.23437(8)	5.12705(5)
Middle	8.23423(6)	5.12693(4)
End	8.23433(7)	5.12707(8)

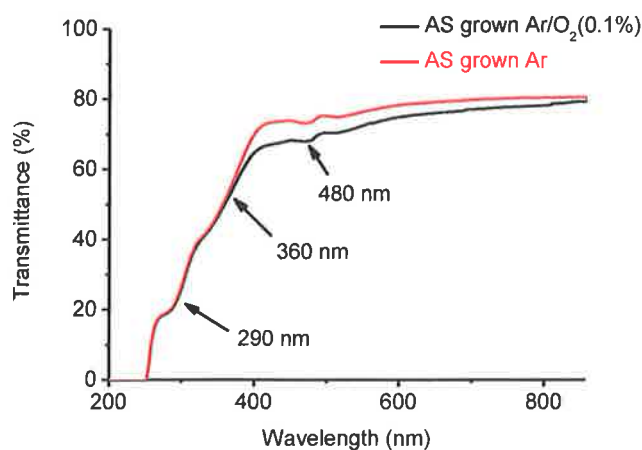


Fig. 3. Transmission spectra of LGT crystal grown under Ar/O₂ (0.1%) and Ar atmosphere.

be uniform in composition and properties. A characteristic feature of this structure is that Ga resides in three positions octahedral, (partially occupied by Ta atoms); tetrahedral; and trigonal-pyramidal. The La atoms sit in the center position of dodecahedra. There are several reports concerning the crystal growth of

LGT by micro-pulling-down method [6], by vertical Bridgman method [7], and by Czochralski method [2,4,8,9]. That the composition of LGT crystals depends significantly on preparation conditions such as a charge preparation, growth atmosphere and growth conditions. The present paper reports the growth of LGT langatate crystals by Czochralski (Cz) technique.

2. Experimental

The starting materials were powdered oxides of lanthanum, gallium and tantalum (99,99% purity). 1mol% excess of Ga₂O₃ oxide was added to compensate the losses of this material during the crystal growth process. The mixture corresponding to the composition La₃Ga_{5.5}Ta_{0.5}O₁₄ was calcined at 1350 °C for 24. The charge was melted in a cylindrical iridium crucible with internal diameter 60 mm, height 70 mm and thickness 1.5 mm. To reduce the oxidation of iridium, the furnace was purged with argon before growth. During growth, a small partial pressure of oxygen was maintained by adjusting the flow rate of argon, the pressure in the furnace was kept slightly higher than the ambient pressure in order to prevent invasion of oxygen.

Single crystals of the LGT compound were grown by the Czochralski technique. The crucible was equipped with passive iridium after heater and inductively heated by a generator (40 kW). Process control was achieved by a double-loop PID system controlling both of output power of the generator and the growth rate of the crystal to maintain high thermal stability during growth. The input signal of the control circuit was the differential increase of the weight of the growing crystal provided by an electronic balance. A CCD camera focused onto the melt surface was used to directly visualize the growth process, and to monitor the tricky process of manually making contact between the cylindrical seed and the surface of the melt during the first stage of the process. The pulling rate is varied between 1 and 3 mm/h, and the rotation rate between 10 and

30 rpm depending on crystal size. Phases identification was performed using room temperature X-ray powder diffraction with a BRUKER D8 ADVANCE diffractometer equipped with a copper anticathode operating at the $K\alpha_1$ wavelength of copper: $\text{Cu } \lambda$ ($K\alpha_1$) = 1.5406 Å, the 2θ angle varying between 10 and 70°. The lattice parameters were calculated from the XRD pattern using Si powder as an internal standard. The optical transmission of ≈ 3 mm thick plane-parallel Z-cut plates polished on both sides was measured in the range 200–1100 nm on a Perkin Elmer Lambda 900 spectrophotometer. The spectra were analyzed using Lambda 900 software.

3. Results and discussion

Typical LGT crystals weighted 250–400 g and were approximately 30–35 mm in diameter and 80–110 mm-long were grown from the melt by Czochralski technique. Depending on the pulling rate, the average total process duration including crucible installation, charge melting, the growth and crystal cooling is about two weeks. Fig. 1a shows the as grown LGT crystal under pure argon atmosphere gas. The geometry of the bottom (end) of the grown crystals and the tail length depend on the growing parameters program selected in the pulling software [10]. The profile of the grown boules is cylindrical with good symmetry and uniformity. The cylindrical profile has been adjusted by varying the crystal growth parameters, so that the heat power and pulling rate are changed. The crystals grown in pure argon atmosphere are colorless and contain some grain boundary and cracks. On another hand the crystal (Fig. 1b) grown in mixed argon- O_2 (0.1%) is transparent with orange color. No visible defects such cracks, grain boundary and inclusions were observed in the crystal grown in the mixed argon- O_2 (1%) gas atmosphere. The surface at the end of the shoulder was rather rough and this is related to the Ga vaporization which is reactive to the crystal. The coloration of LGT grown in argon- O_2 (0.1%) atmosphere confirm the impact of the oxygen on LGT crystals coloration. The utilization of mixture of oxygen gas with argon will minimize the decomposition of Ga_2O_3 and limit the evolution of the composition in the La_2O_3 - Ga_2O_3 - Ta_2O_5 ternary equilibrium diagram. If the growth atmosphere contains more than 1% oxygen, the Ir crucible was oxidized and small iridium particles were observed in the crystal surface and the solidified melt.

The room temperature powder X-ray diffraction of crashed LGT crystals was performed in order to identify the secondary phases. Samples from the beginning, middle and the end of the ingot were collected and analyzed (Fig. 2). All diffraction peaks of the XRD pattern of different parts of crystal were identified as langatate-type structure and only $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ single phase in good agreement with JCPDS file: 00-047-0532 was observed. Table 1, summarizes the lattice parameters measurement at different position of the LGT crystal grown in mixed argon/ O_2 (0.1%) gas. The average lattice parameters were around $a = 8,23431(8)$ Å and $c = 5,12701(5)$ Å, respectively. So we haven't observed strong variation of lattice parameters corresponding to variation

composition along the crystal axis which confirmed the homogeneity of the grown crystals.

The transmission spectrum of a samples taken from a crystal pulled under argon and Ar + 0.1% O_2 atmosphere are shown in Fig. 3. Three absorption bands around 290, 360 and 480 nm are observed. The band at 480 nm is most intense in the sample grown in argon atmosphere corresponding to the higher transmission. According to this results, growing crystal in argon atmosphere gives rise to the increase of oxygen vacancies. The variation of the color from colorless to orange is due to the different concentration of oxygen vacancies. According to Buzanov et al. [11] it is most likely that the formation of color centers in LGT crystals involves not only oxygen vacancies but also the processes related to the cation sublattice (formation of cation vacancies and charge exchange in cations). This band may be due to charge transfer of Ta^{5+} to Ta^{3+} , that is, if the growth atmosphere contain oxygen-rich contents, few of Ta^{5+} cations turn to Ta^{3+} cations which create the color of crystal and the band around 480 nm, alternatively, without oxygen no Ta^{3+} cations in the crystal, thus the crystal is colorless and the band disappears.

4. Conclusions

LGT single crystal were successfully grown by Czochralski technique in argon and argon/ O_2 (0.1%) atmosphere. The atmosphere affect the crystal quality. Growing crystals in mixed argon/ O_2 (0.1%) allows the obtainment of orange high quality LGT single crystal without macroscopic defects such cracks and inclusions. Using inert argon atmosphere, the crystals were colorless and contain visible macroscopic defects such cracks and inclusions. The difference of the color from colorless to the orange is attributed to the gas growth atmosphere because of the concentration of oxygen vacancies.

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