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Growth of piezoelectric crystals by Czochralski method

D. COCHET-MUCHY

Crismatec, Usine de Gières, 2 rue des Essarts, 38610 Gières, France

Abstract : The Czochralski method is one of the most widely used industrial technique to grow single-crystals, since it applies to a very large range of compounds, such as semiconductors, oxides, fluorides, etc... Many exhibit piezoelectric properties and some of them find applications in Surface-Acoustic-Waves or Bulk-Acoustic-Waves devices. That explains the large amount of work made on the development of the corresponding growth processes and the high levels of production achieved in the world today. We will review the basic principle, main features and parameters of the Czochralski method, and the configuration which is used by Crismatec. Then we will discuss in more details the growth parameters for the two piezoelectric crystals that we are producing, LiNbO_3 and LiTaO_3 , and present the state-of-the-art for both crystals : pulling axis, diameter and quality. We will also discuss some preliminary results on the growth of the new $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ langasite crystal.

1. INTRODUCTION

The need for piezoelectric crystals has been raising since around 20 years due to their use in several mass-produced electronic equipments : TV, watches, radio receivers and communication systems, etc... Among their advantages, they allow low-cost, compact-size and reliable devices to be manufactured, such as frequency filters, resonators and oscillators. Mainly the crystals having the highest electro-mechanical coupling coefficient and the lowest temperature coefficient are interesting candidates. The materials which are known to have one of these properties or which exhibit a good compromise [1] are shown in Table I.

The growth of these compounds as large single-crystals is the first requisite to their use by the electronic manufacturers. For this reason, the growth techniques have been widely investigated, and, when possible, the Czochralski technique was used as it is one of the most convenient method for industrial production. Undoubtedly, the best accomplishments of these efforts towards the growth of piezoelectric crystals by Czochralski method were obtained with LiNbO_3 and LiTaO_3 . They are now on a large scale produced and processed into wafers for Surface-Acoustic-Waves (SAW) devices, mainly in Japan, but also in US and Europe. More recently it appeared that the promising $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ could also be grown with good results [2].

After a discussion of the main issues associated with the Czochralski method, we will focus on our experience in growing these piezoelectric crystals.

Table I
Characteristics of some piezoelectric crystals

Crystal	Cut-plane	Electromechanical coupling coefficient K^2 (%)	Temperature coefficient (ppm/°C)	Propagation mode	Growth method
SiO ₂	ST AT	0,15 0,65	~ 0 ~ 0	SAW BAW	hydrothermal
AlPO ₄	170° rotated X	0,5	~ 0	SAW	"
Li ₂ B ₄ O ₇	X	1,0	~ 0	"	Czochralski
LiNbO ₃	128° rotated Y	5,5	- 73	"	"
LiTaO ₃	X	0,75	- 18	"	"
Pb ₂ KNb ₅ O ₁₅	X	2,0	~ 0	"	"
La ₃ Ga ₅ SiO ₁₄	~ Y	2,5	~ 0	BAW	"

2. THE CZOCHRALSKI METHOD

2.1 Basic principe

The Czochralski method is a crystal pulling technique from the melt. The process is based on a liquid-solid phase transition driven by a seed crystal in contact with the melt. Basically, the seed is to be considered as a heat sink, by which the latent heat of solidification escapes, and as a nucleation center : the solidified fraction at the surface of the seed will reproduce its single-crystal structure. By raising the seed slowly, a crystal is "pulled" from the melt. Decreasing the melt temperature makes the crystal diameter increasing and vice versa. A sketch of this process is shown in Fig. 1.

2.2 Limitations

2.2.1. Technological considerations

When bringing this relatively simple process into operation, one have to solve several major technological problems :

- (1) finding a crucible which is compatible with the melt to crystallize (higher melting point and chemical stability) and the surrounding atmosphere.
- (2) selecting insulator materials acting as a thermal barrier all around the crucible and controlling the thermal field in the crystallization area.
- (3) finding a heating source compatible with the environment described above.

(4) controlling the diameter of the growing crystal.

2.2.1.1. Crucible

For oxide crystals, noble metals give the best compromise between chemical stability and mechanical strength. Platinum, Platinum-based or Iridium crucibles are used, depending on the melting point of the oxides (T_m). When a choice is possible between several crucible materials, cost is generally the key factor. Total cost includes the raw metal, the manufacturing of the crucible, the metal loss and repairing during the lifetime of the crucible. Strong variations of some of these elements occurs from time to time and can change the optimum choice. Table II shows the possible crucibles for the piezoelectric crystals discussed in this article.

Table II
Crucibles used for some piezoelectric oxides

Oxide	T_m (°)	Crucible	T_m (°C)	Atmosphere
LiNbO ₃	1253	Platinum	1769	preferably oxidizing
LiTaO ₃	1650	Iridium Platinum-Rhodium (~ 30 %)	2454 1930	neutral preferably neutral
La ₃ Ga ₅ SiO ₁₄	1470	Platinum	1769	preferably neutral

The choice of the pulling atmosphere is a compromise between what is preferable for the crystal and what is preferable for the crucible. According to the crystal chemistry, it is of course preferable to pull an oxide under an oxidizing atmosphere, but it is not a prerequisite, since oxygen vacancies which can be formed during pulling under neutral atmosphere are generally removed with an oxidizing post-annealing. Often, either problems such as metallic impurities, inclusions into the crystal (e.g. Rh, see [3]) or the stability of the crucible materials at the operating temperature determined the atmosphere. When iridium crucibles are used, a neutral atmosphere is required to avoid the volatilization of IrO₂.

2.2.1.2. Insulators

The refractory materials which surround the crucible are commonly alumina-silica, pure alumina or zirconia ceramics, depending on the operating temperature. The design of these ceramics is a major feature of the pulling process for a given crystal, since it determines the thermal gradients (see 2.4.3).

2.2.1.3. Heating source

There are two ways of generating the heat to melt the compound inside the crucible : resistance heating and induction heating.

Resistance heating is commonly used up to ~ 1400°C with the advantages of a very universal heating technique : low-cost, reliability and standardization, both for the heating elements and the power control equipments. In addition the distribution of the hot zones, easily

controlled, enables to get high uniformity of the thermal field (i.e. low gradients).

Induction heating uses a r.f. generator to generate r.f. currents into a coil surrounding the crucible, which acts as a susceptor. Obviously, the crucible must be conductive, which is the case with noble metals. Heat is generated into a "skin depth" at the outer surface of the crucible. This makes the thermal field control more difficult. In order to get the desired gradients, one should pay more attention to the design of the ceramics and, sometimes, extra-heaters ("after-heater") must be introduced, such as secondary metallic susceptors (or reflectors) over the crucible, or resistance heated zones. The position of the crucible with respect to the coil also plays a significant role to (see 2.4.3).

Contrary to the resistance heating, induction heating is not temperature limited. Moreover, the environment of the crucible is preserved very clean. Therefore, crystals with very high level of purity can be produced.

2.2.1.4. Diameter control

The diameter control is required to obtain crystals as close to the dimensions of the final products as possible. We said above that the diameter fluctuations are due to variations of the melt temperature. The way of correcting the melt temperature is obviously to adjust the power of the heating source. Theoretically, with a correctly designed pulling furnace, no variation of the heating power gives no variation of the diameter. In practice, this situation is ideal, and designers should try to reach it, but, as usual in reality, full stability does not exist. Also, over a long time period, a constant heating power will make the melt temperature regularly increase (i.e. the diameter decrease) since the quantity of compound to be kept molten decreases while crystallization is running.

Measuring the melt temperature and using a feedback regulation system to keep up a constant temperature (setpoint) is a way to control the diameter. However, this method, easy to apply in the case of resistance furnace, is not the most routinely used. One generally prefers control systems which take directly into account a diameter setpoint. Such systems are using optical sensing or weighing techniques. The latter is nowadays the most commonly used as it is rather simple to put in operation and reliable whatever the pulling configuration is. For the weighing technique, a load cell is used to measure the weight of the crystal growing, or of the crucible emptying, at regular time period. From these data, a growth rate is permanently calculated and adjusted. Under the assumption of steady growth conditions, one can also calculate a growth rate setpoint from the diameter setpoint :

growth rate (gr/hr) =

$$(1) \quad \text{pull rate (cm/hr)} \times \frac{\pi \cdot d_m \cdot d_s \cdot \varnothing_{\text{crucible}}^2 \cdot \varnothing_{\text{crystal}}^2}{4 (d_m \cdot \varnothing_{\text{crucible}}^2 - d_s \cdot \varnothing_{\text{crystal}}^2)}$$

where	$\varnothing_{\text{crystal}}$	= crystal diameter setpoint	(cm)
	$\varnothing_{\text{crucible}}$	= crucible diameter	(cm)
	d_s	= density of the solid crystal	(gr/cm ³)
	d_m	= density of the molten compound	(gr/cm ³)

The difference between the real growth rate coming from weighing and the growth rate setpoint calculated from (1) gives an error signal from which the heating power can be regulated. The crystal weighing method is more difficult to implement than the crucible weighing one, because the load cell must be located at the end of the translating and rotating seed-holder, but it gives the best sensitivity.

2.2.2. Materials considerations

The Czochralski method is convenient for all compounds having a congruent melting, a low vapor pressure and exhibiting no structural change between the solidification temperature and the room temperature.

The congruent melting means that the liquidus and solidus curves merge on a single-point on the temperature-composition phase diagram (fig. 2). The composition corresponding to this point is named the congruent composition. Its determination is of high importance, in order to pull homogeneous crystal. In case the melt does not have the congruent composition, the crystal composition will vary from the top to the end, as indicated on fig. 2.

Usually the congruent composition is near to, but not identical to the stoichiometric composition given by the usual chemical formula of the compound.

A low vapor pressure means that the liquid remains stable over the time period required for the growth. Precisely, the composition should not vary due to preferential evaporation of one part of the compound.

2.2.3. Geometrical considerations

One limitation of the crystal size comes from the dimensional limitation of the crucible.

A convenient ratio between the crucible diameter and the crystal diameter is $\varnothing_{\text{crucible}}/\varnothing_{\text{crystal}} = 2$. However, for cost-effective reasons, one should generally try to lower this ratio, which makes the pulling process more challenging.

The crystal length is also limited, the solidified fraction of the starting melt being always less than 1. A reason for this limitation is the melt level drop while crystallization runs. It affects the thermal gradient at the solid-liquid interface in such a way that spiral growth may occur (fig. 3) and, generally speaking, the single-crystal perfection decreases. This risk is higher with $\varnothing_{\text{crucible}}/\varnothing_{\text{crystal}} < 2$, as the melt level drops quicker. A way of increasing the solidified fraction is to use a crucible lift. The position of the crucible can be adjusted during the growth period so that the position of the solid-liquid interface and the gradient remain constant.

The problem of crystal perfection is or is not an issue according to the applications. For instance, for piezoelectric purposes, defects are much more permitted than for optical purposes. Thus, longer crystals can be pulled decreasing significantly the cost price of the material.

2.3 Advantages

Despite of the limitations described in the previous section, we have shown that many difficulties in operating the Czochralski process can be overcome. One can emphasize that the Czochralski pulling is one of

the most versatile, reliable and productive crystallization technique. Large size cylindrical crystals with a very high level of perfection can be manufactured on an industrial basis. Examples of routinely produced materials include zero dislocation $\varnothing$ 200 mm silicon, zero dislocation $\varnothing$ 100 mm $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) and $L = 200$ mm $\text{Nd}^{3+} : \text{Y}_3\text{Al}_5\text{O}_{12}$ (Nd:YAG) laser crystal, with a tenth of the wavelength wavefront distortion on a single pass...

2.4 Process parameters

2.4.1. Pull rate

The pull rate is an accurately controlled variable as it is the velocity at which the seed is lifted up. Through diameter control, the growth rate is related to the pull rate by equation (1) (When the crucible lifts, the equation should be modified for that). Cost constraints dictate that the growth rate should be as high as possible. The absolute limit is given by the capacity of the system to take out the latent heat of solidification generated at the growth interface. Another limit may exist if compositional changes happen during solidification as it is the case with a non-congruent composition, or if an impurity with a distribution coefficient different from 1 is in or added to the melt (dopant). Beyond these pulling limitations, many macroscopical defects may appear into the crystal because of local refusions.

For piezoelectric crystals, which are usually pulled at congruent composition and without any dopant, the pull rate is the highest compatible with the required crystal quality, generally ≈ 0.5 cm/hr.

2.4.2. Rotation rate

Even so all the elements of a Czochralski furnace are designed with an axis of symmetry being the seed axis, there may exist a small misalignment between the two axis, or some asymmetry in the temperature distribution. At first, one rotates the seed to smooth these asymmetries and prevent disturbances of the geometry and of the stress distribution in the crystal. Secondary, rotation creates a forced convection flow opposite to the natural convection flow of the liquid in the crucible. The natural flow is due to density gradients which are themselves related to the distribution of temperature (higher on the edge of the crucible) and it makes the liquid/solid interface convex. As a growth with a planar interface is usually preferred, one can adjust the rotation rate to compensate both natural and forced convection flows. Depending on the crystal diameter and the configuration, rotation rates range from 5 to 40 rpm typically.

2.4.3. Thermal gradients

The existence of a non-uniform temperature distribution inside and above the crucible is an absolute requisite to the crystallization process : the temperatures in the liquid are obviously above the melting point, and those in the crystal below, the interface being at T_m . Despite of this requisite, the gradients have also some drawbacks. In the liquid, they lead to convection movements which may generate quick changes of temperature in the interface region and, therefore, growth rate variations. Such variations induce small lattice parameter variations into the crystal (called striations) especially if the melt is not perfectly congruent. Other structure defects can also appear : dislocations, subgrain boundaries. In the crystal, thermal stresses

caused by gradients, if above the elastic limit at any temperature between T_m and room temperature, can originate structure defects or even cracking.

The challenge of the crystal grower is to get a thermal profile which is a good compromise between the above mentioned requisite and drawbacks. Reasons of the difficulty to reach the optimized gradients stand from the lack of prediction models and the few possibilities of measurements. One usually gives a description of the thermal profile by measuring the axial vertical gradient with a thermocouple. Fig. 4 shows an example corresponding to a pulling configuration used for LiTaO_3 , for various crucible versus r.f. coil positions. Though it is a very limited handling of the thermal gradients, this method has proved to be useful in many cases.

2.5 The Crismatec growth station

The standard Crismatec growth station is shown on fig. 5. One can see from the left to the right : the r.f. generator for induction heating, the water-cooled walls of the furnace with the pulling head above, and the control bay. The pulling head groups the weighing and mechanical functions, except the crucible lift. One find on it a direct-drive torque motor which rotates a precision lead-screw to give the translation movement. This translation movement is communicated to the seed through a mechanical sub-assembly which, from the seed to the pulling head, includes : a seed-holder, an alumina rod, a load cell and a direct-drive torque motor for rotation. The control bay consists of a computer for weight signal acquisition and r.f. power regulation (diameter control), and the motors power-supply. This Czochralski growth station is suitable to all types of oxide pulling and it allows crystals of large size and high quality to be grown, including piezoelectric, when correct process parameters are used.

3. GROWTH OF PIEZOELECTRIC CRYSTALS

Crismatec has experiences in growing LiNbO_3 and LiTaO_3 for piezoelectric uses, and is now developing the Czochralski process to pull the promising $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (langasite). In such crystal growth developments, one should first take into account the physicochemical features of the compounds (see 2.2.3.), with emphasis on the following points : crystal structure, congruent composition, melting temperature and thermal expansion coefficients.

3.1 Physicochemical features

3.1.1. LiNbO_3 and LiTaO_3

Lithium niobate and lithium tantalate are two ferroelectric compounds studied since 1949 [4], having a rhombohedral structure. Below the Curie temperature (T_c), their structure belongs to the space-group $R3c$. It is build on a succession of oxygen octahedra along the three-fold axis, containing the cations in the following sequence : Li, Nb or Ta, an empty octahedron. The origin of the ferroelectricity lies in the displacement of the cations from the center of the octahedra. Above the Curie point, in the paraelectric state, the cations move to the center of the octahedra, and the structure becomes centrosymmetric ($R\bar{3}c$).

This description of the atomic arrangements corresponds to the stoichiometric compounds, LiNbO_3 or LiTaO_3 , but a large solid solution range exists for both phases. The maximum range for the Li_2O content is

45-51 % for LiNbO_3 near 1200°C, and the same for LiTaO_3 near 1600°C. As indicated previously, the crystal grower should use the composition which, among these ones, melts congruently and gives homogeneous crystals. The easiest way to check the homogeneity is to use the strong and linear variation of the Curie temperature with the composition of the LiNbO_3 or LiTaO_3 crystals. Those having homogeneous T_c from the top to the end are grown at the congruent composition. Surprisingly, several different congruent compositions have been reported in the literature for both compounds [5-8]. We explain these discrepancies by the multiple potential errors when weighing the raw materials for the melt preparation. The usual raw materials are Li_2CO_3 and Nb_2O_5 or Ta_2O_5 , which may have large moisture contents, variable elemental isotopic ratios (Li^6 versus Li^7) and also variable stoichiometries (Li_2O versus CO_2). As a consequence, the crystal grower should have its own equipment to measure the T_c , so as to check by himself the congruency of the composition he used.

Table III summarizes the relevant data in view of crystal growth. When necessary, we give the average figures of the several published results.

A consequence of the strongly anisotropic crystal structure of LiNbO_3 and LiTaO_3 is a strongly different behavior upon crystallization when different pulling axis (i.e. seed axis) are used. Therefore, one should consider the crystal growth operations for different pulling axis as separate processes.

The anisotropy of the thermal expansion coefficients creates high thermal stresses during growth and cooling of the crystals. Generally speaking, one should use very low thermal gradients to prevent the crystals from cracking and having too many structure defects. Even like so, zero dislocations LiNbO_3 can not be achieved and subgrain-free crystals are considered as the top quality. The issue of the thermal gradients is more or less tight depending on the pulling axis.

3.1.2. $\text{La}_3\text{Ga}_5\text{SiO}_{14}$

Considerably less data are available on $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, since it was synthesized for the first time during the 80s, in the former Soviet Union. Table III summarizes the data available from [2].

3.2 Crystal growth

3.2.1. LiNbO_3

Up to $\varnothing$ 80 mm crystals have been grown by Crismatec along the $[12.0]$, 128° rotated $[12.0]$ and $[00.1]$ axis. These pulling axis have been chosen because they correspond to the normal direction of the cut plane used for the Surface-Acoustic-Waves substrates. For cost reasons, one should obviously cut the wafers perpendicularly to the axis of the cylinder, i.e. pulling axis. The available final products are $\varnothing$ 76.2 mm wafers (3 inches), respectively Y-cut, 128° rotated Y-cut and Z-cut.

For these SAW-wafers, raw materials of 99.95 % purity are largely enough. Li_2CO_3 and Nb_2O_5 are mixed together and prereacted during several hours at high temperature for solid-state formation of polycrystalline LiNbO_3 . This prereacted powder is used to fill the crucible and pull the crystal. The vertical gradient just above the liquid surface is around $15^\circ/\text{cm}$.

Table III
Physicochemical features of LiNbO_3 , LiTaO_3 and $\text{La}_3\text{Ga}_5\text{SiO}_{14}$

		LiNbO_3	LiTaO_3	$\text{La}_3\text{Ga}_5\text{SiO}_{14}$
Crystal structure		Rhombohedral	Rhombohedral	Trigonal
Lattice parameters (nm) at RT (hexagonal)	a	0.5147	0.5154	0.8162
	c	1.3856	1.3782	0.5087
thermal expansion coefficients at RT	a-axis	14.1×10^{-6}	16.1×10^{-6}	-
	c-axis	6.0×10^{-6}	4.1×10^{-6}	-
melting point	(°C)	1253	1650	≈ 1470
congruent composition		48.5 % Li_2O	48.75 % Li_2O	$\text{La}_3\text{Ga}_5\text{SiO}_{14}$
Curie point for the congruent composition	(°C)	1143	610	-

Once the good thermal profile is obtained, the following requisite for succeeding the growth of LiNbO_3 is to avoid the formation of extended structure defects like twins. Many attention should be paid to the quality of the seed and to the temperature of the melt when dipping the seed into the melt, since twinning very often occurs at the early stage of the crystallization. For that reason, the LiNbO_3 furnace includes a window in the ceramics assembly to see every details of the process. When it occurs, twinning is easily visible on the shoulder of the crystal going from the seed diameter to the final diameter. If so, the shoulder is remelted and a new dipping is made.

After growth, cooling of the crystal down to room temperature is completed within around 30 hours, in a resistance after-heater with nearly zero thermal gradients.

The typical crystal quality is shown by X-ray topography on fig. 6. Only a few small-angle misorientations are visible.

To check the homogeneity of crystals, we have developed an equipment based on the measurement of the ϵ_{33} dielectric constant. ϵ_{33} passes through a sharp maximum at the Curie point [9]. By measuring the dielectric capacitance of a conveniently oriented sample placed in a furnace, between two platinum electrodes, one can follow the variation of ϵ_{33} with the temperature and make T_c determinations. A plot of the measured capacitance versus temperature is shown on fig. 7.

3.2.2. LiTaO_3

We have succeeded in growing $\varnothing$ 105 mm and $\varnothing$ 80 mm crystals along the [12.0] and [10.0] axis, for Y-cut and X-cut, $\varnothing$ 100 mm and $\varnothing$ 76.2 mm

wafers, respectively. The process parameters are almost the same than for LiNbO_3 , with a vertical gradient of $15^\circ/\text{cm}$ above the melt surface (see fig. 4). A difference is that, with diameter as large as $\varnothing 105$ mm, the melt level drop more rapidly into the crucible, and the gradient tends to fall down. In that situation, spiral growth may occur (see fig. 3). We suppress this tendency by using the crucible lift which help to keep the gradient constant (fig. 4).

Fig. 8 shows a $\varnothing 105$ mm x 75 mm SAW-grade crystal pulled along the $[10.0]$ axis, together with a processed wafer.

3.2.3. $\text{La}_3\text{Ga}_5\text{SiO}_{14}$

Crystals oriented along $[00.1]$ have been grown with satisfactory results. The size reaches $\varnothing 60$ mm x 140 mm and the quality, as seen by visual inspection, is crack-free and inclusion-free. More detailed investigations have been performed on this material and the results are reported at this conference [10]. Fig. 9 shows one of our $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystals with a flat interface. As indicated in [2], the $[00.1]$ crystals are strongly faceted with an hexagonal shape.

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Fig. 1 - The Czochralski process

Fig. 2 - Temperature-composition phase diagram showing a binary compound with congruent melting

Fig. 3 - As-grown $\text{Ø } 105 \text{ mm LiTaO}_3$ crystals - Left : without the use of the crucible lift - Right : with it

Fig. 4 - Axial vertical gradient measured with a thermocouple in the LiTaO_3 pulling configuration. x = crucible versus r.f. coil position

Fig. 5 - The standard Crismatec growth station

Fig. 6 - X-ray topography on a 3 in. Z-cut LiNbO_3 wafer

Fig. 7 - Variations of the capacitance of LiNbO_3 along c -axis on heating and cooling. Peak at T_c

Fig. 8 - $\varnothing 105$ mm $[10.0]$ LiTaO_3 crystal and 4 in. processed wafer

Fig. 9 - $\varnothing 60$ mm $[00.1]$ $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ crystal