Czochralski growth of oxides

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Abstract

The first oxide grown using the Czochralski technique (CaWO4) was in 1960. Since that time, the Czochralski technique has become the method of choice for the growth and production of many bulk oxide materials used in the electronics and optical industries, e.g. lasers, substrates, scintillators, nonlinear and passive optical devices. This paper will trace the development of the initial process from its beginnings in the early 1960’s to its present state and highlight some of the significant advances over the years that have allowed the oxide crystal growth industry to develop. It will conclude with an assessment of the current status and outline directions for further research and development.

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1. Introduction

The use of the Czochralski [1] process to grow semiconductor crystals (Si and Ge) was well established by the mid-1950s [2–4]. The first reported oxide material grown using the Czochralski technique (CaWO4) was in 1960 [5]. This initial paper was followed quickly by numerous other papers dealing with the growth of a variety of oxide materials such as LiNbO3 [6], LiTaO3 [7], BGO [8], YAG (Y₃Al₅O₁₂) [9], Nd:YAG [10] and Al₂O₃ (Sapphire) [11,12]. By the mid-1960s, the Czochralski process for the growth of oxide materials was becoming well established. Today, the Czochralski technique, also known as crystal pulling, has become the method of choice for the growth and production of many bulk oxide materials used as components for the electronics and optical industries, e.g. lasers, substrates, scintillators, nonlinear and passive optical devices.

To achieve this progress, numerous advances to the understanding of the role that liquid and crystal composition, interface shape/fluid dynamics, thermal geometry and puller design have on the quality of the resulting crystal had to be determined. This paper will trace the development of the initial process from its beginnings in the early 1960s to its present state and highlight some of the significant advances over the years that have allowed the oxide crystal growth industry to develop so that today the size and variety of materials has expanded to include 125 to 150 mm diameter oxide single crystal that can weigh as much as 50 kg. It will then conclude with an assessment of the current status and outline directions for further research and development.

2. Crystal composition

One of the first problems encountered during the growth of various crystals was that the...
properties were found to vary through the crystal length as well as from crystal to crystal and from one researcher to another. It was always assumed that the composition of these oxide materials was stoichiometric; hence, the initial starting melt composition was also stoichiometric. The first oxide material identified to show variations in properties due to stoichiometric variations of the liquid was LiTaO₃ [13]. Fay et al. [14] found similar results for LiNbO₃ and that the Curie temperature and birefringence would vary over a wide range of starting melt compositions. A detailed investigation of the phase diagram in the region of the stoichiometric composition for LiNbO₃ by Carruthers et al. [15] showed that the congruently melting composition was 48.6% Li₂O and crystals grown from this melt composition showed much lower variations in the optical properties. The phase diagram (Fig. 1) shows the shift in the composition in the Li₂O–Nb₂O₅ phase diagram from stoichiometric to congruent [16]. Using a similar approach (Curie temperature vs. composition) for LiTaO₃, Miyazawa and Iwasaki [17] showed that the congruently melting composition was also nonstoichiometric. Up until the early 1970s, these two materials were believed to be the only examples of an oxide material that had a nonstoichiometric, congruently melting composition.

With the discovery in the early 1970s that rare-earth iron garnets had sufficient growth-induced anisotropy to support small, circular magnetic domains (magnetic bubbles) and that thin films of these materials could be grown using a liquid phase epitaxy (LPE) technique [18], the need for a suitable substrate for the deposition of thin films of these materials became apparent. The rare-earth gallium garnets provided an excellent lattice match for the various rare earth iron garnet films and therefore became the material of choice for substrate use [18]. The first gallium garnet that was grown for substrate use was GGG (Gd₃Ga₅O₁₂). When the lattice parameter of the Czochralski grown material was compared to that of flux grown material, a significant difference was found (12.376 Å for the flux material vs. 12.384 Å for the Czochralski grown material) [20]. Brandle and Barns [19] showed that as the ionic radius of the rare-earth ion decreased, the departure of the lattice parameter for flux grown material vs. Czochralski grown material increased (Fig. 2). Analysis of the Czochralski grown material showed that it contained an excess of rare earth that was substituting on the octahedral site in the garnet structure and that the congruent melting composition was gradually shifting to the rare-earth rich region of the phase diagram as the ionic size of the rare-earth ion decreased (Fig. 3) [21]. The actual congruently melting composition is represented by \( \{\text{RE}\}_3\{\text{Ga}_{2-x}\text{RE}_x\}\text{Ga}_3\text{O}_{12} \) where
} signifies the dodecahedral site, [] signifies the octahedral site, and () signifies the tetrahedral site in the garnet structure. Thus, this class of materials became the second known group to exhibit nonstoichiometric behavior at its melting point.

Another example of a further shift from the stoichiometric composition is given by GSGG (Gd$_3$Sc$_2$Ga$_3$O$_{12}$). In the mid-1980s, this material was of interest as a laser host for Nd and Cr; however, growth striations associated with optical variations in the material limited its use. Fratello et al. [22] showed that the congruent composition of GSGG was {Gd$_{2.957}$Sc$_{0.043}$}[Sc$_{1.862}$Ga$_{0.138}$](-Ga)$_3$O$_{12}$. As one can see, this material shows that multiple substitutions can occur on the various garnet sites. Fig. 4 shows a section of the phase diagram in the region of the congruent melting composition [22] whereas Fig. 5 shows a comparison of the growth striations in a crystal grown from a stoichiometric melt composition and that grown using a congruent melt composition. Similar results have been shown for other Sc-based garnets [23]. Although these materials are still garnets, they clearly show that as the complexity of the cation substitution increases, the probability for multiple substitutions on various sites also increases and hence, the shift from a stoichiometric melting composition to a congruently melting nonstoichiometric composition is more likely to occur.

Other examples of nonstoichiometry continue to be reported in the literature [24–26]. Unlike what was believed in the 1960s and 1970s, a nonstoichiometric, congruently melting composition appears to be the rule rather than the exception and very few oxide materials exist as line compounds. Thus today, our current understanding of composition is:

- For most oxides, the congruently melting composition most probably is not the stoichiometric composition.
- The more complex the crystal structure, the higher the probability for nonstoichiometry to exist at the melting point.
- Materials with a crystal structure that have similar cation coordination sites are most likely to show nonstoichiometry at its melting point.
- Only simple oxides such as Al$_2$O$_3$ tend to have congruent melting composition that is stoichiometric.

3. Interface shape/fluid dynamics

With the growth of oxide materials in the early 1960s, very little attention was paid to the shape of
the growth interface and its influence on the quality of the resulting crystal. The growth systems were small and the crystals usually were 1–2 cm in diameter. Given such small growth systems, most early crystals were grown with a high thermal gradient and the shape of the growth interface was conical. Furthermore, it was assumed that a conical interface was necessary to maintain stable growth and that a flat or convex interface shape would result in unstable growth. One of the first attempts to modify the shape of the growth interface was by Cockayne et al. [27]. They showed that under the proper conditions, the shape of the growth interface could be controlled by the crystal rotation rate. At sufficiently high rotation rates (150 rpm), the normally convex interface in YAG could become very shallow. Using a similar approach, Brandle and Valentino [19] were able to grow GGG (Gd₃Ga₅O₁₂) with a flat interface and maintain stable growth conditions.

For GGG, the main purpose of changing the interface shape was to reduce or eliminate the facets and the strain associated with these facets that normally form on the growth interface as well as minimize growth striations. Since facet strain and growth striations were replicated by the epitaxial iron garnet film [28,29], their reduction or elimination was necessary to produce more uniform magnetic garnet films. By changing the shape of the growth interface, the position of the facets on the growth interface is changed thereby moving them from the central section of the crystal to the outside surface. In this manner, the strain associated with the facets can be removed during the fabrication step yielding a strain free central section that can be processed into substrates or optical parts. Fig. 6 is a schematic of the position of the facets on the growth interface of a garnet crystal at a slow and fast rotation rate.

For a given thermal environment, changing the shape of the growth interface through varying the rotation rate of the crystal implies one is altering the fluid flow within the crucible. Carruthers [30] and Carruthers and Nassau [31] were among the first to simulate the fluid hydrodynamics of a Czochralski growth system. By the early to mid-1970s, numerous papers had been published dealing with the influence of the crystal rotation rate on the fluid flow during the growth process and its impact on the crystal interface shape [32–36]. Fig. 7 shows schematics of typical flows observed in an oxide melt at various crystal rotation rates [37]. This type of surface structure as illustrated in Fig. 7 has been studied extensively in the Bi₁₂SiO₂₀ system [38]. The outer annular area consists of fluid flow driven by natural convective forces of the heated fluid whereas the main driving force for the inner area is forced convection driven by the rotating crystal. Fig. 8 shows an example of the sudden melt back of the conical growth interface of GGG that is produced by the reversal of the fluid flow as a result of the crystal rotation [39]. Also, visible at the top of the crystal in Fig. 8 is the facet strain associated with the formation of the (211) facets that form on the conical portion of the growth interface as illustrated in Fig. 6.
Fig. 6. Change of the position of interface facets in ⟨1 1 1⟩ grown garnet as a function of interface shape (a) conical (b) flat.

Fig. 7. Surface and bulk flow observed in water/glycerin simulations (a) slow rotation (b) moderate rotation (c) fast rotation. From Brandle, Ref. [37].
Another factor that has been shown to have a pronounced effect on the fluid flow is the liquid depth within the crucible. By placing baffles within the liquid, effectively changing the liquid depth and disrupting the natural convection, Whifflin and Brice [40] have pointed out that the ratio of liquid depth to crucible height has a most pronounced effect on the thermal oscillations in the liquid. Their experiments in zinc tunstate melts in the late 1960s and early 1970s showed that the melt stability is increased when a baffle in positioned within the liquid or as the liquid level within a given crucible size is reduced; however, growth under these conditions becomes more difficult. Numerous researchers [32,33,36,41] have found that using a crucible with approximately a 1:1 aspect ratio, i.e. crucible diameter to crucible height provides the best compromise between melt stability and growth difficulty.

Given the success of the earlier fluid flow simulations, numerous authors [42–45] simulated the flow that resulted in the rapid interface melt back and transition from a conical to flat interface with the general conclusion that such interface transitions were the result of going from natural convection to forced convection under the region of the rotating crystal interface.

By the mid-1970s, numerical simulations of fluid dynamics became practical and as computational power increased so has the complexity of the models. Kobayashi [46] was among the first to examine the features of forced convection generated by a rotating crystal or crucible such as seen in a Czochralski growth configuration. A more recent example of modeling effort is that of Derby and Brown [47]. This trend has continued and been quite successful for Si-based systems and has been successful in explaining the general behavior of molten oxide-based systems.

Also, included in the many factors that influence the interface shape is the composition of the growth atmosphere. By changing the O₂ partial pressure, one can vary the concentration of various oxide species in the liquid and hence change some of the liquid properties such as viscosity and surface tension. Fig. 9 gives an example of the change in interface shape of Al₂O₃ as a function of O₂ partial pressure [39]. In this case, it is believed that by changing the O₂ partial pressure, the equilibrium concentration between Al₂O₃ and Al₂O in the liquid is shifted resulting in a change in the surface tension of the melt and perhaps its viscosity. This change in fluid properties then impacts the fluid flow within the crucible and hence the interface shape.

Based on the information gathered over the past 30 years, our current understanding is:

1. Hydrodynamics and fluid properties are crucial elements in defining the interface shape and crystal quality.
2. The interface shape can be altered by changing the thermal environment, growth atmosphere and/or the crystal rotation/growth rates.
3. The interface shape can be controlled and tailored to the end use of the crystal.

4. Diameter control

Of the many mechanical advances that were made in the growth system and furnace construction for oxide materials, the one that has made the most contribution to the growth and quality of oxides has been the development of a useful method for active control of the diameter of the growing crystal. Initial control systems were based solely on control of the power input based on the assumption that if the power input into the furnace was constant then the resulting temperature during growth would also be constant and hence the diameter would also be constant. For the early low melting oxides such as CaWO₄, a thermocouple was placed in the liquid and provided the signal for diameter control [48]. A schematic of a furnace using this form of control is shown in Fig. 10 whereas an actual photo of the growing crystal is shown in Fig. 11. Note that the furnace assembly is very open and thus the crystal is growing in a very high thermal gradient. Diameter control was achieved by manually changing the temperature control set point based on visual observations of the change in diameter in the crystal. This early system of diameter control had the advantage that the control circuit was simple and based on readily available instrumentation. However, its disadvantages were many:

1. The power had to be controlled manually requiring constant operator attention.
2. Diameter control was based on visual observation of the growing crystal, thus the crystal/liquid boundary had to be visible. This in turn required a growth furnace in which the crystal/liquid boundary was easily visible throughout the entire growth process.
3. Power/temperature corrections for diameter control were made after a visible change in diameter. This in turn required a skilled operator to detect these changes as early as possible.

4. Because each type of crystal had different thermal properties, it behaved differently during growth and thus many growth tests were required to gather the necessary data to produce a crystal of reasonably uniform diameter, i.e., to predict the temperature changes necessary to compensate for the changing thermal environment during crystal growth.

5. For the higher melting oxides, a means, other than a thermocouple had to be used for power control. This required either RF power pickup loops or such devices as optical pyrometers focused on the bottom of the crucible.

Examples of early crystals grown using these types of control are shown in Fig. 12.

With the demand for larger crystals and the need for higher quality, work began in the late 1960s and early 1970s on alternate methods of diameter control. One early system used an optical sensor to detect the position of the crystal/liquid interface. This system was mechanically linked to the puller so that it would gradually change the viewing angle during growth to compensate for the liquid level drop [49–51]. This type of diameter control has the unique advantage that the control system is truly sensing the diameter changes of the crystal and not some other variable. However, this system still required a clear, unobstructed view of the crystal/liquid interface during the entire growth process.

Another approach taken for diameter control was based on a weighing method. The first type of weighing control was based on a melt weighing technique [52–57]. The weight of the crystal was not measured directly but determined through the loss of weight of the melt. The entire furnace assembly was placed on an electronic balance. During the growth process, the rate of weight loss from the balance was monitored and the balance output was then used as the diameter control signal. This signal was then processed to provide the final control signal to control the furnace power and therefore the crystal diameter.

The melt weighing technique had numerous advantages over the manual technique:

1. It provided active control feedback of the weight (diameter) of the growing crystal.
2. The puller head and crystal rotation required no modifications for active diameter control.
3. It didn’t require the attention of a skilled technician to make power adjustments for diameter control.
4. Since diameter control was no longer dependent upon the visual observation of the crystal/liquid interface, there was more freedom in designing the furnace and thermal gradients.

Despite these obvious advantages, the melt weighing technique had two serious disadvantages:

1. Except for a unique crucible position, the balance output was sensitive to power changes due to the levitation of the crucible when an RF generator was used. These levitation weight changes required a second circuit to compensate for the power changes that were required for diameter control.
2. As the size of the crystal increased, there was a corresponding increase in the weight of the furnace assembly with a corresponding decrease of sensitivity until the point was reached that this approach became impractical.

As the need for larger crystals developed and hence larger furnace assemblies, the above-men-
tioned disadvantages became real obstacles to the growth of large diameter crystals. In the mid-1970s, the crystal weighing technique for diameter control and the mechanical assemblies required for this approach were developed. A schematic [39] of such a system is shown in Fig. 13. With the continued advances in load cell technology and refinement of the mechanical design, coupled with digital control, this type of approach to diameter control has become the method of choice (Fig. 14).

Its advantages are many:

1. The load cell can be matched to the final expected weight of the crystal without any reduction of sensitivity.
2. It can provide a completely automatic operation from seeding to cool down.
3. Complex algorithms provide excellent diameter control as well as providing the capability for a predetermined cone shape.
4. As in all weight control techniques, there is no need to see the crystal/liquid boundary for diameter control.
5. Commercial systems are now currently available.

Despite these many advantages, this does not imply that the growth of new materials and compositions has become routine. The best diameter control system will not compensate for poor furnace design, compositional shifts or thermal problems. It can only produce high-quality crystals if these other issues have been addressed.

5. Future directions

As the demand for oxide crystals and their uses increases, the need for the growth of larger crystals (> 75 mm diameter) with improved quality will also increase, i.e. the oxide crystal growth industry will follow the same path as the semiconductor industry with cost becoming the main driver. This has already happened for several materials such as Nd: YAG, Sapphire (Al₂O₃), LiNbO₃ and several garnets (GGG and SGGG). However, unlike the semiconductor industry, adequate models for the design of these large oxide crystal growth furnaces did not exist and their ultimate configuration was based on a trial-and-error methodology that, for these large systems, can become very costly. For example, the investment in one large Iridium crucible could be as much as $100,000. Thus, it becomes imperative that models be developed that can be used for scaling purposes for the design of large oxide crystal growth systems. Presently, such
models do not exist. The reasons for this lack of understanding are many and can be broken into two distinct groups. The first group deals with the oxide material itself while the second group deals the physical design of the furnace and the method of heating.

5.1. Hydrodynamics

As pointed out in an earlier section, computational analysis of convection in molten oxide systems has shown general agreement with the characteristics of fluid flow observed within these systems as well as the simulation experiments. However, if these models are to be used to accurately design and scale a given oxide Czochralski system to produce large diameter crystals, one must have accurate thermal properties as a function of temperature for both the liquid and its solid. Such data is very difficult to obtain because the operating temperature is in many cases above 1800°C. Because of this difficulty, only a limited amount of data has been reported for the physical properties of a few molten oxides [58,59]. Some of the differences reported in the literature might be explained by the influence of the atmosphere on the liquid properties although for some cases the reported differences are not fully understood and could be associated with the method of measurement [60,61]. In addition, the thermal properties of the various furnace components must be known since these also enter into any calculations to determine the thermal environment.

5.2. Physical design

The high operating temperature required for the growth of many oxide materials generally requires that the crucible becomes the active source for heat generation within the furnace, i.e. the crucible is heated by RF energy. The coupling of the crucible to the RF field is strongly dependent upon the diameter and length of the RF coil as well as the shape (diameter and height) of the crucible. Also, the position of the crucible within the RF coil strongly influences the thermal gradients generated within the liquid [62]. Here again, no adequate models exist that can accurately predict the impact of changing the RF coil size or the crucible size and/or shape that can be used for the design of large systems. General “rules of thumb” exist for smaller systems (~3” diameter crystal); however, they are unproven as one goes to larger systems that are capable of producing 25–40 kg crystals. One of the most difficult tasks in designing these large systems is the establishment of a suitable radial thermal gradient in the liquid that allows good seeding and controlled growth during the “shouldering” phase when the crystal is being brought out to the required diameter. In general, as the size of the system increases, the radial liquid thermal gradient decreases [63]; hence, making control of the start more difficult. At present time, adequate models do not exist that can utilize information derived from smaller systems to predict a design of a furnace for the growth of large crystals that would establish the “correct” growth conditions.

6. Summary

Over the past 40+ years of Czochralski oxide growth, significant progress has been made in understanding the various factors involved in the growth of these materials. Each decade has addressed a series of pressing problems that have advanced the Czochralski growth of oxide materials (Table 1). We have progressed from the growth of small (1 cm diameter × 3 cm length) 100 g crystals suitable for research purposes to the growth of large oxide crystals that now are 75 mm or larger in diameter that can weigh as much as 30 kg. We have a much better understanding of the impact of stoichiometry, growth atmosphere and furnace design on the quality of the resulting crystal. At the same time, significant advances have been made in the design of control systems and equipment that today allows complete automatic control of the crystal growth process. Materials first conceived and grown in the late 1960s and early 1970s, e.g. Nd:YAG, LiNbO3 and Al2O3 to name a few have become important materials in today’s modern world; however, much work still needs to be done. The design of the furnace, the aspect ratio of the crucible, the size of
the RF coil, the placement of the crucible within
the work coil are still based on general “rules of
thumb” that may or may not be true for larger
growth systems. Although a large base of knowl-
edge has been developed for these systems,
accurate predictive capability that can be used
for design purposes does not exist and must still be
developed.

As the optical and electronic industries merge,
the demand for new materials will increase coupled
with the demand for increased performance,
smaller component size and lower cost. Currently,
new materials are being developed that utilize the
knowledge gained over the past decades. These
new materials are being “engineered” for im-
proved properties to satisfy a given set of
applications by using such techniques as coupled
substitution, selective ion replacement or solid
solutions. With each of these new materials come
new challenges which continue to drive a better
understanding of the growth process.

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