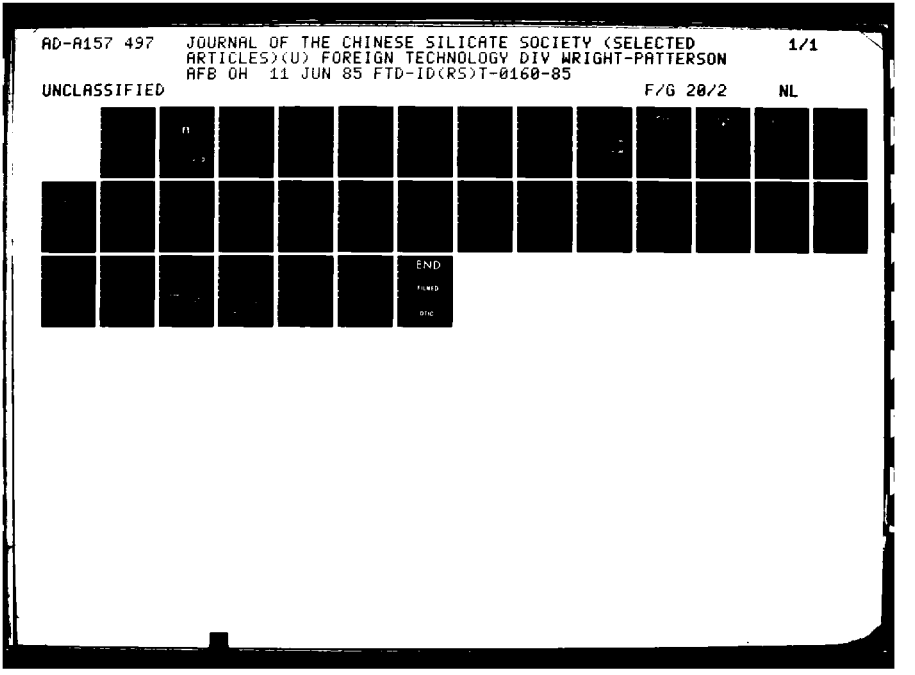
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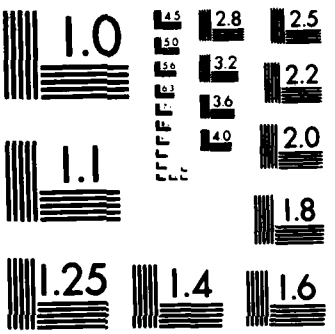

MICROCOPY RESOLUTION TEST CHART

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THE EFG GROWTH AND APPLICATION OF SMALL DIAMETER SAPPHIRE CRYSTALS IN TUBULAR AND ROD SHAPES*

Zhang Shouqing, Tang Lianan, Wang Wen, Le Xiuhong
(Shanghai Institute of Ceramics, Academia Sinica)

Small diameter sapphire crystals in tubular or rod shapes have been grown by the EFG (Edge defined, Film-Fed Growth) method. The effect of growth parameters on the perfection of the crystal has also been studied in detail. The quality of small diameter sapphire crystals grown by this method has been found to be comparable to that of flame fusion sapphire. The tubular crystals are used in making special light sources while the growth technology of rod-shaped sapphire crystals has been extended to the production of instrument jewel bearings. Since the EFG growth method can simplify the crystal post-growth machining techniques and achieve the multiple EFG growth, it lowers production cost and obtains better cost-effectiveness.

I. Preface

Crystals grown from crystal melt are generally in lumps or bars. In actual practice they must be machined into strips or other specific shapes. As a result they must undergo special

*Received on June 7, 1982.

machining such as cutting and grinding. Thus, not only is there considerable crystal material loss, but also labor and equipment cost is increased. This is particularly true for crystals like sapphires, which are hard and difficult to machine. The material loss resulting from processing is even greater. Consequently, to develop new crystal growth methods that would directly produce crystals of desired shapes and forms has long been the goal of many scientists and many research efforts have been expended in this field. In 1977, H.E. Labelle, Jr., et al. [1] of the United States reported for the first time the successful development of the EFG growth method. This method has several unique characteristics: it is able to grow crystals of various special cross-sectional shapes, which contributes to saving crystal material and simplifies further machining; it is capable of multiple EFG growth, simultaneously growing many crystals from the same crucible; and it provides a fast growth rate, and the stability of the growth process is good.

In recent years, there has been substantial progress in the use of this method to grow silicon chips for solar batteries, sapphire linings for silicon expitaxial use in semi-conductor circuits, Lithium Niobate chips for surface wave apparatus and piezoelectric transducer, etc. Some of the applications are already in the production stage.

In 1976 we embarked on the research of using the EFG method to grow special shaped sapphire crystals. The study in growth of chip-shaped crystals was published in an earlier article [2]. The EFG method growing device for tubular and rod-shaped sapphire is the same as that described in Reference [2]. This article concentrates on the introduction of the results of research in the growth technique of tubular and rod-shaped sapphire crystals, the relationship between growth parameters and crystal quality, the mechanical, optical and electrical properties of crystals, the

structural perfection of crystals as well as the practical results obtained in the development of special light sources and the production of instrument bearings, etc. using tubular and rod-shaped crystals.

II. Study of the Growth of Tubular Crystal

The sapphire crystal has a high melting point and good transparency. It is mechanically strong, chemically stable, and highly resistant to high-temperature alkali vapor corrosion. Therefore, it is an excellent material for making special light sources.

It is very difficult and expensive to machine bar-shaped crystals grown by the drawing technique or flame fusion method into lamp tubes. The tubular crystals grown by the EFG method, on the other hand, can greatly reduce machining and consequently provides favorable conditions for the development of special tubular light sources.

The die shape used for the growth of tubular-shaped sapphire crystals is shown in Fig. 1. It consists of two Mo cylinders of different diameters with the smaller one placed inside the larger one. The gap of about 0.8 mm in width between the cylinder walls is used on the capillary melt-feeding slot. Based on usage demands, we have grown tubular crystals with the inner diameter ranging from 1 to 10 mm, the length from 150 to 200 mm, and the wall thickness of 1 mm (Fig. 2). Due to the fact that growth orientation significantly affects the shape of crystals grown, [0001] axis was selected in order to improve the roundness of tubular crystals. When growing small diameter tubular crystals, there must be a higher degree of temperature control accuracy and growth mechanism stability. It is especially important not to allow the crystal melt to enter the small hole in the center of the

die during the melt-feeding and growth period, otherwise the tubular crystal grown will not be of a uniform diameter.

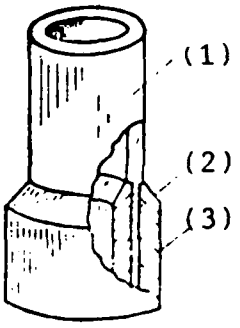

Fig. 1. Die for the growth of tubular crystal.
Key: (1) Tubular crystal; (2) Melt; (3) Die.

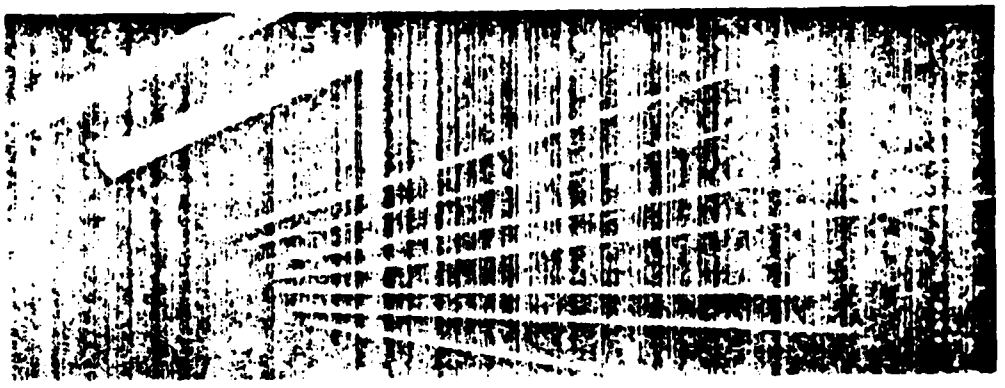

Fig. 2. Rod and tubular sapphire crystals grown by EFG method 0.3x.

In the earlier tubular crystals grown by the EFG method, numerous voids about 10 m in diameter can be seen under a high-powered microscope (Fig. 3).

Fig. 3. Microvoids in the crystal 50x.

The density of the sapphire crystal is 3.95 g/cm^3, yet the density of its molten state is only 3.05 g/cm^3. A 20% volume contraction results as the molten crystal solidifies. Because of this abrupt contraction, and coupled with the relatively fast drawing rate when the EFG method is used to grow sapphire single crystal it is very easy to leave voids in the crystal. The faster the drawing rate, the more voids; and in serious cases even cellular structures are formed (Fig. 4). By slowing down the growth rate (generally down to about 45 mm/h), voids in the center region of the crystal wall can be eliminated; however, this technique does not completely eliminate voids located near the crystal inner and outer edges. It is observed, from the void distribution characteristics, that the locations where voids appear correspond with the die tops (Fig. 5). This is because crystalization latent heat does not dissipate easily from the solid-liquid phase boundary which corresponds with the die top. In addition, the phase boundary is concave and impurities like voids gather easily in such a place. If the die top temperature is too high and the drawing rate too fast, void formation will be even more serious. Sometimes a series of small voids might attach to each other to form fine, strip-shaped cavities in the crystal.

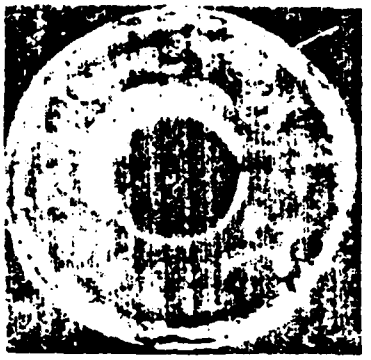

Fig. 4 Cellular structure in the crystal 15x.

Fig. 5. Correspondence of the void distribution locations with the die tops.

The dislocation density was measured for a slice cut from the (0001) plane of tubular crystal. The slice was mechanically polished and then allowed to be corroded in boiling phosphorous acid or molten potassium hydroxide. This resulted in regular, triangular corrosion spots. The distribution of dislocation showed a higher density near the edge of the tubular walls and in some cases grain boundaries were formed (Fig. 6). This is probably due to microvoids and the presence of greater thermal stress near the edge of the tubular walls.

Fig. 6. Dislocations in crystal 500x.

For tubular crystals grown by the EFG method, the dislocation density on (0001) plane is generally around $3x10^5/cm^2$, as compared with a dislocation density of around $2x10^6/cm^2$ on the corresponding crystal plane for sapphire grown by the flame fusion method.

Tubular sapphire crystal have been manufactured into Na lamps, CO_2 lasers, etc. Small CO_2 lasers made from tubular sapphire of 1 mm in inner diameter and 100 mm in length have displayed a continuous power output of 1 W.

III. Study of the Growth of Rod-Shaped Crystal

Sapphire single crystals has excellent thermal conduction capacity. Its thermal conductivity is 0.06 Cal/cm.s.^oC. It also has good electrical insulation capacity and low dielectric loss, which makes it one of the ideal materials for making the retaining rod of the waveguide. By employing the EFG method to grow sapphire filaments of 0.1 mm in diameter has been reported abroad. However, they are dendrite crystals with imperfection and can only be used as reinforcement material. To satisfy the need for test-making the waveguide, in 1977 we employed, for the first time, a three-rod die to simultaneously grow three small rods of sapphire with diameters ranging from 1.5 to 2.0 mm. These rod-shaped crystals were 250 mm long with uniform diameters and excellent straightness. Based on the experiments of three-rod dies, dies with six rods which are easily machined were also designed later (Fig. 7).

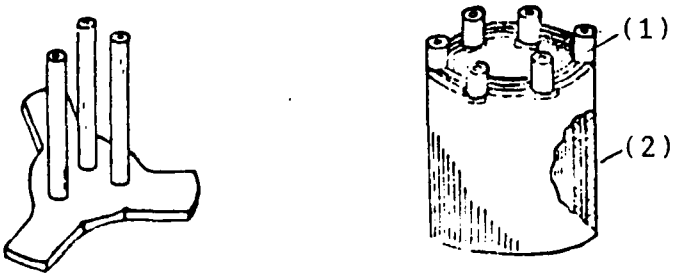

Fig. 7. Schematic diagram of the multi-rod dies for growth of rod-shaped crystals.
Key: (1) Die tops; (2) Circular melt-feeding slot.

Rod-shaped crystals grown along the [0001] growth orientation sometimes appear in a near hexagon shape. Crystals grown along the 60° growth orientation usually display a flat-cut plane on the surface. This is because sapphire is an epitaxial crystal. Its (0001) plane and {1120} plane are two groups of low index planes with high crystal plane network density, and they are easily exposed when the growth rate is low. Crystal plane exposure does not necessarily affect crystal quality; however, it does present certain machining problems later. Experiments have shown that improvements in heat retention of the die top portion as well as proper raising of die top temperature all contribute to the prevention of flat surface occurrences.

Microvoids and sub-grain boundaries are also potential defects commonly found in rod-shaped crystals. Especially for rod-shaped crystals grown along [0001] axis by the drawing method, if the growth technique is improper, large residual stress tends to remain in the crystal, which in turn causes serious formation of grain boundaries. This is the main cause for the increase in crystal brittleness and the gradual change in crystal growth orientation.

Figure 8 is a polarized microscopic picture of crystal grain on a slice cut from a rod-shaped crystal of greater brittleness. Many grain boundaries are present. The occurrence of this phenomenon can also be explained by the research results of the relationship between chip-shaped crystal growth orientation and formation of the grain boundary [2].

Fig. 8. Grain boundaries in a rod-shaped crystal 15x.

The experiments of making instrument bearings with rod-shaped sapphire grown by the EFG method have been successful. Considering the roundness of bearings after machining, it is also required to grow rod-shaped crystal along an optical axis. As stated above, this is obviously not a favorable growth orientation from the growth standpoint. Selecting excellent seed crystal, increasing temperature control accuracy and setting proper temperature field are essential to effective prevention of the occurrence of numerous grain boundaries during the growth process. In addition, the crystal drawing orientation may be set to deviate a certain angle, within an acceptable range, from the optical axis. Figure 9 shows isogyres taken under normal polarization of a slice cut from a rod-shaped crystal grown by the EFG method. The isogyres are basically regular without deformity, which indicates better crystal structure perfection. Since the crystal growth axis is allowed to deviate a little from the optical axis, the center of the black cross interference pattern in the figure is also shifted to one side.

Fig. 9. Isogyres of crystal 15x.

The following table lists comparisons in characteristics between rod-shaped sapphire grown by the EFG method and flame fusion method.

Item	Rod grown by EFG method	Rod grown by flame fusion method
Microhardness(H_v)(kg/mm²)	2038	2038
Compressive strength(kg/cm²)	13300 ~ 19800	3000 ~ 12700*
Bending strength(kg/cm²)	4900 ~ 5100	2700 ~ 3400
Dielectric constant	9.5	9.4
Dielectric loss	5×10^{-3}	3×10^{-3}*
Dislocation density(0001)(cm⁻²)	3×10	2×10^{5}

* Quoted from references[3, 4]

Practical applications have demonstrated that instrument bearing productions using rod-shaped sapphire grown by the EFG method display the following advantages:

(1) Since the diameters of rod-shaped crystals grown are very close to those required for the end products, machining techniques are simplified. Techniques such as slicing, cutting, and rounding, etc. required for crystals grown by the flame fusion method have been either simplified or eliminated.

(2) Since the crystal brittleness has been improved, the percentage of acceptable products has increased from 60-70% for

crystals grown by flame fusion to 80% for crystals grown by the EFG method.

(3) Crystal usage rate is markedly increased. According to the preliminary estimate from production units, to produce the same number of jewel bearings a 70% saving in crystal material has been achieved when rod-shaped crystal grown by the EFG method is used instead of corundum boules grown by the flame fusion method.

(4) Consumption of energy and other supporting materials during crystal machining processes have been greatly reduced.

IV. Conclusions

Small diameter tubular and rod-shaped sapphire single crystals have been grown by the EFG method. The effects of growth parameters on the perfection of crystal has been investigated. The quality of crystals grown by the EFG method is found to be comparable to that of crystals grown by the flame fusion method.

Tubular crystals are used in the development of special light sources. A small CO_2 laser has been successfully built.

The EFG growth technology of small rod-shaped crystals has been extended to the factory and used for the production of instrument bearings. Since the EFG method can simplify the crystal fast-growth machining techniques, it contributes to the conservation of raw material, supporting material and energy, and thereby markedly reducing bearing production costs and obtains apparent cost-effectiveness.

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The Chinese Ceramics Society Sent Representatives to Attend the International Congress on Glass Held in West Germany

The Chinese Ceramics Society sent representatives to attend the Second International Workshop - Glasses and Glass Ceramics from Gels in Wuerzburg, West Germany from July 1 to 2, 1983; from July 3 to 8, 1983 the XIII International Congress on Glass in Hamburg, West Germany; July 13 to 15, 1983 the International and VII University Conference "Glass Science" in Clausthal-Zellerfeld, West Germany. Also attending the aforementioned conferences were three representatives from the Chinese Academia Sinica (Shanghai Institute of Ceramics, Shanghai Institute of Optics and Fine Mechanics, Chungchun Institute of Optics and Fine Mechanics), one from the Chinese Ministry of Education (East China Institute of Chemical Engineering), one from Zhejiang Provincial Council of Science (Zhejiang University), and two from the Ministry of Light Industry.

There were about 110 representatives from various countries who attended the Second International Workshop - Glasses and Glass Ceramics from Gels and 29 papers were presented. Gan Fusi of the Chinese delegation presented his paper entitled "The Synthesis of ZrO_2-TiO_2-SiO_2 Glass Using Low Temperature Gels Method with $Zr(NO_3)_4.5H_2O$, $Si(OC_2H_5)_4$, and $Ti(OC_4H_5)_4$ as Raw Materials".

There were about 800 representatives from various countries who attended the XIII International Congress on Glass. 164 papers were presented with another 105 papers on display. Gan Fusi presented his paper entitled "The Study of Laser Stimulated ESR Narrow Lines Spectrum of Cr^{3+} Ions in Glasses, Li Jiazi presented his paper entitled "The Relationship between Phase Segregation of Certain Microcrystal Glasses and Crystallization", Zheng Jijian presented his paper entitled "The Phase Segregation and Microcrystallization of Certain Sulfurous Oxide Glasses", Ding Zisang presented his paper entitled "The Affects on the

Characteristics of Flat Glass with Small Quantity of P_2O_5 Dopants" and Jiang Zhonghong presented his paper entitled "The Study of Making High Silicon Glasses by CO_2 Laser Fusion".

There were about 125 representatives from various countries who attended the International and VII University Conference "Glass Science". Forty-six papers were presented with another 30 papers on display. Gan Fusi presented his paper entitled "The Development of Certain Semiconductor Glasses and Alloys by Means of Laser Radiation Method", Li Jiazi presented his paper entitled "The Manufacture and Characteristics of Certain Glasses of the Li-Al-Si-O-N System, Zheng Jijian presented his paper entitled "The Microscopic Structure and Characteristics of Selenite Glasses with Controlled Precipitation" and Jiang Zhonghong presented his paper entitled "The Study of Certain Reddish Halogenate Glasses".

During the XIII International Congress on Glass, the Executive Committee and Board of Directors of the International Commission on Glass elected Mr. Gan Fusi, Director of the Shanghai Institute of Optics and Fine Mechanics, as a full member of the Executive Committee. Mr. Gan reported in these two meetings the preparation work for the International Seminar of Glass and the Annual Conference of the International Commission on Glass to be held in Bcijing, China, in 1984.

(From the Journal)

STUDY OF THE SURFACE MICROTOPOGRAPHY OF CORUNDUMS GROWN BY THE VERNEUIL METHOD*

Huang Degun, Wang Haobin, Hou Huaying**
(Shanghai Institute of Optics and Fine Mechanics, Academia Sinica)

Model Dx-3A scanning electron microscope and Model LMA10 laser probe have been used to observe and analyze the "emulsion surface" and "small spot" on the side surface and "grain lines" on the top growth surface of corundum boule grown by the Verneuil method. The experimental results showed the essential of these microtopographies. Incorporating the actual process of crystal growth, this study explained their formation mechanisms and their relationships with the quality of crystals.

The microtopography of corundum boule grown by the Verneuil method has long been the focus of corundum researchers [1, 2]. People can make, based on the boule surface characteristics, certain qualitative judgements on the quality of crystals.

We used a Model DX-3A scanning electron microscope (hereinafter called SEM) and a Model LMA10 laser probe to observe

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**Hou Huaying is a graduate of Shanghai Science and Technology University, class of 1982. Special thanks to Zhu Guangyong of the Jewel Plant, First Shanghai Glass Instrument Factory, who provided all the samples for this study.

and study corundum surface microtopography. This study showed the essential of corundum surface microtopography and explained its formation mechanism and the relationship with the quality of crystals.

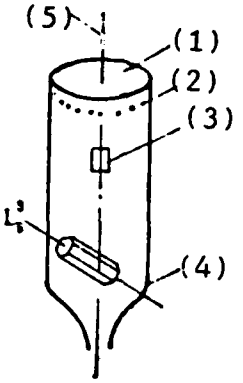

Fig. 1. Form of corundum boule grown by Verneuil method.
Key: (1) Top; (2) Small spot; (3) Sample area; (4) (0001) face; (5) Growth axis.

I. "Emulsion Surface" on Side Surface of Corundum Boule

The surface of corundum boule grown by the Verneuil method often appears emulsive. This surface condition is usually called "emulsion surface". Samples for SEM observation are taken from two typical regions on boule surface: one is the spinal region which is basically parallel to the cleavage plane of the boule (3); the other is the (0001) exposure plane (4). See Fig. 1 for details. Many small crystal grains are found attached to the crystal surface when making a SEM observation of the "emulsion surface" of the boule. Most of the forms of these grains are regular polyhedron with a few irregular ones. Crystal grain sizes range from several microns to tens of microns. Figure 2 (Ill. 6) is a SEM photograph

of a boule "emulsion surface". It can be seen that these regular polyhedral grains are essentially of consistent growth orientation. In addition, Fig. 2 (1) shows that the angle between the crystal grain [0001] orientation (optical axis) and the boule growth orientation is close to 50^{o}, i.e. the grain [0001] orientation is consistent with the optical axis orientation of the boule substrate. In Fig. 2 (2), small crystal grains on (0001) face are all of regular polyhedrons. This indicates that the optical axis orientations of both the small crystal grain and the substrate are identical. Also, the orientation of the two L_2 axes is the same. Accordingly, we believe that the orientation of polyhedral crystal grain coincides with that of the surrounding boule substrate.

Undoubtedly, the small crystal grains adhered to the surfaces of the boule are all precipitates of raw material powder that drops from the feed bin and through the H_2 - O_2 torch onto the boule surface.

When the temperature gradient in the crystallization zone inside the furnace is relatively small, the molten layer temperature is close to that of the crystallization layer below. Therefore, substance particles adhered to the surface of the crystallization layer will have greater surface mobility. As the powder particles hit the solidification surface, they obtain the required activation energy for rearranging their fixed crystal lattices and then realign growth orientation to become the continuation of the substrate crystal lattice. We call these crystal grains "adherent crystal grains of compatible structure".

As shown in Fig. 2 (3) (Ill. 6), there are also crystal grains of irregular forms adhered on the "emulsion surface" of the boule. During the single crystal growth process, if the powders fall on the crystallization layer whose surface temperature has been markedly lowered, the effects of surface dynamics are only enough

to keep the powders adhered but not enough to cause realignment of growth orientation according to the substrate crystal lattice. We call these crystal grains "adherent grains of incompatible structure".

Sometimes the surface of the corundum boule grown by the Verneuil method is shiny and transparent (partial or entire surface). Figure 3 (Ill. 6) shows the SEM photograph of a smooth corundum boule surface. On such a surface only a few small bumps and craters are present and no regular polyhedral crystal grains can be found.

The reason why these smooth surfaces are formed is: since the temperature gradient in the crystallization zone is relatively large during the crystal growth process (especially in the solidification zone adjacent to the molten layer), it causes crystal surface temperature to drop rapidly as the distance between the crystal surface and the molten layer increases. The surface temperature of the crystal surface has dropped too low to provide the incoming powders with sufficient activation energy; therefore, they will not adhere to the crystal surface.

Usually, when the hydrogen to oxygen flow ratio of the H_2 - O_2 torch is improper, e.g. when this ratio is greater than 2.6:1, the torch flame shortens causing the temperature gradient of the crystallization zone in the furnace to increase. Crystals grown under this condition tend to form smooth surfaces.

Since boules with a smooth surface pass through zones of a greater temperature gradient during the growth process, serious residual stress and structural defects in the crystals are resulted. Boules with "emulsion surface" are of better quality because the temperature gradient in the crystallization zone is small during the crystal growth process.

II. "Small Spot" on Side Surface of Corundum Boule

About 3-5 mm below the top of the corundum boule, sometimes a ring of scattered small spots appear on the side surface. The diameters of these small spots range from 0.5 to 1.0 mm and they may appear in either sapphire or ruby. The shapes of these spots were observed by means of SEM and their content was analyzed using a laser probe.

Figure 4 (Ill. 6) is the surface topography of a small spot observed under SEM. The small spot is found to be a cluster of incompatible dendritic microcrystals occasionally with a few polyhedral crystal grains. The following table shows the analytical results of impurity contents using a laser probe in both small spot and substrate (the region outside the small spot). As indicated, either in sapphire or ruby the contents of the four elements Ti, Fe, Mg, and Ca in the small spots are higher than those in the substrate. Ti and Fe are added on purpose into raw material to improve the crystal machining quality. Mg and Ca, however, are assumed to have come from the refractory linings of the furnace during raw material firing.

Element (%)		Ti	Mg	Fe	Ca	Cr	Si
Sapphire	Small spot	0.1~1	0.1~1	0.01~0.1	0.01~0.1	—	0.001~0.01
	Substrate	<0.001	<0.001	0.01~0.1	•	—	0.001~0.01
Ruby	Small spot	0.1~1	0.1~1	0.001~0.01	0.01~0.1	1~5	0.01~0.1
	Substrate	<0.001	<0.001	•	•	1~5	•

• Content lower than the limit of test

Since the segregation coefficients of these impurity elements are all less than 1, they tend to concentrate in the molten layer

during the growth process and cause the melting point of region rich in impurities to drop slightly. When the furnace temperature fluctuates (temperature fluctuations tend to occur between the end of crystal growth and the termination of heating), part of the melt in said regions starts to permeate through the side surface of the boule. Due to the effects of surface tension, the permeated melt solidifies and forms small spots on the boule surface.

Therefore, the small spots on the side surface of corundums are actually the result of slight "overmelting". Since the small spots do not affect the internal structures of boule and the furnace temperature fluctuations are small during crystal growth, it can be concluded that there is no significant relationship between the appearance of small spots and the boule quality.

III. "Grain Lines" on Top Surface of Corundum Boule

SEM observations how the true forms of "grain lines" on the corundum boule growth surface are a series of concentrated microsteps as shown in Fig. 5 (Ill. 6). The tread of each step at the center of the top surface is 100 μm. For those steps near the edge, the tread is about 10~30 μm. The average rise of each step is approximately 5 μm.

It can be clearly observed in Fig. 5 that there are many kinks on the growth surface of corundums grown by the Verneuil method and each kink is a crystal growth source. Therefore, this crystal growth mechanism resembles that of the multiple seeds, 2-dimensional step growth. Since the crystal is affected by factors such as added impurity elements, temperature changes, etc. during the growth process, these microsteps appear rough and irregular on a microscopic scale.

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GROWING OF EXCELLENT Nd:YAG CRYSTALS BY TEMPERATURE GRADIENT TECHNIQUE (TGT)*

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(Shanghai Institute of Optics and Fine Mechanics, Academia Sinica)

The melt of Al_2O_3-Y_2O_3 ternary system is a complex phase equilibrium involving many compounds and especially the doping of Nd ions leads to instability of the four-fold coordination of the aluminum in the Yag structure. There is much difference between the crystalization condition of YAG and that of sapphire. In consideration of potential problems in the growth of Nd:YAG single crystals and the features of vertical solidification technique, we have properly designed a new growing device and a heater; and combined with the selection of growth parameters as well as careful preparation and treatment of the raw material, excellent Nd:YAG laser crystals with more homogeneous Nd dopants, good optical perfection, less scattering particles and low dislocation density have been stably grown with success.

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**Comrade Hwang Zhiguang also participated in this experimental work. Special thanks to Comrade Zhong Yongzhen who supported this work, and Comrades Wu Guangzhao and Zhang Xiuzong who provided the Nd concentration test data.

(I)

Thus far, Nd:YAG crystals are still the best and the most widely used laser base crystals. Currently the laser crystal bars used are primarily obtained from the raw crystals grown by the Czochralski technique. However, due to the presence of fluid effects and surface tension effects, certain difficulties still exist in the growing of large diameter and large surface area crystals with good optical homogeneity.

In 1979, J. L. Caslavsky, et al. [1] of the U. S. Army Material Mechanics Research Center reported the growing of larger diameter Nd:YAG crystals using an improved heat exchange technique. The main problem reported was the difficulty in the doping of Nd ions into crystal lattices (i.e. at Nd dopant concentration of 0.6~0.8 atom%, the volume of the non-scattering center occupies more than 90% of the entire crystal body; however, at Nd doping concentration of 1.1 atom%, the volume of the non-scattering center is only about 50%). In addition, during the crystal solidification process the complex phase equilibrium of the Al_2O_3-Nd_2O_3-Y_2O_3 ternary systems easily leads to overcooling of its compounds resulting in second phase precipitates, and consequently could not grow Nd:YAG single crystals with good optical qualities. Large crystals that weigh 2,180 g with a diameter of 76.2 mm and a height of 105 mm have been grown using this method. However, the crystal can only be machined into small rods of 3 mm in diameter and 30 mm long. They are used in laser tests and the laser slope efficiency of their long pulse work is $\eta \approx$ 0.2%.

We used the guided temperature gradient technique and successfully grew excellent sapphire single crystals [2]. The technique is already in broad use [3]. Sapphire single crystals are grown from pure Al_2O_3 single compound melt. Nd:YAG single crystallization, however, is a process of complex phase equilibrium

involving many compounds. The author has considered various parameters of Nd:YAG single crystal growth (e.g. the difficulty in the doping of Nd ions into the crystal lattices, the effects of the shape of solid-liquid phase boundary on the growth of facets, and the second phase precipitation of Al_2O_3, $NdAlO_3$, and $YAlO_3$, etc.) and made reasonable improvements on the growing device. Currently excellent Nd:YAG crystals that weigh approximately 680 g with a diameter of 50 mm, a height of 80 mm and a Nd dopant concentration of 0.9-1.3 atom% have been stably grown with success using the TGT method, and thus provide excellent crystal chips and bars for laser capacity tests.

(II)

The TGT method is a high temperature technique for growing crystals from melt. The advantages of this technique are a simple growing device and convenience of operation. It uses a vacuum resistance furnace equipped with a fine temperature procedure controller to grow single crystals. In addition, the growing device of the TGT method is kept under relatively stable conditions; neither the crucible nor the seed crystal turns; the temperature gradient coincides with earth's gravity field; consequently, there is neither forced convection resulting from mechanical blending nor natural convection caused by density difference in the melt. For a single compound melt like sapphire, the stable growth parameters create an appropriate temperature gradient for single compound molten sapphire to grow crystals of perfect structure, good optical homogeneity as well as very little thermal stress and scattering particles.

But the Nd:YAG single crystals are grown from the melt of Al_2O_3-$Nd_2O_3Y_2O_3$ ternary system with complex phase equilibrium. Moreover, the doping of Nd ions causes instability of four-fold coordination of aluminum in the YAG structure. Verified by the experiments of J. L. Caslavsky, et al. [4], two mutually insoluble

fluids, Al_2O_3 and $YAlO_3$, are always formed after a YAG crystal lump is melted at high temperature. The melting point of a YAG crystal is 1,940$\pm$7°C. At a temperature around 1,916$\pm$7°C, $YAlO_3$ exhibits an inconsistent melting transformation temperature with its liquidus at 1,934$\pm$7°C, which is very close to the YAG melting point. During the Nd:YAG growth process, facets are formed on the convex solid-liquid phase boundary. Yet, on the other hand, a flat solid-liquid phase boundary hinders the elimination of impurities (e.g. small Nd segregation coefficient and its heterogeneous mixing, chemical composition deviation of part of the compound, etc.) and crystal lattice defects (e.g. second phase precipitation caused by compound overcooling, and voids, grooves, etc.). Based on these considerations, the author designed a new heat retaining device and a new heater to ensure that a slightly convex solid-liquid phase boundary is maintained throughout the entire crystal growth process. It is also necessary to consider the relative stability of the temperature filed when designing the heat retaining device. The purpose is to reduce the overcooling of compounds due to temperature fluctuation caused by heat convection. Tests have shown that maintaining a slightly convex solid-liquid phase boundary contributes to the elimination of impurities and dislocation, and that at the same time it prevents the growth of facets in the center of a crystal, thereby improving crystal optical qualities.

Highly purified oxide powders (Al_2O_3, Y_2O_3, Nd_2O_3) are first weighed according to proper chemical composition, then carefully ground together until the powders are thoroughly mixed. The mixture is then sintered.

A seed crystal is a specially selected single cylindrical crystal with a fixed orientation to be placed at the bottom of the crucible. The premixed raw materials are few into the crucible, which is fixed on a platform. The system is then sealed and air is

evacuated until a vacuum of 10^{-5} Torr is reached, and at such time heating of the system begins. Air evacuation is continued until a preset temperature is reached, then argon is introduced into the system. Heating continues until the materials start melting. A constant melting temperature is maintained. The entire single crystallization process is automatically completed by the fine temperature procedure controller according to the preset cooling procedures. Temperature must be strictly controlled during the entire single crystal growth process. Eliminating as many factors as possible that disturb thermal stability and maintaining a steady solid-liquid phase boundary rise are also critical. These precautions contribute to less growth marks, avoiding zones of inconsistent melting temperature as well as less scattering particles and second phase precipitates.

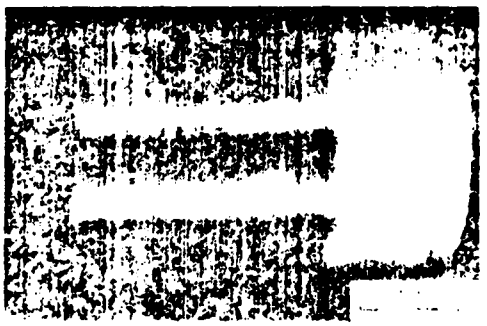
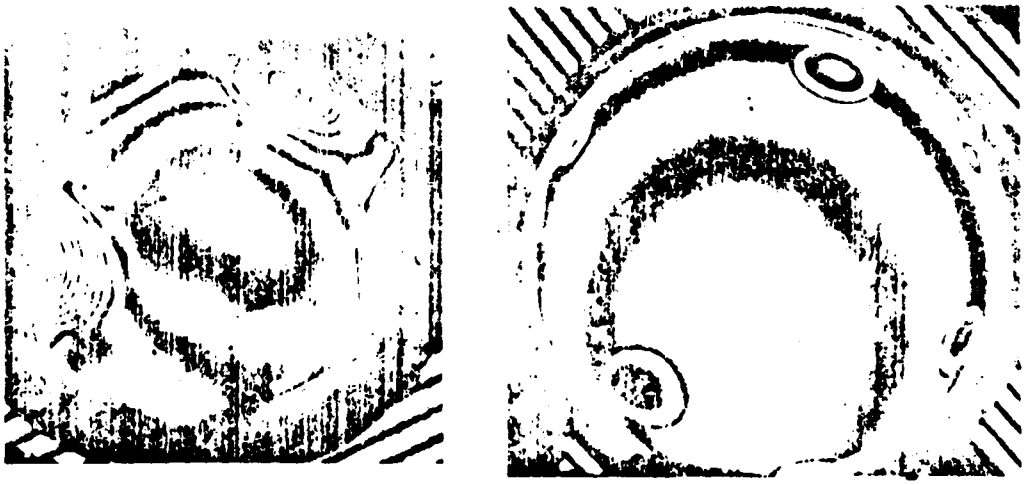


Fig.1.Crystal embryo of Nd:YAG grown by TGT method.

Fig.2. Crystal slice with the two end surfaces polished (Ø 50 x 62 mm)

The form of Nd:YAG crystals grown by the TGT method is cylindrical (see Fig. 1). The transparency of the crystal after the two end surfaces are polished is good (see Fig. 2). Crystal

optical tests have shown that no nuclei cased by facets are found in the center region of a crystal embryo. A crystal embryo was machined into a ∅ 50x50 mm crystal segment and observed on the Tyman-Green interferometer. Facets were only found near the crystal edge with the remaining region displaying good optical homogeneity. Six ∅ 5x50 mm excellent laser crystal rods with zero-order interference patterns and two 7 mm thick, 16 mm wide, and 50 mm long excellent laser crystal chips with zero-order interference patterns have been machined from this crystal segment. The interference patterns are shown in Fig. 3 (1). Facet growth can be controlled to concentrate only in a very small region after the furnace temperature field is further improved, and thereby obtaining large surface area crystals with good optical homogeneity (see Fig. 3 (2)). When a 20 mW He-Ne laser beam (6,328 Å) passes through the above samples, essentially no scattering particles can be seen (see Fig. 4). Under a 200~400x microscope, however, tiny scattering particles are visible. Generally speaking, there are very few scattering particles in these crystals and their dislocation densities are relatively low less than $10^2/cm^2$.



(1) Facets at the edge of a crystal

(2) In this crystal boule the facets are in very small region

Fig. 3. Observation of optical homogeneity (by Tyman-Green interferometer).

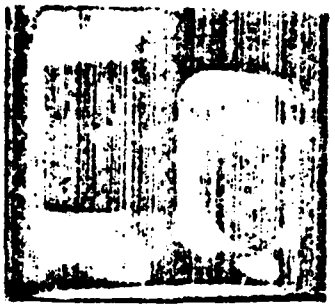


Fig. 4 The figure shows that when a 20 mW He-Ne laser beam (6,328Å) passes through the sample from the left, "light path" caused by the scattering particles in the Nd:YAG grown by TGT (left) cannot be seen, while in the sapphire grown by the Czochralski technique "light path" can be seen (right).

(III)

The growing of Nd:YAG crystals by the TGT method is still at an early research stage. However, tests on crystals grown have shown that there are no optical strain-induced patterns in the center region of a crystal embryo. Therefore, chip and lump-shaped crystals with large surface area and good optical homogeneity are obtained. Since the gain coefficient of Nd:YAG crystal is higher than that of the Nd glass and the crystal has better thermal conduction capacity, it is feasible to properly increase, through technique improvements, the crystal size so that it can be used for chip-shaped laser stimulator and amplifier.

In conclusion, the author considers it possible, based on the existing technology of growing Nd:YAG single crystals, by the TGT method to further enlarge the growing device to grow excellent crystals of much larger size (e.g. 80 mm in diameter, 100 mm in height; when machining crystal chips of larger size, laser crystal bars of about 70 mm in length can also be cut at the same time).

Accordingly, the author plans to do research work in the area of further reducting scattering particles and Nd concentration gradient in crystals. In addition, a new growing device capable of growing excellent single crystals will be designed in order to obtain both large-sized laser crystal chips with good optical homogeneity and provide excellent laser crystal bars.

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