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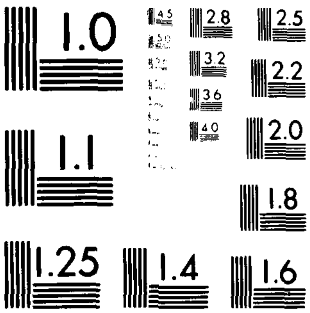

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CRYSTAL GROWTH AND CHARACTERIZATION

by

Wu Qian-zhang, Chen Qing-han, Tian Wan-chun

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CRYSTAL GROWTH AND CHARACTERIZATION

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Abstract

Imperfections such as cracks, inclusions, growth striations, color centers, inhomogeneity and cellular structures, that frequently occur in artificially grown crystals are discussed. The phenomena of constitutional super-cooling are dealt with in more detail. The origins of the occurrence of these imperfections and the measures adopted to overcome them are recommended. It is stressed, moreover, that the work on growth of crystals and their characterization must be closely coordinated so that the final goal of obtaining perfect crystals may be attained through successive stages of experimental research.

1, Introduction

The objective of the scientific study of the growth of crystals is to understand and thoroughly master the principles inherent in the structure of crystals in order to facilitate the growth of high-quality crystals which possess specially determined capabilities. What is meant by high quality is crystals which have few imperfections, have a high degree of uniform completeness, and, of course, also have good functional properties (with the exception of a few cases).

The branch of science dealing with the growth of crystals, from the last century to the present, has undergone a long, slow process of development; it has only been after the decade of the 1950's, due to semiconductor technology, and particularly after the rapid development of light excitation technology, that there has been a pressing need for all types of high quality single-crystal materials in order to pursue on a large scale the surging development of this branch of science and to cause the technical skill of "growing crystals", which had been carried out on the basis of experience, to gradually become relatively more scientific. This has been particularly true in the last ten years; because of requirements for crystals which were relatively difficult to grow as well as ever-higher requirements for the quality of crystals, there has been undertaken a series of relatively profound research projects into many of the basic phenomena involved in the growing process; the theory of the growth of crystals has achieved a great development, and the technology of growing crystals has also been greatly improved. In the area of various problems such as the theory of constitutional super-cooling (1,2), phase diagram theory (3), etc., it has already been possible to apply these advances to guide the actual execution of the growing of crystals, and excellent results have already been achieved. Despite this, however, in the work of growing crystals, at present, operations based on experience are still the principal trend. Why has there still been no complete solution of the problem of controling the quality of crystals during the process of growth in order to achieve an ideal level? This is the question.

Because of this problem, at present, every type of approach is being employed which might speed up the development of the science of crystal growth (including both the aspects of theory and actual technical experimentation), and these problems completely occupy the minds of workers in the field of crystal growth.

Concerning the relationship between crystal growth and characterization as well as the influence of these two factors on the development of the science of crystal growth, we have compiled from the literature on the subject as well as from work done here in China a good deal of experience and instruction which approach the problem from all angles. Here, we take very seriously the discussion of the close organic relationship which exists between the work of characterizing crystals and the growing of them. For the sake of speed and convenience, we tried to carry out an analysis using several different types of commonly seen imperfections in crystals; after that, we carried out some preliminary discussions on the relationships that must exist between the operations of characterizing crystals and growing them.

2, Imperfections Which Commonly Appeared in the Initial Phase of Experimental Crystal Growth and Methods of Overcoming Them As Well As the Relationship Between These Imperfections and Correction Methods and Crystal Charactarization

Crystals, especially crystals which are particularly difficult to grow, in the initial phase of experimental growth, often exhibit imperfections the most common of which are the types listed below: 1) cracks, 2) inclusions, 3) growth striation, 4) color centers, 5) inhomogeneity, and 6) constitutional super-cooling imperfections or cellular structures. Below we will distinguish between these conditions and discuss them.

1. Cracks

When attempting to grow any type of crystal material, the first type of problem one runs into is frequently cracks. For example, when we try to grow crystals such as Nd: YAG, $LiNbO_3$, $KNbO_3$ and so on, the first crystals grown all encountered problems with cracking. According to the principles of elastic mechanics, cracks obviously occur due to the fact that stresses within the crystals exceed, in localized areas, the extreme limits of material failure.

However, this kind of general knowledge is not enough to concretely guide the improvement of growth experiments. Because there are a great many reasons for increases in localized stresses, looking from the angle of growing crystals, measures for overcoming the problem of cracking may not all be the same; there may be several types of measures to accomplish this, even precisely opposite ones.

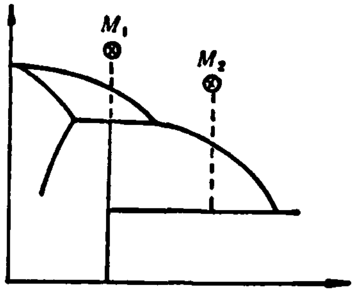
After crystal growth, the problem of cracking during the process of cooling to room temperature is an example. It is the general experience that very slow cooling is advantageous to the reduction of thermal stress and is, therefore, advantageous in avoiding cracking of crystals and other imperfections. Particularly is this so where it concerns crystals with relatively different rates of heat conductivity. However, practically speaking, if, in the cooling process, the interior of a crystal developed certain "changes", then, it would be possible to drop the temperature relatively quickly and, even so, still have the effect of being advantageous to the prevention of cracking. For example, SNN single crystals, during the post-oven cooling process, develop the chemical reaction below:

$$3Sr_2NaNb_5O_{15} \xrightarrow{\sim 1000^\circ C} SrNa_3Nb_5O_{15} + 5SrNb_2O_6$$

This type of eutectoid decomposition reaction causes changes in volume and creates cracks in crystals. Dropping the temperature relatively quickly, for example, dropping the temperature at a rate of 300°C/hr through the eutectoid decomposition region prevents the eutectoid decomposition reaction from taking place, however, and brings the crystals to room temperature with their stability intact and cracking prevented.(4) And again, as an example, $LiNbO_3$, during the cooling process after growing, when the crystals are going through their solidification line period, if cooling is done gradually, then, there develops the precipitation of a secondary compound $LiNb_3O_3$(5); because of this, cracks can easily be caused(6). However, if the temperature is dropped relatively more quickly through this time period, then, the crystals again arrive a room temperature stable and uncracked.

However, with regard to another set of "changes", the methods above cannot be employed. For example, $KNbO_3$ crystals, during the process of after-oven cooling, due to cubic $\xrightarrow{435^\circ C}$ square $\xrightarrow{225^\circ C}$ perpendicular structural changes in crystals, there are caused rather large and sudden changes in the point drop constant(7). When the cooling is quick, the structural stresses produced can easily produce cracking in crystals. Only a very slow cooling, causing stresses to slowly be released, can prevent cracking. Many ferro-electric crystals, for example BNN crystals, when cooling goes through its ferro-electric temperature change (T_c=560°C), due to the Curie point vicinity, and the fact that the heat pulsation coefficient polarity is different in different directions, rapid cooling (for example, 100°C/hr) will cause the crystals to crack. However, if the temperature is brought down very slowly, (for example, 30°C/hr), then, cracking can be avoided(8).

Concerning the situation where there exists a peritechtoid reaction which leads to cracking, for example, $6Bi_2O_3 \cdot TiO_2$(9) and $LiBaF_8$(10) as well as $KNbO_3$(11,12), the method for preventing this cracking should be to accurately select, on the basis of the phase diagram (Fig 1), the compounding ratio of fusion bodies and, thereby, prevent the occurrence of the peritechtoid reaction (as shown by M_2 in Fig 1).



1 图 1 包晶体相图示意图
2 M_1—化合物配比，产生包晶反应，
3 M_2—实际配料组分，可避免包晶反应

1. Fig 1 An Illustrative Peritechtoid Phase Diagram 2. M_1—Ratio of chemical components producing peritechtoid reaction 3. M_2—The actual mix of constituents which prevent peritechtoid reaction

When bubbles, striation or high levels of impurities or inhomogeneity exist within crystals, the cooling process can also easily cause cracking. For example, when crystals are grown by the extraction method, and the Nd:YAG concentration is excessively high in the tail portion of the crystals develop bubbles or cloudy striated layers, there is frequently cracking during the growth or cooling processes; at this time, there is a need to first improve the technology of growing crystals (for example, improving heat fields, etc.) in order to reduce this type of imperfection in crystals.

Generally speaking, even if the reasons for the phenomenon of cracking in simple crystals are very complex, it is all the more necessary to carry out characterization concerning this phenomenon. Only after carrying out observation and experimental analysis will it be possible to finally uncover the reasons for this phenomenon and the appropriate measures for overcoming it.

2. Inclusions in Crystals

The term crystal inclusions refers to bubbles, liquid phase inclusions, as well as solid phase granules, etc. Under stress, these inclusions can cause cracking; however, most just seem to be scattered granules within crystals. They are second phase inclusions within crystals; because of this, reduction of second phase impurities in fusion bodies would obviously help reduce this type of imperfection. However, as was the case with the problem of cracking, the causes of this problem of inclusions come from the actual concrete situation and nothing else; because of this, methods of overcoming this problem can only be discovered relatively quickly if the work of characterization is closely coordinated with this attempt.

For example, in GGG (or Nd:YAG) crystals grown using an iridium compound, there frequently occur triangular or hexagonal iridium granules; this is due to the oxidation and reduction reactions carried out between the iridium compound, the fusion bodies and the gases in the furnace(13), these reactions cause the iridium to enter the fusion bodies; later, they finally enter into the crystals. Experimentation demonstrates that, in the case of certain solid phase granules, these granules can only be easily captured by the crystals when there exists a critical speed of growth V_c(14), and V is greater than V_c. Therefore, the reduction of the speed of growth and its fluctuations is also an important measure in the reduction of solid phase granules. Also, to give another example, in Nd:YAG crystals grown in a molybdenum compound in a graphite resistance oven, there are also often discovered granules of molybdenum and carbon. Research demonstrates that, except for the proper establishment of methods for the reduction of pollutants in fusion bodies, change in fluctuation speed of crystals has a very obvious influence on the amount of solid phase granules in crystals which are grown, and this fact should command attention.(15)

In Nd:YAG crystals, large bubbles; minute, widely dispersed, invisible small bubbles; and depressed boundary surfaces or constitutional super-cooling imperfections are all known to occur. However, in TeO_2 and $Pb_5Ge_3O_{11}$ crystals, it is reported that(16), in the case of convex boundary surfaces, it is very easy for crystals to give rise to bubbles; moreover, whether bubbles appear or not is related to the purity of the raw materials used. When the purity of the raw material TeO_2 is raised from 99.8% to 99.99%, it is no longer certain that bubbles will appear, and so on. It is clear that the precise causes of the phenomena of the appearance and disappearance of bubbles can only be determined after the carrying out of detailed research.

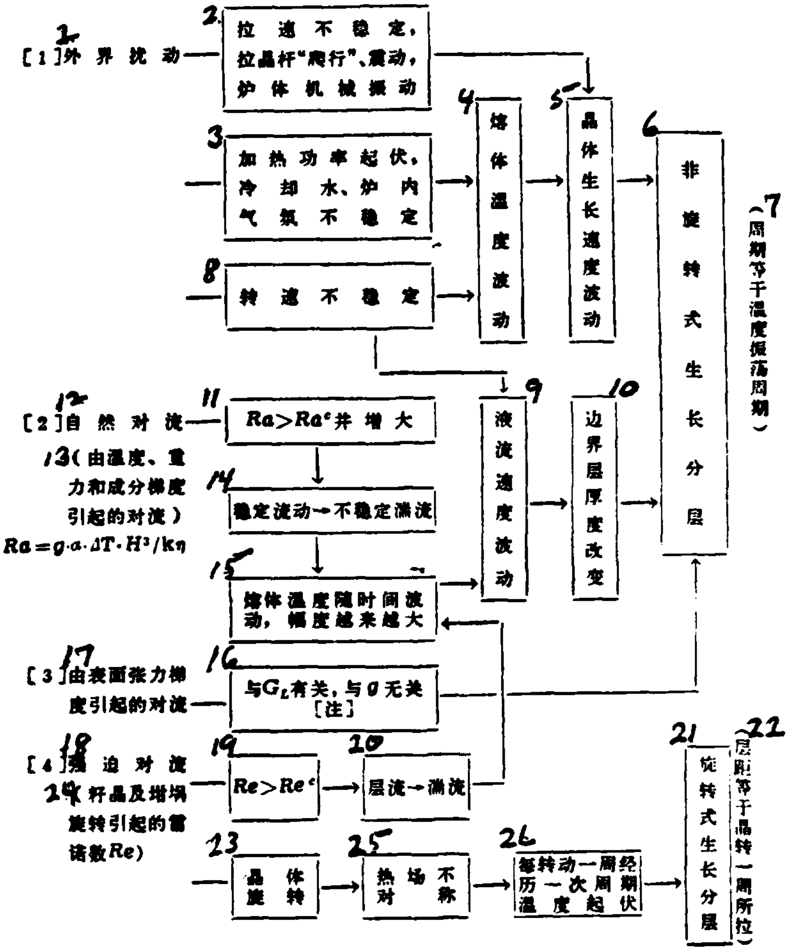
Concerning liquid phase inclusions which are caused by the phenomenon of constitutional super-cooling, we will temporarily cease the discussion of it here and hold that discussion until later.

There is still another type of crystal which, in the cooling process, gives rise to second phase granules, for example, the precipitation of $LiNbO_3$ crystals which is mentioned above as well as the products of the general decomposition reaction of a compound of niobic acid, strontium and sodium, etc. Normally, researchers use optical microscopes to observe the external form of granules in order to differentiate between metallic granules, liquids, bubbles, etc. In other cases, researchers use electron probes, ion probes, optical excitation spectroscopy and similar analytical methods of minute dicrimination in order to characterize the constituents and phase of granules, thereby, helping to determine the causes of granules; however, sometimes, there are difficulties with making fine distinctions. In such cases, it is possible to employ supplementary experimentation, observing the principles of transformation which govern imperfections under particular conditions; in this way, it is frequently possible to bring a very powerful discrimination capability to the "precise diagnosis" of the imperfection. For example, the precipitation phenomenon produced when $LiNbO_3$ crystals very slowly pass through the solidification line, cause transparent crystals to become cloudy; however, when the temperature is raised back over the solidification line, crystals again return to a transparent state; after this, if the temperature is dropped relatively quickly, then, crystals can return to room temperature preserving their single-crystal phase stability and transparency. This kind of transformational plasticity, on the one hand, points out a method of overcoming precipitation and, at the same time, also makes a powerful determination of the character of this type of imperfection. Moreover, the bubbles, liquid phase inclusions and solid phase granules in crystals do not, then, basically change during these types of temperature changes.

3. Growth Striations

Concerning the appearance in crystals of the striated formation of different layers, this type of phenomenon is called growth striation. Concerning transparent crystals (for example, Nd:YAG), diffences in constituents lead to changes in the index of refraction; under vertically polarized light, when one observes a slice of such a sample one sees several lines of different brightnesses (actually, they are different layers); their outlines actually represent the shape of the boundary between solid and liquid at each instant. Careful observation can then discover that the forms of growth striations are very complicated. It is frequently possible to divide them into several groups. Some structures are relatively simple and have good periodicity; some forms are very complicated and have no strict periodicity, even to the point of being completely without governing principles. Concerning their classification and the causes of their production, although there has been unceasing work on the subject since the 1960's, it is only recently that there has been a relatively high degree of understanding of this subject. In order to make the presentation convenient, we have drawn Fig 2 in order to explain the results of international research on this problem in the last few years.

The cause of growth striation is the difference between solid phase crystals and



a. 图 2 引起晶体生长分层的几种原因和机制

b. [注] 但g大(在地面上)则g的影响掩盖表面张力，g小(宇航中)则表面张力作用占优势

a. Fig 2 Various Causes and Mechanisms for the Occurrence of Crystal Growth Striation 1. (1) External boundary disturbance 2. Pull speed uneven, Crystal pull rod "crawl" and vibration, Oven body mechanism vibration 3. Decline in the rate of heat increase, Instability of gases within the furnace 4. Fluctuations in temperature of fusion bodies 5. Fluctuations in the speed of crystal growth 6. Non-rotational type growth striations 7. (Period is equal to the period of temperature oscillation) 8. Rotational speed uneven 9. Fluctuations in speed of liquid flow 10. Changes in thickness of boundary layers 11. Ra > Ra^c and enlarged 12. (2) Natural convection 13. (Convection caused by temperature, gravity and constitutional gradient) 14. Stable flow ⟶ unstable turbulance 15. Constant fluctuation in temperature of fusion bodies, amplitude greater and greater

16. Related to G_L, unrelated to g (See note) 17. Convection caused by surface tension gradient (3) 18. (4) Forced convection 19. (As stated) 20. Laminar flow ⟶ turbulance

21. Rotational type growth striation 22. (Striation distance equals the pull in one crystal rotation period) 23. Crystal rotation 24. (Reynold number Re caused by seed crystals and rotation of the crucible) 25. Incorrect heat field 26. Each rotational period produces one periodic temperature fluctuation b. (Note) Even though, when g is large (on the surface), the influence of g conceals surface tension; when g is small, the effects of surface tension are dominant

liquid phase components, as well as so-called fusion substance segregation phenomena. It is related to growth conditions. Under stable conditions, the BPS formula, which has already been developed$^{(18)}$ is:

$$C_s = K \cdot C_B \qquad (1)$$

$$K = \frac{K^*}{K^* + (1-K^*)\exp\left\{-\frac{\delta V}{D_L}\right\}} \qquad (2)$$

In these equations, C_S is the concentration of "impurities" in crystals; C_B is the average concentration of "impurities" in fusion bodies; K is the coefficient of effective liquation of "impurities"; K^* is the coefficient of liquation or segregation of "impurities" on boundary surfaces; at low pull speeds $K^* \approx K_0$ (equilibrium liquation coefficient); D_L is the distribution coefficient of "impurities" in fusion bodies; δ is the thickness of "impurity" boundary layers; and, V is the speed of crystal growth.

Changes in the periodicity of K cause the very slow, smooth changes in C_S and then forms the inhomogeneity in the crystals as a whole.

It is necessary to point out the fact that use of the BPS equations is very limited in most fusion body growth systems; they are suitable for use in situations where changes in the speed of growth (or the thickness of diffusion layers), amplitude and frequency are all relatively small. However, most fusion body growth systems all have very large fluctuations in speed of growth and have very obvious non-equilibrium properties; because of this, the BPS model is certainly an inappropriate one to use. However, qualitatively speaking, the BPS equation certainly has meaning as far as leading one to a way of overcoming growth striations. Habitually, growth striations are divided into two types; one is the rotational type growth striation, and this can be ascribed to rotary movement of the crystal or the crucible (the period is the same in either case). The second is non-rotary growth striation; whether the period or time interval of this type is equal or unequal to the period of external boundary turbulance or fusion body temperature oscillation is a very complicated question. Let us explain a few things about Fig 2.

1) The ability to eliminate growth striation imperfections is the problem of first importance concerning the existence of materials with same-component points and the locating and matching of these points with fusion bodies. When $K^{*} \cong K_{0} = 1$ hr, theoretically speaking, liquation phenomena would not exist. In such a situation, since the growth conditions are not sufficiently stable, clear growth striation phenomena would not appear either(19).

2) Sudden changes in rotation speed can cause the state of liquid flow and temperature in fusion bodies to exhibit changes. Experimentation has already revealed that (20) when the speed of rotation is intermitently changed 1 turn per minute, then, clear growth striation occurs. Moreover, using automatic control methods to very slowly change the rotation speed ($\frac{\Delta\omega}{\Delta t} \doteq 0.3$ rotations per hour), it is then possible to reduce this type of growth striation to a very low level. Therefore, a stable rotational speed has particular importance for the elimination of growth striations.

3) Instability of liquid flow. Even if, in symmetrical heat fields, instability of external boundary conditions is eliminated, it is still possible for growth striation phenomena to occur. Because, in the type of fusion body which is normally employed and is cold on top and hot on the bottom, there exists unstable heat convection, particularly in the case of fusion bodies with high melting points, relatively large temperature fluctuations, which are caused by heat-convection instability, are frequently a principal cause of the occurrence of growth striation in crystals. In order to control the influence of unstable heat convection, the method of crystal rotation is often employed; the forced convection produced by rotation of crystals can take the interface between solid and liquid and "isolate" them from each other, also causing the thickness of boundaries to become uniform. However, forced convection, in and of itself, can cause new growth striation.

Another method is to find a way to reduce heat convection; for example, reducing the temperature gradient in fusion bodies(21-24), adding inhibitors to fusion bodies in order to inhibit the flow in those bodies(25-27), lowering the depth of fusion bodies(21, 28), etc.

Of course, if there is no gravitational field, there will be no heat conduction either. Therefore, those persons who have grown crystals in space ($g \doteq 0$) have achieved excellent results(25, 29). However, at the present time it is still impossible to eliminate convection caused by surface tension gradients(30).

Among the methods available for the observation of growth striation are optical microscopes, X-ray imaging techniques, electron probes and ion probes as well as other methods. Among these, the use of optical methods and X-ray imaging are the most common. One of the important new findings uncovered by these observations is the amplitude of the changes in the period and components of growth striation. This not only requires the analysis of what types of changes there are in the conditions of growth which can cause a certain type of periodic striation; it also requires a comparison of the levels of importance of the various types of factors involved in the striation which is caused. This is always a very delicate and, sometimes, a very difficult thing to do. Sometimes, it even reaches the point where there is no discernible order to it. Because of this, the only thing that remains is to characterize the growth striation and analyze the conditions of growth, then, put these efforts together in a timely fashion, carry out many analyses and repeated growth experiments; only then is there the possibility of discovering precise causes and making progress toward overcoming the problem. For example, Takagi(31) and others discovered that the 230 micron-period growth striations which appear in GGG crystals are produced by small, sudden changes in the potentiometer power readings for each rotation; this is one example.

It is easy to produce another example; growth striation is ordinarily a damaging imperfection; however, in the last few years there has also been discovered a very effective use for it, which is called boundary surface marking technology. This technique sets up in the crystal a very clear, temporary mark. It can be employed to accurately determine minute growth speeds and changes in those speeds; it can distinguish simultaneously between different types of growth areas, etc. At present, there are three methods that can effectively control striation; they are the vibration method, the temperature method, and the thermoelectric method. In order to gain a better understanding one should consult the literature(32).

4. Color Centers

The problem of color centers in crystals includes a great deal of material; concerning optical crystals, color centers can lead to supplementary optical absorption which can profoundly influence the optical capabilities of crystals. For example, a crystal made from a compound of neodymium, aluminum and yttrium is a reddish-brown color when it comes out of the oven and puts out almost no light excitation . There are some Nd:YAG crystals which, due to the light absorption of color centers cause the light excitation efficiency of the crystals to drop, severely effecting the quality of the crystals.

The causes of color centers in crystals can be divided into two types; one is impurities; the other is imperfections in the crystal structure; this phenomenon is also related to the conditions of growth.

For example, a content of only 4 ppm of Ce^{3+} ions is enough to make Nd:YAG crystals carry a yellow color. Moreover, approximately 10 ppm of Dy^{3+} and Fe^{2+} ions, in the 1.06 micron optical absorption range, can cause the optical excitation of Nd:YAG to be destroyed(33).

Besides this, oxide crystals often form color centers because of shortages of oxygen.

If one is growing $KNbO_3$ crystals and if the fusion body content of K_2O is too high, even if other conditions are relatively suitable, the crystals will often appear to have a blue color because of a shortage of oxygen; under these circumstances, it is necessary to employ special heat refining measures (maintaining temperatures higher than the 150°C melting point for 24 hr); only after these measures are taken is it possible to obtain pure, high-quality colorless crystals(7). The results of research by several units here in China is that when fusion bodies are initially employed they always result in a blue-colored crystal; however, if use of the fusion bodies is repeated several times, even at relatively low refining temperatures, it is possible to obtain colorless crystals. The reason for this is still not very clear.

Due to the fact that color centers are difficult to directly characterize, it is necessary to employ supplementary experimentation and to closely correlate crystal growth experiments in order to aid "diagnosis". For example, one has the idea of adding a certain type of impurity, observe changes in the color center situation, and, by this means, precisely determine which kind of trace elements produce which types of color centers and the reasons for these relationships. Again, taking Nd:YAG crystals grown in a graphite resistance oven as an example, (34)when the crystals come out of the oven, they unexpectedly have an absorption peak of 3700 angstroms; often, simultaneously, there is an absorption peak of 4800 angstroms and the crystals have a brown color. However, somewhat later, in the air, annealing and ultra-violet tests reveal(36): the 3700 angstrom absorption peak becomes an even more intrinsic characteristic; only under certain conditions does the 4800 angstrom absorbtion peak exist and the crystals have their brown color. If these conditions do not exist, the 4800 angstrom absorbtion peak will not appear. Concerning the cause of the 3700 angstrom absorption peak, an analysis of gases in the furnace reveals(35) that the oxygen partial pressure in the furnace is extremely low, the reduction of the gases is very strong and that the combination of high temperature and air annealing can completely destroy the 3700 angstrom absorbtion peak. Because of this, it can be conjectured that(35,36): given these kinds of oven gases, the color centers which form in the large oxygen spaces which form in the crystals are the major cause producing the 3700 angstrom absorbtion peak. Subsequent experimentation also revealed that, in the growth process, the CO contained in the furnace is always added. This simply confirms even more the possibility of fusion bodies in the growth process or oxygen shortage in the crystals as reasons for the formation of color centers(37). However, the extremely low oxygen partial pressure in the gases of the oven as well as the strong reduction are both theoretically capable of causing oxygen spaces; references(35)speculate that the extremely low oxygen partial pressure is the principal cause. In order to make progress in actual characterization, specimens of material (34)from the top and bottom portions of crystals, and seperate samples were taken from this material in order to determine the heights corresponding to the peak values of the 3700 angstrom absorbtion band; it was discovered that, in low temperature areas of the top of the crystals, the peak absorbtion values were all relatively small; it was demonstrated by the analysis of temperature-related changes in gases that lowering of the temperature causes a lessening of the reduction of the $CO-CO_2$ system; at the same time, the partial pressure of O_2 is lowered. Looking from this point of view, the appearance of the 3700 angstrom absorbtion peak is primarily due to strong reduction of the gases in the oven and is not primarily due to the size of the O_2 partial pressure. This is in very good agreement with the results of annealing experiments on the gases in a graphite resistance oven under high temperature. Because of this, one of the greatest possibilities is that, with forced or natural gases, the internal oxygen-space imperfections, which are created in the formation of crystals, could, in this way, explain all the experimental results and point out methods for the elimination of color centers(34).

5. Overall Constitutional Inhomogeneity of Crystals

In systems where the total amount of impurities in fusion bodies does not change, the average distribution of solvent in crystals closely corresponds to the formula below:

$$C_S = C_{B_0} \quad (1-g)^{K-1} \qquad (3)$$

C_{B_0} is the initial concentration of solvent in fusion bodies; g is the solidification fraction, that is, the fraction of the total initial volume of the fusion body which is occupied by the solidified part (assuming that the volume at the time of crystal formation does not change); C_S is the solidification fraction which is the solid component of g. From the formula above, it is possible to determine that, when $K \neq 1$hr, C_S changes gradually. Besides this, the uneven evaporation of constituents can likewise cause the solid bodies produced in crystal formation to exhibit a kind of gradual change.

Concerning the macroscopic inhomogeneity of crystal components, samples of the crystals can be put through qualitative analysis.

Concerning situations where the solvent coefficient of liquation is very small, ordinarily, fusion bodies with relatively large amounts of compund cause crystals which are pulled out to only occupy a small fraction of the fusion body; in this case the change in the value of g is not great; this causes the change in the concentration of impurities in crystals to be relatively small; therefore, this improves, across the board, constitutional inhomogeneity. For example, Nd:YAG crystals are usually handled in this way.(38)

Moreover, $LiNbO_3$ crystal inhomogeneity is related to the chemical composition of the fusion bodies. Crystals which are grown from fusion bodies which have ideal compositional mixes (Nb_2O_5 and Li_2O each constituting 50%), change on the order of $3x10^{-4}$/cm due to the dual index of refraction produced by constitutional changes. This severely limits the effective phase match length of crystals. Moreover, fusion bodies which use the same composition (51.5% Nb_2O_5, 48.5% Li_2O) grow crystals which can have changes as low as 4×10^{-6}/cm or less due to the dual index of refraction produced by compositional changes(16). Again, if one is growing BNN crystals from a compound of niobic acid, barium and sodium, crystals which are grown with fusion bodies made with an ideal compositional mix have from one end to the other a curie point difference created by dissimilar constituents of $\Delta T_c = \pm 15^\circ C$, moreover, crystals grown with fusion bodies using the same constituent mixes have corresponding curie point differences of less than $\pm 5^\circ C$(39).

Gentile(40) has also used a "constant-temperature-long-bubble" method to cause thorough constitutional uniformity in KTN crystals. It works as follows: under conditions in which the crucible is hot on the bottom and cold on the top, there is placed at the bottom of the crucible considerable constituent material close to the solid material for crystal formation. The liquid flow takes the saturated liquid phase on the bottom and sends it to the top; there, where the temperature is relatively low, crystals form on the seed crystals. Due to the fact that the temperature of the seed crystals is constant, it is possible to obtain crystals which are completely uniform in their constituents. Concerning the curie point differences which are caused by constitutional inhomogeneity, horizontally $\Delta T < \pm 3^\circ C$, vertically $\Delta T \doteq 0^\circ C$ (the measurements of the crystals is 40x40x 30 mm).

If the surface layer is uneven, it will then be found that the inhomogeneity mentioned above not only manifests itself vertically, but also radially. A typical example would be Nd:YAG crystals grown on a concave surface at $\langle 111 \rangle$ direction; the centers and edges of these crystals often give rise to core centers and side centers formed by $\{211\}$ small crystal surfaces. The concentration of Nd^{3+} in the core centers will come out approximately 20% higher than in neighboring areas that have no small crystal surfaces. This is due to the segregation coefficient and the crystal surface index being different and causing disparities. In order to overcome this type of inhomogeneity, using crystals grown on flat boundary surfaces to control the appearance of small crystal surfaces is a workable and effective method.

Another very sensible method is the one reported by Fukuda and others(41); they employed the guide model method (EFG technique) to grow $Li(Nb_{1-x}Ta_x)O_3$ (x=0.05), and achieved specimens which were relatively uniform throughout. However, the basic principle behind this method is to determine the liquation coefficient on the basis of surface tension; the different types of ions in various fusion bodies give different liquation coefficients due to the fact that they have different surface tensions; this method certainly does not have universal aplication to the problem of overcoming overall inhomogeneity in crystals.

3, Constitutional Super-cooling and the Imperfections It Causes

ae phenomenon of constitutional super-cooling is one subject in the theory of crystal which has been researched relatively successfully. The relationship between crystal fections and growth conditions which this research has uncovered has already received e amounts of experimental verification and has successfully been used to guide the improvement of growth thechnology.

In the work of experimentally growing crystals, constantly preventing the phenomenon constitutional super-cooling is necessary if one is to greatly increase the quality of ystals grown. However, regrettably, this important phenomenon was neglected by people or a long time; therefore, some people are of the opinion that those who work with the rowth of crystals should be made to constantly remind themselves of this phenomenon and that the words "Constitutional Super-cooling" should be carved on the door of every laboratory(42).

What follows combines our own work and reports from abroad, taking the growth of crystals by fusion as the main subject, in a discussion of this problem.

1. Theoretical Analysis of the Phenomenon of Constitutional Super-cooling

Considering only stable state growth systems, if the constituents of the crystals and the fusion bodies are different, we take and simplify it into a single two-element system for purposes of consideration. In this system, one part is seen as an impurity in the broad sense; its concentration is noted as C; if its effective liquidation coefficient is less than one, then, during the growth process, due to the "rejection" function of the boundary surfaces, a concentration gradient can be produced; therefore, this causes the equilibrium solidification temperature at various points on the fusion bodies to undergo changes (see Fig 3).

If the positive temperature gradient on fusion bodies is not large enough, as in straight line I, then, there can still exist in the fusion body a super-cooled area (the shaded section in the figure). This type of super-cooling phenomenon, which is caused by constituent changes, is refered to as constitutional super-cooling. From Fig 3 one can see that conditions under which constitutional super-cooling does not appear are when the rates of slope of the temperature distribution curve for the fusion bodies and the equilibrium solidification temperature curve are at least equal on the boundary surfaces. That is, in the formula

$$\frac{G_L}{V} > \frac{mC_s}{D_L}\left(\frac{1-K^*}{K^*}\right)K \qquad (4)$$

except for the symbols which have already been used, G_L is the vertical temperature gradient in fusion bodies in the vicinity of the boundary surface between solid and liquid; m is the rate of slope of the liquid phase line. In Fig 3 x is the distance from the boundar surface between solid and liquid.

Pay attention to $K^*=C_S/C_{L_0}$ (when x=0, $C_L=C_{L0}$) and $K=C_S/C_B$, equation (4) can be rewr ten to be

$$\frac{G_L}{V}>\frac{m}{D_L}(C_{L_0}-C_S) \qquad (5)$$

At low pull speeds, $K^*\approx K_0$, that is, $C_{L_0}\rightarrow C_L$, therefore, in the equation below

$$\frac{G_L}{V}>\frac{m}{D_L}(C_L-C_S) \qquad (6)$$

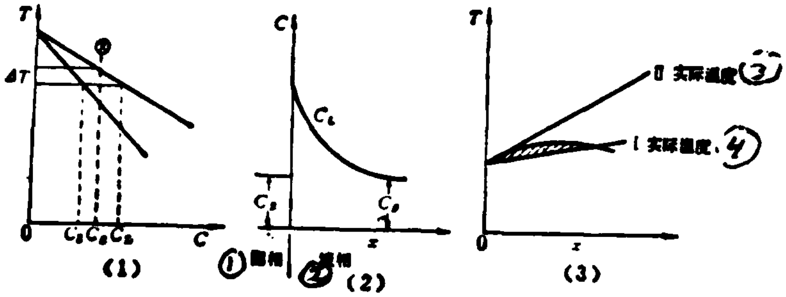
$_L$ and $_S$ are the equilibrium concentrations of the two phases, solid and liquid. It can en that G_L/V as well as C_L and C_S, which are required for the prevention of constitutio er-cooling, are also related.

It should be noted that what is employed here is a very rude model of steady state th. Because of this, later there will be others later who will do more perfect perturb- on analysis in order to consider the influences of other factors. However, under norma ing conditions, simple constitutional super-cooling as defined by equation (4) and de iption of that phenomenon by a complete perturbation analysis would differ very lit

, Experimental Facts and Discussion Related to the Phenomenon of Constitutional Super-cooling

Concerning the conditions of constitutional super-cooling, during the [illegible] pe- from the boundary layer into the fusion body, the level of super-cooling is inc- because of this, if there happens to form on the boundary surface a convex edge, will grow somewhat faster, and the fusion body between the convex edges, due to ncy of the convex edge to reject impurities, will have an increased concentratio ties, its melting point will be lowered, and it will have difficulty solidifying the boundary surfaces become even more unstable.

sent it is already known that constitutional super-cooling, under the most sev can make crystals exhibit bush-like growth with the presence of branches and ,46); after this comes cloudy striation (severe but intermittent constitution ng)$^{(47)}$, network-like structures of uneven weight (regular cellular structure



(1) (2) (3)

Fig. 3

1. Solid
2. Liquid
3. II Actual temperature
4. I Actual temperature

and irregular cellular structures)(48), and, as shown in Fig 4, this leads directly to minute "threads" and "dots", which can only be seen under a microscope.(47,49).

Generally speaking, it is very easy to make people realize that severe network-like structures are caused by constitutional super-cooling, and minute-scale imperfections like "threads" and "dots" are, therefore, frequently overlooked. In reality, these types of imperfections are also the results of constitutional super-cooling, although the severity of the effects is less.

2) Large amounts of experimental data demonstrate that [50-52], on a graph relating C_B and $\frac{G_L}{V}$, there exists a line of demarcation determining whether or not network-like structures appear or not. As is shown in Fig 5(1), if one takes these data and uses them to construct a chart reflecting the relationship between G_L, C_B and V, then, it can be easily seen that the occurrence-non-occurrence line for network-like structures follows changes in C_B or G_L; see Fig 5(2) and 5(3). For example, under the growth conditions indicated at P, if C_B is a short time, crystals have no network-like structures; if C_B is a large amount of time, then, network-like structures do appear.

Konodo(53)and Niizeki(54), while growing $Rh:LiNbO_3$ crystals, also discovered that, when G_L/V is somewhat longer time, there also exists an analogous occurrence-non-occurrence line for growth striation (see Fig 6, extracted from graphs in refemces (48) and (53)). This seems to indicate that growth striation is caused by increased temperature gradients promoting convection instability of fusion bodies.

Of course, it is entirely possible for there to exist this kind of situation: that is, when the value of G_L/V, which is needed to overcome constitutional super-cooling, is, at the same time, large enough to cause growth striation. Almost all the crystals which we saw containing the growth striation phenomenon were most likely of this type. For example, for certain GGG crystals, after using optical methods to examine them from several directions, we could not see any growth striation. However, on an X-ray diffraction scan, growth striation was still found to exist.(55) At the very least, the $Rh:LiNbO_3$ example demonstrates that, among the prerequisites for overcoming constitutional super-cooling, the reduction of the temperature gradient is effective in raising the quality of the crystals.

However, the value of G_L/V cannot approach too closely the critical point. We still must consider the temperature oscillation produced by fusion body convection instability; therefore, causing temperature gradient oscillation. This type of oscillation creates the possibility for having the discriminator line which runs across the middle of Fig 6 and describes instantaneous growth speeds, thereby producing instantaneous constitutional super-cooling. Concerning the critical maximum value of G_L/V, this question is in great need of attention. Because of this, in order to raise the quality of the single crystals produced,

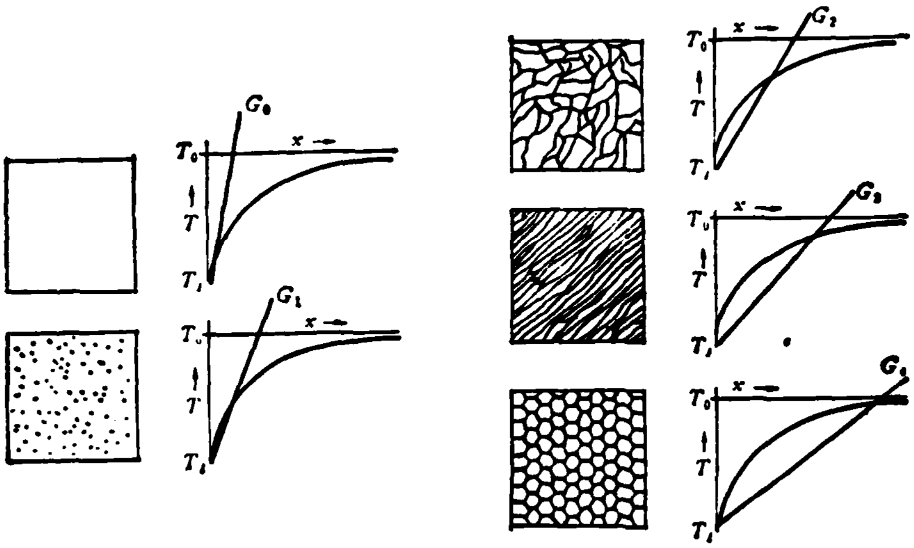
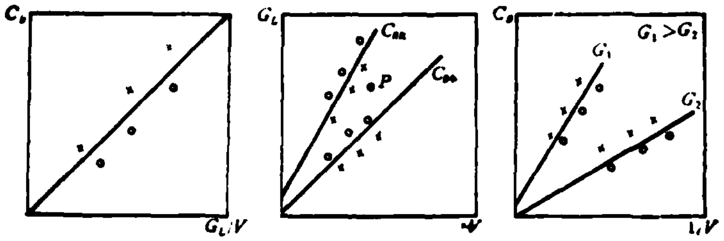


Fig 4

Fig 4 Relationship Between Constitutional Super-cooling and Crystal Imperfections [48]



(1) (2) (3)

1 图 5 晶体中网络结构出现与否和生长条件的关系

×一表示晶体中出现网络结构，○一表示不出现网络结构

Fig 5

1. Fig 5 The Relationship Between the Occurrence of Network-like Structures in Crystals and Growth Conditions x-stands for the occurrence of network-like structures in crystals 0- stands for the absence of network-like structures

we must first use an optimum value of G_L.

3) If we take a group of values of G_L/V which have been employed to eliminate constitutional super-cooling during the growth of various crystals, as these values have been

reported in several articles, and arrange these values in order from largest to smallest, it is possible to arrive at a pattern like the one in Table 1.: the size of G_L/V is definitely related to the ease of crystal growth. When materials were used in which the value of G_L/V was very large, crystal growth was exceedingly difficult (however, the values of G_L measured by various people can, because of the different methods used, be different; also, the values of V used are not necessarily critical values; therefore, these comparative values can only offer a brief outline of a comparison).

A point worthy of attention is that, due to equation (6), the crystal material which has particularly large constitutional differences between solid and liquid phases requires relatively large critical values of G_L/V; because of this, there is considerable difficulty with crystal growth. Real attention is already being paid to this point$^{(41)}$.

4) In equation (4), what, in fact, does C_B represent? Giving tentative consideration to the simplified, two part phase diagram (Fig 3(1)), the liquation coefficient of the impurities in this system (impurities in the broad sense) is $K_0 < 1$; therefore, under conditions in which there is a fixed degree of super-cooling during crystal growth, the situation is as displayed in Fig 3(1). As C_b increases, C_L-C_S also increases. Therefore, C_B, in this meaning of it, represents the relative sizes of the constitutional differences of the solid and liquid phases. Concerning crystals which have impurities in them, this is nothing but the amount of impurities contained in them with $K_0 < 1$. Concerning the general situation with impurities, we can say that any factor which is able to cause constitutional differences between solid and liquid phases can be considered to be represented by C_B. For example, the amounts of Li_2O or Nb_2O_5 which are deviations from the same constituent mix and are present in $LiNbO_3$ fusion bodies$^{(59)}$. These could also be called "constitutional impurities" in order to reflect their difference from the other types of impurities that have been discussed. Moreover, CBr_4 crystals and liquid phase component distinctions can be influenced by the addition of a second compound, C_2Cl_6, which can be added$^{(66)}$. Therefore, we can just as well call them "compound impurities". Again, concerning the situation of fusion body growth of crystals like $Li(Nb_{0.35}Ta_{0.65})$ and many other multi-constituent crystals, growth of these crystals is very close to growth of crystals by the solution method; C_L-C_S is relatively large; growth speeds are all very small, creating the complicated factors creating constitutional super-cooling; we could just as well call these "solution impurities." There have also been those who have raised the "structural super-cooling" viewpoint$^{(68)}$, which says that fusion bodies or solutions first form crystal formation units of different sizes; the parts or sections grow to the top of the crystals and stop in the diffusion layer where they have a function analogous to that of impurities.

3. Several Measures for Overcoming Constitutional Super-cooling

Mehtods which are employed to overcome constitutional super-cooling and which have

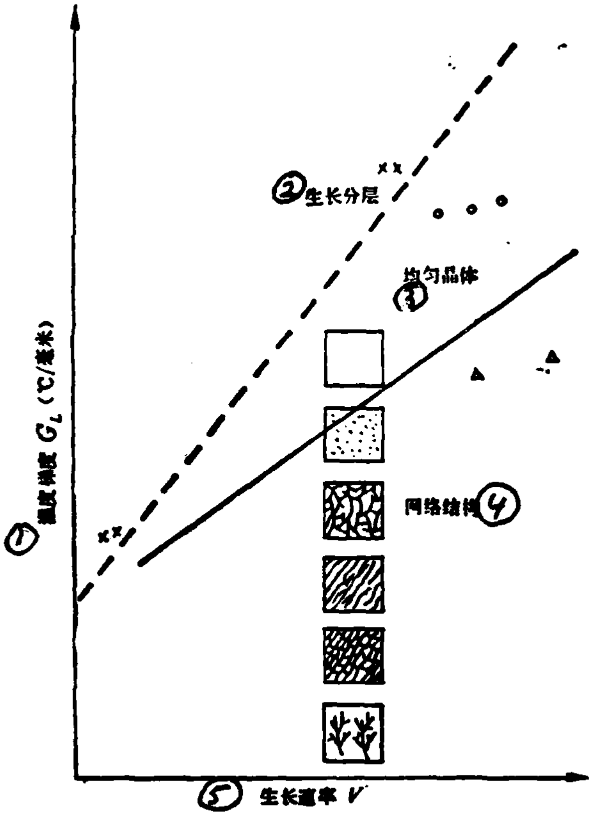


Fig. 6

Schematic diagram of component supercooling and growth layer in G_L - V chart

1. Temperature gradient G_L (C/millimeter)
2. Growth layer
3. Homogeneous crystal
4. Network structure
5. Growth speed V

been used according to theoretical estimates based on successes in understanding the theory of constitutional super-cooling can frequently obtain satisfying results. According to equation (4) and equation (2), most of the methods increase G_L and reduce C_B, δ or V. Below, the various methods are distinguished and introduced.

1) C_B (Fusion body constituent). If impurities are added purposely in order to give particular capabilities or characteristics to crystals, then they are not a parameter which can be regulated. The only thing is that, due to the fact that constitutional super-cooling has limited the specific growth conditions, the concentration of impurities cannot be too high. Besides this, other "impurities" should all be reduced as much as possible.

Concerning compounds which all possess the same constitutional points, their compositions should be precisely analyzed, and, then, using rigorous mixing techniques, the composition of crystals should be made as close as possible to the composition of fusion bodies. Concerning the composition of fusion bodies around crystals, it is even more neccessary to carry out their selection according to actual phase diagrams and experimentation.

There are those who say that, due to many reasons, it is very difficult to acheive the ideal composition of fusion bodies which is required; because of this, it is suggested that a "volley fire" method be used for carrying out experimentation(69). Initially, estimate the outer boundaries of the vicinity of the numerical value, on the basis of this estimate, make up several fusion bodies of different compositions, and then, from the results of actual crystal growth, carry out a comparison.

Concerning fusion bodies of a fixed composition, change the value of G_L/V, and obtain the discriminator point for the occurrence or non-occurrence of network-like structures. Taking a series of these discriminator points, line them up and one gets a discriminator line; suppose that the discriminator line and the vertical constitutional axis of a fusion body intersect at a point A (Fig 7), then, when the fusion body constituent is A, it is possible to allow very large growth speeds and still not cause the occurrence of constitutional super-cooling ($G_L/V \rightarrow 0$). Therefore, A corresponds to the optimum composition of fusion bodies at which $C_B \longrightarrow 0$ (that is, the composition points are the same).

In actual application, due to the fact that it is difficult to get a precise analysis of G_L, and, due to the influence of factors such as fusion body convection or cold air in the observation window or differences between the gas temperature and the liquid temperature, it is frequently very difficult to get uniform numerical values from one observation to the next. Therefore, we may as well say that the temperature gradient is fixed and only change the pull speed. For example, if one uses different pull speeds to grow different parts of the same crystal, as shown in Fig 8; one can then extract, using the method in Fig 7, the optimum composition of fusion bodies.

2) δ and liquid flow speed are related; the faster the liquid flow speed, the smaller δ is. It has already been said above that there are two kinds of convection in fusion

1 表 1 避免组分过冷所用的G_L/V值

2 晶体和熔体		G_L/V(°C·小时/毫米²) 3	4 资料来源
Al_2O_3(纯) 5		~1	[56]
$LiNbO_3$	φ≤20毫米 6	~1.1	[57]
	φ 40毫米 6	~2.5	[58]
	Li_2O=54%(分子) 7	~2*	[59]
	Li_2O=60%(分子) 7	5.5	[59]
	Rh:$LiNbO_3$	>2	[53]
	Mg:$LiNbO_3$	1.6~3	[54][60]
$LiTaO_3$	φ不大 8	1~2.3	[61]
	φ38毫米 6	1.16~	[62]
$Gd_3Ga_5O_{12}$(GGG)		2.5~3.5	[63]
$Ba_2NaNb_5O_{15}$(BNN)		2.5~4	[64][65]
$KNbO_3$		~6	[12]
$Sr_4NaLiNb_{10}O_{30}$		15~20	[4]
$Li(Nb_{0.95}Ta_{0.05})O_3$		20~25	[41]

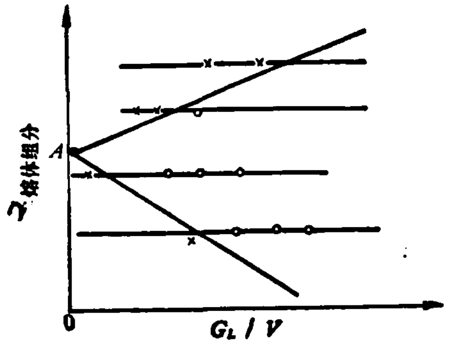
Table 1

1. Table 1 Values of G_L/V Used to Eliminate Constitutional Super-cooling 2. Crystals and Fusion Bodies 3. $^0C \cdot hr/mm^2$ 4. Reference source 5. pure 6. mm 7. molecular 8. not large

bodies: heat convection and forced convection. Forced convection is strengthened as the speed of crystal rotation increases. Heat convection is strengthened as the temperature gradient is increased. These two types of convection are mutually opposed; therefore, under any given speed of crystal rotation, the two types of convection reach a balance, causing the liquid flow of the fusion bodies to greatly weaken; δ is obviously increased, and it is at this time that the phenomenon of constitutional super-cooling appears; this must be prevented by any means possible (15). In the growing of Nd:YAG crystals, the critical rotation speed value $w_c \sim [ga\Delta TR^3 \pi^{-2}]^{1/2} d^{-2}$ has already been confirmed; in this case R is the diameter of the crucible. Ordinarily, one employs relatively low pull speeds (very convex boundary layers) or slightly high critical values for rotation speed (flat boundary surfaces) in order to prevent constitutional super-cooling. The actual choice of a high or low speed of rotation ought to consider the possible production of other imperfections as well as the size of their influence.

3) G_L and V

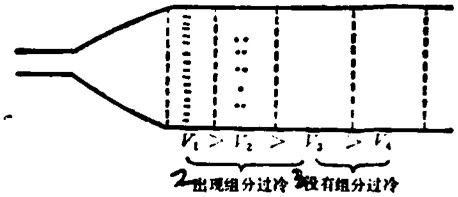
A moderate range adjustment of G_L and V is the most effective, simplest and most convenient method for overcoming constitutional super-cooling. For example, Nd:YAG crystals normally have a growth speed of approximately 1mm/hr; however, under similar conditions, when Nd and Lu:YAG crystals are mixed, they may produce the phenomenon of constitutional super-



1 图 7 寻找最佳熔体组分的"排炮法"示意图
×—晶体内有网络结构，○—晶体内无网络结构

Fig 7

1. Fig 7 Illustrative Chart of the "Volley Fire" Method of Determining the Optimum Composition of Fusion Bodies x- network-like structures appear in crystal O-network-like structures do not appear 2. Fusion Body Composition



2 图 8 用不同拉速生长同一晶体的情况示意图

Fig 8

1. Fig 8 Illustrative Chart of the Situation When Different Pull Speeds Are Used to Grow the Same Crystal 2. Constitutional Super-cooling Occurs 3. Constitutional Super-cooling does not Occur

cooling. Comperchio and others(70) took the growth speed and lowered it to 0.03mm/hr thereby successfully overcoming constitutional super-cooling and obtaining crystals of excellent quality. However, excessive increasing of G_L and lowering of V can also bring with it disadvantageous influences, such as, instability of heat convection, pull rod "crawl", fluctuations in temperature, the influence on V will become excessively clear, etc., etc.

When there is no other way, we may as well initially employ a relatively large G_L in order to overcome constitutional super-cooling. Because the influence of constitutional super-cooling on crystals will normally be greater than the imperfections caused by thermal stress, the subsequent use of a high-temperature, long-duration annealing method eliminates the thermal stress produced by the size of G_L.

4) Recently, Jackson and others(71) also employed periodic remelting and regrowth techniques; in experiments, they were able to determine the optimum period for and extent of remelting ; they were also able to take imperfections on the surface of crystals and eradicate them. Therefore, under conditions in which the original inclusions produced and constitutional super-cooling were not changed, they were still able to achieve relatively good results. It seems that this is a new avenue of approach in the overcoming of the phenomenon of constitutional super-cooling.

4, Conclusions

Above we have already seen that characterization is extremely important to the development of the work of growing crystals and ought to receive adequate and serious attention; however, on the other hand, if observation and research on imperfections does not grow apace and become related to the parameters of growth and the basic problems of growth, then, that research and observation cannot be of much help in the growing of crystals; moreover, the formation and principles of organization of many imperfections cannot be grasped with complete clarity (for example, the various kinds of imperfections caused by instability of liquid flow, which are at present being extensively researched, are of this kind); because of this, without progess in each of these areas, observation and research alone can be useless in both the areas of crystal growth and characterization.

We hope that, in the period of experimental growth when crystals are still being grown badly or not well enough, we will be able to closely cooperate in both areas, take observed imperfections and relate them to conditions of crystal growth, as well as carrying out appropriate numerical analysis, thereby obtaining the optimum values for several important conditions, which can be used in carrying out yet more growth experimentation and, through repetitions of this cycle, obtain crystals of excellent quality. At the same time, we hope to, step by step, precisely determine and experimentally verify the causes of imperfections; perhaps we will be able to discover in the characterization process a type of imperfection which has a large influence on the capability of crystals (such as, granular diffusion in Nd:YAG, which severely influences its optical excitation capability) and immediately "feedback" to the growth process a precise correction of growth parameters and obtain sooner an even more perfect crystal of superior quality.

This is nothing more than being able to gain relatively deep understanding of the process of crystal growth from observations of imperfections and, thereby, guiding more growth experimentation. Or, to turn it around, only after repeated experimentation in crystal growth is it possible to check out this knowledge, which then makes it possible to offer even more clues for the improvement of this knowledge. In recent years, the science of crystal growth has been in the process of a gradual maturation; the gap between theory and practice has been gradually narrowed; in some areas these two aspects have already been unified (critique of attendence at the 1977 Fifth Session of the International Crystal Growth Conference). The problem of constitutional super-cooling which this article concentrates on discussing is an example. Not only can the theory of constitutional super-cooling be used to explain the formation of network-like structures which can be seen by the naked eye, but it can also be extensively used to explain the occurrence of several types of imperfection. By taking the results of these observations of imperfections and putting them through an effective analysis of constitutional super-cooling, one can link them to many aspects of the conditions of crystal growth, can obtain optimum values for these observed quantities and, thereby, grow crystals of high quality.

Due to the gradual maturation of conditions, at present, internationally, every day brings more serious attention to the dual problems of crystal growth and characterization. For example, at present there are, already published, both books and periodicals called "Crystal Growth and Characterization"(54,72); however, there seem to be currently only two all together and these are of simple content; this is very inadequate. In order to quicken the development of the science of crystal growth in China, we suggest that workers in the fields of crystal growth and characterization cooperate closely and join their minds in collective effort to rapidly raise the level of the work of crystal growth and characterization.

Generally speaking, the international trend has been, in recent years, to take several crystals which have practical value and grow them well and in large quantities; at the same time, in the process of investigating new materials, there gradually appeared many crystals which were relatively difficult to grow; their application capability was rather good, and they had a future; however, there was still no satisfactory growth method which allowed the obtaining of large, high-quality single crystals; this limited their application and spread. Among these crystals were inclusion crystals such as $KNbO_3$(7,12), $Sr_2NaNb_5O_{15}$(4), YIG, $BaTiO_3$ and so on (according to preliminary estimates, among the several thousand oxides already known, inclusion crystals account for about half)(74). Again, as in the phase diagram, crystals whose solid phase line and liquid phase line have large distances between them, such as, KTN($KTaO_3$-$KNbO_3$)(75) and so on, as well as crystals which have complicated compositions and structures, such as, $KMg_3(AlSi_3)O_{10}F$ (artificial mica)(68), $Sr_4NaLiNb_{10}O_{30}$(4) and protein crystals, etc., as well as crystals whose components and structure easily give rise to changes, such as, $CaCO_3$, KIO_3, etc. (sic) This is a technical problem taken from actual practice; at the same time, it gives to the science of crystal growth a new subject for in-depth research. We feel that it is already time to take research into crystals that are relatively difficult to grow and put it on a daily work schedule. If this type of problem in crystal growth could be solved, on the one hand, it would be helpful to the work of investigating new crystal materials, and, on the other hand, would promote the steady development of crystal growth theory and technology.

Besides this, characterization methods are very numerous; however, each method has advantages and disadvantages, and we must choose the strong and improve the weak; we cannot overemphasize one method to the neglect of the others. Speaking comparatively, optical methods run from 2000-3000 angstroms and X-ray and electron beam methods can reach 0.5~1 angstroms. Therefore, concerning very minute imperfections, it is necessary to use X-ray scan or electron microscope technology. However, optical methods are simple, convenient and visual; moreover, they can explain the distribution forms of large-scale imperfections(15); sometimes, it can also easily and simply explain problems which are not easy to explain using X-ray technology, for example, the perpendicular a,b,and c axes of crystals as determined by a light cone diagram(4).

According to preliminary estimates, concerning crystals in general (includes crystals whose level of perfection and growth are experimental), among their imperfections, it is possible to use optical methods of observation in about 70-80%; those which require the use of an electron microscope acount for about 10%; those requiring the use of X-ray scaning techniques is about 10%; and other methods (the corrosion method, the "rag ornament" method, etc.) account for approximately 5%.

Sometimes, relying exclusively on direct observation (that is, observation after a crystal has already completed its growth) makes it difficult to precisely characterize imperfections and easy to make mistaken judgments. If, during the process of adding heat we observe changes in the crystals' light cone diagrams, we can also visually observe phase changes in the crystals and determine the temperatures at which these phase changes take place(4). In the process of adding heat, we can also observe imperfections in the crystals "in operation", so to speak.(76) If progress is made in the application of magnetic fields, electric fields or the carrying out of strong light irradiation, neutron activating irradiation, and so on, and experimentation and observation is carried out in these areas, then, there will be even more news to bring to the attempt at precise characterization of imperfections.

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Summary

CRYSTAL GROWTH AND CHARACTERIZATION

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Imperfections such as cracks, inclusions, growth striations, color centers, inhomogeneity and cellular structures, that frequently occur in artificially grown crystals are discussed. The phenomena of constitutional super-cooling are dealt with more details. The origins of occurance of these imperfections and the measures adopted to overcome them are recommended. It is stressed, moreover, that the work on growth of crystals and their characterization must coordinate intimately so that the final goal of obtaining perfect crystals may be attained through successive stages of experimental research.