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CZOCHRALSKI GROWTH OF $LaAlO_3$

FINAL REPORT

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TABLE OF CONTENTS

LIST OF FIGURES

I. SUMMARY

The objective of this program was to explore the possibility of growing high optical quality $LaAlO_3$ by the Czochralski method. The techniques developed for ruby growth were found to be directly translatable to $LaAlO_3$ with no apparent limitations imposed by the use of a crucible. Undoped and doped (Cr^{3+}, Eu^{3+}) crystals of various orientations were grown.

Two major defects were encountered: color centers and twinning. Color centers were eliminated by using high purity starting materials in combination with selected growth and post-growth treatment. Two mechanisms for forming color centers are proposed and their relation to $LaAlO_3$ defect chemistry is discussed. The dominant twin planes have been identified to be those of the (100) system. Their relation to the crystal structure of $LaAlO_3$ has been elucidated.

Isolated attempts were made to grow $BiAlO_3$ and $PrAlO_3$ to determine if twinning might be a problem in these potential host compositions; other growth problems were encountered indicating that an answer could be obtained only by an extensive effort beyond the bounds of the present program.

II. INTRODUCTION

Of the many known III-III perovskites (ABO_3), only one ($LaAlO_3$) has been found to exist in the ideal cubic phase; however, the cubic phase exists only at elevated temperatures. At room temperature, $LaAlO_3$ is rhombohedral, having a rhombohedral angle of 60°6' referring to the primitive rhombohedral cell or 90°5' referring to the face centered rhombohedral cell.

Because the departure of the unit cell from the cubic is so slight, it has been hoped that such a material would provide an attractive laser host for substitutional doping of trivalent ions in either the A or B sites. $LaAlO_3$ has been shown to be an attractive host in that fluorescence data from Cr^{3+} doped $LaAlO_3$ is reported to be

25[1) - 34[2) milliseconds at room temperature as compared to 3 milliseconds for Cr^{3+}: Al_2O_3, while for Nd^{3+} doped $LaAlO_3$, the lifetime of the dopant is enhanced by a factor of two relative to that in $CaWO_4$ and Y_2O_3[2).

However, $LaAlO_3$ heretofore available was unattractive optically because of a twinning defect. The material on which fluorescence data were obtained was Verneuil grown. The present work was undertaken to explore whether Czochralski-grown material suffered the same defect or whether, by virtue of reduced stresses during growth, twinning would be avoided. In the course of this program it became apparent that the structural basis for twinning needed elucidation. Hence this aspect of the problem received attention.

III. CRYSTALLOGRAPHIC DATA

A. Structure

Geller and Bala[3) have done an extensive survey of rare-earth aluminates and in particular $LaAlO_3$. They reported that $LaAlO_3$ is rhombohedral belonging to the space group $R\bar{3}m$ and having unit cell dimensions of $a = 5.357Å$ $\alpha = 60°6'$ at room temperature. The above symbols mean that the unit cell has a 3 fold inversion axis along the body diagonal and a mirror plane parallel to this axis as symmetry elements.

The Al^{3+} occupy the eight corners of the rhombohedron and its center (Figure 1). In addition to being on the 3 fold axis, they occupy the inversion center of the unit cell. The La^{3+}, however, do not occupy an inversion center, but are approximately 0.01Å from it along the body diagonal, as indicated by arrows in Figure 1.

[1) F. Forrat, R. Jansen and P. Trévoux, Comptes Rendus Acad. Sci. t 256 1271 (1963).

[2) Laser Materials Final Report - Korad Corporation No. AD 439901.

[3) S. Geller and V. B. Bala, Acta Cryst., 9 1019 (1956).

Derighetti, et al.[4], however, report the most probable space group to be $R\bar{3}c$ on the basis of electron paramagnetic measurements. In this space group, the mirror plane is replaced by a glide plane; however, the Al^{3+} positions remain the same as in $R\bar{3}m$. The structure would thus have equivalent La^{3+} sites and Al^{3+} sites. In either space group, the Al^{3+} are the only atoms located on an inversion center and long fluorescence lifetimes can only be predicted for atoms substituted on the B site. This, in fact, seems to be the case for Cr^{3+} and not for rare-earth dopants on the A site.

B. Phase Change

In addition to the room temperature data on $LaAlO_3$, Geller and Bala took high temperature x-ray powder patterns of $LaAlO_3$. Here they found a gradual change from the rhombohedral to the cubic cell with increasing temperature. They were unable to detect any additional change above 350°C. Wood[1], however, observed a phase change at 435°C ± 25°C. DTA showed no indication of a phase change implying that there is no appreciable heat of transition. Such results would probably indicate a second order transition.

Visible observations of the phase change of crystals from 1/2-inch to 2-inches in length in the present work showed it to be a gradual change as reported by Geller and Bala; however, the rhombohedral phase could be seen up to 512°C ± 3°C. This value is 77°C above that of Celler and Bala, 65°C above that reported by Gränecker and Müller[5] and 22°C above that reported by Bondar and Vinogradova[6].

C. Density

The theoretical x-ray density for $LaAlO_3$ using the cell constants as reported by Geller and Bala was calculated in this work to be 6.51 g/cc while the

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[4] B. Derighetti, J.E. Drumheller, F. Laves, K.A. Müller and F. Waldner, Acta Cryst. 18 557 (1965).

[5] H. Gränicher and K.A. Müller, Nuova Cim., Suppl. 6 Serx. X 1216 (1957).

[6] I.A. Bondar and N.V. Vinogradova, Izr. Akad. Nauk. SSSR, Ser. Khim. 5 785 (1964).

measured density of the solid crystal boules was found to be 6.16 g/cc. This agreement confirms the doubly primitive (two molecules per unit cell) rhombohedral unit cell chosen by Geller and Bala. Bondar and Vinogradova report a density of 5.84 g/cc, probably applying to powder samples.

IV. EXPERIMENTAL

A. Crystal Growth

The crystal growth chamber used for pulling ruby was found to be directly applicable to $LaAlO_3$ without change of design or materials. The chamber provides for atmosphere control (neutral or H_2-containing atmospheres were used for $LaAlO_3$ growth) and temperature control. The crucible was charged with La_2O_3 powder and crystalline Al_2O_3 (Verneuil crackle) in stoichiometric ratio. The melting point of pure $LaAlO_3$ was read to be 2075-2080°C, uncorrected pyrometer values. Several melts were checked for stoichiometry after having been held for 6-8 hours above the melting point and were found to have maintained stoichiometry with no detectable departure therefrom. There was no visible attack of the crucible and no crucible contaminant was found in the frozen melt by emission spectroscopy.

Crystals ranging from 8.5 to 43 grams and from 1/2-inch to 4-inch length were grown. A total of five different boule axis orientations were obtained; referred to the pseudo-cubic unit cell (transformations from cubic to rhombohedral to hexagonal indices are given in Appendix I) these were as follows: $\langle 111\rangle$, 20° from $\langle 111\rangle$, $\langle 2\bar{1}\bar{1}\rangle$, 10° from $\langle 2\bar{1}\bar{1}\rangle$, and $\langle 3\bar{1}\bar{1}\rangle$.

Several doped crystals were pulled in the "10° from $\langle 2\bar{1}\bar{1}\rangle$" orientation. Two different dopants were used separately: Cr^{3+} as a B site dopant and Eu^{3+} as an A site dopant, each introduced into the original charge as the sesquioxide. The melting point of the Cr-doped charge was higher than that of pure $LaAlO_3$ and increased with the Cr concentration in the range .07-2.2 wt % Cr_2O_3. The Eu-doped charge (0.1 to 1 wt % Eu_2O_3) did not show a melting point difference relative to pure $LaAlO_3$.

The La_2O_3 used initially for growth of $LaAlO_3$ was obtained from American Potash and had a purity rating of 99.99 and 99.997% with respect to rare earths (Code 528 and 529 respectively). Calcium, magnesium and silicon impurities were found to be present in concentrations of from 100 to 200 ppm each. All crystals grown from this material were a dark yellow-brown in color. At the present time a special grade of La_2O_3 has been obtained which has a total non-rare earth impurity level of about 60 ppm, the majority of this being silicon while the calcium and magnesium total less than 15 ppm. Crystals grown with this material are clear and colorless.

It was noted that during the initial heating of the unreacted oxides, two characteristic "breaks" could be seen in the heating curve. The first break occurred at about 1650° to 1660°C and was accompanied by a complete change in the character of the charge. The material would "puff" to perhaps twice its original volume. At about 1715°C, the exact reverse would occur, i.e., the "puffed" material would collapse into a dense charge and thereafter no change was noted until the melting point was reached.

The "puffed" material was very plastic at that temperature and it is believed the "puffing" is a result of a solid-solid reaction between the oxide components of the charge. The collapse of the charge is believed due to the increase in plasticity of the material with increasing temperature.

B. Crystal Quality

During the course of the first few tests, it became apparent that the seed orientation strongly affected the overall quality of the crystal. In the first few crystals pulled, a central defect could be seen which usually ran the length of the crystal. This defect was then terminated at the growth interface by a small depression. Figure 2 shows a photograph of such a depression. Examination of the figure will show that the depression is composed of many facets giving it an overall appearance of hopper growth. These facets have been found to be the (100) faces of the pseudo-cubic unit cell. It is believed that the central defect is a result of an overgrowth of the "hopper" section of the growth interface.

Such defects as described above have been found on all undoped crystals of $LaAlO_3$ that were grown along a low index direction. The crystals which have been grown along a high index direction did not show this defect and had few, if any, bubbles. Such results as described above would suggest that growth along a high index direction is desirable.

Another factor which strongly affected the crystal quality was the type of dopant used. When Cr^{3+} was placed in the melt, two things became apparent. First, as mentioned before, the melting point of the material was raised and more important the crystal quality of the boule dropped considerably. The addition of Cr^{3+} to the melt enhanced the faceting tendency of $LaAlO_3$ to such an extent that the (100) face was formed on the growth interface even though growth was in a high index direction. This faceting again led to the formation of oriented voids and bubbles throughout the entire crystal. A photograph of the growth interface of a Cr^{3+} doped crystal is shown in Figure 3.

One approach which can be taken is to grow at much slower rates. Several attempts at slow growth rates yielded promising results and crystals of Cr^{3+} doped $LaAlO_3$ have been grown with only a few bubbles and voids; however, examination of these crystals still showed twinning to about the same extent as in the undoped crystals.

Doping on the "A" site is an entirely different matter. Good quality Eu^{3+} doped crystals of $LaAlO_3$ have been pulled with no evidence of facets as were seen in the Cr^{3+} doped samples, though both were grown off the same seed rod. Examination of ionic sizes of Eu^{3+} and Cr^{3+} as compared to La^{3+} and Al^{3+} respectively shows a much better "fit" for Eu^{3+} than for Cr^{3+}. This fit could be part of the reason for the ease at which Eu^{3+} doped $LaAlO_3$ can be grown.

A third parameter which strongly affects crystal quality is the pulling rate. Crystals of undoped $LaAlO_3$ have been pulled at rates from 1/16 to 1 1/2-inches per hour. The crystals pulled at a rate of greater than 0.60-inches per hour showed a slight lineage structure in the center and as the pulling rate was increased so did the lineage increase until a point was reached where the entire crystal becomes opaque due to lineage. Figure 4 shows the effect of pulling rate on crystal quality.

C. Crystal Defects in $LaAlO_3$

Two defects exist in $LaAlO_3$ which would be detrimental to its use as a laser host. These defects are color centers and twinning. Both of these must be eliminated before single crystals of $LaAlO_3$ can be used for a laser host material.

1. Color Centers

The first of these defects which must be eliminated are color centers which give the crystal a yellow-brown color. Forrat, Jansen and Trévoux[1)] report that these color centers are due to vacancies on the La^{3+} site and can be removed by substituting on the vacant site mono-, bi-, or trivalent ions. Furthermore, they state that these are V color centers which implies a positive ion vacancy-hole combination. In addition to the La^{3+} ion vacancy, it has been found that the purity of the starting materials strongly affects the color of the final boule. As has been found in other crystal growth problems, e. g., Al_2O_3 and YAG, the presence of alkaline earths such as calcium or magnesium greatly affects crystal clarity.

The problem then becomes one of (1) eliminating the impurity atoms which cause the discoloration of the crystal or (2) permanent "bleaching" of the color from the crystal. Of the two choices, the first is by far the best. As already mentioned above, the first objective has been accomplished by use of a special grade La_2O_3.

"Bleaching" of the color from the boules has also been accomplished by growth in a hydrogen atmosphere or by heating the boules under vacuum to 1800°C for about 1 1/2 hours. The vacuum heated crystals, when removed, from the furnace were colorless; however, exposure to UV light caused them to again return to their original color.

The hydrogen "bleached" crystals were colorless as grown; however, as in the vacuum heated case, UV light caused them to turn to the characteristic yellow-brown color. Unlike the vacuum heated crystals, however, the color was not permanent and the crystals gradually became colorless after several hours. It was also found that prolonged heating in air at 450°C caused both the vacuum heated and hydrogen "bleached" to become permanently discolored. It should be pointed out that these dark crystals were grown from Code 528 or 529 La_2O_3.

2. Twinning

The other major defect in $LaAlO_3$ is twinning of the crystals which is a direct result of the phase change from the ideal, cubic perovskite structure to the rhombohedral structure. This phase change is accompanied by a gradual shift of the La^{3+} ion along the body diagonal of the pseudo-cubic unit cell and a shift in the opposite direction of the adjacent "body diagonal" La^{3+} ion. Such shifts as described above are accompanied by a distortion of the cubic cell. The rhombohedral-cubic-transformation and the direction of the La^{3+} ion shift are shown in Figure 1. The twins result when the initial shift of the La^{3+} ions at various parts of the crystal are along different, equivalent cube body diagonals. It should be pointed out that the twins formed have identical structures and the only difference lies in the orientation of one part of the crystal with respect to another part.

To determine the sets of twins present, disks of three different orientations were cut from a boule: (100), (110), (111), these indices defining the planes parallel to the disk surface. The (100) disk, shown in Figure 5b, showed two distinct sets of twin planes. These sets are at right angles to each other and are perpendicular to the disk surface. The (110) disk, shown in Figure 5a, showed two sets of twin planes. One set is perpendicular to the disk surface while the other set is inclined from the surface. A difference in the extinction angle between the two parts of the crystal separated by the perpendicular twin plane was found to be 30 ± 10 arc minutes. Figure 5c shows the (111) disk which has three separate sets of twin planes present. All these sets are inclined with respect to the disk surface, i.e. (111) plane.

Several attempts have been made to remove the twinning by annealing. Although heat treatment does not remove the twinning, it does tend to produce large areas where only one direction of twin planes are present and reduce the twinning to some extent.

D. Spectroscopy of Doped Samples

The fluorescent spectra of both the Cr^{3+} and Eu^{3+} doped samples of $LaAlO_3$ were taken using an ARL Quantograph and agreed closely with that reported by Korad Corporation. The Cr^{3+} doped sample of $LaAlO_3$ showed a line at 7350Å and had a line width of approximately 8Å at room temperature. No low temperature data was taken nor were lifetimes measured.

The Eu^{3+} doped sample showed four strong lines which are: 4462Å, 5175Å, 5930Å and 6175Å however no line widths were measured. As in the case of the Cr^{3+} sample, no low temperature data was taken nor lifetimes measured.

E. Growth of Related Hosts

1. $BiAlO_3$

At the start of this program, a search of the literature revealed numerous references to rare-earth aluminates. It was found that all these were of rhombohedral or lower symmetry, but as the rare-earth ionic radius increased, the material tended toward the cubic phase as shown in Figure 6 which shows the pseudo-cubic angle as a function of the "A" ionic radius.

If the curve can be extrapolated, an ionic radius of 1.20Å of a 3 plus ion could yield a cubic III - III perovskite at room temperature. Such an ion is Bi^{3+} which is reported to have an ionic radius of 1.20 in some literature. Furthermore a reference(7) was found in which $BiAlO_3$ was reported. With these facts in mind, an attempt was made to form $BiAlO_3$.

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(7) Naray-Szabo, Publ. Univ. Tech. Sc. Budapest 1 30 (1947).

One to one mole ratios of Bi_2O_3 and Al_2O_3 were mixed together and heated in a platinum crucible for 1 to 5 hours and at temperatures of from 800 to 1200°C. Examination of the frozen melt did show small hexagonal crystals, however, these were found to be α - Al_2O_3 only. Further attempts to produce $BiAlO_3$ gave only the α - Al_2O_3 crystals.

2. $PrAlO_3$

$PrAlO_3$ is reported to have the same space group as $LaAlO_3$; however, the distortion from the cubic is slightly more, the rhombohedral angle being 90°17' as compared to arc 90°5' for $LaAlO_3$ 1). The symmetry of the Al^{3+} site remains the same as in $LaAlO_3$, and therefore Cr^{3+} doped $PrAlO_3$ should exhibit the same fluorescence characteristics as Cr^{3+} doped $LaAlO_3$.

Furthermore, it was reported that the rhombohedral angle at 950°C was 90°9' 1). It was thought that a way to avoid the twinning problem in $LaAlO_3$ was to grow Cr^{3+} doped $PrAlO_3$ if the material melted while still in the rhombohedral phase. This value would be about 1950°C. The melting point of $PrAlO_3$ was found to be 2050°C or very close to the melting point of $LaAlO_3$. The material was much harder to grow than $LaAlO_3$ and had an emerald green color whose origin was not identified. The sample that was pulled was of insufficient optical quality to determine if twinning was present or not. Because of the difficulty of growth, no additional attempts were made to grow $PrAlO_3$.

V. DISCUSSION

A. Color Centers

As stated before, it was found that the problem of color centers in $LaAlO_3$ can be linked directly to the non-rare earth impurities in the starting material, in other words, the higher the non-rare earth impurity concentration, the more color centers produced. As a result of this observation, the color center problem in $LaAlO_3$ can be eliminated by careful selection of the starting material, giving particular attention to the concentration of calcium, magnesium and silicon.

If an alkaline earth impurity, either calcium or magnesium, is chosen as the color center producing agent, two possible mechanisms can be formulated to explain the experimental results. The first proposed mechanism consists of the diffusion of hydrogen into the crystal lattice and the association of the hydrogen with the lattice defect (color center). This mechanism is very similar to that proposed by Forrat, Jansen and Trévoux and can be represented by the following equations using the nomenclature of Kröger and Vink8).

$$H_2 \rightleftarrows 2H_i \qquad (i = \text{interstitial}) \tag{1}$$

$$H_i \rightleftarrows (H_i^+)^{\cdot} + e^- \tag{2}$$

$$(Ca^{3+}_{La^{3+}}) \rightleftarrows (Ca^{2+}_{La^{3+}})' + e^+ \rightleftarrows V \text{ color center} \tag{3}$$

$$(Ca^{2+}_{La^{3+}})' + (H_i^+)^{\cdot} \rightleftarrows (Ca^{2+}_{La^{3+}}\; H_i^+)^{\circ} \tag{4}$$

$$e^+ + e^- \rightleftarrows \text{ground state} \tag{5}$$

If such a mechanism existed, heating a "hydrogen containing crystal" would tend to drive off the hydrogen and produce color centers. Likewise, exposure to UV light could supply enough energy to break up the complex formed in equation (4); however, in this case, the hydrogen would be retained and could again complex with the calcium defect. This mechanism does not explain the disappearance of the color centers when heated in a vacuum. In fact, one would predict on the basis of the above mechanism an increase in the number of color centers in the crystal due to the evolution of hydrogen under vacuum.

The second mechanism results in the formation of oxygen vacancies due to the reduction of the oxygen partial pressure by the hydrogen. These vacancies would then tend to produce electrons in a similar manner as did the hydrogen. The increase in the concentration of the electrons would tend to reduce the hole concentration and therefore the color center concentration. This mechanism can be represented as follows:

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8) F. A. Kröger and H. J. Vink, Solid State Physics 3 307 (1956).

$$(V^{2-}_{O^{2-}})^{\circ} \rightleftarrows (V_{O^{2-}})^{\cdot\cdot} + 2e^{-} \qquad \text{(V = vacancy)} \tag{6}$$

$$(Ca^{3+}_{La^{3+}}) \rightleftarrows (Ca^{2+}_{La^{3+}})' + e^{+} \rightleftarrows \text{V color center} \tag{7}$$

$$e^{+} + e^{-} \rightleftarrows \text{ground state} \tag{8}$$

In a neutral atmosphere, the following equilibrium can be thought to exist between the solid and gas:

$$(La^{3+})_{1-2\delta}\,(Ca^{2+}_{La^{3+}})'_{2\delta}\,(Al^{3+})\,(O^{-2})_{3} + 2\delta e^{+} \rightleftarrows$$
$$(La^{3+})_{1-2\delta}\,(Ca^{2+}_{La^{3+}})'_{2\delta}\,(Al^{3+})\,(O^{-2})_{3-\delta}\,(V_{O^{-2}})^{\cdot\cdot}_{\delta} + \frac{\delta}{2}O_2\,(g) \tag{9}$$

Any reduction of the equilibrium oxygen vapor pressure in the atmosphere would tend to drive the above reaction to the right producing more oxygen vacancies in the lattice. Such a reduction can be accomplished by either vacuum heating or growth in a reducing (hydrogen) atmosphere. If such a sample were heated in air, a decrease in oxygen vacancies would result with a corresponding increase in the number of holes.

Of the two mechanisms proposed, the second appears more likely than the first since identical results can be accomplished by the use of CO as reported by Forrat et al. 1) Also the second mechanism appears more probable when compared to other perovskites such as $SrTiO_3$ which are known to have an oxygen vacancy-oxygen partial pressure equilibrium.

B. Twinning

The other major defect found in $LaAlO_3$ which greatly affected the optical properties of the boules was the twinning which resulted from the phase transformation from cubic to rhombohedral. Buerger[9, 10] has shown that crystals connected by a high-low phase transformation possess related symmetries, i.e. the symmetry of the low temperature form is a subgroup of the symmetry of the high temperature form. This implies that the symmetry of one form can be derived from that of another form by the suppression of one or more symmetry element sets in the unit cell. Furthermore, derivative structure theory can provide a basis for the prediction of the twin boundaries formed by such a phase transition and the prediction that the suppressed symmetry element can become the symmetry element of the twin.

For the case of $LaAlO_3$, the high temperature form is the cubic perovskite form which belongs to the point group m3m, space group Pm3m, while the low temperature (rhombohedral) form belongs to the point group $\bar{3}m$ and either the space group $R\bar{3}m$ or $R\bar{3}c$. The International Tables for x-ray Crystallography, Vol. I[11] shows that the point group $\bar{3}m$ is a subgroup of the point group m3m and likewise for the space group. Thus the suppressed symmetry set which results from the phase transformation is the set of mirror planes (m) perpendicular to the cube axes. The mirror planes perpendicular to the face diagonals remain as does the three fold axis. An inversion three fold axis arises due to the doubling of the original cubic unit cell to form the rhombohedral cell. Therefore, one would predict the twin planes to be mirror planes (as are most twin planes) perpendicular to the ⟨100⟩, ⟨010⟩ and ⟨001⟩ directions of the original cubic unit cell. Such twins are referred to as transformation twins and result in a change of direction (approximately 70°) of the ⟨111⟩ axis (body diagonal) of the true rhombohedral cell at the twin boundary. These predictions on the twin boundaries agree with the results observed on the (100) disk, the (110) disk and the (111) disk as shown in Figure 5.

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9) M. J. Buerger, Am. Min. 30 469 (1945).

10) M. J. Buerger, J. Chem. Phys. 15 1 (1947).

11) International Tables for X-Ray Crystallography, Vol. I p 36 (1952).

Two other forms of twins could exist. One of these forms occurs along the face diagonals of the cube that are not in the same plane as the body diagonal. However, such a twin requires the La^{3+} ions on the twin plane (mirror plane placed in the (110) plane) to occupy a special position on the twin plane. This form of twinning is more disruptive to the crystal than the transformation twin since it does require the La^{3+} ions to occupy their "cubic positions" on the twin plane. Since such a position would be highly unstable, the La^{3+} ion would tend to "flip" to one of the other rhombohedral directions and form a (100) twin.

The third form of twinning which might occur is along the (111) face of the cubic unit cell or the faces of the rhombohedral unit cell. This form of twin represents a gross distortion from the original cubic phase and can not be formed by a simple change of direction of the La^{3+} ion shift and therefore can only be formed during growth of the crystal. Such a twin is called a growth twin and is shown in Figure 7 along with the other forms of twinning discussed.

Of the three forms of twinning possible, only the transformation twin has been found in the crystals grown.

APPENDIX

I. CUBIC-RHOMBOHEDRAL-HEXAGONAL TRANSFORMATION

Because the departure of the rhombohedral unit cell is so slight when compared to the cubic cell, it is easier to refer different crystal directions to the cubic cell. The following matrix represents the transformation from the cubic to the rhombohedral unit cell. It should be stated that this transformation applies only for a rhombohedral angle of between 59 and 61°.

Transformation matrix

Transformation equations

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 1 & 0 \\ 0 & 1 & 1 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_R &= h_C + \ell_C \\ k_R &= h_C + k_C \\ \ell_R &= k_C + \ell_C \end{aligned}$$

where h, k, and ℓ refer to the Miller indices while C and R refer to the cubic and rhombohedral phases respectively. The inverse of the above matrix is:

$$\begin{bmatrix} 1/2 & 1/2 & -1/2 \\ -1/2 & 1/2 & 1/2 \\ 1/2 & -1/2 & 1/2 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_C &= 1/2\,(h_R + k_R - \ell_R) \\ k_C &= -1/2\,(h_R - k_R - \ell_R) \\ \ell_C &= 1/2\,(h_R - k_R + \ell_R) \end{aligned}$$

Likewise a similar transformation exists for a rhombohedral to hexagonal unit cell relationship. Unlike the cubic-rhombohedral transformation, this applies to any hexagonal or rhombohedral system. The hexagonal-rhombohedral transformation matrix is given as follows:

$$\begin{bmatrix} 1 & -1 & 0 \\ 0 & 1 & -1 \\ 1 & 1 & 1 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_H &= h_R - k_R \\ k_H &= k_R - \ell_R \\ \ell_H &= h_R + k_R + \ell_R \end{aligned}$$

where H refers to the hexagonal unit cell. The inverse of the above matrix is:

$$\begin{bmatrix} 2/3 & 1/3 & 1/3 \\ -1/3 & 1/3 & 1/3 \\ -1/3 & -2/3 & 1/3 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_R &= 1/3\,(2h_H + k_H + \ell_H) \\ k_R &= 1/3\,(-h_H + k_H + \ell_H) \\ \ell_R &= 1/3\,(-h_H - 2k_H + \ell_H) \end{aligned}$$

Again a similar matrix can be found for the cubic-hexagonal transformation and is as follows:

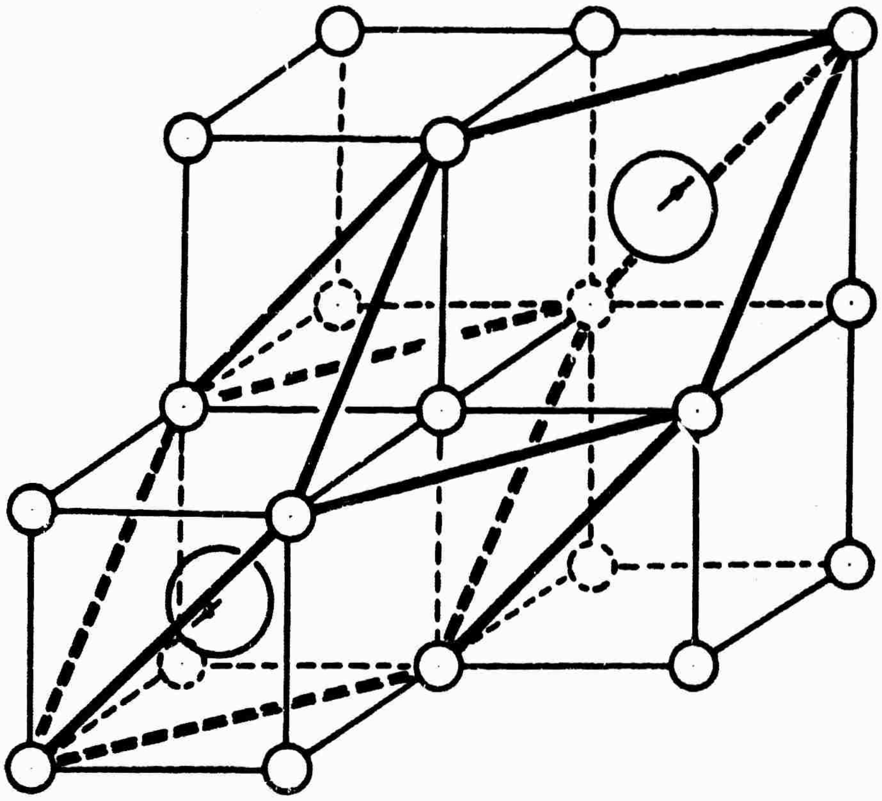
$$\begin{bmatrix} 0 & -1 & 1 \\ 1 & 0 & -1 \\ 2 & 2 & 2 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_H &\quad - k_C + \ell_C \\ k_H &= h_C - \ell_C \\ \ell_H &= 2(h_C + k_C + \ell_C) \end{aligned}$$

which is subject to the condition that the distortion is very slight. The inverse can be given as:

$$\begin{bmatrix} 1/3 & 2/3 & 1/6 \\ -2/3 & -1/3 & 1/6 \\ 1/3 & -1/3 & 1/6 \end{bmatrix} \quad \text{or} \quad \begin{aligned} h_C &= 1/6\,(2h_H + 4k_H + \ell_H) \\ k_C &= 1/6\,(-4h_H - 2k_H + \ell_H) \\ \ell_C &= 1/6\,(2h_H - 2k_H + \ell_H) \end{aligned}$$

FIGURE 1

CUBIC-RHOMBOHEDRAL UNIT CELLS



Small circles represent Al^{+3}

Large circles represent La^{+3}

The arrows show direction of La^{+3} shift

FIGURE 2

Growth Interface of Undoped Boule (Low Index)

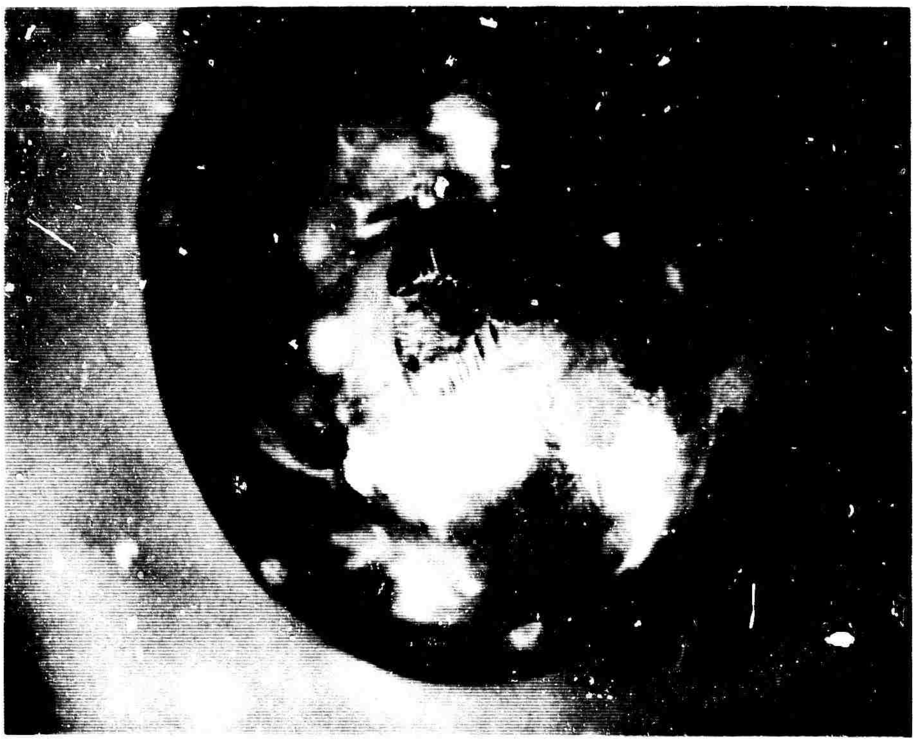


FIGURE 3

Growth Interface of Cr^{+3} Doped Boule (High Index)

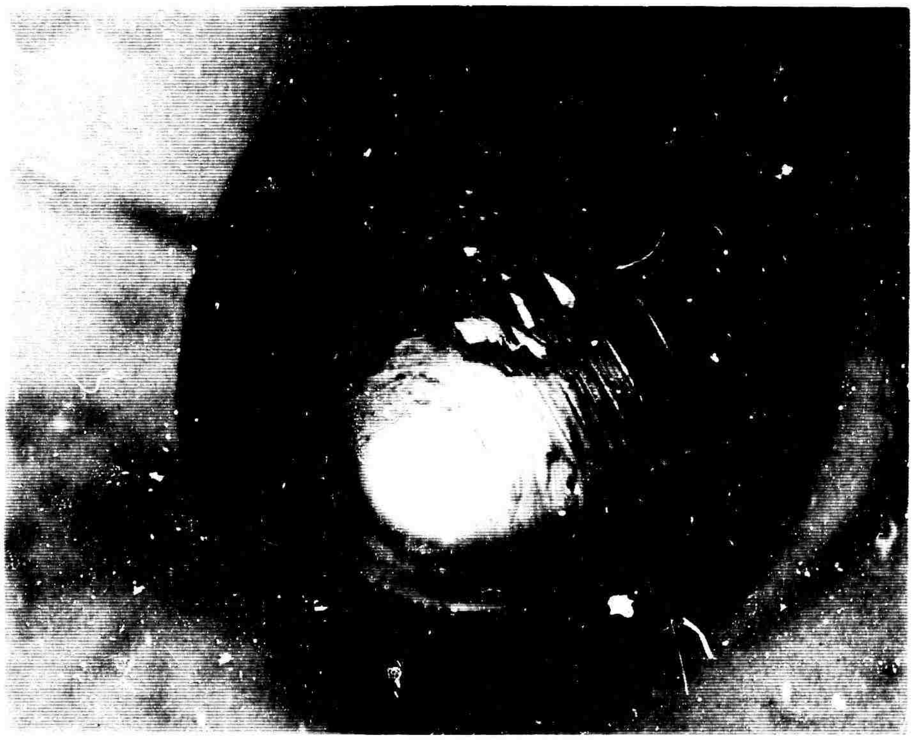


FIGURE 4

Effect of Pulling Rate on Lineage (IX)

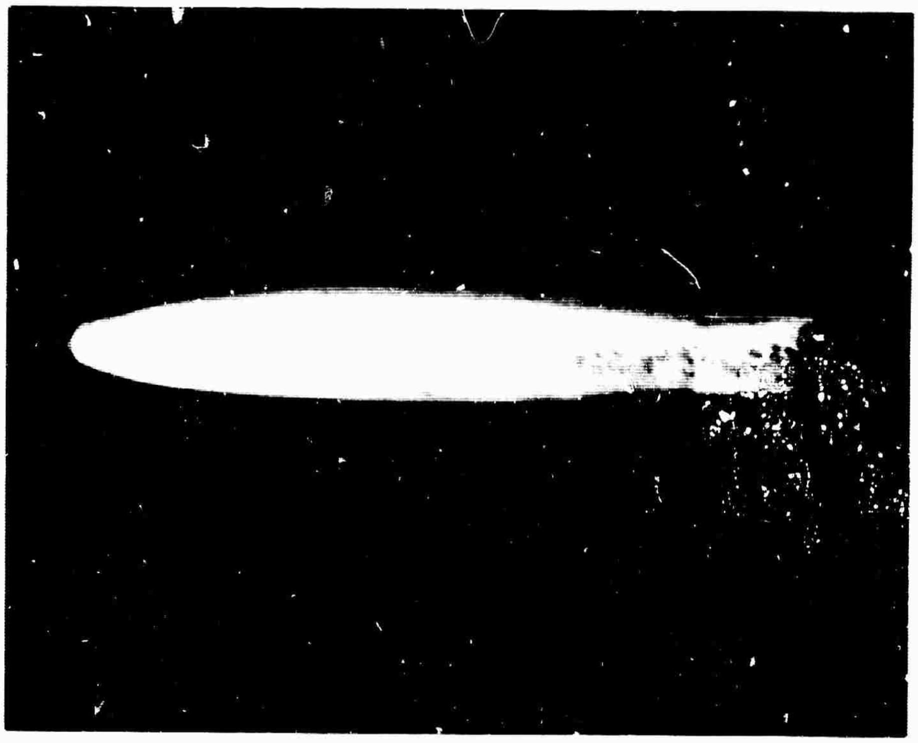
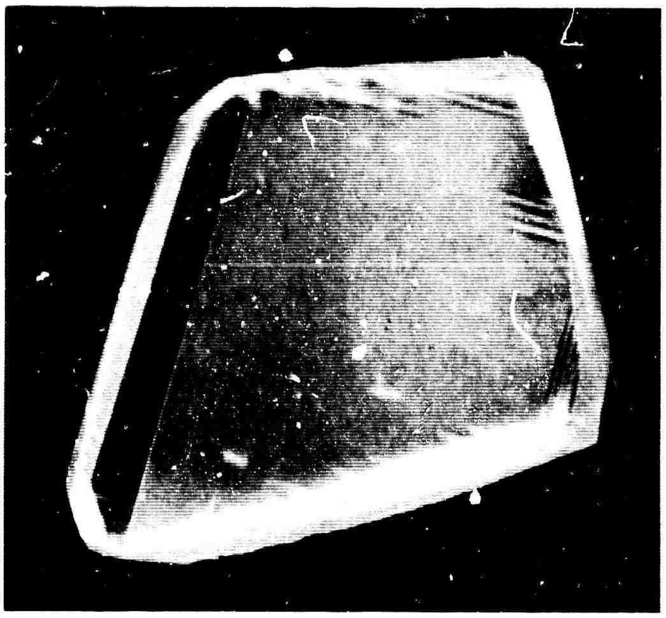


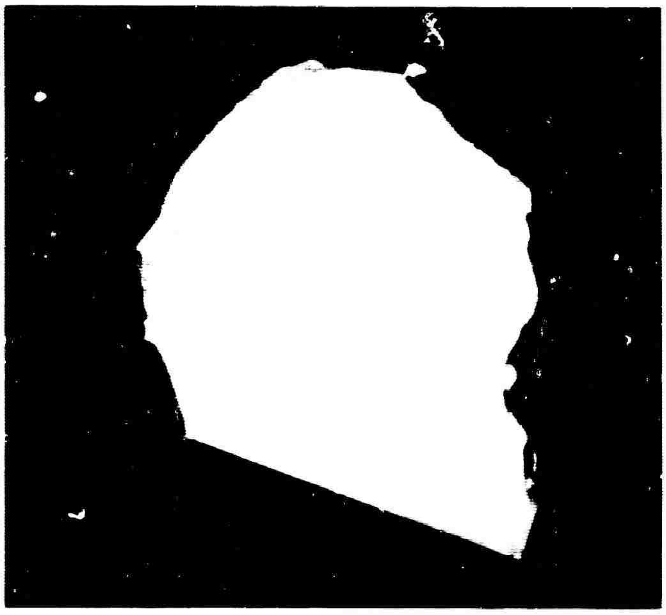
FIGURE 5

Twin Boundaries in Various Crystal Orientations



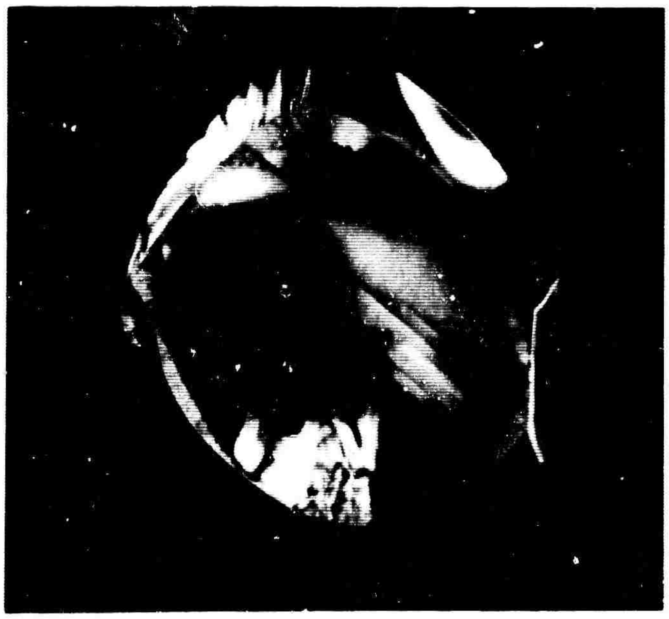
a

(110) Disk showing perpendicular and 45° twin boundaries. Approximately 7x



b

(100) Disk showing both sets of perpendicular twin boundaries. Approximately 7x



c

(111) Disk showing three sets of twin boundaries, each set 120° from the others. Approximately 7x

FIGURE 6

PSEUDO CELL ANGLE FOR RARE EARTH ALUMINATES

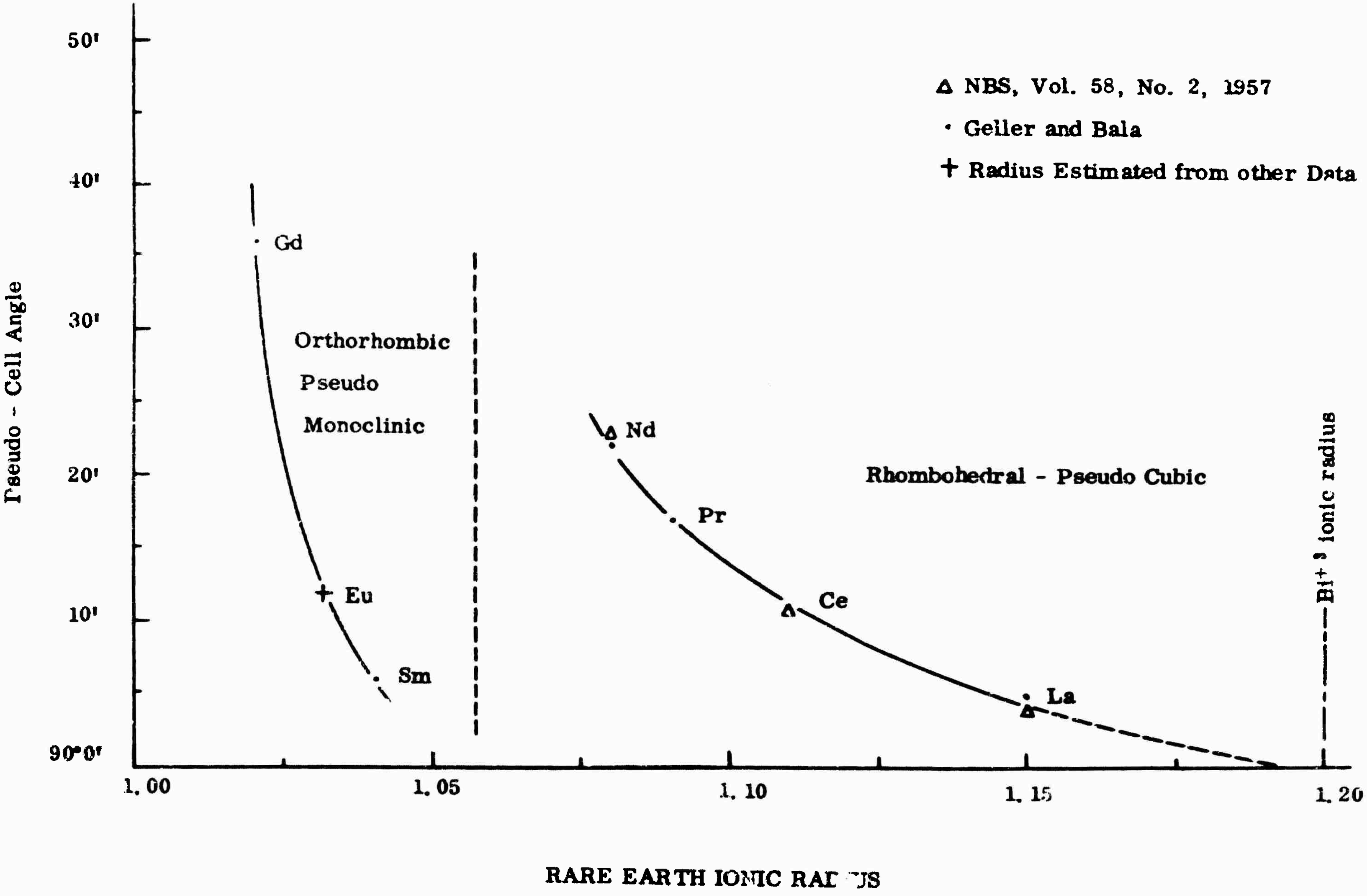
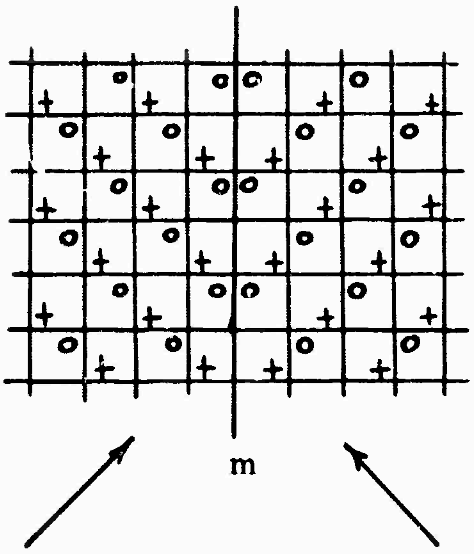


FIGURE 7

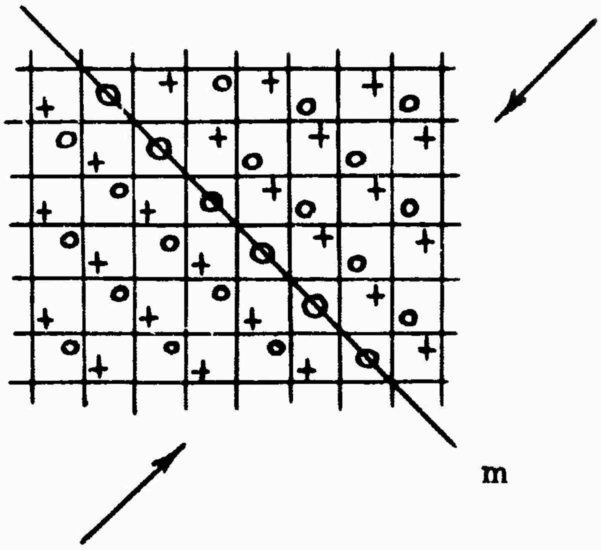
VARIOUS TYPES OF TWINNING

TRANSFORMATION TWINS

(100) Twin

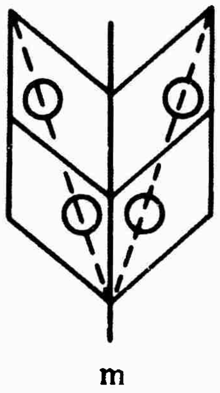


(110) Twin



GROWTH TWIN

(111) Twin



The grid on the first two figures represents the original cubic unit cell. The arrows represent the direction of the ⟨111⟩ axis. The circle (o) represents a shift of the La^{+3} ion in the direction indicated below the plane of the paper, the positive sign (+) a shift above the plane of the paper. The twin boundaries are represented by m (mirror planes). In the lower figure the large circle (O) represents the La^{+3} ion.

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13. ABSTRACT

The objective of this program was to explore the possibility of growing high optical quality $LaAlO_3$ by the Czochralski method. The techniques developed for ruby growth were found to be directly translatable to $LaAlO_3$ with no apparent limitations imposed by the use of a crucible. Undoped and doped (Cr^{3+}, Eu^{3+}) crystals of various orientations were grown

Two major defects were encountered: color centers and twinning. Color centers were eliminated by using high purity starting materials in combination with selected growth and post-growth treatment. Two mechanisms for forming color centers are proposed and their relation to $LaAlO_3$ defect chemistry is discussed. The dominant twin planes have been identified to be those of the (100) system. Their relation to the crystal structure of $LaAlO_3$ has been elucidated.

Isolated attempts were made to grow $BiAlO_3$ and $PrAlO_3$ to determine if twinning might be a problem in these potential host compositions; other growth problems were encountered indicating that an answer could be obtained only by an extensive effort beyond the bounds of the present program.

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3 0988   COLUMBUS 1, OHIO                                       54
4 0988   ATTN BMI-DEFENDER                                      54

1 1030   HEADQUARTERS, USAELRDL                                 54
2 1030   FORT MONMOUTH, NEW JERSEY 07703                        54
3 1030   ATTN SELRA/SAR,NO-4, X, AND PF                         54

1 1032   COMMANDER, U. S. NAVAL ORDNANCE TEST STATION           54
2 1032   CHINA LAKE, CALIF                                      54
3 1032   ATTN MR. G. A. WILKINS /CODE 4041/                     54

1 1036   J. C. ALMASI                                           54 *
2 1036   GENERAL ELECTRIC COMPANY                               54
3 1036   ADVANCED TECHNOLOGY LABORATORIES                       54
4 1036   SCHENECTADY, N. Y.                                     54

1 1039   PROF. RUBIN BRAUNSTEIN                                 54 *
2 1039   UNIVERSITY OF CALIFORNIA                               54
3 1039   DEPARTMENT OF PHYSICS                                  54
4 1039   LOS ANGELES 24, CAL.                                   54
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1 1040   N. I. ADAMS                                               54 *
2 1040   PERKIN-ELMER CORP.                                        54
3 1040   NORWALK. CONN.                                            54

1 1046   E. P. REIDEL                                              54 *
2 1046   QUANTUM ELECTRONICS DEPT.                                 54
3 1046   WESTINGHOUSE ELECTRIC CORP.                               54
4 1046   RESEARCH LABORATORIES                                     54
5 1046   PITTSBURGH, PA.                                           54

1 1047   PROF. H. G. HANSON                                        54 *
2 1047   UNIVERSITY OF MINNESOTA                                   54
3 1047   DULUTH, MINN                                              54

1 1048   P. SCHAFFER                                               54 *
2 1048   LEXINGTON LABORATORIES, INC.                              54
3 1048   84 SH   MAN ST.                                           54
4 1048   CAMBRIDGE, MASS.                                          54

1 1049   L. E. RAUTIOLA                                            54 *
2 1049   LINDE COMPANY, DIVISION OF UNION CARBIDE                  54
3 1049   EAST CHICAGO, IND.                                        54

1 1050   F. S. GALASSO                                             54 *
2 1050   UNITED AIRCRAFT CORP RESEARCH LABS.                       54
3 1050   400 MAIN ST.                                              54
4 1050   EAST HARTFORD, CONN.                                      54

1 1051   J. W. NIELSON                                             54 *
2 1051   AIRTRON, DIVISION OF LITTON INDUSTRIES                    54
3 1051   MORRIS PLAINS, N. J.                                      54

1 1052   E. M. FLANIGEN                                            54 *
2 1052   LINDE COMPANY                                             54
3 1052   DIVISION OF UNION CARBIDE                                 54
4 1052   TONAWANDA, N. Y.                                          54

1 1053   W. PRINDLE                                                54 *
2 1053   AMERICAN OPTICAL COMPANY                                  54
3 1053   14 MECHANIC ST.                                           54
4 1053   SOUTHBRIDGE, MASS.                                        54

1 1054   DR. ALAN HAUGHT                                           54 *
2 1054   PLASMA PHYSICS                                            54
3 1054   UNITED AIRCRAFT CORP.                                     54
4 1054   EAST HARTFORD 8, CONN.                                    54

1 1055   PROF. N. BLOEMBERGEN                                      54 *
2 1055   HARVARD UNIVERSITY                                        54
3 1055   DIVISION OF ENGINEERING & APPLIED PHYSICS                 54
4 1055   CAMBRIDGE 38, MASS.                                       54
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1 1056   PROF. R. J. COLLINS                                    54 *
2 1056   UNIVERSITY OF MINNESOTA                                54
3 1056   DEPARTMENT OF ELECTRICAL ENG.                          54
4 1056   MINNEAPOLIS 14, MINN.                                  54

1 1057   DR. ALAN KOLB                                          54 *
2 1057   U. S. NAVAL RESEARCH LAB.                              54
3 1057   WASHINGTON, D. C.                                      54

1 1058   PROF. J. M. FELDMAN                                    54 *
2 1058   CARNEGIE INSTITUTE OF TECHNOLOGY                       54
3 1058   DEPARTMENT OF ELECTRICAL ENGR.                         54
4 1058   PITTSBURGH 13, PENNA.                                  54

1 1059   PROF. ARTHUR SCHAWLOW                                  54 *
2 1059   STANFORD UNIVERSITY                                    54
3 1059   STANFORD, CALIFORNIA                                   54

1 1060   J. ATWOOD                                              54 *
2 1060   ELECTRO-OPTICAL DIV.                                   54
3 1060   PERKIN-ELMER CORP.                                     54
4 1060   NORWALK, CONN.                                         54

1 1065   RESEARCH MATERIALS INFORMATION CENTER                  54
2 1065   OAK RIDGE NATIONAL LABORATORY                          54
3 1065   POST OFFICE BOX X                                      54
4 1065   OAK RIDGE, TENN. 37831                                 54
5 1065   ATTN MR. T. F. CONNOLLY                                54

1 1066   J-5 PLANS AND POLICY DIRECTORATE                       54
2 1066   JOINT CHIEFS OF STAFF                                  54
3 1066   REQUIREMENTS AND DEVELOPMENT DIVISION                  54
4 1066   ATTN SPECIAL PROJECTS BRANCH                           54
5 1066   ROOM 2D982, THE PENTAGON                               54
6 1066   WASHINGTON, D. C., 20301                               54

1 1067   ADVANCED RESEARCH PROJECTS AGENCY                      54
2 1067   RESEARCH AND DEVELOPEMENT FIELD UNIT                   54
3 1067   APO 143, BOX 41                                        54
4 1067   SAN FRANCISCO, CALIF.                                  54

1 1068   ADVANCED RESEARCH PROJECTS AGENCY                      54
2 1068   RESEARCH & DEVELOPMENT FIELD UNIT                      54
3 1068   APO 146, BOX 271                                       54
4 1068   SAN FRANCISCO, CALIFORNIA                              54
5 1068   ATTN MR. TOM BRUNDAGE                                  54

1 1082   AIR FORCE MATERIALS LABORATORY                         54 *
2 1082   AIR FORCE SYSTEMS COMMAND                              54
3 1082   WRIGHT-PATTERSON AIR FORCE BASE, OHIO                  54
4 1082   ATTN MAAM /LT. JOHN H. ESTESS/                         54
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1 1083   DR. C. H. CHURCH                                     54 *
2 1083   WESTINGHOUSE ELECTRIC CORPORATION                    54
3 1083   RESEARCH LABORATORIES                                54
4 1083   PITTSBURGH 35, PENNA.                                54

1 1084   PROF. DONALD S. MCCLURE                              54 *
2 1084   INSTITUTE FOR THE STUDY OF METALS                    54
3 1084   UNIVERSITY OF CHICAGO                                54
4 1084   CHICAGO 37, ILLINOIS                                 54

1 1085   DR. DANIEL GRAFSTEIN                                 54 *
2 1085   GENERAL PRECISION, INC.                              54
3 1085   AEROSPACE GROUP                                      54
4 1085   LITTLE FALLS, NEW JERSEY                             54

1 1087   DR. R. C. LINARES                                    54 *
2 1087   PERKIN-ELMER CORPORATION                             54
3 1087   SOLID STATE MATERIALS BRANCH                         54
4 1087   NORWALK, CONN.                                       54

1 1088   DR. R. C. OHLMANN                                    54 *
2 1088   WESTINGHOUSE RESEARCH LABORATORIES                   54
3 1088   PITTSBURGH 35, PENNA.                                54

1 1089   PROFESSOR S. CLAESSON                                54 *
2 1089   UPPSALA UNIVERSITY                                   54
3 1089   UPPSALA, SWEDEN                                      54

1 1106   COMMANDING OFFICER                                   54
2 1106   OFFICE OF NAVAL RESEARCH BRANCH OFFICE               54
3 1106   BOX 39, FPO                                          54
4 1106   NEW YORK, NEW YORK 09510                             54

1 1122   DR. C. B. ELLIS                                      54 *
2 1122   GPL DIVISION                                         54
3 1122   GENERAL PRECISION, INC.                              54
4 1122   63 BEDFORD ROAD                                      54
5 1122   PLEASANTVILLE, NEW YORK                              54

1 1172   MR. C. M. STICKLEY                                   54
2 1172   AIR FORCE CAMBRIDGE RESEARCH                         54
3 1172   LABORATORIES - CROL                                  54
4 1172   LAURENCE G. HANSCOM FIELD                            54
5 1172   BEDFORD, MASSACHUSETTS 01731                         54

1 1177   DR. WAYNE H. KEEN                                    54 *
2 1177   WESTINGHOUSE DEFENSE & SPACE CENTER                  54
3 1177   /SURFACE DIVISION/                                   54
4 1177   P. O. BOX 1897                                       54
5 1177   BALTIMORE, MARYLAND 21203                            54
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1 1178   DR. C. J. KOESTER                                          54 *
2 1178   AMERICAN OPTICAL COMPANY                                   54
3 1178   RESEARCH CENTER                                            54
4 1178   SOUTHBRIDGE, MASSACHUSETTS                                 54

1 1179   DR. RAY HOSKINS                                            54 *
2 1179   KORAD CORPORATION                                          54
3 1179   3520 COLORADO AVENUE                                       54
4 1179   SANTA MONICO, CALIFORNIA 90406                             54

1 1180   DR. J. W. CARSON                                           54 *
2 1180   HUGHES AIRCRAFT COMPANY                                    54
3 1180   CULVER CITY, CALIFORNIA                                    54

1 1181   DR. MARVIN LASSER                                          54 *
2 1181   PHILCO CORPORATION                                         54
3 1181   RESEARCH LABORATORIES                                      54
4 1181   BLUE BELL, PENN.                                           54

1 1183   PROF. A. SMAKULA                                           54 *
2 1183   CRYSTAL PHYSICS LAB                                        54
3 1183   MASSACHUSETTS INSTITUTE OF TECHNOLOGY                      54
4 1183   CAMBRIDGE, MASS                                            54

1 1184   DR. F. MCCLUNG                                             54 *
2 1184   HUGHES RESEARCH LABORATORIES                               54
3 1184   3011 MALIBU CANYON ROAD                                    54
4 1184   MALIBU, CALIFORNIA 90265                                   54

1 1185   DR. M. C. TOBIN                                            54 *
2 1185   PERKIN-ELMER CORPORATION                                   54
3 1185   NORWALK, CONNECTICUT                                       54

1 1186   PROF. G. W. STROKE                                         54 *
2 1186   ELECT. ENGINEERING DEPT.                                   54
3 1186   THE UNIVERSITY OF MICHIGAN                                 54
4 1186   ANN ARBOR, MICHIGAN 48107                                  54
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FURTHER ADDITIONS TO LIST 54*

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National Bureau of Standards
Washington, D.C.

N.D. Schoenberger
Precision Instrument Company
3170 Porter Drive
Palo Alto, California

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*Authorized by letter

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NR 017-708
30 November 1964

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13 Nov 1964