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Growth Striations in Vertically Pulled Oxide and Fluoride Single Crystals

B. COCKAYNE, M. P. GATES
Ministry of Aviation, Royal Radar Establishment, Malvern, Worcs, UK

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Temperature oscillations have been detected in oxide and fluoride melts which can be directly correlated to the movement of convection patterns visible on the melt surface. It is shown that such oscillations cause growth striations in single crystals grown from these melts. Additional experiments are reported in which the effect of changes in growth parameters upon the oscillations and melt temperatures have been investigated.

1. Introduction

Growth striations or bands of impurity which occur parallel to the solid/liquid interface of both vertically pulled and horizontally grown single crystals are well known in semiconductor crystals [1, 2]. More recently, these striations have been observed in a wide range of higher-melting-point materials such as CaF_2 [3], $CaWO_4$ [4], $Y_3Al_5O_{12}$ [5], and Al_2O_3 [6]. In vertically pulled and rotated, semiconductor single crystals, two types of striation have been identified. The first type is well defined and corresponds to the amount of crystal grown per revolution. These are attributed either to thermal assymetry in the melt or to departure of the rotation axis from the thermal centre of the melt. The second type is more finely spaced (10 to 100 μm) and shows a smaller change in impurity concentration. Several mechanisms have been proposed to explain their formation. These include (i) the formation of an impurity-rich layer of either thermally [7] or constitutionally [8, 9] cooled melt ahead of the growing interface, followed by rapid growth of the layer, and (ii) the occurrence of turbulent thermal convection in the liquid ahead of the growing crystal, which causes temperature fluctuations and results in growth-rate changes which modulate the height of the impurity boundary layer [3, 10, 11]. This latter mechanism is also a suggested cause for growth striations in CaF_2 single crystals [3]. More recently, it has been conclusively shown [12-14] that temperature fluctuations are the cause of the fine striations in semiconductor crystals, but the fluctuations do not arise from turbulence. Instead, they are caused by a form of convective instability superimposed upon steady convection, which can result in oscillations rather than fluctuations in temperature. The present work, reported very briefly elsewhere [15], establishes that the same mechanism conclusively explains the occurrence of growth striations in vertically pulled $CaWO_4$ and CaF_2 single crystals.

2. Experimental Details

Temperature fluctuations have been studied in $CaWO_4$ and CaF_2 melts using the apparatus previously described for the single-crystal growth of these materials [4]. The materials were melted in a 40 mm diameter, iridium crucible, under respective atmospheres of argon/5 vol % oxygen and pure argon, using induction heating at 450 kc/sec. Constant power conditions were maintained by feeding the output of a power-monitoring coil into a Honeywell-Brown proportional controller arranged to control the output power of the induction heater. Temperature measurements were made with Pt-Pt/13% Rh thermocouples in conjunction with a variable chart speed recorder. An R-C filter circuit was employed to remove any rf interference picked up by the thermocouple. Two independent thermocouples were used which could probe all parts of the melt or be incorporated into a crystal growing from the melt.

Crystal and/or crucible rotation was possible, and the afterheater described earlier [16] was mounted for certain experiments. The crystals were grown at a standard rate of 12.5 mm/h since, at greater rates, $CaWO_4$ crystals develop cellular structures which obscure the growth striations.

The $CaWO_4$ was obtained as chemically precipitated powder from Levy-West Laboratories Ltd; whilst the CaF_2 was crystalline material supplied by Barr and Stroud. Neodymium was the impurity element used for the striation studies. 2 at. % Nd was added to the melt, as NdF_3 for the fluoride crystals, and as $Nd_2(WO_4)_3$ for the mixed oxide crystals, since this quantity is known to give readily visible striations when these materials are used as laser host lattices. The striations were exposed by etching mechanically polished crystal sections in orthophosphoric acid at a temperature of 250° C.

3. Results

3.1. Growth Striations

The spacing and intensity of growth striations has been studied in Nd-doped $CaWO_4$ and CaF_2 single crystals grown under a wide range of conditions. Crucible and/or crystal rotation rates in the respective ranges 0 to 24 and 0 to 200 rev/min have been employed. The results of these studies, presented in table I, show that there is no direct correlation between the measured spacing and the amount of crystal grown per revolution, which is in agreement with the results previously reported for Nd-doped $Y_3Al_5O_{12}$ [5]. In addition, striation formation is observed to be independent of crystal rotation rate, since their intensity remains unaltered if the rate is increased or decreased during crystal growth in discrete steps of 50 rev/min within the range 0 to 200 rev/min. Crucible rotation, on the other hand, enhances the formation of striations even at rates as low as 5 rev/min. Fig. 1 shows the increased intensity of striations (XX) when 10 rev/min crucible rotation is introduced during the growth of a crystal being rotated at 50 rev/min; no afterheater was used in this case. Fig. 2 shows the occurrence of striations at the onset of 10 rev/min crucible rotation in a crystal grown into an afterheater. The effects produced in the crystal by crucible rotation are independent of the sense of rotation of the crucible with respect to the crystal. Striations are seen rarely in crystals grown into an afterheater when crystal rotation only is used; if present, they are only faintly visible. The striations remain unaffected by changes in the flow rate of the gas ambient from 0 to 50 to 100 to 250 to 500 cm³/min or vice versa.

3.2. Temperature Oscillations and Their Relation to Growth Striations

In non-rotating melts of $CaWO_4$ and CaF_2, from which 8 to 10 mm diameter crystals were growing, temperature oscillations of the type

TABLE I

Crystal rotation (rev/min)	Crucible rotation (rev/min)	Striation intensity	Measured spacing (cm × 10^{-3})	Calculated spacing (cm × 10^{-3})
$CaWO_4$				
50	0	w	4.20	0.42
50	10	s	4.30	0.53
50	20	s	5.00	0.70
0	10	s	5.00	2.12
0	20	s	5.50	1.06
0	0	w	4.50	—
10	10	s	3.70	—
20	20	s	3.30	—
100	0	w	4.20	0.21
100	20	s	3.70	0.26
200	0	w	4.35	0.11
CaF_2				
50	0	w	4.90	0.42
100	0	w	5.10	2.12
200	0	w	5.75	0.11
50	20	s	5.25	0.70

w: weak; s: strong.

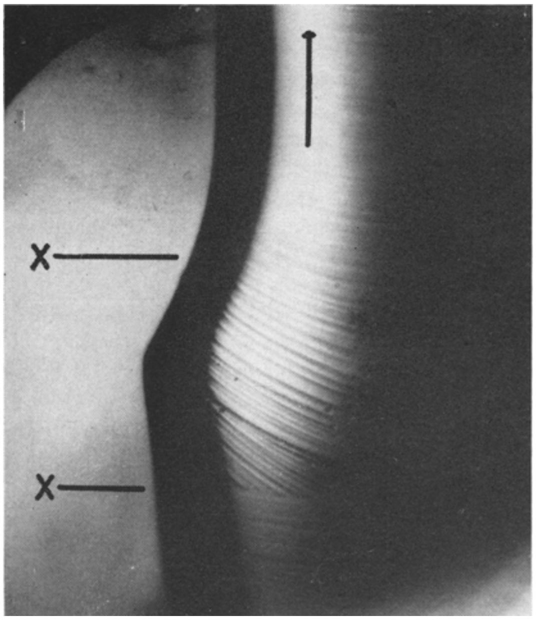


Figure 1 The change in intensity of growth striations during crucible rotation (XX) in Nd-doped $CaWO_4$ (×27). The arrow specifies the growth axis.

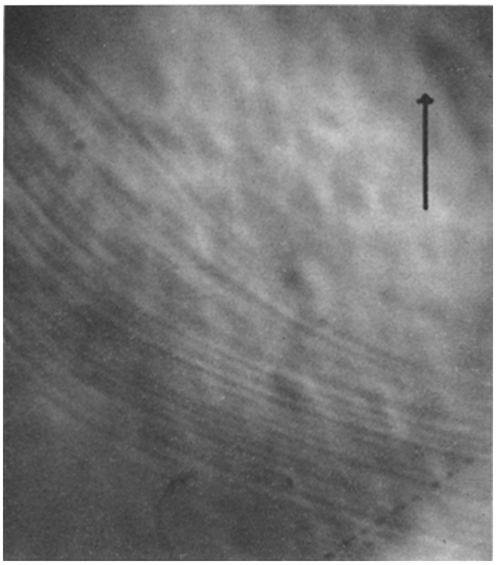
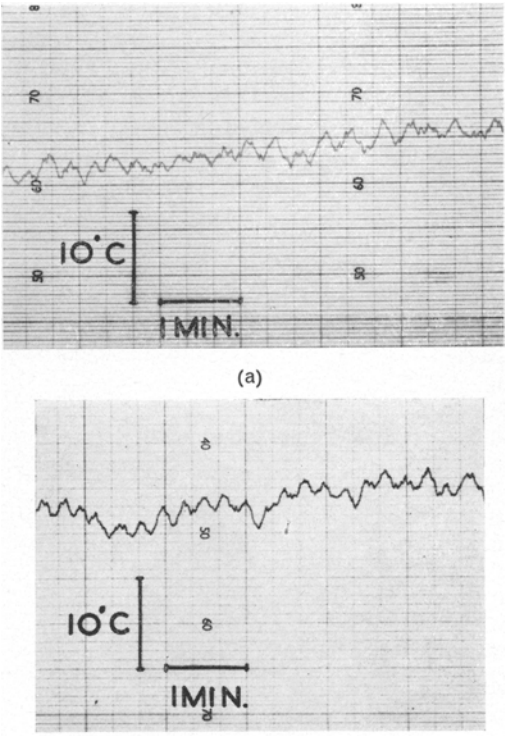


Figure 2 The onset of growth striations with crucible rotation in Nd-doped $CaWO_4$ grown into an afterheater (×27). The arrow specifies the growth axis.

shown in fig. 3 have been recorded. Amplitudes of 3 to 5° C and periods of 10 to 15 sec have been observed for these oscillations, which are independent of thermocouple position in the melt, but disappear in the solid when the growing interface encompasses the thermocouple. The oscillations are also unaffected by the presence of up to 5 at. % Nd in the melt. The period of oscillation remains unaltered by the introduction of crystal rotation but, at a rate of 200 rev/min, the amplitude is reduced slightly to 2 to 3° C. The amplitude is, however, markedly increased to 12 to 15° C by the introduction of crucible rotation at rates up to 24 rev/min, as shown in fig. 4, irrespective of crystal rotation speed; the period of oscillation remains in the range 10 to 15 sec.

It may be deduced from table I that, at a growth rate of 12 mm/h, the striation spacings of 3.3 to 5.75×10^{-3} cm correspond to time intervals of 9.5 to 16.5 sec, which is almost identical to the range of periods observed for the temperature oscillations. A direct correlation between the oscillations and the striations was shown to exist by growing Nd-doped crystals from non-rotating melts and introducing crucible rotation at discrete points during growth for known time intervals. This allows a reference



(a)

(b)

Figure 3 Temperature oscillations in non-rotating melts of (a) $CaWO_4$ and (b) CaF_2.

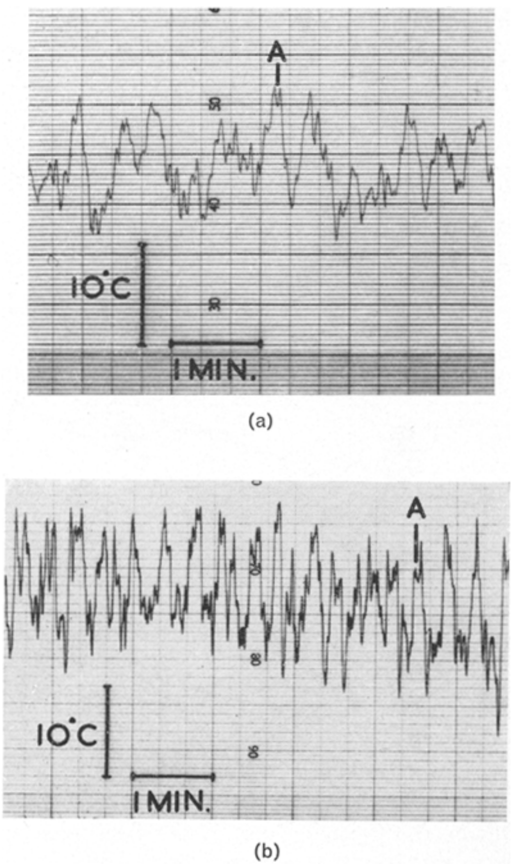


Figure 4 Temperature oscillations in melts of (a) CaWO and (b) CaF_2, in the presence of crucible rotation.

point to be established between the crystal and the temperature recording, because crucible rotation induces an immediate temperature drop in addition to producing a change in the shape of the freezing interface, which becomes more convex with respect to the melt, as in fig. 1. Conversely, when crucible rotation is stopped, the temperature rises and the interface reverts to the original shape, causing a slight melt back of the interface in the centre of the crystal, which is again apparent in fig. 1. In all cases, the number of striations formed during the period of crucible rotation was exactly equal to the number of temperature oscillations recorded by a thermocouple placed approximately 1 mm from the crystal interface.

Occasionally, very finely spaced striations, 10^{-3} cm apart, are observed between the striations so far described. These are present only in crystal grown using crucible rotation, and when present they occur at the same points in time as the 2 to 3° C oscillations typified by A in fig. 4.

In the presence of an afterheater, temperature fluctuations rather than oscillations are recorded. These are small in magnitude, being of the order of 1° C, which is consistent with the observation that striations are rarely visible in crystals grown into an afterheater.

All the oscillations described in this section are present whether the melt is transparent, as for undoped CaF_2, or opaque, as for the other melts. The oscillations remain unaffected by changes in the flow rate of the gas ambient within the limits specified in section 3.1, which again is consistent with such changes having no effect upon the striations.

3.3. Temperature Oscillations and Their Relation to Convection Patterns on the Melt Surface

In opaque oxide and fluoride melts, a general radial flow of material from the walls to the centre of the crucible is observable as a dark, spoke-like pattern, which is represented schematically in fig. 5. In unrotated melts, the centre of the pattern, i.e. the thermal centre, is not stationary but moves backwards and forwards along a line such as AB. The movement is typically 2 to 3 mm, and causes a thermocouple, placed at A, to undergo cyclic temperature variations with periods in the range 10 to 15 sec, which is identical to that reported for the temperature oscillations in section 3.2. The magnitude of the oscillations is slightly greater in the absence of a crystal, and amplitudes of 7° C have been recorded. The 2 to 3 mm movement of the thermal centre is the most common, but, occasionally, much greater movement has been observed. In such cases, motion takes place from A by a distance of 10 mm to

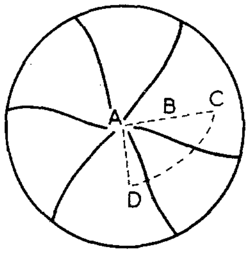


Figure 5 Diagrammatic representation of the spoke-like pattern on the melt surface.

C and back again to A via D. Such cycles have periods of 1 to 3 min, and produce temperature changes of 10 to 20° C at the centre of the crucible; a typical temperature recording for these circumstances is given in fig. 6.

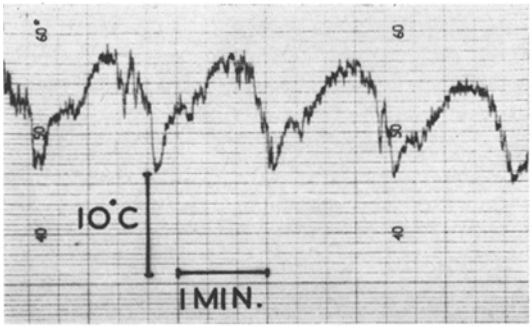


Figure 6 Temperature oscillations observed during enhanced motion of the thermal centre of a $CaWO_4$ melt.

Other, higher frequency oscillations with periods less than 5 sec are observed in these melts, which can be correlated with movements of the dark spokes of the radial pattern. The spokes are not stationary but tend to move backwards and forwards in a non-uniform manner over a distance of approximately 1 mm perpendicular to the radial flow. A thermocouple placed in the vicinity of one of the spokes experiences a temperature drop of 2 to 3° C every time the spoke passes through the bulb, showing that the spokes are regions of slightly lower temperature. This type of motion may well account for the apparent noise on the signal in fig. 6. These oscillations and the spoke-like pattern both disappear when an afterheater is placed above the melt. The pattern is enhanced, however, when crucible rotation is introduced, and particularly when a crystal is in contact with the melt. In this case, the spokes rotate and, as the rotation rate is increased from 0 to 24 rev/min, the pattern changes progressively from a two-spoke to a four-spoke structure, in the manner illustrated by fig. 7. Each time a spoke passes through the thermocouple, a temperature drop is recorded, which can be correlated with the occurrence of the very fine striations (see section 3.2) and which is typified by the points marked A in fig. 4. This effect is superimposed upon the main oscillations induced by crucible rotation. The amplitude is dependent upon thermocouple position, being 15° C near the crucible wall and 2 to 3° C at the crystal.

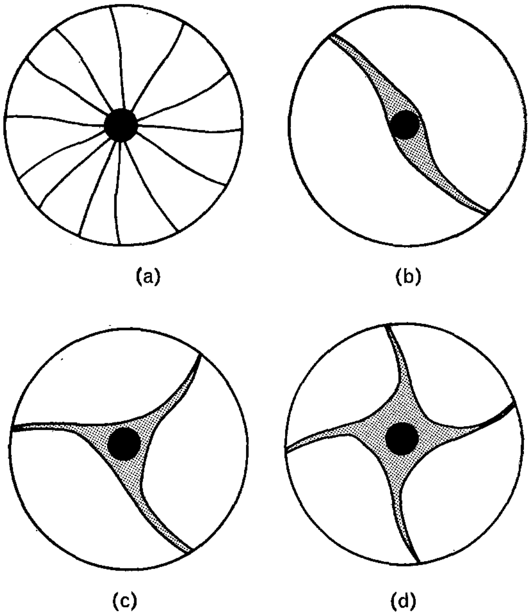


Figure 7 The progressive change in the spoke-like pattern as clockwise crucible rotation is increased through the range: (a) 0 rev/min; (b) 8 rev/min; (c) 14 rev/min; (d) 20 rev/min.

3.4. The Effect of Rotation upon Melt Temperature

During the present work, it has been observed that crucible rotation not only produces a marked difference in the temperature oscillations but also in the melt temperature. For instance, a temperature drop of 11° C is recorded in a $CaWO_4$ melt, 1 mm below the solid/liquid interface, as soon as 10 rev/min crucible rotation is commenced. At 20 rev/min, the temperature is 23° C below that measured at 0 rev/min. Crystal rotation, however, produces only a 3° C temperature drop at the same point in the melt when the rate of rotation is increased from 0 to 200 rev/min. These observations suggest that, in the presence of a strong thermal flow, crucible rotation greatly enhances the flow of cooler material from near to the crucible base up to the crystal interface, whilst crystal rotation produces little or no material transport. The present results thus confirm the flow patterns observed in a model vertical-pulling system [17] using $KMn0_4$ as a flow pattern indicator in a crucible of water at temperatures in the range 0 to 30° C.

4. Discussion

The work described above establishes that the impurity striations observed in certain oxide and fluoride single crystals arise from oscillations in melt temperature which can be directly correlated with the movement of thermal convection patterns on the melt surface. No evidence has been found to support the argument that the striations are related to the rotation of the crystal through an asymmetric thermal field.

The problem of thermal convection in a confined fluid heated mainly from the sides, as in a crucible, has not been treated theoretically. However, the simpler problem of a semi-infinite fluid heated from the bottom (the Bénard cell), so that a temperature gradient develops parallel to the gravitational axis, has been extensively investigated and is fully reviewed by Chandrasekhar [18]. In the simple case, steady convection occurs only above a critical temperature gradient, when a cellular pattern forms on the melt surface which is similar to the spoke-like pattern described here. The onset of steady convection is determined by the Rayleigh number of the system, R, which is a dimensionless parameter defined as

$$R = \frac{\alpha}{K\nu} \cdot g \frac{dT}{dz} \cdot d^4$$

where g is the acceleration due to gravity, d is the depth of liquid, dT/dz is the temperature gradient, and α, K, and ν are the coefficients of volume expansion, thermal diffusivity, and kinematic viscosity, respectively. Steady convection occurs at values of R greater than 1708, but no temperature oscillations are predicted or observed at the onset of this instability. Such oscillations can be induced, however, by rotating the liquid with respect to the gravitational axis and the temperature gradient [18]. This situation is applicable to the crucible rotation experiments, although it must be emphasised that the present bounding conditions for the liquid are very different from those in the simple cell.

Recently, Quinn [19], using gas as the fluid medium, and Hurle [20], using liquid gallium, have shown that stable temperature oscillations can develop in a fluid heated from the base but with boundary conditions which approximate to those used here. These oscillations are superimposed upon steady convection and occur at values of R greater than 2×10^4. The physical constants, α, K, and ν, are not known for molten $CaWO_4$ and CaF_2, but values are available in the literature for molten salts of lower melting point. Substitution of these values in the above equation for a measured temperature gradient of 100° C/cm and a known cell depth of 3 cm gives an approximate value of R equal to 10^6, which exceeds the value required for the onset of oscillations. It is possible that this type of oscillatory motion accounts for the observed periodic motion of the thermal centre, in which case, the melt appears to behave as one, single, convection cell.

Thus, although no theory of thermal convection exists for the conditions examined in the present work, theoretical and experimental studies of comparable systems predict that temperature oscillations arising from unstable thermal convection are permissible.

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