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Interface shape changes during the Czochralski growth of gadolinium gallium garnet single crystals

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It is shown that interface shape changes, often induced during the growth of gadolinium gallium garnet single crystals in order to control defects, can occur naturally under specific conditions. Changes in both crystal weight and melt temperature, associated with changes in interface shape, are consistent with a melting-back process arising from modification to the flow patterns in the melt.

1. Introduction

In earlier papers [1–3], the present authors have shown that the macroscopic shape of the solid/liquid interface during the Czochralski growth of oxide single crystals can exert a marked influence upon the quality of the crystals produced. A particularly important example has been the deliberate inducement of changes in interface shape to control both facet and dislocation formation in gadolinium gallium garnet ($Gd_3Ga_5O_{12}$) crystals, which are used as substrates for magnetic garnet bubble-domain devices. In this particular work [3] the interface shape was modified from convex towards the melt to planar by increasing the rate at which the crystal rotated whilst in contact with the melt. This paper describes conditions under which the change in interface shape can occur without altering the rotation rate of the crystal and reports upon changes in melt temperature and crystal weight which provide information pertinent to the melt flow conditions established as the interface alters its shape.

2. Experimental details

All the $Gd_3Ga_5O_{12}$ crystals, temperature measurements and crystal weight changes discussed herein were obtained using a standard Czochralski crystal growth apparatus which has been fully described elsewhere [4].

The crystals were prepared in the correct molar proportions from the carefully dried component oxides, Ga_2O_3 and Gd_2O_3, supplied respectively by Johnson-Matthey Chemicals Ltd and Rare-Earth Products Ltd. A cylindrical iridium crucible, 38 mm diameter x 33 mm deep x 1.6 mm wall thickness and heated by rf from an 18 kW 450 kHz generator, was used to contain the melt. The gas ambient was nitrogen containing 5 vol% oxygen flowing at a rate of 0.7 litre min^{-1}. Crystals were grown at a pulling speed of 6 mm h^{-1}. The principal variable was crystal rotation rate and rates within the rage 30 to 100 rpm were employed. The crystal growth apparatus was fitted with a standard weighing cell of the type used for automatic diameter control [5, 6] which, in conjunction with a Servoscribe chart recorder, allowed crystal weight changes to be measured to ± 0.02 g.

Temperature measurements were obtained using an Ir–Ir/40%Rh thermocouple; an R–C filter circuit was used to eliminate possible rf interference with the thermocouple output. The thermocouple was rigidly attached to a micromanipulator capable of translation in three mutually perpendicular directions so that a melt volume approximating to a 1 cm cube could be probed.

3. Results and discussion

3.1. Weight changes during interface shape modifications

Under the growth conditions specified above, $Gd_3Ga_5O_{12}$ single crystals have a solid/liquid interface shape which is convex towards the melt at low crystal rotation rates, typically < 30 rpm.

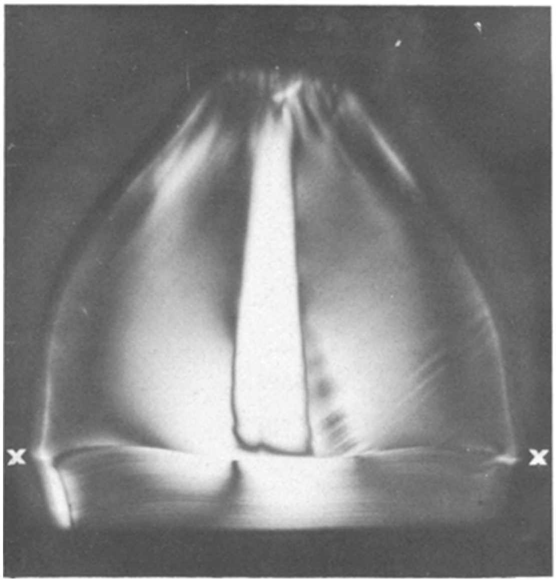

Figure 1 A longitudinal section of a ⟨1 1 1⟩ axis $Gd_3Ga_5O_{12}$ single crystal showing the change in interface shape from convex to planar at XX due to an increase in crystal rotation rate from 30 to 80 rpm (crystal diameter = 1.8 cm).

However, as the crystal rotation rate is increased, the degree of convexity diminishes and at approximately 80 rpm, a planar configuration is achieved. An induced shape change of this type was used in an earlier study by the present authors [3] to control facet formation and dislocation generation. The change in shape, as delineated by growth striations and shown in Fig. 1, appears to be due to a sudden melting-back process, otherwise the striations would change gradually from the V-section typical of a convex interface to a planar section rather than the abrupt change shown by the incomplete V-sections at XX.

The volume of crystal which is lost in the melting-back approximates to a cone with a base radius equal to the crystal radius and a height which can be measured by using the thermocouple as a mechanical probe to find the difference in the depth of the interface centre below the melt surface (h) before and after melt back. For a 1.4 cm diameter crystal, h was measured as 0.33 ± 0.03 cm with a rotation rate increase from 30 to 100 rpm which gives a volume decrease of 0.17 cm^3 and corresponds to a weight decrease of 1.20 g (the density of $Gd_3Ga_5O_{12}$ is 7.07 g cm^{-3}).

Fig. 2 shows the change in weight recorded by the weighing cell whilst the change in interface shape was taking place upon increasing the crystal rotation rate from 30 to 100 rpm and then reversing the process. The figure shows that the process is reversible and gives a directly measured weight loss of 1.11 g during the melt-back which is in good agreement with the calculated value.

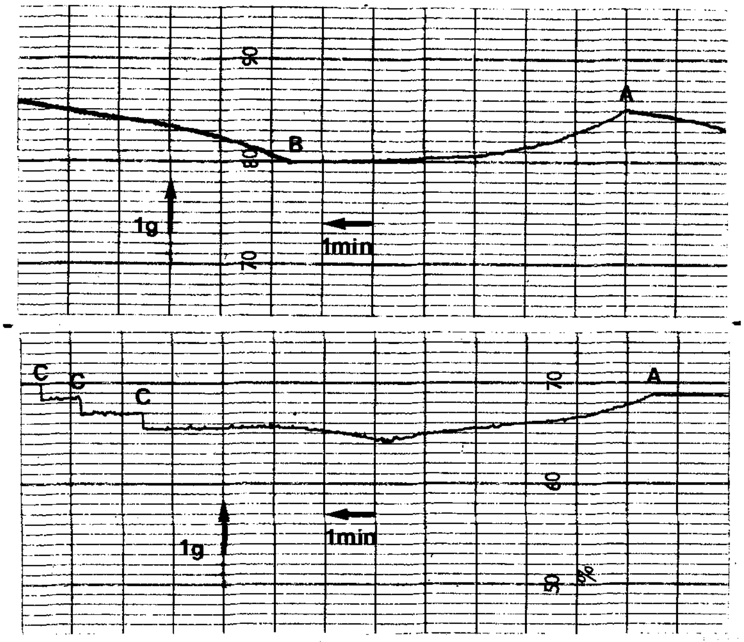

Figure 2 The weight change recorded by the weighing cell during changes in crystal rotation rate at (A) from 30 to 100 rpm and (B) from 100 to 30 rpm showing respective losses and gains as melt back and regrowth occur. (C) indicates the calibration made by adding three separate weights of 0.28 g each to the weighing cell.

The weight calibration, shown at C in Fig. 2, was obtained by adding three equal weights separately to the weighing cell whilst the crystal was in contact with the melt so that buoyancy effects were identical for calibration and measurement.

3.2. Interface melt-back

There is substantial evidence reported for the Czochralski growth of oxide single crystals [1–3] to suggest that the melting-back process is due to hot liquid being drawn upwards to the crystal interface from hotter regions nearer to the crucible base by the centrifugal action of the rotating crystal. This centrifugal flow must be sufficient to overcome the natural convective flow from the crucible walls towards the crystal for melt-back to be possible. In most instances, the relationship between interface shape and fluid flow has been inferred by studying growth striations and defect distribution as a function of crystal rotation rate or by examining flow patterns in model systems at or near room temperature [7]. The present work has established a more direct correlation for such a relationship by measuring the temperature changes which occur in the vicinity of the crystal interface as the rotation rate of the crystal is altered.

If the melt-back is due to an increasing dominance of a centrifugally generated flow over convective flow, the temperature within a central column of liquid beneath the crystal interface should rise as the crystal rotation rate is increased. Fig. 3 shows that this is precisely the observed case; a temperature pulse of 40 to 50° C, but with a somewhat lower general temperature rise, occurs on increasing the rate of rotation from 30 to 80 rpm; a reverse change from 80 to 30 rpm produces corresponding decreases in temperature.

The effect of a recorded temperature increase alone does not conclusively prove that a change in flow has occurred. A rise in temperature could merely reflect the increased distance between the interface and the thermocouple position as melt-back occurs so that the thermocouple would find itself in a relatively deeper and therefore hotter region of melt. However, the weight change in Fig. 2 suggests that the melt-back occurs slowly, taking some 5 min. Hence the relative change in position of thermocouple and interface must also occur slowly, as would any temperature changes due to this effect. In contrast, the observed temperature changes are rapid, instantaneous upon rotation rate changes and usually slightly precede the start of the weight change. A rapid change of this type is, therefore, consistent with a change in fluid flow. There is also visual evidence to support the idea of the flow change as the radial spoke-like pattern on the melt surface associated with natural convection is disrupted in the vicinity of the crystal immediately the rate of rotation is increased.

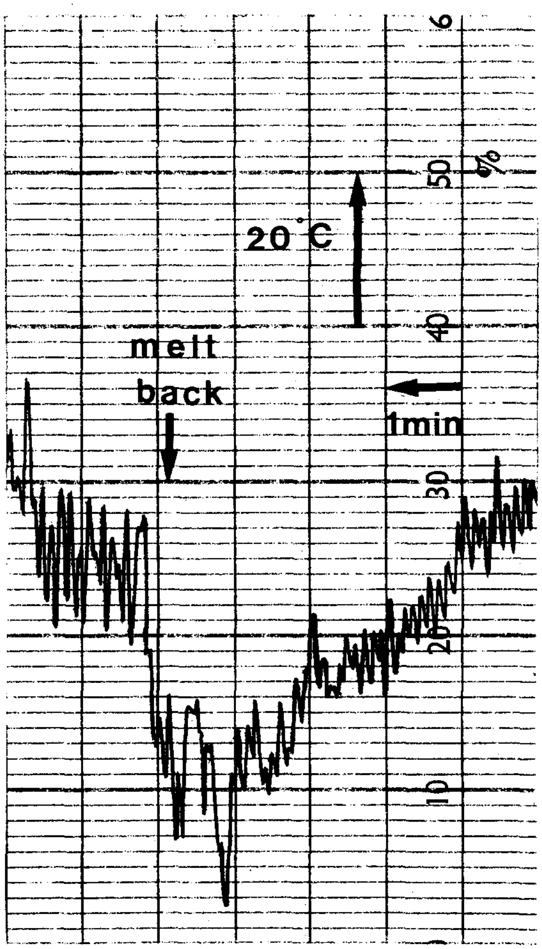

Figure 3 The temperature pulse and rise recorded by the thermocouple positioned immediately below the crystal interface as the rotation rate is increased from 30 to 80 rpm.

The positioning of the thermocouple in order to detect the described temperature changes appears to be very critical. Reproducible results were obtained only in a central column, 2 to 3 mm wide, below the interface. In the other parts of the melt investigated temperature changes were detected but, in any given position, no consistent rise or fall in temperature was observed with rotation rate alterations.

3.3 The influence of crystal diameter

For a crucible of given diameter, the centrifugal stirring effect of the crystal depends not only upon crystal rotation rate but also upon crystal diameter. Hence for a given rotation rate, a change in interface shape from convex to planar should occur without artificial inducement, provided that the crystal diameter is allowed to increase steadily to the point where the centrifugal flow generated by the crystal can predominate over the convective flow. Fig. 4 shows a crystal which was grown at a constant crystal rotation rate of 80 rpm and a change of interface shape occurs which is identical to that artificially induced in Fig. 1. A thermocouple placed 3.5 mm below the interface at the beginning of growth recorded a temperature rise of 25° C at the point corresponding to the critical diameter (Fig. 5).

The dependence of the critical diameter upon crystal rotation rate was established by growing crystals at constant rotation rates within the range 30 to 100 rpm. The results, presented in Fig. 6, suggest that the relationship is linear over this range.

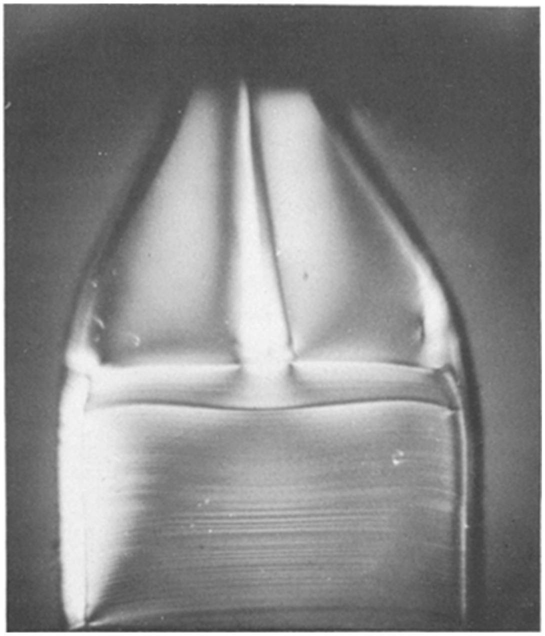

Figure 4 A longitudinal section of a ⟨1 1 1⟩ axis single crystal of Gd$_3$Ga$_5$O$_{12}$ grown at 80 rpm throughout, showing the change in interface shape from convex to planar as the critical diameter for fluid-flow reversal is reached (crystal diameter = 1.8 cm).

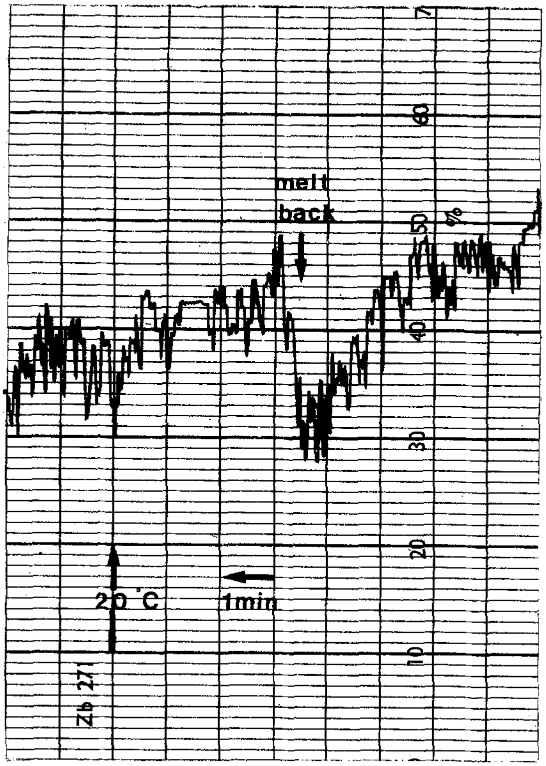

Figure 5 The rise in temperature recorded by the thermocouple positioned beneath the crystal interface when the interface is changing shape at constant crystal rotation rate (80 rpm). A rapid temperature increase is clearly visible on an otherwise general trend of decreasing temperature as the crystal grows towards the thermocouple.

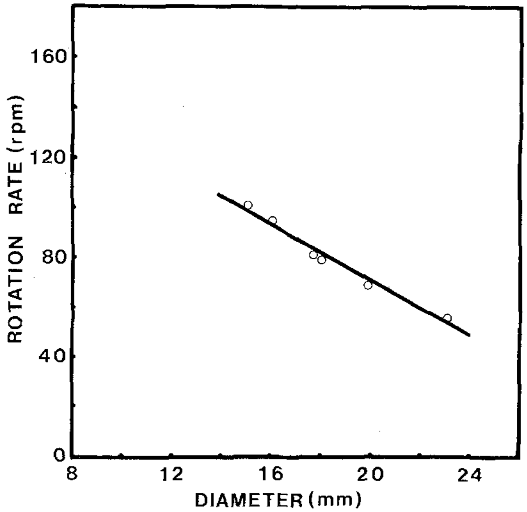

Figure 6 The experimentally determined relationship between the diameter at which the interface shape modificiation occurs and crystal rotation rate.

4. Conclusions

Changes in crystal weight and melt temperature, which occur coincidentally with a change in interface shape from convex to planar during the Czochralski growth of $Gd_3Ga_5O_{12}$ single crystals, have been observed. The sense and relative times over which these effects occur are consistent with the idea that the interface shape modification is caused by a melting-back process, arising from hot liquid being drawn towards the crystal interface from hotter regions of the melt by the centrifugal stirring effect of the rotating crystal.

The requisite change in the shape of the solid/liquid interface can be artificially induced by a sudden increase in crystal rotation rate or can occur naturally during growth as the crystal diameter is increased. In the latter case an experimentally derived linear relationship exists between crystal diameter and rotation rate.

Acknowledgements

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References

1. B. COCKAYNE, M. CHESSWAS and D. B. GASSON, *J. Mater. Sci.* **4** (1969) 450.
2. B. COCKAYNE, *J. Crystal Growth* **3, 4** (1968) 60.
3. B. COCKAYNE and J. M. ROSLINGTON, *J. Mater. Sci.* **8** (1973) 601.
4. B. COCKAYNE, M. CHESSWAS and D.B. GASSON, *ibid.* **2** (1967) 7.
5. W. BARDSLEY, G. W. GREEN, C. H. HOLLIDAY and D. T. J. HURLE, *J. Crystal Growth* **16** (1972) 277.
6. W. BARDSLEY, B. COCKAYNE, G. W. GREEN, D. T. J. HURLE, G. C. JOYCE, J. M. ROSLINGTON, P. J. TUFTON, H. C. WEBBER and M. HEALEY, *ibid.* **24/25** (1974) 369.
7. D. S. ROBERTSON, *Brit. J. Appl. Phys.* **17** (1966) 1047.

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