

# The Growth of Oxide Single Crystals

## USE AND CARE OF PLATINUM APPARATUS

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*With new techniques of crystal growth new problems have been encountered with the platinum apparatus used in crystal production. Some of these difficulties are discussed in this paper, including attack by bismuth oxide,  $\text{Bi}_2\text{O}_3$ , and dissolution of the platinum in the leaching acids, together with methods of prolonging the life of platinum crucibles.*

For many years single crystals of oxides have been grown by the high temperature solution technique. The conditions of growth and the properties of the solvents have been enumerated by White (1). Basically the solvents are very corrosive, which necessitates the use of platinum containers and thermocouples. In the last few years a modification of this growth technique, namely liquid phase epitaxy, LPE (2), has come to the forefront for the growth of single crystal thin films. The development of this latter technique has been accompanied by new problems with the

care of the platinum. In this paper we indicate the problems and possible solutions that we have found to be of use to extend the life of the platinum. Only some of the new problems have been indicated because there are already review articles on this subject (3, 4). This paper is split into the various stages of material preparation and the difficulties encountered. No attempt has been made to be exhaustive but this paper is designed to help the crystal grower in general.

### The Premelting Stage

Growth of a garnet, as a typical example of the oxides under consideration, would be from a  $\text{PbO}$ ,  $\text{PbF}_2$  and  $\text{B}_2\text{O}_3$  flux and a typical composition for thin film growth is given in Table I. With this type of flux a well-known problem has been its attack on the platinum. In general the attack is caused by a metal or non-metal (Pb, Bi, As, Sb, B, etc.) which reacts with the platinum to form a low melting point platinum-rich alloy. Since the reaction takes place preferentially on grain boundaries, only very small amounts of the element are required to cause destruction of the crucible. The formation of lead may be the result of the non-stoichiometry in the lead compounds or of the contamination with reducing organic material, such as lead acetate, which is readily reduced to lead on heating. The organic lead salts can be removed sufficiently by washing the  $\text{PbO}$  and then redrying.

The non-stoichiometry has been overcome to some extent by the addition of small quantities of  $\text{PbO}_2$  (5) in order to prevent the formation of free lead in the melt.

**Table I**  
**A Typical Composition for Growing  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  Thin Films on  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  Substrates from a Lead Borate Flux**

$\text{PbO}$	275.0 g
$\text{B}_2\text{O}_3$	6.88 g
$\text{Fe}_2\text{O}_3$	25.0 g
$\text{Y}_2\text{O}_3$	2.8 g

To overcome the difficulties of the lead salt solvents and, in particular, their volatility at the crystal growth temperatures (1000 to 1400°C), much work has been done to find new fluxes. One such system is BaO/B<sub>2</sub>O<sub>3</sub> (6) and another is BaO/B<sub>2</sub>O<sub>3</sub>/Bi<sub>2</sub>O<sub>3</sub> (7). The addition of Bi<sub>2</sub>O<sub>3</sub> to the melts has increased the number of problems because the platinum is attacked more severely and the attack is even worse with the use of platinum alloys.

Although liquid Bi<sub>2</sub>O<sub>3</sub> (and PbO) should be thermodynamically stable with respect to the metal (8) up to about 1800°C, this attack can only be explained by the formation of metallic bismuth. This means that circumstances exist that prevent the system from attaining thermodynamic equilibrium. In this respect, slow heating during melting might be helpful. It has been found that there was little attack on the pure platinum crucible if a composition containing Bi<sub>2</sub>O<sub>3</sub> was premelted in a slowly heated resistance furnace in an oxygen atmosphere (9). We have performed a series of tests with these fluxes in pure (99.99 per cent) platinum crucibles. In the case of fast heating with an R.F. coil in air, a failure rate of about 75 per cent was found. Even the addition of BaO<sub>2</sub> (decomposition temperature 800°C) could not prevent failure with fast heating. Heating at a rate of 100°C/h in a resistance furnace in an oxygen atmosphere produced no failures, even after a soaking period of 200 hours at 1150°C. The heating rate is clearly a very important factor to consider during premelting. The use of crucibles fabricated from platinum that contains certain additives in order to minimise grain growth requires more care in combination with these corrosive melts. These additions tend to dissolve preferentially and cause fast leakage by the crucibles. A similar effect applies to crucibles fabricated from rhodium-platinum alloys. In this latter case a platinum lining of the crucibles will reduce failures, as mentioned in the next section.

At all times gloves should be worn when platinum is handled in order to reduce contamination by grease. This organic

material would cause a local reduction of the flux components when heated and hence an attack on the crucible at the grain boundaries. It would help to remove this danger during the premelting stage if crucibles were first annealed in an oxygen atmosphere at about 800°C for several hours. This not only relieves the strains produced by a previous 'run' but also the carbon-containing materials are oxidised and a protective oxide layer is formed on the platinum surface by reaction with the atmosphere (10) and this may help in some cases.

## The Growth Stage

During the growth of crystals or films over long periods (i.e. several weeks above 900°C), certain new difficulties have been found. These include mechanical failure of pure platinum crucibles. This is because the lead salt fluxes are very dense and melts can weigh up to several kilograms. This problem can be overcome by supporting the crucible in a ceramic vessel with alumina powder as padding. However, it is often undesirable to have aluminium-containing materials in the furnace, since these can lead to contamination

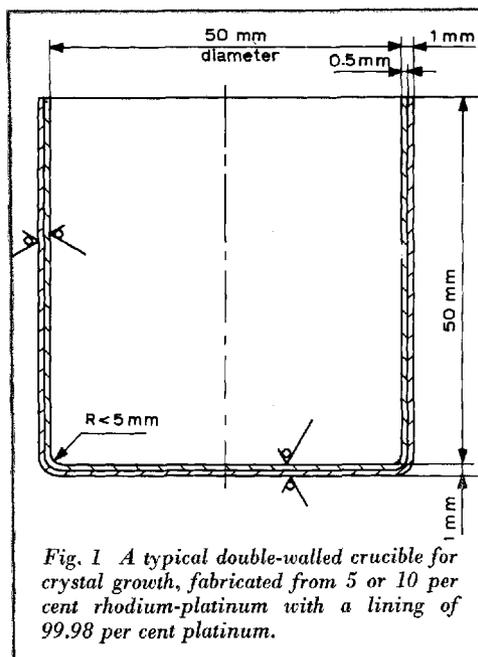
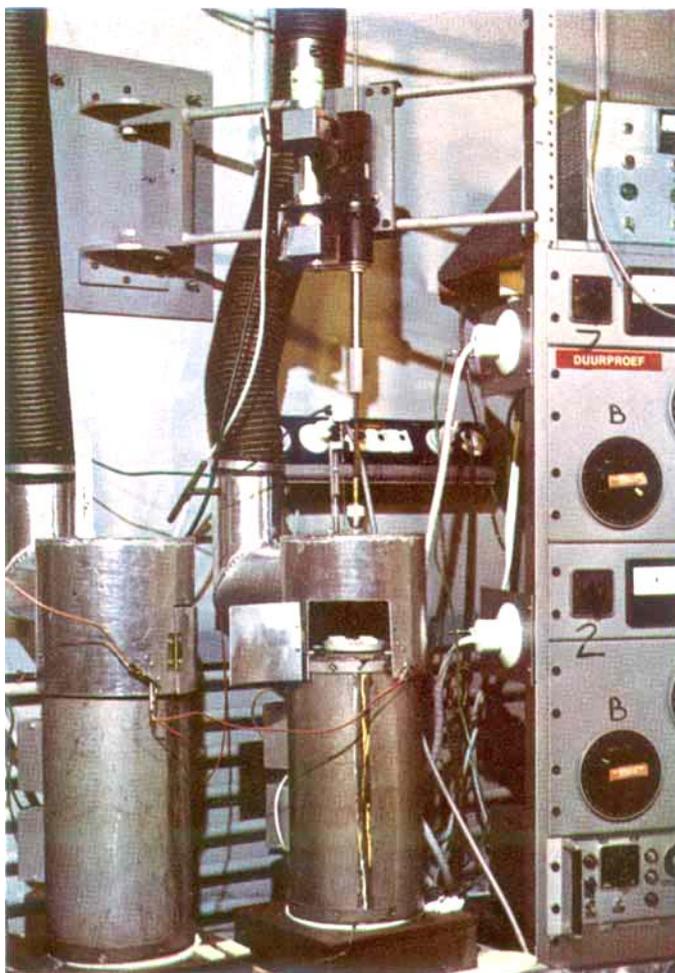


Fig. 1 A typical double-walled crucible for crystal growth, fabricated from 5 or 10 per cent rhodium-platinum with a lining of 99.98 per cent platinum.

*Fig. 2 Liquid-phase epitaxial growth of single crystal films is carried out in this furnace at Philips Research Laboratories, Eindhoven. The internal arrangement of the furnace is shown in Fig. 3*

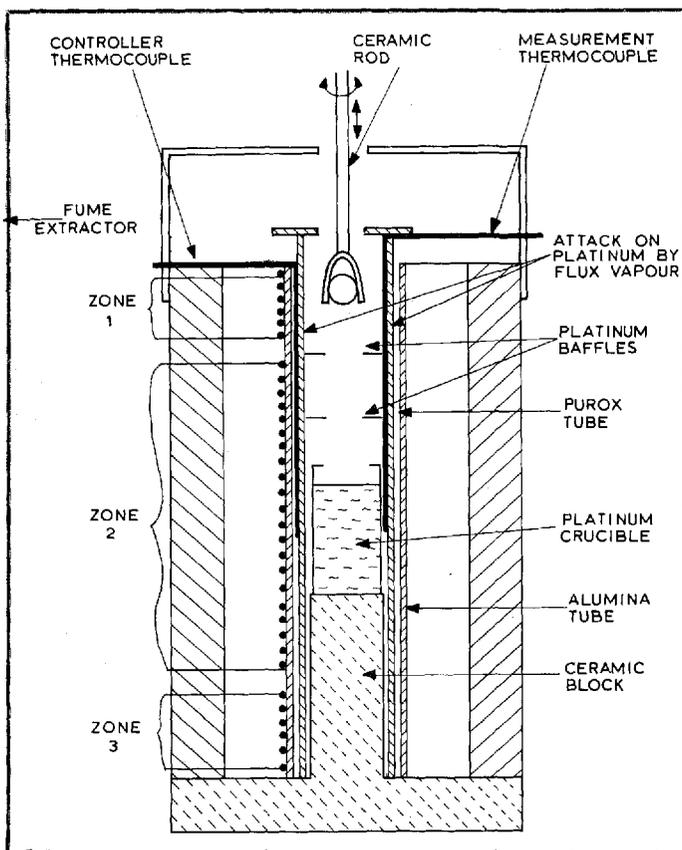


of the desired crystals. In that case it would be better to use alloys of rhodium and platinum. However, chemical analysis has shown that the rhodium contaminates the melts, and hence the crystals. To overcome this we have successfully used double-walled crucibles, as shown in Fig. 1. The pure platinum liner stops the contamination while the 10 per cent rhodium-platinum alloy gives the strength. The rounded edge inside the base of the crucible facilitates cleaning.

In the double-walled form of crucible it is still possible to get contamination by diffusion of the rhodium through the platinum liner. It has been shown (11) that at 1000°C with a 0.5 mm thick platinum liner it takes of the order of  $10^4$  hours, and that at 1400°C and the same wall thickness it takes of the order of  $10^2$  hours, for 2 per cent of rhodium to diffuse through to the inner surface of the platinum liner when a 10 per cent rhodium-platinum alloy also 0.5 mm thick is used on the outside.

It has been observed that during the stirring of a LPE melt above the saturation temperature, which speeds up the homogenisation process, a crystalline form of platinum collects on the stirring rod. Also, at the end of a 'run' lasting three or four weeks there is usually a large deposit of platinum at the bottom of the crucible. It is clearly seen that the crucible wall is thinned below the level of the melt surface. This transport is not fully understood but it would appear that the stirring action accelerates the transport of platinum from the wall of the crucible to the bulk of the melt.

Here we should make some remarks about platinum : 10 per cent rhodium-platinum



*Fig. 3 A furnace for liquid-phase epitaxy growth of single crystal thin films of garnets. The approximate position is indicated of the condensed lead flux vapour where it attacks the platinum baffles and thermocouple*

furnaces and the inserted platinum baffles indicated in Fig. 3. As said before, the use of alumina may be undesirable because of contamination of the melt.

thermocouples. Lead salt fluxes are some of the worst to use with platinum thermocouples since they poison them. It is possible to use platinum sheaths but even these fail after a short period of time. The thermocouples should be checked at least once a week against a standard thermocouple. In the LPE process we have found that the greatest failure of the platinum-sheathed thermocouples occurs in the cooler regions of the furnace where the lead oxide vapour condenses, as shown in Fig. 3. It appears that when the lead oxide condenses it attacks the platinum and produces a black powder, resulting in mechanical failure at this point. A typical analysis of the black powder is given in Table II. The life of the thermocouple may be extended by using a thicker platinum sheath or, better, by the use of an alumina sheath. This attack also occurs with platinum-lined

### **Cleaning Crucibles for Re-use**

One of the quickest ways of cleaning the crucibles is to heat them upside down in a R.F. coil with a ceramic pot below to collect the melt. Final cleaning in hot dilute nitric or hydrochloric acid produces a crucible ready for re-use. This latter method creates undesired effects. First, we have found by chemical analysis that 0.25 mg of platinum is dissolved per hour from 100 cm<sup>2</sup> of platinum surface in 6N hydrochloric acid at approximately 80°C. If many crucibles are to be cleaned frequently in this way it would be desirable from the economic point of view to reclaim the platinum. Secondly, iron (one of the many elements present) is very difficult to remove from the surface of the platinum, so a different method of cleaning has to be employed. This is normally done by fusion with potassium pyrosulphate at approximately

**Table II**  
**Spectrochemical Analysis of the Black Powder Produced When the PbO Vapours Condense on Platinum**  
**(All Values in Weight per cent)**

PbO	bulk
Pt	30
Fe <sub>2</sub> O <sub>3</sub>	0.4
B <sub>2</sub> O <sub>3</sub>	0.3
Al <sub>2</sub> O <sub>3</sub>	0.1
Bi <sub>2</sub> O <sub>3</sub>	0.05
MnO	0.006
MgO	0.003
CuO	0.002

700°C, but this produces grain growth in the platinum and dissolution of the platinum. We normally use a bath of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> at a somewhat lower temperature; this does not cause grain growth and only 300 mg platinum dissolves in 1 kg of K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> in two months of

continuous use. With the rhodium alloys the dissolution of rhodium in K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> is much greater because it is more readily oxidised. Another fusion method is the use of a borax melt for 0.5 h at 1000°C. Grain growth has not been detected when using this method.

### Effect of the Gas Atmosphere

The growth of garnets under various pressures of oxygen (12) and argon has produced many new and interesting results. In particular, chemical analysis of the crystals produced under these conditions has shown some interesting facts. A typical set of results is given in Table III. It is seen that the argon atmosphere produces less contamination of the crystals. However, observation inside the pressure vessel of the furnace (13) shows that with the argon the transport of platinum to the cooler regions of the furnace is far greater than in the case of oxygen atmospheres. The platinum also becomes very brittle when used in argon atmospheres and should be annealed in oxygen before re-use.

**Table III**  
**Chemical Analysis of Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> Crystals Grown from a PbO-PbF<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> Flux under Various Pressures of Oxygen and Argon**  
**(All Values in Weight per cent)**

Contaminants	Oxygen			Argon			
	6 atm	10 atm	15 atm	2 atm	6 atm	10 atm	15 atm
PbO	0.4	0.3	3.0 *	0.2	2.0 *	0.4	0.2
Pt	0.2	0.2	0.2	<0.002	<0.002	<0.0002	<0.0002
B <sub>2</sub> O <sub>3</sub>	0.03	0.02	0.1 *	0.03	0.1 *	0.04	0.04
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.02	0.02	<0.001	<0.001	0.001	<0.001
SiO <sub>2</sub>	0.01	0.03	0.03	0.03	0.03	0.04	0.03
Al <sub>2</sub> O <sub>3</sub>	0.008	0.006	0.009	0.006	0.02	0.01	0.01
Rh	0.002	0.02 **	0.004	<0.001	<0.001	<0.001	<0.001
Eu <sub>2</sub> O <sub>3</sub>	<0.002	0.05 **	<0.002	<0.002	<0.002	<0.002	<0.002
MnO	0.0004	0.0003	0.0003	0.0007	<0.0005	0.0002	0.0002
MgO	0.0007	0.0006	0.0004	0.0005	0.0006	0.0004	0.0003

\* The large content of PbO and B<sub>2</sub>O<sub>3</sub> is due to bulk inclusions of flux.

\*\* These higher values are probably due to chemical batch differences.

Results in Table III are of general interest to the garnet crystal grower. They show the effect of gas species and pressure on the incorporation of impurities in the crystals and are the subject of a future publication.

## Conclusions

It is possible for platinum ware to have a long life and no mechanical failures if some care is taken by crystal growers as follows:

- (1) At all times handle the platinum ware with gloved hands.
- (2) Premelt the fluxes *slowly* in an oxygen atmosphere and preferably in a resistance-heated furnace, and also check the stoichiometry of the starting compounds used.
- (3) Use platinum-lined rhodium-platinum alloy double-walled crucibles for strength, but preferably for limited periods to reduce the risk of rhodium contamination of the melt.
- (4) From the point of view of corrosion of the apparatus and volatility, the use of barium salt fluxes has to be considered.
- (5) The use of a gas atmosphere different from air has to be considered, since it

plays a role in the attack on the platinum.

Finally, it is suggested that the leaching acids should be retained because it may be economic to reclaim the dissolved platinum.

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## The Reliability of Dry Reed Switches

The dry reed switch is in general a highly reliable device, the inert gas contained in the glass capsule preventing any undesirable reactions that might affect contact behaviour. Because of their excellent resistance to erosion, rhodium plated contacts are commonly used on the reeds. However, the purity of the gases in the capsule may still be a cause of uncertainty, and an investigation of the effects of such impurities on the contact resistance of rhodium was reported to the 19th Annual Holm Seminar on Electric Contact Phenomena in Chicago by Hayashi, Tanaka and Hara of Fujitsu Laboratories, Kawasaki.

Gaseous impurities that can exist in the capsule included oxygen, methane and carbon dioxide, arising either from atmospheric contamination of the sealing gas or from adsorbed gases on the walls of the glass or on the reeds. The effects of these gases, in

varying concentration in purified nitrogen, on the contact resistance of electrodeposited rhodium were measured, while the contact surfaces were checked for impurities by electron probe micro-analysis.

In the presence of oxygen in concentrations as low as 50 p.p.m. in nitrogen contact resistance was found to increase, while a similar effect was given by methane, and oxygen and carbon were respectively detected at the mating point of the contacts. Carbon dioxide did not appear to affect contact resistance even after many operations. Hydrogen, of course, led to no increase in contact resistance, but brought the value back to normal after operation in oxygen or methane.

Similar results were obtained in experiments using bulk rhodium instead of an electrodeposit, and an improved sealing technique to avoid contamination is discussed.