Platinum Containers for the Growth of Single Crystal Oxides

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The growth of single crystal oxides for optical and magnetic purposes is commonly carried out using platinum containers. Modifications to container design have been important factors in improving growth conditions. A new composite three-layer crucible has been fabricated in platinum and iridium for growing crystals of sodium barium niobate, and a platinum container which can be drained of flux has been developed for growing rare earth iron garnets.

Single crystals are of basic importance as integral parts of semiconductor devices, oscillators, transducers, detectors, delay lines and power limiters. There is also an interest in nearly perfect optical crystals for coherent light sources (lasers), non-linear optical applications (second harmonic generators and parametric oscillators) and as light beam modulators, deflectors and phase shifters. Further, there are a number of uses for large, uniform, single crystals of yttrium or rare earth iron garnets having controlled magnetic properties.

The emphasis placed on size and uniformity has motivated a search for ways to improve crystal growth. One important part of this effort has been to modify the container design. A melt (or fused mixture of the components of a crystal) can conveniently be contained in a platinum crucible-susceptor that is heated by radio frequency induction. In Fig. 2 a boule of lead molybdate ($PbMoO_4$),

Fig. 1 The furnace in which single crystal garnets are grown in a platinum crucible. The operator is preparing to drain off the flux by puncturing the seal in the container bottom

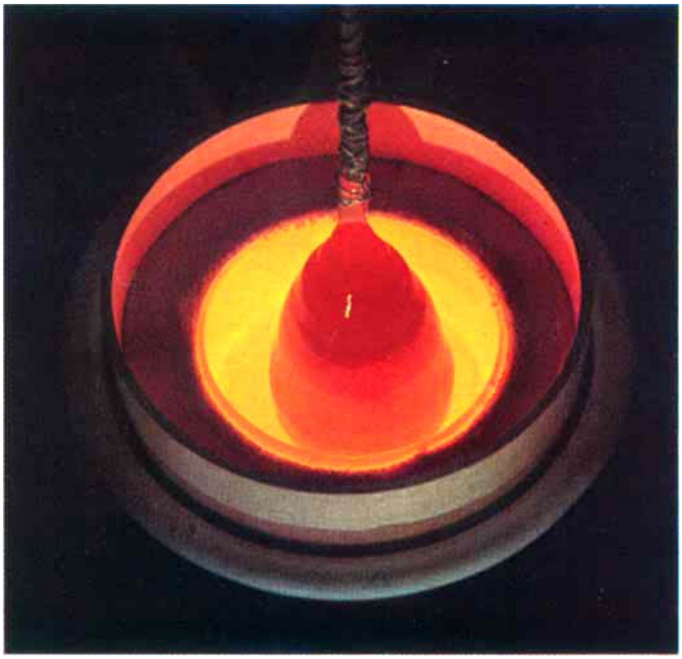

Fig. 2 A single crystal of lead molybdate being pulled from the melt. The platinum crucible susceptor is heated by a radio frequency induction coil, the top turn of which is visible here

which is particularly useful for acousto-optic applications, is shown being pulled from a melt contained in a platinum crucible that is 3 inches in diameter and 3 inches high (1). The crucible is embedded in zirconia granules that are contained by a quartz liner that is closely fitted by a multi-turn r.f. coil (only the top turn is evident).

Little difficulty is encountered with the crucible in growing $PbMoO_4$ (melting point 1065°C). However, when growing sodium barium niobate ($NaBa_2Nb_5O_{15}$, an important material for non-linear optical applications) the platinum crucible expands extensively over the several hours required to complete the growth run (2). This shortens the useful lifetime of the crucible and increases the difficulty of maintaining uniform crystal growth conditions. The melting point of $NaBa_2Nb_5O_{15}$ is near 1450°C, about 285°C closer than that of $PbMoO_4$ to the melting point of platinum at 1773°C. It is essential to use platinum in contact with the $NaBa_2Nb_5O_{15}$ melt, rather than the higher melting point noble metals (such as rhodium or iridium) to avoid contamination by oxides of the latter that colour the crystal. Fortunately, the surface stability of platinum can be combined with the rigidity of iridium by using composite crucibles.

Several crucibles are shown in Fig. 3. The first (A) is a new 1.5 inch diameter × 1.5 inch height × 0.060 inch wall platinum crucible. The second (B) is a similar crucible that has been used to grow $NaBa_2Nb_5O_{15}$ crystals for about 50 hours. This crucible has expanded to nearly twice its original volume. The third (C) is a new, composite, three-layer crucible. It was constructed by close fitting a 0.040 inch wall platinum crucible inside a 0.040 inch wall iridium crucible which in turn was close fitted inside a 0.020 inch wall platinum crucible. The inner and outer platinum crucibles were joined at the top. The fourth crucible (D) is such a container after 20 hours of use. The outer wall expanded due to internal gas pressure and subsequently burned through. The fifth crucible (E) was also constructed in the same manner as crucible C. However, several tiny vent holes were drilled through the outer platinum layer to permit entrapped gas to escape during heating. The crucible shown (E) has been used to grow $NaBa_2Nb_5O_{15}$ crystals for more than 200 hours without expanding or suffering distortion beyond that experienced using iridium alone as the crucible material.

Crystals that do not grow well from the melt are often best prepared by growth from a solvent or flux. The yttrium or rare earth

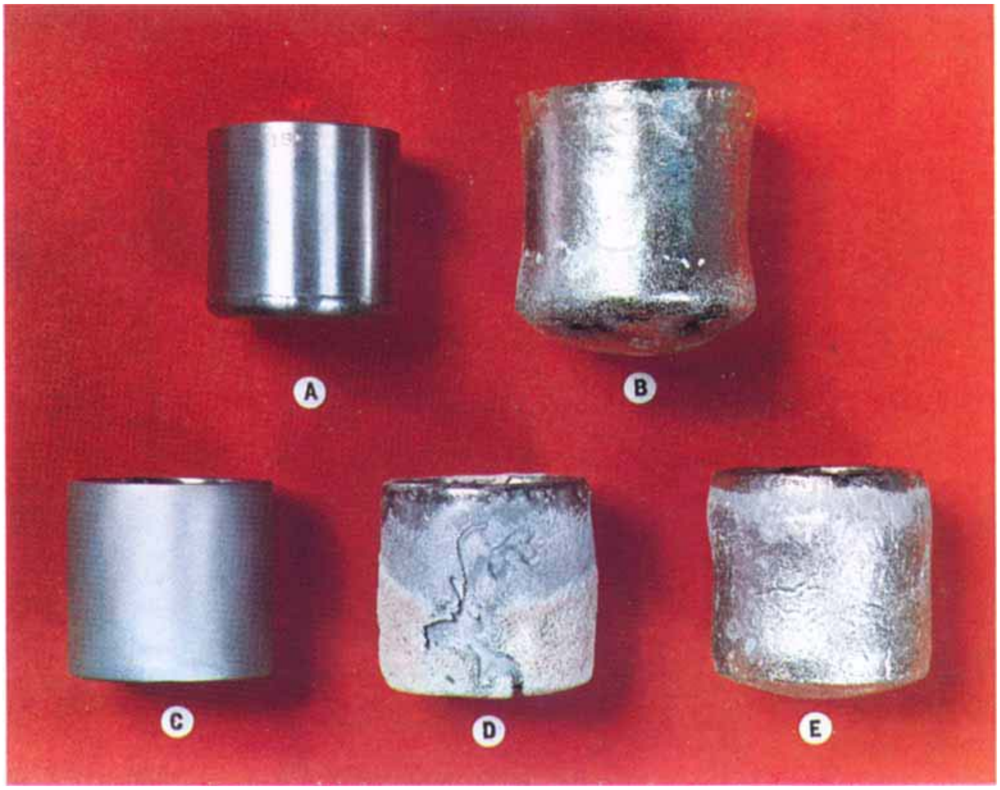

Fig. 3 Platinum and composite platinum-iridium-platinum trilayer crucibles compared.

A New platinum crucible

B Platinum crucible after 50 hours growing sodium barium niobate crystals

C New composite crucible

D Composite crucible after 20 hours use

E Composite crucible with vent holes to permit escape of entrapped gas during heating. After 200 hours use it was distorted no more than one made of iridium

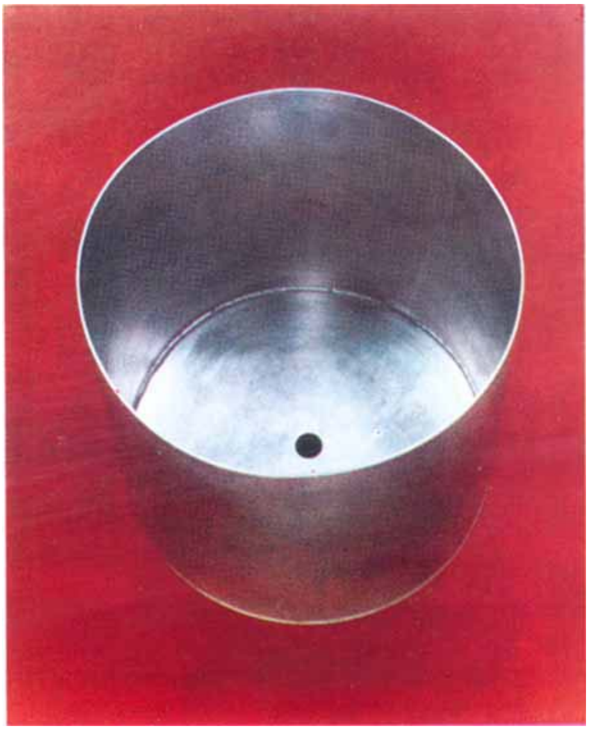

Fig. 4 A platinum container used for the flux growth of large garnet crystals has been designed to permit draining at high temperatures

Fig. 5 Garnets grown by the technique which includes draining of the flux are used in microwave devices, delay lines, tunable lasers and bubble domain devices. Demand for them is increasing steadily

iron garnets (e.g. $Y_3Fe_5O_{12}$) are such materials. These crystals are grown by slowly exsolving the crystal components from a $PbO{\cdot}PbF_2{\cdot}B_2O_3$ flux by cooling at about 15°C per day from 1300°C to 950°C (3). Below the lower temperature the garnets tend to redissolve and therefore they should be separated from the flux. However, large crystals will crack if they are subjected to thermal shock. This can be avoided by removing the flux at 950°C while the crystals remain in the furnace.

A platinum container that has been designed to permit draining at high temperatures is shown in Fig. 4. The 8 inch diameter $\times$8 inch height$\times$0.060 inch wall container weighs about 15 pounds. The hole in the centre leads into a ½ inch long stand-off that can be fitted with a welded-in insert. The insert is punctured to drain off the flux. The covered crucible is mounted on a hollow pedestal in a vertical muffle resistance furnace during crystal growth. The operator shown in Fig. 1 is preparing to drain the flux by puncturing the seal in the bottom of the container. The flux drains quietly into the catch tray. After the flux is drained the furnace is shut down and allowed to cool to room temperature. Garnets that have been grown under these conditions are shown in Fig. 5. The crystals have found use in microwave devices, delay lines, tunable lasers and bubble domain devices.

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