was not recognized by the writer in either stone during microscopic examination of material in the United States National Museum and the British Museum.

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GROWTH OF BERYL FROM MOLTEN SALT SOLUTIONS

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INTRODUCTION

Single crystals of beryl, $Be_3Al_2Si_6O_{18}$ are of interest for physical and optical studies, microwave maser devices, gemstones and other applications. A variety of techniques have been described for the growth of beryl including melt (Gentile *et al.*, 1963 and Wilson, 1965), hydrothermal (Van Praagh, 1947) and flux (Hautefeuille and Perry, 1888, Schiebold, 1935, Linares *et al.*, 1962 and Lefever *et al.*, 1962).

The growth of beryl from fluxes is particularly attractive because it readily allows growth by seeding techniques. Beryl and emerald crystals have been grown from molten V_2O_5 solutions by seeding (Linares *et al.*, 1962). It appears from the present investigation that in the beryl-V_2O_5 phase diagrams beryl is stable only in a region of liquid immiscibility in which a silicate liquid is also stable. Since this liquid formation seriously interferes with crystal growth, new fluxes for beryl were investigated.

During the course of this investigation a new family of fluxes were found having the general formula of $(1-x)\ MO \cdot xR_2O_5$, where M could be Pb, Ca, Sr or Ba, and R could be V or up to 50 percent P or Nb.

EXPERIMENTAL

The system PbO-V_2O_5 was chosen for the most extensive investigation since early experiments showed it to be more promising than others. Batches were prepared in which the PbO-V_2O_5 ratios and the temperature range of crystallization were varied. In these runs, the source of beryl was clear natural beryl crystals which were added in excess of the solubility limit at the growth temperature. Cr_2O_3 was added to the melt so that any beryl which crystallized would be chromium doped and, therefore, easily distinguishable from the source material by its green color. The appropriate mixture of PbO-V_2O_5, beryl and Cr_2O_3 were heated at 1100–1250°C in a platinum crucible for a period of 4 hours to insure chemical equlibrium. Next, the batch was cooled at 5°/hour to a predetermined temperature, the crucible was removed from the furnace and the remaining solution poured off. After cooling to room temperature, the beryl crystals were cleaned by leaching off the remaining flux with hot nitric acid. The residues were then identified by X-ray diffraction and microscopic examination.

RESULTS

Growth Compositions: At temperatures from 1100°C to 700°C the beryl was the only crystalline phase found in fluxes containing from 15 to 70 mole percent V_2O_5 ($x=0.15$ to 0.70). With less than 15 percent V_2O_5, no crystals are found and the melt freezes to form a lead glass. With more than 70 percent V_2O_5, the region of liquid immiscibility reappears.

At temperatures from 1250°C to 1100°C beryl was found from 35 to 65 percent V_2O_5 ($x=0.35$ to 0.65). At the higher temperatures however, beryl always coexisted with some other crystalline phase. All of these phases have not been identified; however, BeO, Be_2SiO_4 and $BeAl_2O_4$ are among them. These runs were repeated using the beryl component oxides rather than natural beryl as the feed material with the same results.

Variations were made in the ratios of the component oxides to attempt to find a region where only beryl crystallized. No such region was found; however, the tolerable variation from stoichiometry was determined. It was found that additions of up to 35 mole percent BeO, 30 mole percent Al_2O_3, or 10 mole percent SiO_2 were the limits of variation from stoichiometry which would yield beryl in useful amounts. These limits were roughly the same at lower temperature range also. Beryl will also grow from compositions in which PbO is replaced by CaO, SrO, or BaO, or in which the V_2O_5 is partially replaced by P_2O_5 or Nb_2O_5. However, with CaO, SrO, or BaO the region of liquid immiscibility reappears.

Crystal growth. Crystals have been grown by both slow cooling and by the gradient method. Fluxes containing between 50 and 66 mole percent V_2O_5 have been found to be the most desirable because: (1) they are not very volatile at the high temperatures; (2) they are well away from the immiscibility region or lead glass region, and (3) they exhibit a desirable solubility for beryl and change of solubility with temperature satisfactory for crystal growth.

Growth by slow cooling has been done mainly using spontaneous nucleation to seed the melt. A few attempts have been made to seed slow cooled melts with promising results. A typical run contained 50 g beryl components and 200 g flux. Cooling at 1°/hour from 1250 to 900°C resulted in crystals 2 mm^3. By scaling up this process a factor of 20, crystals 5 mm^3 have been obtained. The crystals from large batches are of very poor optical quality and are often intergrown with BeO and Be Al_2O_4. It appears that in large batches considerable stratification can occur owing to the high viscosity silicate melt causing layers of liquid of different composition to form, with different compounds being stable in different regions.

In these melts, beryl grows as hexagonal rods with a c/a ratio of about 2 (Fig. 1). The habit obtained is independent of the flux composition and the form of the beryl nutrient (oxide powders or crystals).

In using the gradient method with this flux, it is necessary to take account of the fact that beryl is less dense than the flux. In order to use the ordinary gradient technique, it is necessary to hold the beryl nutrient down on the bottom with a platinum baffle. This works well when solid chunks of natural beryl are used for nutrient and good growth can be obtained. Beryl can also be grown by using an inverted gradient, wherein the nutrient floats on the surface in a hot region and crystal growth occurs on the bottom in a cooler region. Crystals can be grown here by deliberate seeding or by sponteneous nucleation. Using 125 ml crucibles, deposits $2.5\times1.2\times0.3$ cm have been grown on seed crystals. Using larger seeded melts crystals up to $2.5\times2.5\times1$ cm (1 cm total overgrowth) have been grown. It has been possible with this technique to grow crystals with uniform substitution of iron and chromium for aluminum for microwave maser experiments.

Beryl grows in a gradient at growth temperatures from 750 to 1150°C. It appears that the best growth temperature is 1000°C with the dissolving region at 1050°C. Under these conditions, very clear growth has been observed at growth rates of 0.2 mm per day in both the *a* and *c* directions. The growth rate with the inverted gradient is the same as with a normal gradient indicating that the diffusion rate, not convection, determines the rate of growth.

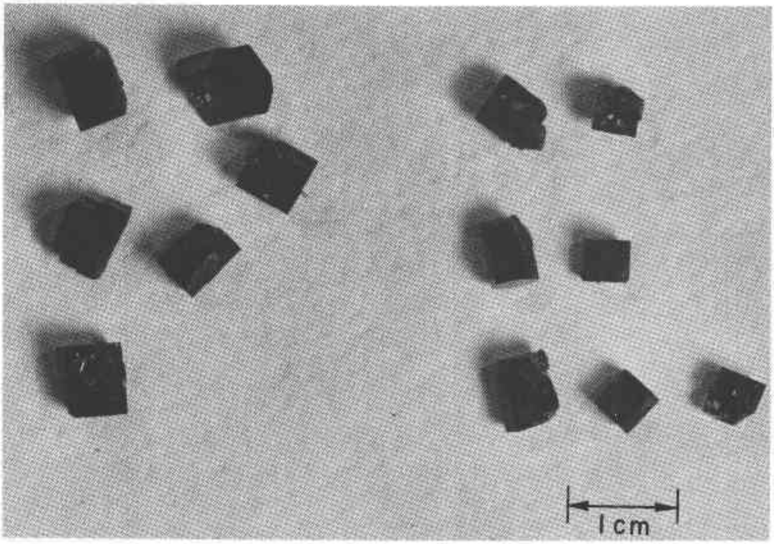

FIG. 1. Spontaneously nucleated emeralds.

Optical properties. Ultraviolet and visible transmission measurements of synthetic emerald show essentially the same spectra as natural emerald. In the infrared, however, there is considerable difference caused by the lack of water bands in the synthetic (Fig. 2). The *ir* cutoff is not affected by the water and begins at 4μ in the natural material and synthetic.

No chromium fluorescence was observed from emeralds grown from vanadate fluxes, when excited with UV light, even though the R lines were observed in absorption. It is believed that there is considerable incorporation of vandium into the emerald which then interacts with the chromium to quench its fluorescence. The same effect has been observed in vandium doped ruby and alexandrite.

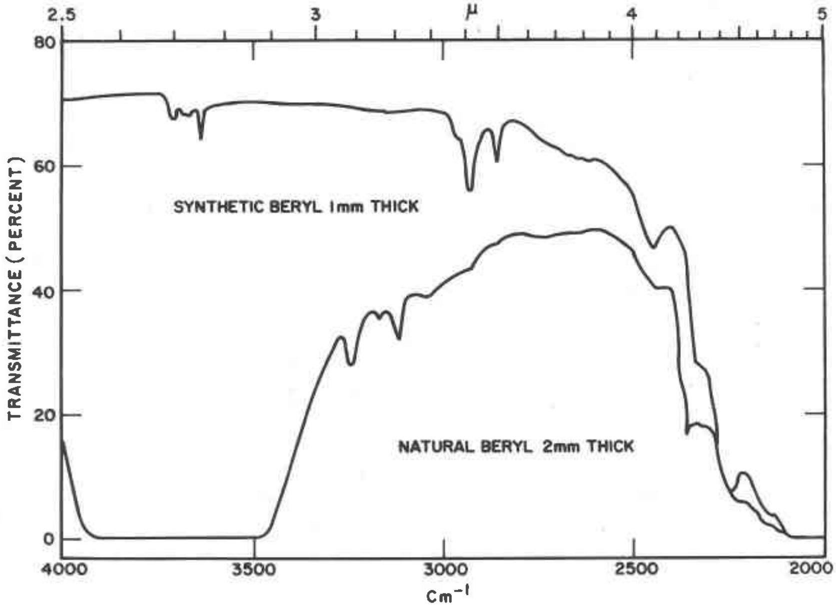

FIG. 2. Infrared transmission of natural and flux-grown beryl.

Synthetic beryl is generally characterized by large areas of flux inclusions. In the case of the vandium-based fluxes, these are reddish to yellow in color and occur as interconnected sheets running through the crystal (Fig. 3). Figure 4 shows the openings of flux inclusions on the 001 face of an emerald grown very slowly on a synthetic emerald seed. These

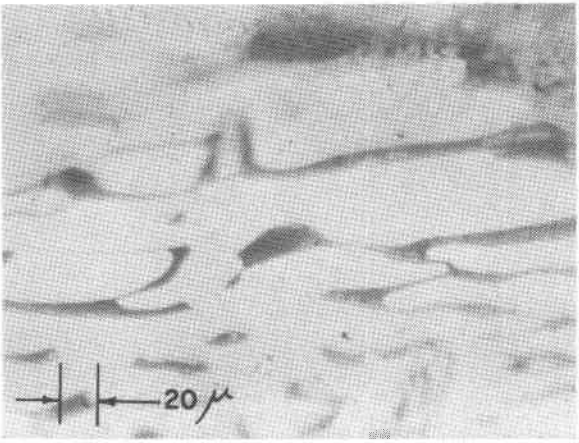

FIG. 3. Flux inclusions in emerald.

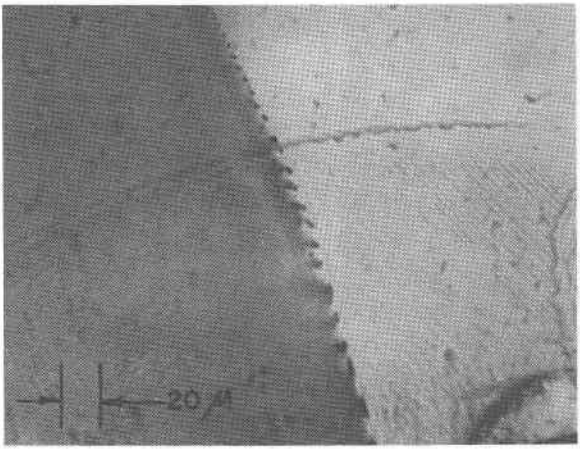

FIG. 4. Openings of flux inclusions on the surface of emerald.

inclusions are found to propagate continually regardless of growth rate, indicating that the defect associated with flux inclusions is inherent in the growth process of beryl itself under these conditions.

CONCLUSIONS

Large beryl crystals can be grown from a $PbO-V_2O_5$ flux using slow cooling or gradient techniques in combination with seeding. The optical properties of these crystals are similar to natural beryl except for the lack of water band absorption in the near infrared. These crystals are also characterized by continuous flux inclusion regardless of growth rate or direction or seed origin.

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