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THE FLAME FUSION SYNTHESIS OF EMERALD

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The synthesis of emerald as a gem material is of considerable economic and academic interest to the mineralogist. Recent applications of chromium-doped beryl, particularly as a maser material, to the field of solid state physics have been evaluated by Geusic *et al.* (1959), Gerritsen (1962) and Goodwin (1961). This has stimulated investigation of techniques for the synthesis of emerald with the objective of synthesizing large single crystals of high quality.

The methods previously investigated have been concerned with the use of fluxes or hydrothermal processes. The first successful synthesis of emerald, using lithium molybdate as the flux, was reported by Hautefeuille and Perrey (1888). In 1930, the I. G. Farbenindustrie synthesized emerald (Schiebold, 1935) by dissolving the oxides in BeF_2 and allowing slow vaporization of the fluoride, thereby crystallizing emerald (Amstutz and Borloz, 1935). At about this time, C. Chatham of San Francisco announced the synthesis of emerald in his laboratory. His secret process which has culminated in the synthesis of large, nearly flawless emeralds leaves Chatham as the world leader in emerald synthesis at present. The Chatham process (1961) requires a run of six months' duration. The hydrothermal synthesis of emerald accomplished in 1928 by R. Nacken of the Mineralogical Institute, Frankfurt University, is discussed by Van Praagh (1947).

Most of the research in recent years has centered on using various fluxes including Li_2MoO_7, $Li_2W_2O_7$, $PbMoO_4$, $PbWO_4$ and V_2O_5. Linares

et al. (1962), have reported a quality of beryl suitable for microwave applications grown in a V_2O_5 flux. Lefever *et al.* (1962), have used $PbO-PbF_2$, B_2O_3, Li_2O-MoO_3 and MoO_3 systems and recently reported good quality and high yield using Li_2SiO_3 and MoO_3 in addition to the oxides of beryllium, aluminum and chromium. Lithium molybdate and sodium vanadate have been used successfully in this laboratory (Andres *et al.*, 1962) for the flux synthesis of emerald. Emeralds approximately the size of a 6-mm cube were grown in runs lasting one month.

The need for large, high quality single crystals of emerald which could be grown rapidly suggested the investigation of emerald synthesis by the flame fusion (Verneuil) technique. This technique has been used on a variety of congruently melting crystals (ruby, spinels, tungstates etc.) with great success. It produces a boule several inches in length by approximately $\frac{1}{2}$ in. in diameter in a matter of three to four hours. The application of this technique to incongruently melting materials remains controversial (Bauer *et al.*, 1950). Initial experimentation by the writers indicates that emerald melts congruently and the melting point, though not accurately determined, generally agrees with that previously reported (*Handbook of Chemistry and Physics*, 1955–56). Safety precautions were taken because of the toxicity of beryllium oxide.

The metal oxides (C. P. grade chemicals) were weighed out as follows:

BeO	16.0 g[1]
Al_2O_3	18.0
SiO_2	67.0
Cr_2O_3	0.5

The mixtures were placed in one gallon jars and rolled on a ball mill rack for eight hours. They were then ground and sintered at 1050° C. for five days. The powder was then removed from the furnace and re-mixed and ground.

After several unsuccessful attempts, two emerald boules were grown. A coating of polycrystalline mullite was formed over the entire boule surface during the latter part of the growth when the conditions were slightly changed. The emerald was identified by means of x-ray diffraction and petrographic microscopy. A portion of the boule is shown in Fig. 1. X-ray powder diffraction films of the flame fusion-grown emerald together with those of other natural and synthetic beryls are shown in Fig. 2.

The Hughes emerald is blue-green in color. The crystal is colorless in thinsection, but thicker sections show pleochroism from blue-green to light green. Since the crystals were grown by the flame fusion technique,

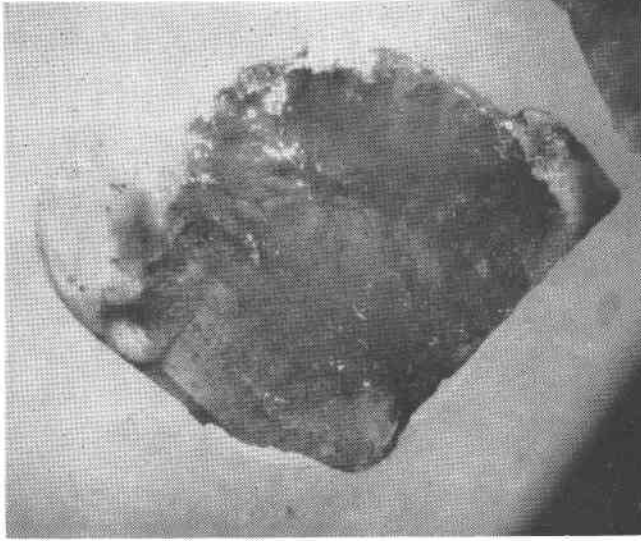[1] Excess BeO was added because of previously observed losses.

FIG. 1. Portion of emerald boule. Note white mullite coating at top. (Magnification 10✕)

no crystal faces were apparent. Crystallographic examination of the
boule indicated growth along the c axis. The thinsection, cut parallel to
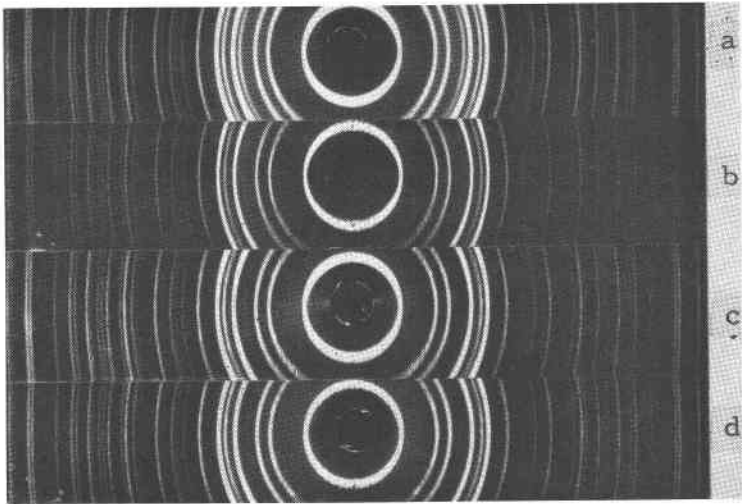the c axis, revealed no cleavage planes. Gas bubble inclusions were ob-

FIG. 2. X-ray diffraction powder photographs. (a) New Hampshire beryl. (b) Single
crystal emerald flux grown in this laboratory. (c) Chatham emerald (d) Hughes flame
fusion-grown emerald.

TABLE 1. REFRACTIVE INDICES OF NATURAL AND SYNTHETIC EMERALD

	ω	ϵ
Hughes emerald[1]	1.561–1.562	1.566–1.567
Lechleitner emerald[1]	1.575	1.581
Chatham emerald[1]	1.560–1.562	1.564–1.565
Igmerald emerald[1]	1.559–1.562	1.563–1.569
Indian emerald	1.586	1.593
Uralean emerald	1.579	1.588
Common beryl	1.564–1.595	1.568–1.602

[1] Denotes synthetic emerald.

served but showed no distinct lineation. Although emerald is uniaxial, a biaxial interference figure was observed in sections of the Hughes and Chatham emeralds. This has been explained by Winchell (1956).

Index of refraction measurements were made on the flame fusion grown emerald using the oil immersion technique. Table 1 shows the measured results together with other reported data (Holmes and Crowningshield, 1960).

The Hughes synthetic emerald has indices of refraction approximating values of most known synthetic emeralds. The close proximity of the indices of the Lechleitner emerald to natural emeralds is expected since the bulk of this synthetic consists of a natural beryl seed with an "emerald" overgrowth (Holmes and Crowningshield, 1960).

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HYDROTHERMAL SYNTHESIS OF ANDALUSITE FROM KYANITE

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Introduction

Lacy (1951) reported the growth of andalusite in slates undergoing hydrothermal treatment at temperatures above 760° C., but the method of identifying the andalusite is not mentioned. Roy (1954) wrote of syntheses of andalusite from various mixtures in the system MgO-Al_2O_3-SiO_2-H_2O. The phase had a mean refractive index of $1.635 \pm .004$, and the x-ray diffraction pattern was reported as very similar to that of natural andalusite. All three Al_2SiO_5 polymorphs were reported synthesized by Coes (1955) at 700°–900° C. and 10,000 to 20,000 atmospheres, but the method of identification is not fully described. The hydrolysis of muscovite mica to pyrophyllite and andalusite at temperatures as low as 420° C. at 15,000 psi water pressure was recorded by Hemley (1959). The x-ray pattern given shows a correspondence with three of the strong reflections for andalusite. More recently, Aramaki and Roy (1959, 1962) have reported the growth of a new aluminosilicate, AS(H)-II, of probable composition Al_2SiO_5. This new phase is stated to be identical to that previously identified as andalusite by Roy (1954). Carr and Fyfe (1960) also noted the synthesis of an "andalusite-like" phase, x-andalusite, and found that whereas the x-ray powder diffraction pattern for andalusite and x-andalusite showed an approximate correspondence between some of the strongest lines, the differences left no doubt that they were dealing with a distinct phase. In the light of these later results it is apparent that previous reports of syntheses of andalusite are open to question.

During the course of some hydrothermal experiments in the system Al_2SiO_5-H_2O the author has observed some results which seem to represent stronger evidence for the synthesis of andalusite than has heretofore been reported.

Experimental Results

The synthesis of andalusite is petrologically significant if it is achieved from other mineral phases under conditions which are not far removed

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