RUSSIAN FLUX-GROWN SYNTHETIC EMERALDS

By John I. Koivula and Peter C. Keller

A relative newcomer to the international gem market is an attractive flux-grown synthetic emerald of Russian manufacture. This article provides a general discussion of the technique used to grow these stones and describes their gemological properties and chemistry. The Russian flux-grown synthetic emeralds were found to be similar to other flux-grown emeralds in refractive index and specific gravity, and therefore to be readily distinguished from natural emeralds on the basis of these two properties.

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Acknowledgments: The authors wish to thank Carol Stockton of the GIA Research Department for providing the chemical analyses of the study samples, and C. W. Fryer for checking the gemological properties reported in this article.

During the 1982 meeting of the International Mineralogical Association at Varna, Bulgaria, a Russian scientist gave one of the authors a spectacular sample of synthetic emerald that had reportedly been manufactured in the Soviet Union. This sample consists of a cluster of self-nucleated hexagonal prisms with pinacoidal terminations radiating from a crust of polycrystalline material (figure 1), not unlike the typical material currently produced by the Chatham Research Laboratory. The individual crystals in the cluster range up to 3 cm in length and 4.2 cm in diameter. The transparent to translucent crystals exhibit excellent bluish green to green emerald color and are only moderately included. The emerald specimen was accompanied by a relatively recent article from a Soviet publication that describes the flux-fusion and hydrothermal methods the Russians have been using to grow emeralds (Bukin et al., 1980); thus far, this article has not appeared in the Western gemological literature.

Recently, significant amounts (at least several hundred carats) of faceted Russian-made flux-grown synthetic emerald have appeared in the world gem markets, particularly in Hong Kong and New York. In March of this year, the GIA Research Department obtained 18 gem-quality faceted stones for study purposes. This article reviews the general history of the flux growth of emeralds and presents what details are known of the Russian technique for growing commercial-size synthetic emeralds by the flux-fusion method. In addition, this article describes the gemological properties of the Russian flux-grown synthetic emerald and identifies the key characteristics by which it can be distinguished from natural emeralds using routine gemological tests.

THE FLUX GROWTH OF SYNTHETIC EMERALDS

A Historical Review. The knowledge that synthetic emerald can be grown from a flux melt has been available since Ebelman (1848) heated powdered natural emerald in a molten boric acid flux and produced minute hexagonal

Figure 1. A cluster of flux-grown synthetic emerald crystals manufactured in the USSR. The largest crystal is 3 cm long × 4.2 cm in diameter. Photo by Susan Gipson.

emerald prisms as the mixture cooled. Hautefeuille and Perrey (1888) did extensive work with lithium oxide and molybdenum oxide fluxes and purified reagent chemicals of beryl to grow emerald crystals up to 1 mm across in 14 days. In 1911, the IG-Farben Company began a study that investigated the use of a lithium molybdate flux with additional molybdenum oxide and reagent-grade chemicals to grow crystals up to 2 cm in length in just 12 months. The IG-Farben study lasted 31 years; the results of this research were not published until 1960, when Espig's report appeared. Simultaneous and almost identical with the IG-Farben work was that of Richard Nacken (Nassau, 1980). As far as we know, however, neither the IG-Farben nor the Nacken work ever resulted in the wide-scale commercial growth of synthetic emeralds, and by the 1940s neither investigation was active. However, the work of IG-Farben and Nacken laid the foundation for the commercially successful flux-grown synthetic emeralds that eventually appeared in the marketplace. The most successful commercial growth of flux-fusion emeralds, probably using a lithium molybdate–vanadate flux technique, was accomplished in 1935 by Carroll F. Chatham of San Francisco, California, and again almost 30 years later, in 1964, by Pierre Gilson of France. It appears that the Russians have now entered the market with a new commercially viable product.

The Russian Method. The flux growth of emerald in the USSR is being carried out by a group under Gennadi Bukin at the Geological Institute of Akademgorod, Novosibirsk. The technique being used by the Russians (K. Nassau, pers. comm., 1985) is accelerated crucible-rotation flux growth (H. J. Scheel and E. O. Schulz-Du Bois, 1971), a variation of the flux-fusion method described by Linares (1967). Rather than using the lithium molybdate–vanadate flux attributed to the Chatham and Gilson products, the Russians have been using a lead vanadate (PbO-V_2O_5) flux similar to that used by Linares, with a nutrient of natural beryl or reagent-grade BeO, $BeCO_3$, Al_2O_3, and SiO_2, together with Cr_2O_3 or $LiCrO_4$ plus Fe_2O_3 as coloring agents.

The basic process for synthesizing flux-fusion emeralds has not changed significantly since the IG-Farben work (Espig's 1960 report is well summarized in Sinkankas, 1981). Espig's report, augmented by published papers of the Linares process and the brief information supplied by the Soviets (Bukin et al., 1980), results in the following generalized description of the Russian process:

The appropriate mixture of PbO-V_2O_5 flux, nutrients, and coloring agents is heated to 1250°C in a platinum crucible. The nutrients sink to the bottom of the crucible since they have a higher density than the PbO-V_2O_5 flux. The necessary silica is supplied in the form of quartz (SiO_2), which floats to the surface of the molten mixture because it has a lower density than the flux. As the quartz slowly dissolves at the top of the flux, the nutrients dissolve from the bottom of the crucible and react with the molten flux to form complex oxides. Convective currents in the crucible carry these complex beryllium oxides to the top of the crucible to react with the dissolved silica and eventually crystallize out as emerald. When the emeralds have reached appropriate size, the mixture is cooled at a rate of 3°C to 10°C per hour to a temperature of 700°C. The crucible is then removed from the furnace and the remaining solution is poured off. As the final step, the crucible is allowed to cool to room temperature and any remaining flux adhering to the emerald crystals is cleaned off using hot nitric acid.

Figure 2. Some of the faceted Russian flux-grown synthetic emeralds used in this study. The largest stone weighs 3.82 ct. Photo ©Tino Hammid.

Linares (1967) never reported the growth of flux crystals larger than 5mm^3, much too small for commercial purposes. The Russian crystal growers, however, have reported success in using a technique similar to that of Linares to grow crystals up to 10 cm long and 6 cm in diameter. The 10-cm-long crystals reportedly require three to four months to grow (K. Nassau, pers. comm., 1985).

MATERIALS AND METHODS

The collection of Russian flux-grown synthetic emeralds available for testing consisted of the large crystal cluster shown in figure 1 and 18 faceted stones: 10 emerald cuts, six pear-shaped brilliants, and two round brilliant cuts, some of which are shown in figure 2. The largest of the faceted stones is a 3.82-ct emerald cut and the smallest is a 0.48-ct emerald cut. The faceted stones are all transparent and range from bluish green to green. All are moderately included; some of the inclusions are visible to the unaided eye and others are easily observed at 10× magnification.

The large crystal cluster and the 18 faceted stones were all subjected to standard gemological testing procedures. Although we found that the Russian flux-grown synthetic emeralds, like other flux-grown emeralds, can easily be distinguished from natural emeralds on the basis of refractive index and specific gravity (see table 1), the test stones were also examined (1) for their reaction to ultraviolet radiation, (2) with a spectroscope,

TABLE 1. Comparison of the key gemological properties of the Russian flux-grown synthetic emeralds with those of natural and other flux-grown synthetic emeralds.

Material	Refractive index		Birefringence	Specific gravity
	o	ϵ		
Russian flux-grown synthetic emerald	1.563	1.559	0.004	2.65±0.01
Other flux-grown synthetic emeralds[a]	1.563	1.560	0.003	2.65–2.69
Natural emerald[a]	1.571–1.593	1.566–1.586	0.005–0.008	2.68–2.77

[a] *As reported in Webster (1983).*

and (3) internally to identify the nature of the inclusions. The results of this examination are reported below.

GEMOLOGICAL PROPERTIES

Refractive Index. The faceted stones and two of the flat faces on the large crystal cluster were tested for refractive index using a Duplex II refractometer, a polaroid filter for birefringence, and a sodium vapor monochromatic light source. In all cases, the reading obtained was $\epsilon = 1.559$, $o = 1.563$. The optic character was determined to be uniaxial negative (−), and the birefringence was 0.004.

Specific Gravity. The faceted stones and a small fragment from the synthetic emerald crystal cluster were tested for specific gravity in a standard 2.67 heavy liquid. All subjects floated in this liquid, with the bulk (approximately 98%) of their volume below the liquid's surface. Next, a heavy liquid of 2.65 specific gravity was used. All of the stones and the crystal fragment sank very slowly in the liquid at about the same rate as a rock crystal quartz indicator. Thus, the specific gravity of these Russian flux-grown synthetic emeralds was determined to be very near 2.65.

Ultraviolet Fluorescence. All of the samples were exposed to long-wave and short-wave ultraviolet radiation. Contrast control glasses were worn during testing. The faceted stones were all inert to short-wave radiation; to long-wave radiation they showed an expected orangy red glow of moderate to weak intensity.

The large crystal cluster also gave an orangy red glow of moderate to weak intensity when the long-wave lamp was used. With short-wave radiation, we observed small patches of bright chalky yellow fluorescence on the faces of some of the emerald crystals, while the crystals themselves were inert. The patches were superficial only and would be cut away during faceting. The exact nature of the fluorescent patches and their cause was not determined. They were not visible with the microscope.

Spectroscopic Examination. The crystal cluster and each of the faceted stones were next examined using a GIA GEM Instruments spectroscope unit. When the emeralds were placed on the opening of the iris diaphragm, we observed that they transmitted red. When looking down the optic axis direction, we saw in all stones a vague general absorption from 440.0 nm down, a sharp line at 477.0 nm, a broad band of absorption between 560.0 and 620.0 nm, and lines in the red situated at 637.0, 646.0, 662.0, 680.5, and 683.5 nm. The bands and lines were visibly weaker in the smallest faceted synthetic stones.

Microscopy. The synthetic emeralds were next studied under magnification and photographed using a gemological stereo microscope. The crystal cluster was studied for both internal and external features, while the faceted stones were examined primarily for their inclusions.

Close scrutiny of the surface of the crystal cluster revealed the presence of three separate and distinct crystalline-appearing solid phases in addition to the synthetic emerald. The most obvious of these phases was a near-colorless transparent, to white translucent, brittle material adhering to the back of the crystal cluster. A small flat-faced fragment of this material was removed, and testing determined that its specific gravity and refractive index matched that of phenakite. The synthetic phenakite contained flux inclusions, and because of its near-colorless and transparent nature the

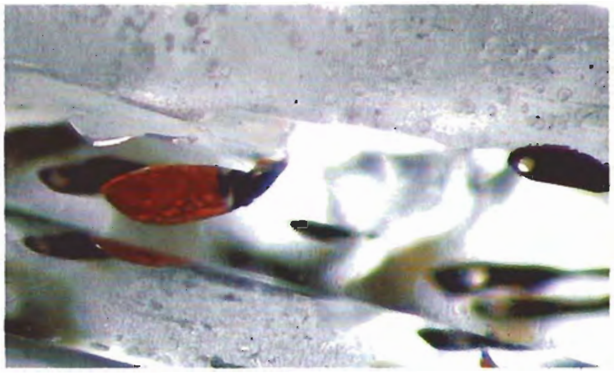


Figure 3. Primary flux inclusions in synthetic phenakite which was found on the back of the flux-grown synthetic emerald crystal cluster. Transmitted and oblique illumination, magnified 50×.

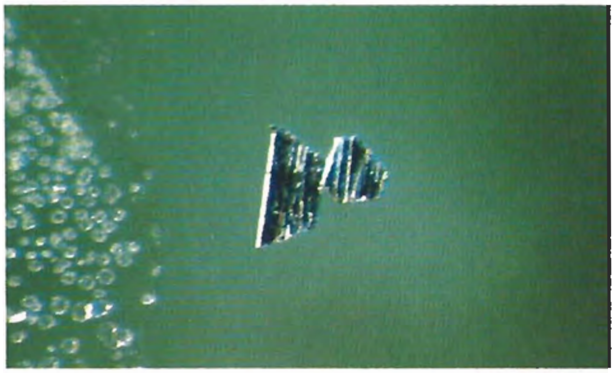


Figure 4. Two tiny platelets of metal (probably platinum) found on one of the prism faces of a Russian flux-grown synthetic emerald crystal. Oblique illumination, magnified 50×.

true color of the dark brown to orange flux used to grow the crystal cluster was easily observed (figure 3).

Also present on the surface of the synthetic emerald crystal cluster were several small singles and groupings of euhedral orthorhombic four-sided prisms, with blunt-ended pyramidal terminations, that showed a distinct color change from brownish red in incandescent light to grayish green in fluorescent light. A small, 2-mm-long crystal was removed from the specimen and tested for refractive index, approximate specific gravity (using 3.32 heavy liquid), and hardness. Because the properties obtained from this small euhedron matched those of chrysoberyl, and a color change had been noted, this associate was identified as synthetic alexandrite. The presence of both phenakite and chrysoberyl are not surprising considering their close chemical relationship to beryl.

The third solid associate, shown in figure 4, was opaque, grayish silver, metallic, malleable and had a hardness of approximately 4–4½ on the Mohs scale. Since it is common practice to use platinum-group metal crucibles or crucible liners for the flux growth of synthetic emeralds, these

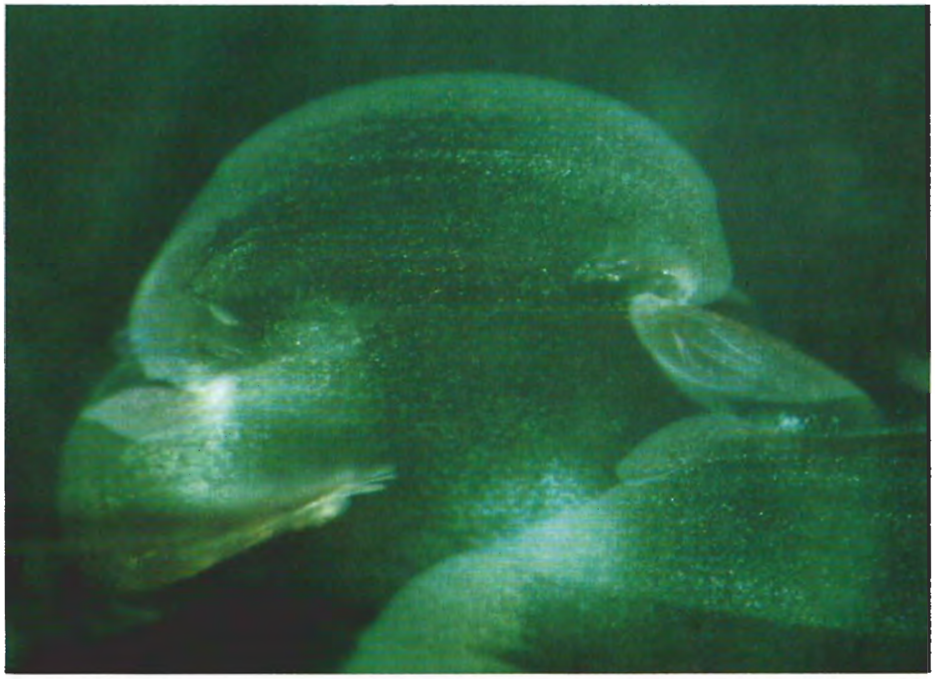


Figure 5. Secondary healed fracture ("fingerprint") in the Russian flux-grown synthetic emerald crystal cluster. Oblique illumination, magnified 35×.

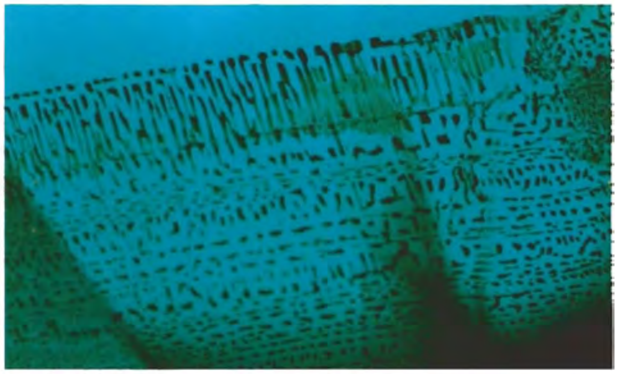
Figure 6. Secondary "fingerprints" of various textures in the Russian flux-grown synthetic emerald crystal. Oblique illumination, magnified 20×.

Figure 7. Primary two-phase inclusions in a faceted Russian flux-grown synthetic emerald. Dark-field and oblique illumination, magnified 35×.

metallic platelets are probably a member of the platinum group, most likely platinum.

Aside from minor growth features and color zoning, the only inclusions observed in the crystal cluster and the 18 faceted stones were flux inclusions. Easily visible at 10× magnification, the flux inclusions were present in two forms: as secondary healed fractures and as primary void fillings. The large crystal cluster contained numerous healed fractures ("fingerprints"). Most of these, as in figures 5 and 6, were extremely delicate, and only in thicker areas was the true, dark, yellow-brown to orangy brown color of the flux visible. Primary flux inclusions were also plentiful. The faceted stones yielded the best view of primary flux inclusions (figure 7). Note in figure 7 the two-phase nature of some of the inclusions, consisting of a contraction (vacuum) gas bubble and glassy flux, and also the color of the glassy flux. Like the crystal cluster, the faceted stones also displayed numerous secondary flux inclusions ("fingerprints"); one of these is shown in figure 8.

Figure 8. Typical secondary "fingerprint" in one of the faceted Russian flux-grown synthetic emeralds. Partial polarized light, magnified 45×.



Takubo et al. (1979) reported on the internal characteristics and surface texture of flux-grown emeralds from the Soviet Union. They also found flux-filled wispy veils ("fingerprints"), as well as silk-like inclusions of unknown composition oriented nearly perpendicular to the c-axis of the crystals. No such silk-like inclusions were observed in the stones examined for the present study.

CHEMISTRY

Microprobe analysis of two of the cut stones from the study collection shows consistency with previous data on other flux-grown synthetic emeralds, except with respect to MgO content (see table 2). The chemical data from Bukin et al. (1980) are also provided in this table. Unfortunately, we have no information regarding the size of the Bukin et al. sample or the method of analysis. This is particularly unfortunate because their data show some significant departures from the analyses obtained for the present study as well as from the limits set forth by Stockton (1984) for the distinction between natural and synthetic emeralds. This may be due either to the techniques of chemical analysis employed by the Russians or to changes in the "recipe" that have been made since Bukin's report was issued in 1980. It is not unusual for such changes to be made by manufacturers of synthetics during the early (and often experimental) years of production. In any case, the recent material analyzed for this study shows no significant differ-

TABLE 2. Chemical data (in wt.%) for synthetic emeralds grown by flux fusion.

Oxide	Present study[a]	Bukin et al. (1980)	Other flux[b]	Natural[b]
Na_2O	nd[c]	0.22– 0.29	≤ 0.04	0.04– 2.3
MgO	0.1	nd	nd	tr– 3.1
FeO	0.2[d]	nd	≤ 0.52[d]	0.06– 2.0[d]
Al_2O_3	19.2	17.86–18.27	18.1–20.1	11.7 –18.2
V_2O_3	<0.1	nr	≤ 0.19	tr– 2.0
Cr_2O_3	0.3	0.31– 0.48	0.2– 2.19	tr– 2.06
SiO_2	66.4	64.4 –65.3	65.7–67.4	63.3 –66.5
BeO	na	13.2 –13.9	na	na
Fe_2O_3	nr[d]	0.14– 0.16	nr[d]	nr[d]

[a] *These data represent an average of the results obtained from four microprobe analyses of two specimens from the study collection.*

[b] *From Stockton (1984) and Schrader (1983) as reported in the former article.*

[c] *nd = not detected; nr = not reported; na = not analyzed.*

[d] *Total iron reported as FeO.*

ences in chemical composition—other than MgO content—from flux-grown synthetic emeralds from other sources.

DISCUSSION AND CONCLUSION

After closely examining the sample crystal cluster and stones from a gemological viewpoint, we determined that these Russian flux-grown synthetic emeralds have properties similar to those of other known flux-grown synthetic emeralds and therefore can be separated from natural stones on the basis of their low refractive index and low specific gravity (see table 1). The presence of flux inclusions only makes identification that much easier.

It is interesting to note that all but one of the faceted stones used in this study were purchased as Russian hydrothermal synthetic emeralds. Russian hydrothermal synthetic emeralds were available at the most recent Tucson Show (February, 1985) and have been seen at the GIA Gem Trade Laboratory (Koivula, 1984). It now appears that Russian flux-grown synthetic emeralds are being sold in the trade as well. T. Chatham (pers. comm.) reported seeing 400 carats of this material at one source in Hong Kong in May 1985.

Even though our test sample consisted of 18 faceted stones and a crystal cluster providing this study with a good data base, it must be remembered that the growth process may be altered in the future; if this were to happen, the overt gemological properties would probably change as well.

REFERENCES

Bukin G.V., Godovikov A.A., Klyakhin V.A., Sobolev S.V. (1980) Synthetic emerald in gem minerals. *Proceedings of the XI General Meeting of the International Mineralogical Association*, pp. 36–44.

Ebelman J.J. (1848) Sur une nouvelle méthode pour obtenir des combinations cristallisées par la voie seche, etc. *Annales de Chimie et de Physique*, Vol. 22, pp. 213–244.

Espig H. (1960) Die Synthèse des Smaragds. *Chemische Technologie*, Vol. 12, pp. 327–331.

Hautefeuille P., Perrey A. (1888) Sur la réproduction de la phenacite et de l'émeraude. *Compte Rendu de l'Academie des Sciences (Paris)*, Vol. 106, pp. 1800–1802.

Koivula J.I. (1984) Gem news. *Gems & Gemology*, Vol. 20, No. 4, p. 245.

Linares R.C. (1967) Growth of beryl from molten salt solutions. *American Mineralogist*, Vol. 52, Nos. 9 and 10, pp. 1554–1559.

Nassau K. (1980) *Gems Made by Man.* Chilton Book Co., Radnor, PA.

Scheel H.W., Schulz-Du Bois E.O. (1971) Flux growth of large crystals by accelerated crucible-rotation technique. *Journal of Crystal Growth*, Vol. 8, pp. 304–306.

Schrader H.W. (1983) Contributions to the study of the distinction of natural and synthetic emeralds. *Journal of Gemmology*, Vol. 18, No. 6, pp. 530–543.

Sinkankas J. (1981) *Emerald and Other Beryls.* Chilton Book Co., Radnor, PA.

Stockton C.M. (1984) The chemical distinction of natural from synthetic emeralds. *Gems & Gemology*, Vol. 20, No. 3, pp. 141–145.

Takubo H., Kitamura Y., Nakazumi Y., Koizumi M. (1979) Internal textures and growth conditions of flux-grown emerald from USSR. *Journal of the Gemmological Society of Japan*, Vol. 6, No. 1/2, pp. 22–28.

Webster R. (1983) *Gems: Their Sources, Descriptions and Identification*, 4th ed. Revised by B.W. Anderson. Butterworths, London.