

RUSSIAN FLUX-GROWN SYNTHETIC ALEXANDRITE

By Karl Schmetzer, Adolf Peretti, Olaf Medenbach, and Heinz-Jürgen Bernhardt

Synthetic alexandrite is being flux-grown in Russia in a molybdenum-, bismuth-, and germanium-bearing solvent by means of the reverse-temperature gradient method. Characteristic properties include habit, twinning, growth patterns, residual flux inclusions, trace-element contents, chemical zoning, color zoning, and spectroscopic features in the visible and infrared ranges. The relationship between production technique and characteristic properties is discussed, and diagnostic properties that can be used to distinguish these synthetics from natural alexandrite are disclosed.

ABOUT THE AUTHORS

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Fine alexandrites are even rarer than fine rubies, sapphires, and emeralds. The major factors determining price are size, clarity, brilliancy, color in daylight, color change in artificial light, and country of origin. The finest alexandrites are characterized by a lively and intense green color in daylight with a prominent color change to purplish red or reddish purple in incandescent light. The most prestigious source of natural alexandrites is Russia, specifically the Ural mountains, where they were first discovered. Fine alexandrites occasionally appear at international auctions. For example, a 31 ct alexandrite sold for almost US\$185,000 at Christie's May 1992 auction in Geneva. Dealers in Idar-Oberstein report the sale of fine, large (over 5 ct) alexandrites for \$10,000–\$20,000 per carat, and even higher for exceptional stones (R. Guerlitz and A. Wild, pers. comm., 1996).

During the past 10 years, new deposits of natural alexandrite have been found in Minas Gerais, Brazil (Bank et al., 1987; Proctor, 1988; Cassedanne and Roditi, 1993; Karfunkel and Wegner, 1993); in Orissa and Madhya Pradesh, India (Patnaik and Nayak, 1993; Newlay and Pashine, 1993); and, most recently, near Songea in southern Tanzania (see "News on the Songea Deposit . . .", 1995; Kammerling et al., 1995). In addition, gem alexandrites are still being recovered from the historic emerald deposits of the Ural Mountains (Eliezri and Kremkow, 1994; Laskovenkov and Zhernakov, 1995).

As greater quantities of gem alexandrite enter the market, significant amounts of faceted alexandrites are being submitted to gemological laboratories for testing. Occasionally, distinguishing natural from synthetic has been difficult, notably for flux-grown synthetics, but especially when a specimen lacks diagnostic mineral inclusions (see Bank et al., 1988; Henn and Bank, 1992; Kammerling, 1995). These difficulties are caused by the similarity of growth structures and healing "feathers" in natural alexandrites from different localities to residual flux feathers in flux-grown synthetic alexandrites. In addition, hematite platelets in natural alexandrites sometimes resemble platinum inclusions in their flux-grown synthetic counterparts.

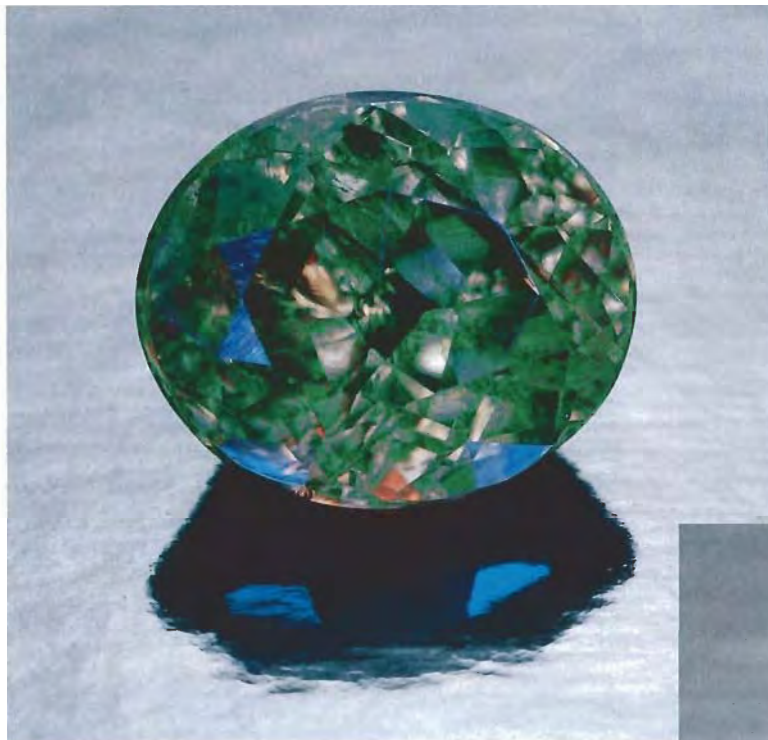


Figure 1. As the number of natural alexandrites in the marketplace increases, so does the quantity of synthetic alexandrites. One of the most convincing synthetic alexandrites is the material that is being flux grown in Russia. Shown here is a 1.08 ct (6.3 × 5.3 mm) faceted Russian flux-grown synthetic alexandrite in fluorescent light (left) and incandescent light. Photos © GIA and Tino Hammid.



The Russian-produced synthetic alexandrites (figure 1) can imitate the highest-quality natural alexandrites—such as those from the Ural mountains. Yet some natural alexandrites have sold for up to 300 times as much as their synthetic counterparts. Consequently, these synthetic alexandrites occasionally are misrepresented in the trade as Uralian alexandrites. One of the authors (A.P.) recently encountered two instances of synthetic alexandrites offered for sale as natural stones in Switzerland.

According to the voluminous scientific and patent literature available to the authors, synthetic alexandrite and synthetic chrysoberyl can be grown from the melt (Czochralski, Verneuil, Bridgman, and floating-zone techniques), hydrothermally, by the flux method, and by chemical vapor deposition (for a good description of most of these modern crystal-growth techniques, see Kimura and Kitamura, 1993). Because of such factors as production costs and the small crystals that result from some of these growth techniques, gem-quality synthetic alexandrites have been grown commercially and released to the market by just a few companies, which use the Czochralski, floating-zone, or flux method.

Two types of flux-grown synthetic alexandrite have been produced commercially for gem purposes. Since the 1970s, Creative Crystals Inc. of San Ramon, California, has produced synthetic alexandrite crystals by a method that uses a lithium

polymolybdate flux, as described in the Cline and Patterson patent (1975).

The second type has been produced at various locations in the former USSR since the late 1970s or early 1980s, using a method originally developed at the Institute of Geology and Geophysics, Siberian Branch of the Academy of Sciences of USSR in Novosibirsk. A few crystals grown by this method were given to one of the authors (K.S.) by Drs. A. Ya. Rodionov and A. S. Lebedev in 1988 and 1991. Preliminary results from the examinations of these samples were never published because of the very small sample base. That situation has changed. Considerable quantities (many kilos) of rough

Russian synthetic alexandrite are now commercially available, either directly from Novosibirsk or indirectly from Bangkok, and large parcels of rough are being cut in Sri Lanka, especially for the American market (G. E. Zoysa, pers. comm., 1995). For the present study, the authors examined more than 200 synthetic alexandrites with properties that indicated that they were all produced by roughly the same method (i.e., using fluxes that were similar in composition). In addition, one commercial source of Russian flux-grown synthetic alexandrite is the Design Technological Institute of Monocrystals, also in Novosibirsk, which works in cooperation with the Institute of Geology and Geophysics. During a 1994 visit to Novosibirsk, one of the authors (A.P.) obtained information first hand at

both institutes and saw demonstrations of part of the growth facilities, including the use of crucibles and furnaces.

The production technique used for Russian flux-grown synthetic alexandrite was briefly mentioned by Godovikov et al. (1982) and later described, in greater detail, by Rodionov and Novgorodtseva (1988) and Bukin (1993). The gemological properties of Russian flux-grown synthetic alexandrites were first described by Trossarelli (1986) and later by Henn et al. (1988), Henn (1992), and Hodgkinson (1995). The present article examines the relationship between production technique and typical properties, and identifies those characteristics that can be used to distinguish these synthetics from natural alexandrite.

TABLE 1. Modern techniques for the flux growth of chrysoberyl and alexandrite.

Authors	Inventors/ assigned to	Flux	Growth conditions ^a		Dopant (oxide)	Remarks
Farrell et al. (1963)		PbO-PbF ₂ PbO	s, sn sn	sc fe	— —	Chrysoberyl Chrysoberyl
Farrell and Fang (1964)		PbO PbO-PbF ₂ Li ₂ MoO ₄ -MoO ₃	s, sn s, sn s, sn	sc sc sc	— — Cr	Chrysoberyl Chrysoberyl Alexandrite
	Bonner and Van Uiter (1968)/Bell Telephone Laboratories	PbO-PbF ₂ -SiO ₂ ± B ₂ O ₃	sn	sc	Cr	Alexandrite
Tabata et al. (1974)		PbO-PbF ₂ ± B ₂ O ₃	sn	sc	—	Chrysoberyl; B ₂ O ₃ is used as habit modifier
	Cline and Patterson (1975)/ Creative Crystals Inc.	Li ₂ MoO ₄ -MoO ₃ (also Li-niobate, tungstate and PbO-PbF ₂)	s, sn	sc	Cr, Fe	Alexandrite
	Machida and Yoshihara (1980,1981)/Kyoto Ceramic Co.	Li ₂ MoO ₄	s	sc	Cr, V	Alexandrite
Godovikov et al. (1982)		"Flux"		tg		Alexandrite
	Hirose (1984)/Suwa Seikosha K.K.	V ₂ O ₅ ± Mo- or W-Oxides				Alexandrite
	Kasuga (1984)/Suwa Seikosha K.K.	Li ₂ MoO ₄ , MoO ₃ , V ₂ O ₅ , LiOH	s		Cr, Fe	Alexandrite
	Togawa (1985)/ Suwa Seikosha K.K.	V ₂ O ₅	s	sc, tg	Cr	Alexandrite
	Isogami and Nakata (1985,1986)/Kyocera Corp.	Li ₂ MoO ₄	s	sc	Fe, Ce, V, Co, W, Cr, Ni, Mn	Cat's-eye; TiO ₂ , SnO ₂ , ZrO ₂ , or GeO ₂ causing asterism
Rodionov and Novgorodtseva (1988)		"Flux"	sn	sc, tg		Alexandrite; two habits according to experimental conditions: platy or equidimensional
Bukin (1993)		Bi ₂ O ₃ -MoO ₃	s, sn	tg (sc, fe)	Cr, Ti	Alexandrite; laser applications

^a fe = flux evaporations, s = seeded growth, sc = slow cooling, sn = spontaneous nucleation, and tg = temperature gradient.

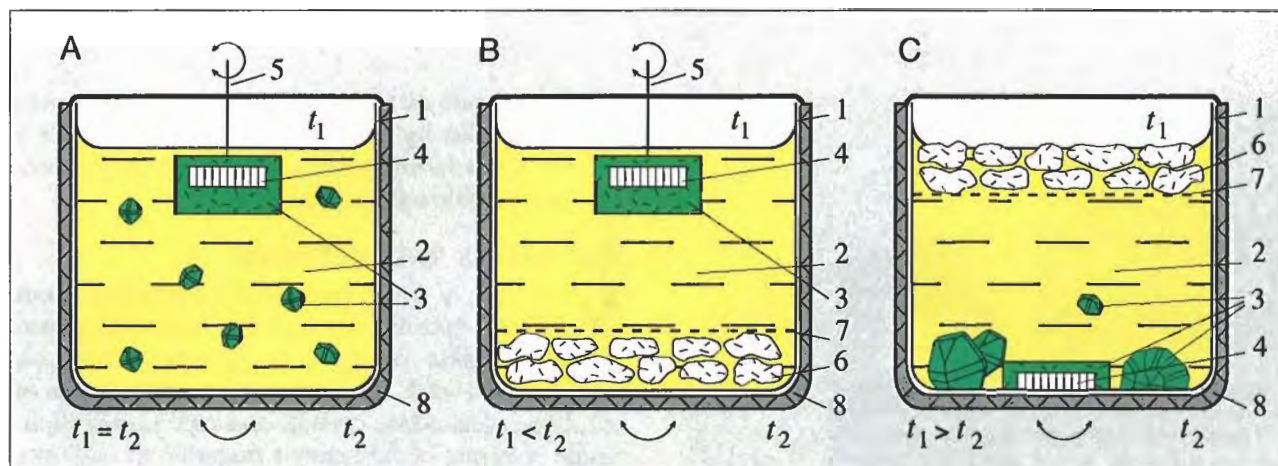


Figure 2. Three main processes have been described for the flux growth of beryllium-bearing oxides and silicates such as synthetic alexandrite and emerald: (A) slow cooling of a saturated melt, with seeded growth or growth by spontaneous nucleation; (B) seeded growth in a temperature gradient, with a growth zone above the dissolution zone; and (C) seeded growth or growth by spontaneous nucleation in a reverse temperature gradient, with a growth zone at the bottom of the crucible below the dissolution zone. Key: 1 = platinum crucible, 2 = flux melt, 3 = growing crystals, 4 = seed, 5 = platinum seed holder, 6 = nutrient, 7 = baffle, 8 = insulation, t_1 = temperature in the upper part of the crucible, t_2 = temperature in the lower part of the crucible. The circular arrows at the top of A and B indicate the possible rotation of the seed holder; arrows at the bottom of all three processes represent the possible crucible rotation. Adapted from Bukin (1993).

FLUX GROWTH OF SYNTHETIC ALEXANDRITE: HISTORY AND DEVELOPMENT

Early 19th-century experiments in the flux growth of synthetic chrysoberyl were summarized by Elwell and Scheel (1975). More modern flux techniques to grow synthetic chrysoberyl and/or alexandrite started in the 1960s (table 1). Most procedures use the slow-cooling technique (figure 2A). First, the solvent of flux and nutrient ($\text{Al}_2\text{O}_3 + \text{BeO} + \text{color-causing dopants}$) is heated above the point at which the flux liquefies and is then held at that temperature for a period sufficient to dissolve the nutrient oxides in the flux (Farrell and Fang, 1964). Next, the melt is cooled slowly at a constant rate until the flux solidifies. Last, the crystals that grew in the flux during cooling are removed from the crucible by dissolving the flux (e.g., in hot nitric acid). Common fluxes used for chrysoberyl and alexandrite are PbO-PbF_2 , $\text{Li}_2\text{MoO}_4\text{-MoO}_3$, and V_2O_5 (see table 1). The temperatures at which the cooling process begins and ends vary according to the composition of the flux used. They generally range from 1350°C to 800°C . Cooling rates are usually between 0.125°C and 3°C per hour. Both seeded growth and growth by spontaneous nucleation are used (again, see figure 2A). Seed crystals may be natural or synthetic chrysoberyl or alexandrite. Cr_2O_3 , Fe_2O_3 , and/or V_2O_3 are used as dopants.

The morphology of synthetic chrysoberyl or alexandrite depends primarily on the composition of the flux and not on the temperatures or cooling gradients used. Tabata et al. (1974) demonstrated the influence of B_2O_3 on the habit of chrysoberyl grown from PbO-PbF_2 solvents: They observed a distinct modification of habit from platy (flux without B_2O_3) to prismatic or equidimensional (flux with B_2O_3).

Isolated attempts to grow synthetic chrysoberyl or alexandrite by the flux evaporation technique have had poor results (see Farrell et al., 1963). In this method, constant heating of the melt in open crucibles leads to supersaturation of the melt and the growth of crystals by spontaneous nucleation.

Godovikov et al. (1982) first mentioned the possible growth of alexandrite by the temperature-gradient method, which works by creating a convection current within the crucible. According to a Japanese patent application by Togawa (1985), the nutrient is placed at the bottom of the crucible, where a certain temperature is reached and then maintained. A seed crystal is placed into the melt in the upper part of the crucible, which is held at a temperature lower than that at the bottom of the crucible (figure 2B). As the nutrient dissolves into the solution, circulation begins between the warmer and cooler areas in the crucible (convection currents). When the solution with the nutrient reaches the cooler area, it becomes supersaturated and crystals begin to form. These different temperatures are



Figure 3. The Russian flux-grown synthetic alexandrite crystals examined were either single crystals (right, 9 × 7 mm) or cyclic pseudohexagonal twins (left, 12 × 11 mm), which are shown here in incandescent light. Photo © GIA and Tino Hammid.

maintained, with the growth zone *above* the dissolution zone, for weeks or even months.

Rodionov and Novgorodtseva (1988) described a reverse temperature-gradient technique—in which the growth zone is located *below* the dissolution zone—for the growth of synthetic alexandrite. In this method, the nutrient is placed in the upper part of the crucible, where a certain temperature is reached and then maintained, while the bottom of the crucible is held at a lower temperature (figure 2C; temperatures are in the same range as those noted above for the slow-cooling process). With this technique, synthetic alexandrite crystals grow by spontaneous nucleation, usually in contact with the bottom of the crucible (Rodionov and Novgorodtseva, 1988), although seeded growth (with a seed placed at the bottom of the crucible) is also possible (Bukin, 1993).

The solvent used in Russia is a complex bismuth-molybdenum flux, mainly composed of Bi_2O_3 and MoO_3 (A. Ya. Rodionov, pers. comm., 1988; Bukin 1993; confirmed during a visit by one of the authors [A.P.] to Novosibirsk in 1994).

The basic growth technique that was developed in Novosibirsk forms synthetic alexandrite crystals with two different habits—thin and platy or more isometric and equidimensional—depending on controlled change in the growth conditions (Rodionov and Novgorodtseva, 1988). Growth rates of 0.13 to 0.35 mm per day in different crystallographic directions have been obtained. For example, a 14 × 8 × 9 mm crystal was grown by spontaneous nucleation over three months with this technique (Rodionov and Novgorodtseva, 1988). According to Bukin

(1993), crystals as large as 2–3 cm (over one inch) can be grown by spontaneous nucleation in a reverse-temperature gradient, and even larger samples are possible with seeded growth.

MATERIALS AND METHODS

In 1994, one of the authors (A.P.) purchased about 50 synthetic alexandrites that had been flux grown in Russia. These samples were selected in Bangkok from six lots, each of which contained hundreds of synthetic alexandrite crystals and represented thousands of carats of flux-grown material. In addition, R. Goerlitz of Idar-Oberstein, Germany, loaned the authors a lot of about 150 rough crystals that he had purchased in Novosibirsk in 1993. This sample of more than 200 Russian flux-grown synthetic alexandrites used for the present study also included material submitted by Novosibirsk scientists to one of the authors (K.S.) in 1988 and 1991. All of the original samples were rough crystals; the few faceted gems studied (see, e.g., figure 1) were fashioned from rough from the Bangkok and R. Goerlitz lots.

About half of the crystals were fully developed single crystals or cyclic twins with one irregular planar surface (figure 3). Compared to the smooth crystal faces, this irregular surface was somewhat rough and uneven; it probably represents the contact plane of the growing crystal with the bottom of the crucible (see the later discussion of growth conditions). Most of the balance of the samples had one irregular plane or surface that was obviously produced by sawing or breaking, probably to remove some impure, non-gem-quality material or to separate the single crystals or twins from larger clusters. Seven smaller crystals (sizes up to 4 mm) were fully developed without any irregular surface plane.

We performed standard gemological testing on about 40 of these crystals. To identify the internal growth planes and the external crystal faces, we studied about 50 crystals with a Schneider horizontal (immersion) microscope, which had a specially designed sample holder as well as specially designed (to measure angles) eyepieces (Schmetzer, 1986; Kiefert and Schmetzer, 1991; see also Peretti et al., 1995). In addition, we examined about 10 samples with an optical goniometer (an instrument used to measure crystal angles). By a combination of these methods, we identified all crystal faces and the most characteristic growth patterns. We studied and photographed the inclusions and internal structural features using the Schneider immersion microscope (with Zeiss optics) and an Eickhorst vertical microscope (with Nikon optics) and fiber-optic illumination.

Solid inclusions and solid phases on the surfaces of the crystals were characterized by X-ray powder diffraction analysis with a Gandolfi camera, by a Cambridge Instruments scanning electron microscope with an energy-dispersive X-ray detector (SEM-EDS), and by energy-dispersive X-ray fluorescence analysis (EDXRF) using a Tracor Northern Spectrace TN 5000 system.

We also performed qualitative chemical analysis of 22 samples using the same EDXRF instrumentation. For quantitative analysis of nine other samples, a CAMECA Camebax SX 50 electron microprobe was used. To evaluate nonhomogeneous chemical compositions of the alexandrite crystals, we measured 2–5 traverses (of 40 to 140 point analyses each) across the samples. For more detailed information, we also had one scan with 625 point analyses.

Polarized absorption spectra in the visible and ultraviolet range were recorded for nine microscopically untwinned single crystals with a Leitz-Unicam SP 800 double-beam spectrometer and a Zeiss multichannel spectrometer. Infrared spectroscopy was carried out on 11 samples using a Philips PU 9800 FTIR spectrometer.

RESULTS

Visual Appearance. The samples varied from slightly yellowish green to green and bluish green in daylight and from slightly orangy red to red and purplish red in incandescent light (again, see figures 1 and 3). No distinct color zoning was apparent in either the rough or faceted samples.

On the faces of some crystals, we observed a fine-grained white crust. In irregular cavities of other samples, we found a fine-grained gray or yellowish gray material.

Crystallography. All samples examined revealed an equidimensional habit, which was formed by three pinacoids *a*, *b*, and *c*; by four different rhombic prisms, designated *s*, *m*, *x*, and *k*; and by the rhombic dipyramid *o* (table 2). The seven small crystals that lacked rough or uneven faces were fully developed single crystals (see, e.g., figures 4 and 5).

All of the crystals with one uneven face—and those crystals that were sawn or broken—had three dominant faces: the pinacoid *a*, the rhombic prism *x*, and the rhombic dipyramid *o*. Frequently, the rhombic prism *k* was also present, and the pinacoid *c* was subordinate. About 90% of these crystals were cyclic twins (figures 6 and 7), which consisted of three individuals twinned by reflection across the rhombic prism (031) and forming a pseudohexagonal

contact twin (figures 6 and 8). The remaining 10% of the samples were untwinned single crystals.

For those crystals that were not broken or sawn, the most frequently observed habit consisted of the *a*, *x*, *o*, and *k* faces (figures 6C and D). Also common was a habit formed by the three faces *a*, *x*, and *o* (figure 6A). Crystals with an additional *c* pinacoid were somewhat rarer (see table 2 and figures 6B and E).

Most of the cyclic twins were somewhat distorted; that is, identical crystal faces varied in their respective sizes between the three individuals of the cyclic twin. Examples are shown in figures 6C and D, in which varying sizes were drawn for the rhombic prism *x*. Consequently, a typical crystal of Russian flux-grown alexandrite is a combination of the two trillings drawn in figures 6C and D, with sizes of the *x* faces varying within the cyclic twin.

In a few single crystals with one irregular face, the pinacoid *b* and the rhombic prism *m* were also observed (see figure 5). In one of these single crystals, an additional rhombic prism *i* was also present (table 2).

Gemological Properties. Table 3 summarizes the gemological properties of the Russian flux-grown synthetic alexandrites examined. The values are more or less within the ranges published by others for crystals of this material (Trossarelli, 1986; Henn et al., 1988; Rodionov and Novgorodtseva, 1988; Henn, 1992; Bukin, 1993).

Specifically, these Russian synthetic alexandrites are distinctly pleochroic. Their color change is

TABLE 2. Morphological crystallography of Russian flux-grown synthetic alexandrites.

	Designation	hkl ^c	Type	
Faces	<i>a</i>	(100)	pinacoid	
	<i>b^a</i>	(010)	pinacoid	
	<i>c</i>	(001)	pinacoid	
	<i>s^a</i>	(120)	rhombic prism	
	<i>m^a</i>	(110)	rhombic prism	
	<i>x</i>	(101)	rhombic prism	
	<i>k</i>	(021)	rhombic prism	
	<i>j^b</i>	(011)	rhombic prism	
	<i>o</i>	(111)	rhombic dipyramid	
<hr/>				
	Faces	Number of crystals		
Habit	<i>a x o</i>	21		
	<i>a x o c</i>	7		
	<i>a x o k</i>	49		
	<i>a x o c k</i>	10		
<hr/>				
Characteristic angles formed by two faces	<i>ax</i>	141°	<i>xx'</i>	78°
	<i>ao</i>	137°	<i>oo'</i>	86°
	<i>kk'</i>	81.5°	<i>kk'</i>	141.5° (re-entrant)

^a Observed only in single crystals.

^b Observed only in one single crystal.

^c Orientation of the unit cell for the Miller indices: *a* = 4.43, *b* = 9.40, *c* = 5.48.



Figure 4. This 3 × 4 mm untwinned synthetic alexandrite single crystal was grown by spontaneous nucleation without crucible contact. (The darkish patches on some crystal faces are the result of carbon coating for microprobe analysis.) Photomicrograph by John I. Koivula.

caused by a change in two of the pleochroic colors—parallel to the a- and b-axes, with the latter making the greater contribution—when illumination is changed from day or fluorescent to incandescent light. The most intense color change was observed for those synthetic alexandrites that revealed a yellowish orange color in daylight and a reddish orange color in incandescent light parallel to the b-axis; a somewhat weaker color change was observed for samples that revealed a pleochroic color of greenish yellow or yellow in daylight and yellowish orange or orangy yellow color in incandescent light parallel to the b-axis (table 3; see also Schmetzer et al., 1980).

Microscopic Characteristics. Structural Properties (Growth Features and Twinning). As mentioned earlier, most of the sample Russian flux-grown synthetic alexandrites were twinned. When examined

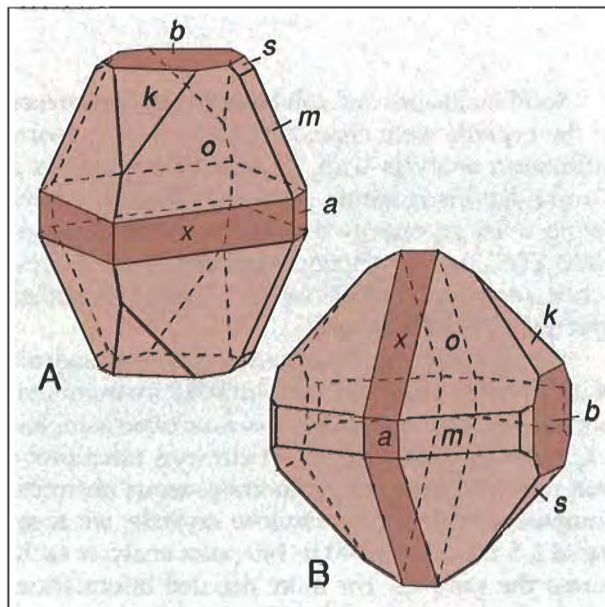


Figure 5. This illustration shows the untwinned synthetic alexandrite in figure 4 in two different orientations (A, B). The second orientation (B) is consistent with the orientation of the cyclic twins in figure 6.

with polarized light, the three individuals of the trilling and their twin boundaries became clearly visible—especially when the polarizer was rotated (figure 8). The angle between twinned individuals is 59.88° (not quite 60°—Goldschmidt and Preiswerk, 1900; Goldschmidt, 1900), which is why the twin boundaries are not exactly planar faces (figure 9). In some samples, the twin boundary between two individuals of the cyclic twin revealed a microstructure of small inclusions of alexandrite crystals oriented parallel to the third individual of the trilling. Most of the twinned samples revealed a 141.5° re-entrant angle formed by two rhombic prism faces *k* and *k'* (figures 6 and 10).

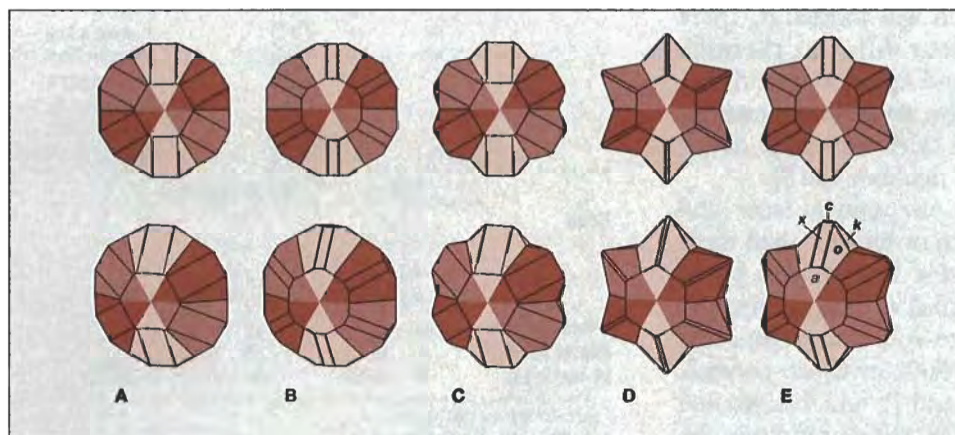


Figure 6. The crystal habits of cyclic-twin flux-grown synthetic alexandrites are shown here in these idealized drawings, as they appear looking down the a-axis (top row) and slightly oblique to the a-axis (bottom row). The habit of the crystals is formed by the pinacoid *a*, the rhombic prisms *x* and *k*, and by the rhombic dipyrmaid *o*; the pinacoid *c* is a subordinate face.

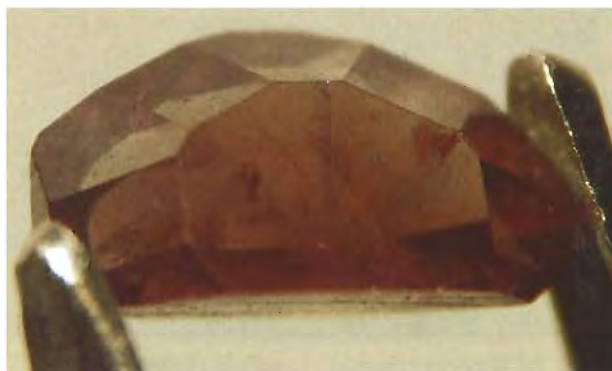
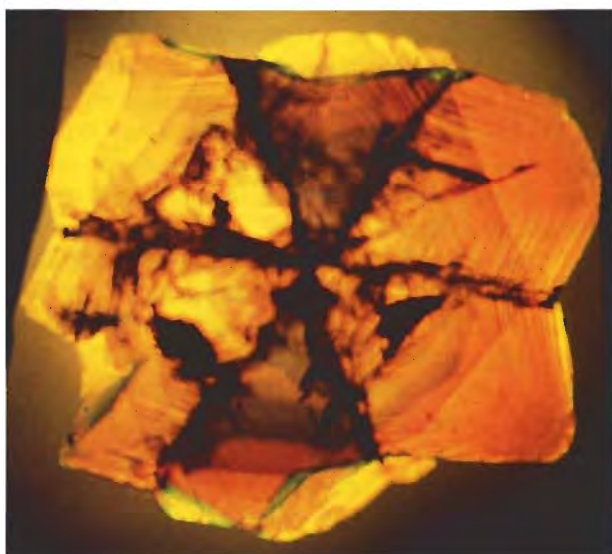


Figure 7. This approximately 3 × 5.5 mm cyclic twin of Russian synthetic alexandrite reveals an irregular contact plane (below) with the crucible; the habit of the crystal is formed by *a*, *x*, and *o* faces (see figure 6A).

The internal growth features of both the rough and faceted Russian synthetic alexandrites corresponded to the external morphology of the crystals. All single crystals or cyclic twins that showed one irregularly oriented uneven plane—that is, all samples that grew in contact with the crucible—revealed distinct internal growth planes parallel to the four dominant faces *a*, *x*, *k*, and *o*.

In a view parallel to the crystals' *a*-axis (i.e., perpendicular to the *a* pinacoid), growth planes parallel to different *k* prism faces were visible in most of the

Figure 8. The three individuals and the twin boundaries of this trilling are clearly visible when this cyclic twin of synthetic alexandrite is viewed parallel to the *a*-axis, using a polarizer and immersion. Magnified 10x.



samples (about two out of three; again, see figures 6 and 10). Two characteristic angles were observed in this orientation: an angle of 81.5° formed by two *k* prism faces of one individual, and a re-entrant angle of 141.5° formed by two *k* faces of two individuals of the twin (see table 2). All of these *kk'* characteristic growth structures also were observed in the faceted synthetic alexandrites (figure 11).

In a view parallel to the *b*-axis (figure 12A), a second characteristic growth pattern *ax* was observed in all samples. This consists of *a* pinacoids and *x* prism faces, which form a 78° angle (figure 13). By rotating the crystal approximately 29° about the *a*-axis (figure 12B), we saw a third characteristic growth pattern *ao*. Visible in all samples, it is formed by *a* pinacoids in combination with *o* dipyrramids (figure 14). In this case, the characteristic angle (formed by the two rhombic dipyrramids *o*) measures 86°. So, three characteristic patterns of growth structures were observed in single crystals and cyclic twins of Russian synthetic alexandrites: *ax* and *ao* in all samples, and *kk'* in approximately two-thirds of the samples.

In about 10% of the single crystals and twins examined, we saw a distinct color zoning—an intense red core (in incandescent light) and a lighter red rim—with the microscope. These areas are separated by a somewhat rounded, very intense red boundary (figure 15). This was the only color zoning seen in any of the samples.

In those small single crystals that were obviously grown without contact with the crucible (again,

TABLE 3. Gemological properties of Russian flux-grown synthetic alexandrites.

Property	Observations	
	Day (fluorescent) light	Incandescent light
Color	Yellowish green or green or bluish green	Orangy red or red or purplish red
Pleochroism		
X parallel to <i>a</i> -axis	Reddish purple	Purplish red
Y parallel to <i>b</i> -axis	Greenish yellow or yellow or yellowish orange	Orangy yellow or yellowish orange or reddish orange
Z parallel to <i>c</i> -axis	Blue-green	Blue-green
Refractive indices		
n_x	1.740–1.746	
n_z	1.748–1.755	
Density (g/cm ³)	3.67–3.74	
UV fluorescence		
Long-wave	Bright red	
Short-wave	Weak red or inert	

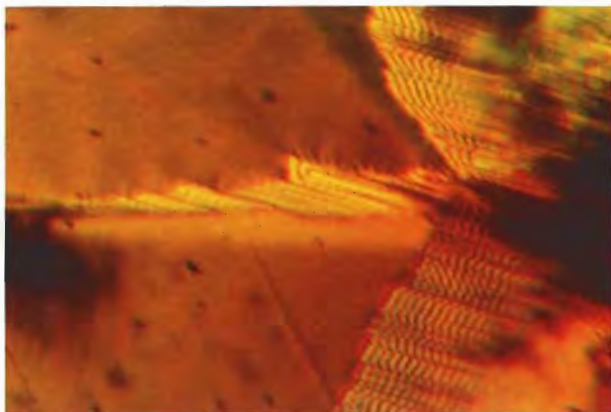


Figure 9. The twin boundaries in this cyclic twin of synthetic alexandrite show a distinct step-like structure. View almost parallel to the *a*-axis; immersion, crossed polarizers, magnified 60 \times .

see figure 4), only very weak growth structures were found parallel to external crystal faces.

Inclusions. Various forms of residual flux were observed in many of the Russian synthetic alexandrites. These include "feathers" or "fingerprints" that consist mainly of isolated droplets or dots, which could be confused with healing features in natural alexandrites. Occasionally, we saw two-phase inclusions of residual flux and spherical bubbles, formed by shrinkage of the trapped flux as it cooled. Feathers of interconnecting tubes or chan-

Figure 11. The view parallel to the *a*-axis reveals characteristic growth structures parallel to the different *k* prism faces of the cyclic twin in this faceted flux-grown synthetic alexandrite. Immersion, magnified 45 \times .

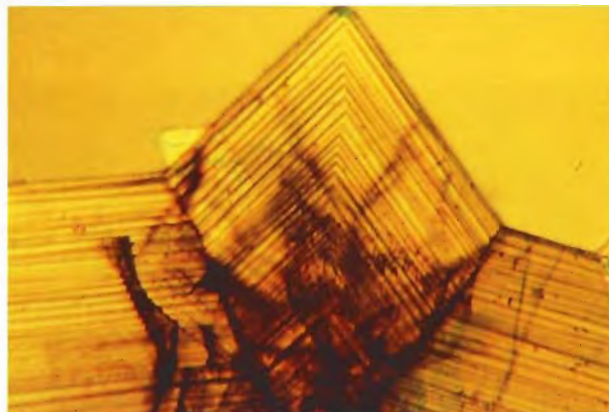
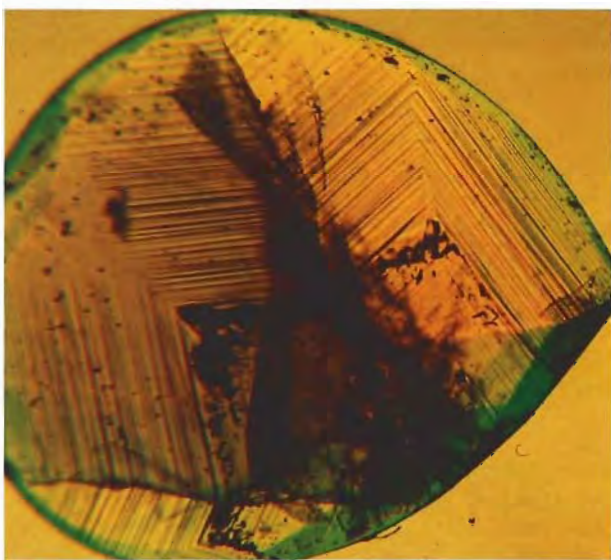


Figure 10. Growth structures parallel to different *k* prism faces form a characteristic angle of 81.5°; re-entrant angles of 141.5° are formed by two different crystals of the cyclic twin. View parallel to the *a*-axis; immersion, magnified 35 \times .

nels (figure 16) also were frequently seen. In some crystals, planar, almost continuous, thin films within a net-like or web-like (i.e., emanating outward from a central point) pattern of flux were observed (figure 17). Occasionally, birefringent refractive components were also found in these flux "nets" (figure 18). In many cases, the flux inclusions took the form of wispy veils (figure 19).

In some of the samples, we observed metallic inclusions (particles or needles). On the basis of EDXRF analyses of similar-appearing solid phases on the surfaces of some of the crystals, we identified these inclusions as platinum.

Chemistry. The EDXRF spectra of the faceted samples and rough crystals with clean faces—that is, without any flux residue on the surface or in open pits or cavities—indicated varying amounts of Cr, V, Fe, Ga, Ge, Bi, and Mo (figure 20), as well as the expected Al. On the basis of these EDXRF results, we added Ge to the list of elements that we measured with the electron microprobe. X-ray fluorescence analysis also confirmed the presence of Sn, traces of which were detected in the course of the microprobe analyses.

Initial scans by electron microprobe revealed zonal variations of all minor-to-trace elements, but zoning of Cr, Fe, and Ge—and sometimes V—was particularly evident. A detailed scan (about 3 mm in length, with 625 point analyses) across one sample (see table 4, sample 7) revealed a distinct zoning and correlation of Cr, Fe, and Ge. In this sample, Ge showed a positive correlation with Fe and a negative correlation with Cr. In other words, when Ge increased, Fe also increased, but Cr decreased as

growth conditions changed. In other samples, however, a negative correlation between Ge and Fe was observed; that is, when Ge increased, Fe decreased. Two synthetic alexandrites had a positive correlation between V and Fe, and one sample showed a positive correlation between Cr and Ge.

Table 4 summarizes the analytical results. In all samples, distinct amounts of Cr and Fe were present as chromophores (see Spectroscopic Features and Discussion sections below); in two alexandrites (samples 2 and 5), minor concentrations of V were also detected. In one single crystal (sample 9), the vanadium content was distinctly higher than the chromium; EDXRF revealed a similar condition of $V > Cr$ in two other small single crystals.

An extreme variation in Cr_2O_3 , FeO , and GeO_2 was observed in two samples (2 and 6). With the microscope, both revealed distinct color zoning: a somewhat irregular, very intensely colored boundary zone between a somewhat lighter core and a somewhat lighter rim (see figure 15). One of these synthetic alexandrites (figure 21) was sawn and polished to match the orientation in figure 12A, so that electron microprobe traverses could be made across

Figure 12. (A) This view parallel to the *b*-axis of a Russian synthetic alexandrite crystal reveals an orientation with a pinacoids and *x* prism faces perpendicular to the projection plane. (B) After a rotation of the crystal through an angle of approximately 29°, the projection plane is perpendicular to a pinacoids and *o* dipyrramids.

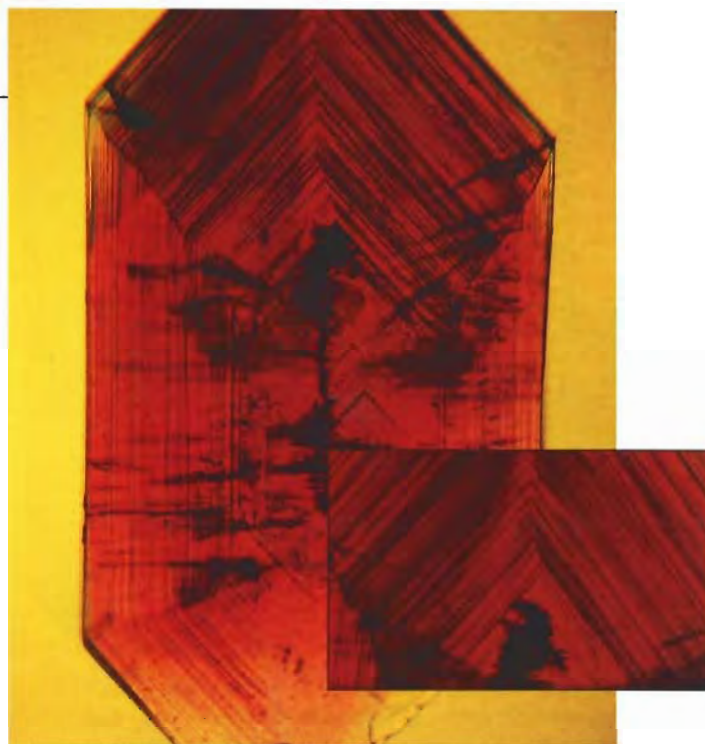
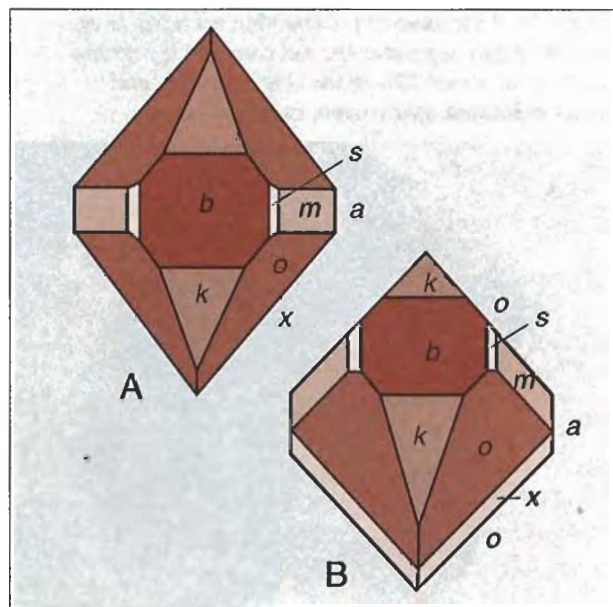


Figure 13. In this crystal, a pinacoids and *x* prism faces (see figure 12A) form a growth pattern characteristic for synthetic alexandrite; the *x* prism faces form a characteristic angle of 78° (see inset). Immersion, magnified 30x and (inset) 50x.

growth zones related to *x* (scan 1) or *a* (scans 2 and 3) faces. The distribution of Cr, Fe, and Ge is shown in figure 22, which represents the analytical data obtained in scan 2. This traverse reveals inner and outer cores, a boundary area, and a rim, similar to the zoning seen with the microscope (figure 21). The inner core had the most GeO_2 as well as distinct amounts of Cr_2O_3 and FeO . In the outer core, GeO_2 content was almost half that of the inner core, and the Cr_2O_3 and FeO contents were somewhat more than that of the inner core (table 5). The rim contained distinctly less Ge and Fe than the core, as well as slightly less Cr. In the boundary zone between core and rim, the Cr content jumped to an extremely high value and then dropped progressively in several steps toward the rim. Scans 1 and 3 (figure 21) revealed similar results (table 5). A scan across a second color-zoned alexandrite (sample 2) showed similar Cr zoning in the boundary area.

All samples had traces of Ga_2O_3 and trace-to-minor amounts of SnO_2 (table 4). MnO and TiO_2 were always close to the detection limit of the microprobe.

Solid Phases on the Surfaces of Rough Crystals. Several types of foreign matter were found on the surfaces of the rough synthetic alexandrites or in cavities, cracks, or pits in the surface.

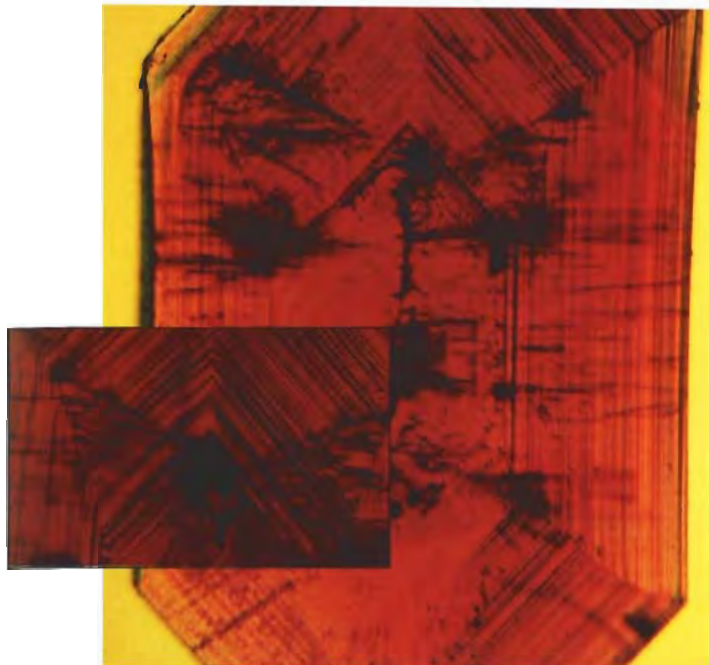


Figure 14. Here, a pinacoids and o dipyramids (see figure 12B) form a growth pattern that is also characteristic for synthetic alexandrite; the o dipyramids form a characteristic angle of 86° (see inset). Immersion, magnified 30x and (inset) 50x.

White polycrystalline crusts were removed from four samples and identified as anatase (TiO_2) by a combination of X-ray powder diffraction analysis, SEM-EDS, and EDXRF. Highly reflective particles on the surface of rough alexandrites (figure 23) were identified by EDXRF as platinum, most probably originating from the crucible. On the surface of a few samples, we also observed a pattern of platinum particles: a tetrahedral particle with a smaller skeleton-like crystal that is trailed by a thin needle. Similar platinum particles occasionally were found as inclusions.

Gray, fine-grained materials in cavities, pits, and cracks were identified in several cases as molybdenum- and bismuth-bearing compounds, that is, as residual flux. In one sample, the X-ray fluorescence spectrum of a crust of this gray, fine-grained material revealed characteristic lines for tungsten as well as for Mo and Bi. The morphology of this particular sample was typical of that described earlier for other samples (see figure 6).

Spectroscopic Features. *Ultraviolet-Visible Spectroscopy.* The polarized absorption spectra for the single crystals of flux-grown synthetic alexandrite were consistent with data reported in the literature for chromium, vanadium, and iron as chromophores in natural and synthetic alexandrites (Farrell and Newnham, 1965; Bukin et al., 1978, 1980; Schmetzer et al., 1980; Powell et al., 1985).

Infrared Spectroscopy. The infrared spectra of the rough and faceted samples showed some characteristic absorption bands in the 2800 to 3300 cm^{-1} range (figure 24). In samples obtained from Novosibirsk (1993), the following absorption maxima were found (in cm^{-1}): 2855, 2921, 2938 (shoulder), 3205 and 3224; samples originating from Bangkok (1994) revealed maxima at 2855, 2921, 2938 (shoulder), 3095, and 3196 cm^{-1} . Because water and/or hydroxyl absorption bands—especially in the 2500 to 3000 cm^{-1} range—are absent from the spectra of synthetic alexandrites, infrared spectroscopy is a powerful tool for separating natural and synthetic alexandrites (Leung et al., 1983, 1986; Stockton and Kane, 1988).

DISCUSSION

Growth Conditions of Russian Flux-Grown Synthetic Alexandrites.

The experimental results of our study are consistent with the descriptions published by Rodionov and Novgorodtseva (1988) and Bukin (1993) of growth techniques for Russian flux-grown synthetic alexandrites. The uniform morphology and chemical properties of our samples indicate that these synthetic alexandrites were grown from a solvent consisting of molybdenum-, bismuth-, and germanium-bearing compounds, most probably oxides. The nutrient contained the main components of chrysoberyl (Al_2O_3 , BeO), as well as color-causing dopants (chromium, vanadium [sometimes], and iron oxides). Cr, V, and Fe are known chro-

Figure 15. An intense red, somewhat rounded, irregular boundary separates the red core and lighter red rim seen in about 10% of the single crystals and twins examined. Immersion, magnified 20x.

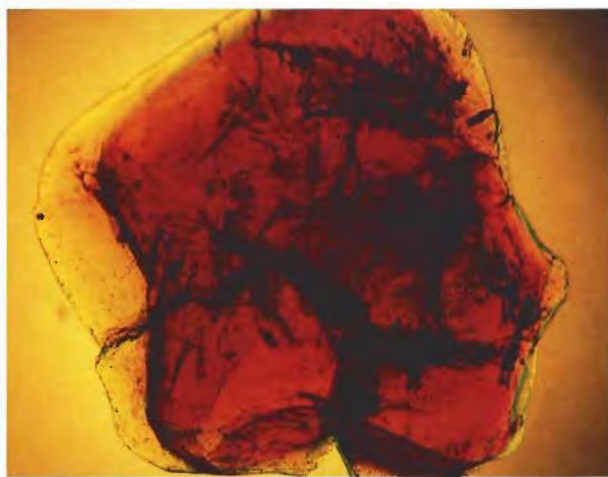




Figure 16. Interconnecting tubes of residual flux form characteristic "feathers" in this Russian flux-grown synthetic alexandrite. Immersion, magnified 40 \times .

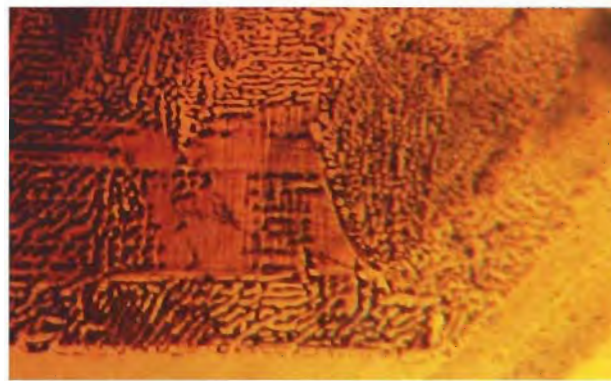


Figure 17. Some of the synthetic alexandrites revealed planar thin films in a net-like pattern of flux. Immersion, magnified 50 \times .

mophores of both natural and synthetic alexandrites (Farrell and Newnham, 1965; Bukin et al., 1980; see also table 1). A varying intensity of color change in different samples is caused by the absolute chromium and iron contents of the samples and by the chromium distribution between two different Al-sites of the chrysoberyl lattice (Solntsev et al., 1977; Bukin et al., 1980; Schmetzer et al., 1980).

We already knew that Mo and Bi were components of the fluxes used in Russia to grow synthetic alexandrite (A. Ya. Rodionov, pers. comm., 1988; Bukin, 1993). However, our chemical data do not agree with those given by Henn et al. (1988) and Henn (1992), who reported the presence of sulfur. It is possible that they mistook the characteristic L_{α} line of Mo (at 2.31 KeV) for the K_{α} line of sulfur (at 2.29 KeV).

Ge has not been mentioned before as a trace element in Russian flux-grown synthetic alexandrites. The only reference we found to Ge in synthetic alexandrite refers to patent applications by Isogami and Nakata (published in 1985 and 1986), who

described a dopant of GeO_2 used to grow synthetic chrysoberyl and alexandrite cat's-eyes. Because Ge is normally found in tetrahedral coordination in oxide structures, the zoning of Ge identified by electron microprobe suggests an isomorphic substitution of beryllium by germanium in the lattice of our samples. This disproves our preliminary assumption that the Ge came from compounds in cavities or fissures ("feathers," "fingerprints") within the synthetic alexandrites. It is most likely that the incorporation of Ge into the chrysoberyl lattice is very sensitive to small temperature changes and/or to small variations in the composition of the flux, as is indicated by the extreme variation in Ge in the microprobe scans (see table 5 and figure 22). Because Ge was positively correlated to Fe in some of the samples, but others revealed a negative correlation between iron and germanium, we could not prove a coupled substitution of beryllium and aluminum by

Figure 18. Birefringence can be seen in some of the components of this net-like pattern of residual flux. Immersion, crossed polarizers, magnified 80 \times .

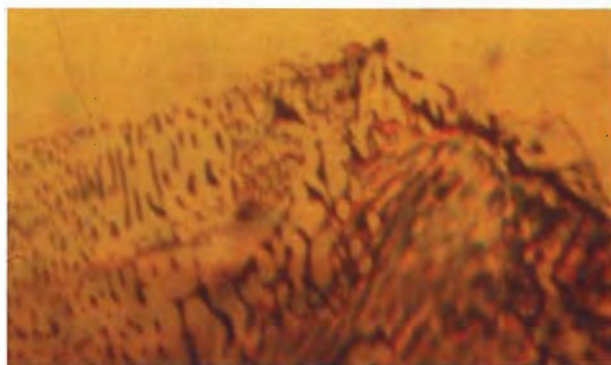
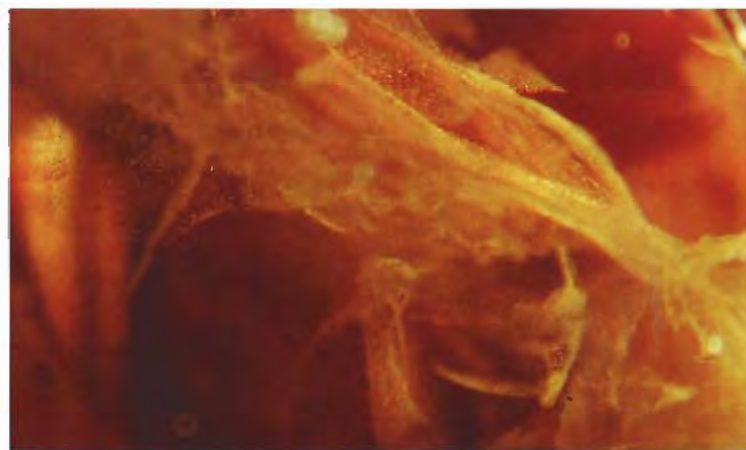


Figure 19. Residual flux takes the form of wispy veils in this Russian synthetic alexandrite. Fiber-optic illumination, magnified 70 \times .



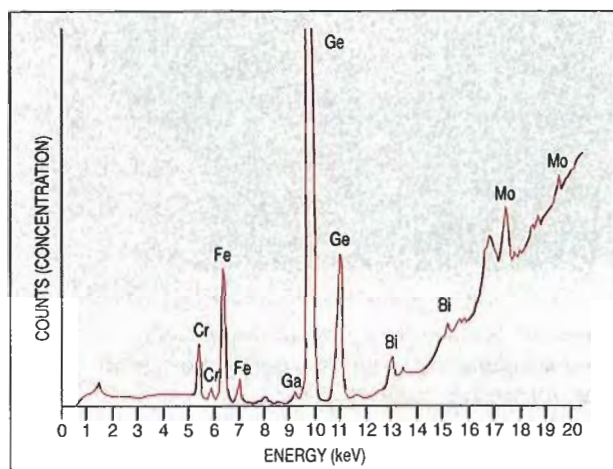


Figure 20. This EDXRF spectrum of a rough synthetic alexandrite was taken from an optically clean crystal face. The spectrum reveals distinct amounts of the chromophores (Cr, Fe), traces of Ga, distinct Ge concentrations, and residues of the flux (Bi, Mo).

germanium and iron (for charge compensation) in all samples. Thus, we do not presently know exactly how Ge is incorporated into the chrysoberyl lattice, but it is probably due to special growth conditions. It is very likely that one of the special growth condi-

tions—mentioned by Rodionov and Novgorodtseva (1988) for the production of more-or-less equidimensional crystals (not thin platelets)—accounts for the presence of a germanium-bearing compound in the solvent, which was found in all samples obtained since 1988 (see table 4).

Our results also indicate that at least some Russian synthetic alexandrites were grown experimentally in a Mo-Bi-W-bearing flux. The use of a tungsten-bearing compound in the solvent was mentioned by Cline and Patterson (1975). Solid phases on the surfaces of the crystals we examined are representative of the major components of the flux (Mo and Bi, sometimes W) and the crucible material (Pt). At this time, however, no explanation is available for the presence of white crusts of anatase on some samples (G. Bukin, pers. comm., 1995), and our chemical analyses of the samples (table 4) do not indicate the presence of titanium in the solvent during growth.

Ga is known as a trace element in natural alexandrites (Ottemann, 1965; Ottemann et al., 1978), but small amounts of Ga recently have been observed in Czochralski- and flux-grown synthetic alexandrite (Schrader and Henn, 1986; Henn et al., 1988; Henn 1992). To the authors' knowledge, Sn

TABLE 4. Electron microprobe analyses of nine Russian flux-grown synthetic alexandrites.

Variable	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6 ^a	Sample 7	Sample 8	Sample 9
Origin	Novosibirsk 1988	Novosibirsk 1991	Novosibirsk 1993	Novosibirsk 1993	Novosibirsk 1993	Novosibirsk 1993	Bangkok 1994	Bangkok 1994	Bangkok 1994
Description	Cyclic twin	Cyclic twin	Cyclic twin	Cyclic twin	Single crystal	Cyclic twin	Cyclic twin	Cyclic twin	Single crystal
Growth zoning	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Color zoning	No	Yes	No	No	No	Yes	No	No	No
Number of scans	4	2	1	1	1	5	1 ^b	1	1
Number of analyses	160	85	66	50	71	560	100 ^b	85	60
Approx. length of scans	3 mm	2 mm	10 mm	3.5 mm	6.5 mm	4–10 mm	2.5 mm	3.5 mm	3 mm
Analyses in wt. % (range)									
Ga ₂ O ₃	0.01–0.07	0.01–0.05	0.01–0.06	0.02–0.07	0.01–0.07	0.01–0.06	0.00–0.13	0.01–0.11	0.01–0.06
Al ₂ O ₃	78.20–79.87	74.03–78.31	76.80–78.08	77.21–79.55	77.59–79.47	74.86–78.65	77.92–79.83	78.05–80.17	76.92–78.52
V ₂ O ₃	0.00–0.03	0.00–0.29	0.01–0.03	0.00–0.03	0.01–0.19	0.00–0.03	0.00–0.03	0.00–0.03	0.70–1.01
GeO ₂	0.00–0.06	0.13–0.50	1.48–3.33	0.30–1.93	0.27–0.85	0.10–1.57	0.27–1.89	0.59–1.16	0.00–0.04
Cr ₂ O ₃	0.17–0.32	0.28–4.64	0.29–0.36	0.33–0.74	0.21–0.27	0.44–4.55	0.28–0.96	0.34–0.43	0.43–0.49
MnO	0.00–0.02	0.00–0.01	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.03
FeO	0.43–0.62	0.33–1.37	0.50–0.56	0.43–0.56	0.73–0.91	0.33–1.42	0.22–0.46	0.51–0.60	1.27–1.42
TiO ₂	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.02	0.00–0.03	0.00–0.02	0.00–0.02	0.00–0.03	0.02–0.04
SnO ₂	0.00–0.04	0.00–0.04	0.32–0.45	0.10–0.36	0.00–0.05	0.00–0.06	0.01–0.15	0.19–0.29	0.03–0.08
Color	Cr, Fe	Cr > V, Fe	Cr, Fe	Cr, Fe	Cr > V, Fe	Cr, Fe	Cr, Fe	Cr, Fe	V > Cr, Fe

^a See also table 5.

^b For this particular sample, an additional detailed scan for GeO₂, Cr₂O₃, and FeO with 625 point analyses was performed.

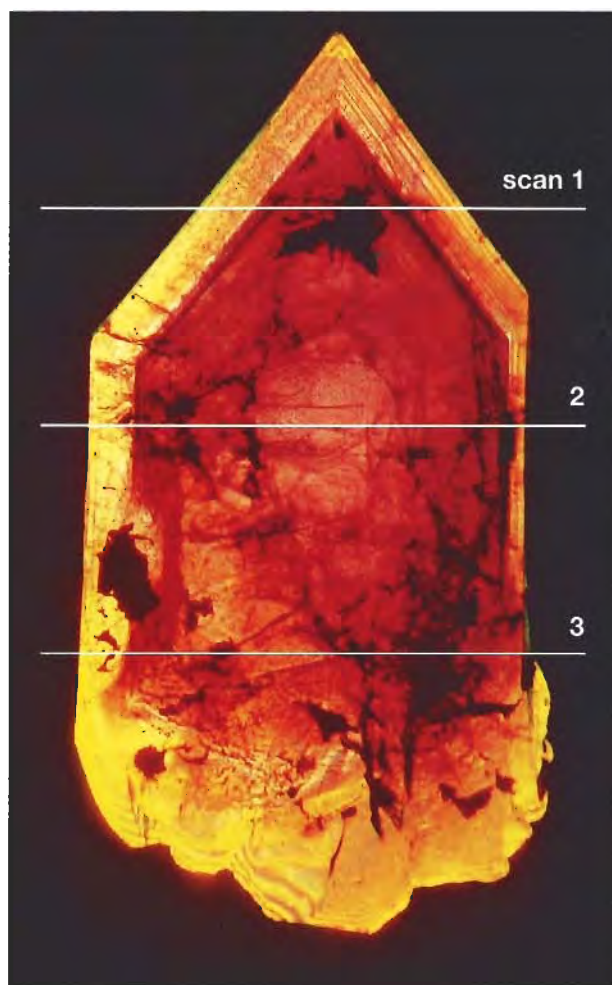


Figure 21. Visible in this color-zoned alexandrite are inner and outer red cores; a narrow, very intense, red boundary; and a light red rim (the yellow in this photo is a function of the immersion liquid and the illuminant). The three electron microprobe traverses across this section covered growth zones confined to x (scan 1) and a (scans 2 and 3) faces. View parallel to the b-axis, immersion, crossed polarizers, magnified 15 \times .

previously was known as a trace element only in natural alexandrites (Ottemann, 1965; Ottemann et al., 1978; Kuhlmann, 1983). Its presence in some of our samples makes it less useful than before as an indicator of natural origin.

The traces of gallium and tin came from impure chemicals used in the nutrient, and were not intentionally added to the solvent system, according to Dr. G. V. Bukin (pers. comm., 1995).

Most of the alexandrites were grown in a negative temperature gradient in contact with the bottom of a platinum crucible, as described for beryllium-bearing oxides and silicates by Bukin (1993; figure 2C). The exception, the seven small single crys-

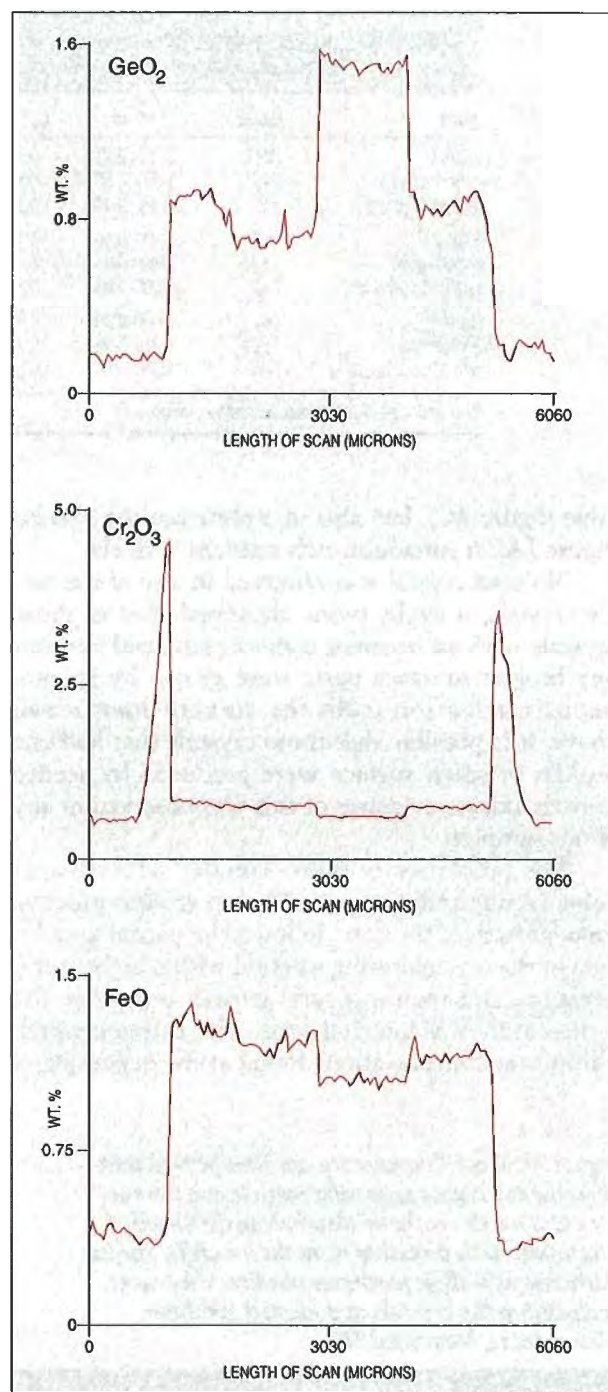


Figure 22. An electron microprobe traverse across the synthetic alexandrite shown in figure 21 (scan 2) revealed distinct zoning of the major trace elements—Ge, Cr, and Fe. The inner and outer cores, a narrow boundary, and a rim are recognizable in these plots (no. of analyses: 120; approx. length of scan: 6 mm).

tals that did not show an irregular surface plane, were grown by spontaneous nucleation without contact to the crucible. This is possible in a temperature-gradient system in the lower part of the cru-

TABLE 5. Electron microprobe analyses (in weight percent) of a Russian flux-grown alexandrite with pronounced color zoning^a.

Scans	Oxide	Left rim	Left boundary	Core	Right boundary	Right rim
Scan 1: growth zone related to prism x	GeO ₂	0.12–0.21	0.15–0.30	0.70–1.12	0.13–0.19	0.11–0.19
	Cr ₂ O ₃	0.50–0.58	0.59–4.20	0.63–0.86	0.62–2.93	0.47–0.59
	FeO	0.38–0.46	0.34–0.43	1.08–1.23	0.34–0.37	0.34–0.42
Scan 2: growth zone related to pinacoid a	GeO ₂	0.12–0.18	0.14–0.21	0.66–1.57	0.15–0.31	0.15–0.24
	Cr ₂ O ₃	0.46–0.61	0.69–4.55	0.57–0.84	0.66–3.58	0.48–0.54
	FeO	0.37–0.45	0.35–0.45	1.03–1.38	0.33–0.57	0.38–0.42
Scan 3: growth zone related to pinacoid a	GeO ₂	0.18–0.24	0.14–0.25	0.42–1.46	0.12–0.23	0.10–0.13
	Cr ₂ O ₃	0.48–0.58	0.71–2.98	0.62–0.82	0.81–3.91	0.44–0.50
	FeO	0.37–0.41	0.34–0.40	1.07–1.42	0.34–0.38	0.37–0.38

^a For other data on this sample, see table 4, sample 6.

cible (figure 2C), but also in a slow-cooling system (figure 2A). A vanadium-rich nutrient is likely.

No seed crystal was observed in any of the single crystals or cyclic twins examined; that is, those crystals with an irregular contact plane and without any broken or sawn parts were grown by spontaneous nucleation from the solvent mentioned above. It is possible that those crystals that had one broken or sawn surface were produced by seeded growth, but no evidence of this was observed in any of our samples.

The properties of those samples with distinct color zoning indicate a multi-step growth process: First, growth of the core, followed by partial dissolution of the crystal during a period with a higher temperature; and then a second growth period, as the temperature was lowered again. The extremely high chromium concentrations found at the beginning of

Figure 23. X-ray fluorescence analysis proved that these white, highly reflecting particles on the surface of a rough synthetic alexandrite consisted of platinum, most probably from the crucible. Similar particles, as well as platinum needles, were seen included in the crystals and faceted synthetic alexandrites. Magnified 50 \times .

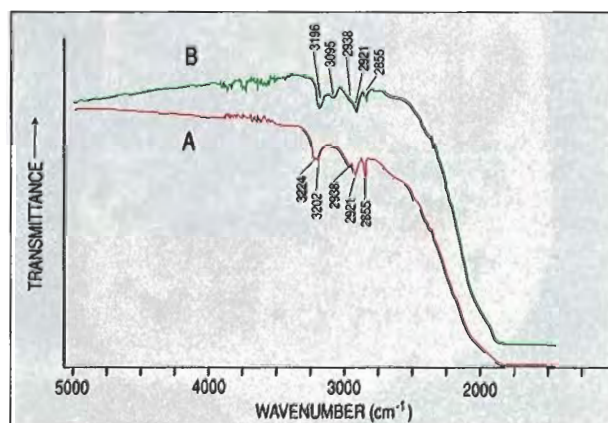
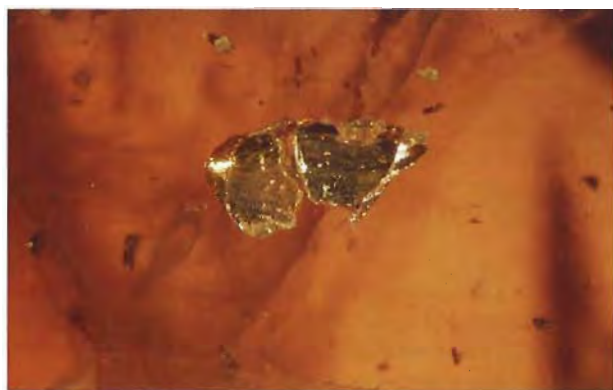


Figure 24. The infrared spectra of Russian flux-grown synthetic alexandrites show characteristic absorption bands in the 2800 to 3300 cm⁻¹ range. Sample A was obtained from Novosibirsk in 1993; sample B was acquired in Bangkok in 1994.

the second growth phase in these samples indicate an increase in the Cr concentration of the flux during the dissolution period.

All samples with this distinct chromium zoning revealed an intense color and a good to very good color change, which is explained by the thin intermediate layer of alexandrite with an extremely high chromium content (which could remain, at least partly, after fashioning).

Diagnostic Properties. Faceted Russian flux-grown synthetic alexandrites may show a number of features that distinguish them from natural alexandrites.

Careful microscopic examination can detect characteristic forms of residual flux and platinum particles (see also Trossarelli, 1986; Henn et al., 1988; Henn, 1992; Hodgkinson, 1995). Although some patterns of residual flux resemble the healing

fractures seen in natural alexandrites (see, e.g., Bank et al., 1987; Henn, 1987; Bank et al., 1988), to date patterns with birefringent components and/or thin films of flux with a net- or web-like structure have been seen only in synthetic alexandrites.

Characteristic growth patterns—which are formed by four dominant crystal faces a , x , k , and o in the Russian synthetic alexandrites—can be observed with immersion microscopy. However, characteristic twin structures and growth patterns in natural gem-quality alexandrites from major localities have not yet been published. Consequently, we do not know how useful these features will be in an identification. Preliminary results indicate that the rhombic prism k (021), which is seen in most Russian flux-grown synthetic alexandrites, is extremely rare in natural samples (see, e.g., Goldschmidt, 1913). Characteristic color zoning—an intensely colored, somewhat rounded boundary between a lighter center and rim—is also diagnostic for some of the Russian samples.

Traces of germanium, molybdenum and/or bismuth, and sometimes tungsten, provide proof of synthesis. All can be readily determined by X-ray fluorescence analysis. Traces of gallium and tin can be found in natural alexandrites and in synthetic Russian samples, as can the chromophores chromium, iron, and sometimes vanadium. Therefore, these trace elements are of no diagnostic value.

Infrared spectroscopy of Russian synthetic flux-grown alexandrites shows some absorption bands in the 2800 to 3300 cm^{-1} range that are characteristic of this material. Like other synthetic alexandrites, this material lacks the water-related absorption bands that are typical of natural alexandrites.

Gemological properties—such as refractive indices, density, pleochroism, and UV-visible

absorption spectra—are of no help in separating Russian flux-grown synthetic alexandrites from their natural counterparts.

CONCLUSIONS

The chemical, physical, and microscopic properties of the more than 200 Russian flux-grown synthetic alexandrites we tested are consistent with known details of the production techniques developed in Russia for this material. Platinum crucibles—with a flux containing molybdenum-, bismuth-, and germanium-bearing components—are placed in a reverse temperature gradient, in which the growth zone is located below the dissolution zone. Almost equidimensional alexandrite crystals grow in this system by spontaneous nucleation in contact with the bottom of the crucible. The nutrients—which consist of Al_2O_3 , BeO , and the chromophores (chromium, iron, and sometimes vanadium oxides)—are placed in the upper parts of the crucibles. The morphology of the crystals, and their chemical and physical properties, are related to the exact compositions of the fluxes and the nutrients, as well as to the temperatures in the upper and lower parts of the crucibles. The manufacturers will not reveal the specific growth conditions, and the details of these conditions cannot be deduced from study of the synthetic alexandrites that result.

A careful microscopic examination of inclusions and structural characteristics (growth patterns and twinning) may be helpful—but is often not conclusive—in separating natural from synthetic alexandrite. However, modern gemological laboratories, especially those with X-ray fluorescence and infrared spectroscopy, should have no problem identifying the synthetic Russian alexandrite material currently available in the trade.

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