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# FLUX-GROWN SYNTHETIC RED AND BLUE SPINELS FROM RUSSIA

By Sam Muhlmeister, John I. Koivula, Robert C. Kammerling, Christopher P. Smith, Emmanuel Fritsch, and James E. Shigley

*Examination of red and blue samples of a relatively new flux synthetic spinel from Russia established criteria by which they can be separated from their natural counterparts. The flux synthetic blue spinels can be recognized on the basis of their inclusions, ultraviolet luminescence, and visible absorption spectrum. Magnification is sufficient to identify the flux synthetic red spinels when flux or metallic inclusions are present; in the absence of such inclusions, however, chemical analysis is required. Red and blue natural spinels both contain significantly more zinc than their flux synthetic counterparts. Also, trace amounts of Pb (from the flux) and Pt and Ir (from the crucible) were found in some of the flux synthetic spinels.*

A

new type of synthetic spinel, grown by the flux method, was first encountered as red crystals by gemologists in the late 1980s. Now commercially available, this material can be difficult to identify by standard gem-testing methods. Preliminary studies indicate that most of the gemological properties of these red synthetic spinels (excluding the presence of possible flux or metallic inclusions) overlap those of natural gem spinels of similar color (see Bank and Henn, 1990; Brown et al., 1990; Koivula et al., 1991; Henn and Bank, 1992). This situation contrasts greatly with that of flame-fusion synthetic spinels—the only type of synthetic spinel previously available commercially—which are easily identifiable even when faceted, on the basis of their distinctive refractive index and specific gravity.

These new Russian flux synthetic spinels are also available in blue and have been grown in other colors that, in some cases, do not correspond to natural spinels. This article reports on identification criteria by which these new, commercially available red and blue Russian flux synthetic spinels (figures 1 and 2) can be separated from their natural counterparts. Other colors are briefly discussed in box A.

## BACKGROUND

Synthetic spinel was first produced in the mid-1800s—not by flame fusion as is usually thought, but by flux growth (Nassau, 1980). These first, small flux synthetic spinel crystals were accidentally grown during an attempted synthesis of corundum. Although they were commercially insignificant at the time, the basic method for growing flux synthetic spinels has been known for almost a century (Wood and White, 1968; Wang and MacFarlane, 1968).

Flame-fusion (“Verneuil”) synthetic spinels have been marketed as faceted stones since the 1920s (Nassau, 1980; Webster, 1983), primarily in light blue colors as an aquamarine substitute. They can be easily separated from natu-

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Figure 1. These faceted Russian flux-grown synthetic red spinels (the largest is 2.27 ct) are representative of those examined during this study. Photo © Tino Hammid and GIA.

ral blue spinel with magnification. It is reportedly far more difficult to grow synthetic red spinel by this method (see Schiffmann, 1972; Brown et al., 1991), because it requires the incorporation of up to five times the amount of alumina normally contained in the spinel crystal structure (Nassau, 1980). As a result of this dramatic difference in composition, most flame-fusion synthetic red spinels have some very distinctive gemological properties, such as a higher index of refraction, as well as a pattern of anomalous birefringence, or internal strain, seen with polarized light (the so-called "cross-hatch effect" or "tabby extinction"—see Webster, 1983; Hurlbut and Kammerling, 1991). Consequently, the separation of natural red

and blue spinels from most flame-fusion synthetic spinels is usually very straightforward.

In contrast, flux growth produces synthetic spinels with the same (one-to-one)  $MgO:Al_2O_3$  ratio as natural spinel (see, e.g., Nassau, 1980); as such, their gemological properties are expected to be very similar. During the past decade, the flux method has been improved by researchers in Russia, with the result that flux synthetic spinels in red and blue are now commercially available in crystals suitable for faceting. GIA researchers first encountered this material in the trade in 1989, when a 17.19-ct red crystal was purchased by one of us (JIK) for gemological investigation (see Koivula and Kammerling, 1989, 1990a; Koivula et al., 1991). Other red crystals as large as 17.96 ct (fashioned to an 8.58-ct cushion antique step cut; J. Fuhrbach, pers. comm., 1990), as well as faceted blue flux-grown synthetic spinels as large as 5.40 ct (Henn and Bank, 1991), have also been reported.

Pinky Trading Co. of Bangkok signed a joint-venture agreement with the Academy of Sciences of the USSR (now the Academy of Sciences of Russia) in the fall of 1989 to market flux-grown synthetic red and blue spinel. They reported to us that as of early July 1993 the following quantities had been marketed: approximately 5,000 ct of rough and 2,700 ct of faceted "red" (actually, light pink to dark red) flux-grown synthetic spinel, and about 1,000 ct of rough and 540 ct of faceted blue material. The faceted stones have included both calibrated and noncalibrated goods, the most popular being ovals and cushion shapes. In red, the most popular sizes have been in the 2–5 ct range, while the greatest demand for blues has been in the 0.5–2 ct range. Pinky Trading also reported that they had no immediate plans to market any additional colors of this material.

The presence of these flux synthetic spinels in the gem market has prompted concern regarding their identification, as evidenced by several brief articles and laboratory alerts issued by the International Colored Gemstone Association (ICA—Bank and Henn, 1989; Koivula et al., 1990a; Henn and Bank, 1991, 1992), and thus the present study.

Note that the blue flux synthetic spinels resemble in color the "cobalt blue" natural spinels found in Sri Lanka. Shigley and Stockton (1984) described but did not clearly define this rare natural gemstone. To provide better identification criteria, we distinguish "cobalt blue" natural spinels

*Figure 2. All of these faceted Russian flux-grown synthetic blue spinels (the largest is 1.73 ct) were examined during this study. Photo © Tino Hammid and GIA*



from the more common grayish blue natural spinels on the basis of the former's saturated color, red luminescence to both visible light and long-wave U.V. radiation, and visible absorption spectrum (which always contains a combination of features due to both Co and Fe, with increasing absorption below about 430 nm and broad absorption bands at about 458, 480, 550, 560–600, and 620–650 nm). In contrast, the more common "blue" natural spinels (i.e., those with a desaturated grayish blue color that is caused by iron) do not luminesce red and have a different visible absorption spectrum (with increasing absorption below about 430 nm, and broad absorption bands at about 458, 480, 555, 590, 635, and 670 nm). There exists

a continuous series from iron- to cobalt-containing natural blue spinels (Schmetzer et al., 1989).

#### **MATERIALS AND METHODS**

The study sample included four red and 16 blue flux-grown synthetic spinel crystals. All of the crystals we examined were euhedral, with relatively flat, smooth faces and sharp edges. At the base of each crystal was an irregular surface in a location normally occupied by a termination of the octahedron (see figure 3). This surface appears to be the point either of attachment or growth nucleation of the crystal; on some specimens, a small secondary crystal that undoubtedly developed during growth of the larger crystal could be seen (figure 4). The

## BOX A: FLUX SYNTHETIC SPINELS OF OTHER COLORS

Besides the red and blue samples described in this article, Russian laboratories have grown other colors of flux synthetic spinel, apparently on an experimental basis (W. Barshai, pers. comm., 1991). We studied three brownish yellow octahedra or octahedral fragments ranging from 0.29 to 3.76 ct, one 3.34-ct greenish blue crystal, one 0.80-ct purple elongated octahedron, and one 1.43-ct pale pink crystal (figure A-1). Their indices of refraction and specific-gravity values were within the ranges measured for red and blue natural and flux synthetic spinels, as described in the article text (except for the pink crystal, which had a low S.G., 3.55). These other colors all showed slight anomalous birefringence ("strain"); three exhibited "snake-like bands" under crossed polarizers. All but the inclusion-free purple and pale pink stones displayed typical orange-brown flux inclusions.

The three brownish yellow spinels fluoresced a weak to moderate chalky yellowish green to long-wave U.V. radiation, and had either a weaker reaction or were inert to short-wave U.V. The larger crystal exhibited a moderate green transmission luminescence when excited by visible light. All three crystals showed weak absorption bands at approximately 430 and 460 nm (in the handheld spectroscope). These absorptions were confirmed by absorption spectrophotometry: The color is predominantly related to a regularly increasing absorption toward the ultraviolet, but the precise cause is unknown. Superimposed on this major feature was a sharp absorption band at approximately 427 nm and two broader bands with apparent maxima at about 458 and 490 nm. EDXRF analysis proved that these crystals contain some Mn. The absorption spectra and luminescence are typical of  $Mn^{2+}$  in tetrahedral coordination, as is found in Mn-doped flame-fusion synthetic spinel (Schmetzer et al., 1989), although the absorption bands are slightly shifted in the flux synthetic material.

The greenish blue flux synthetic spinel crystal was inert to ultraviolet radiation, but showed two bands in the handheld spectroscope, at approximately 590 and 635 nm. EDXRF analysis demonstrated the presence of Ni, Fe, and traces of Mn and V. Visible absorption spectroscopy revealed increasing absorption toward the ultraviolet with a weak, broad band at 470 nm, a broad band with two apparent maxima at 593 and 635 nm, and another one with a maximum at about 875 nm. These features are similar to those recorded by Wyon et al. (1986) on Czochralski-pulled synthetic spinel doped with Ni, and are typical of  $Ni^{2+}$  in octahedral coordination. Therefore, the greenish blue color of this spinel is essentially due to  $Ni^{2+}$ .

The purple crystal emitted a weak red when



*Figure A-1. Russian laboratories have produced flux-grown synthetic spinels in a variety of colors other than red and blue. These samples, reportedly grown on an experimental basis, range from 0.80 to 3.76 ct. Photo by Maha DeMaggio.*

exposed to long-wave U.V. radiation, with a faint red fluorescence to short-wave U.V. It also exhibited a strong red luminescence when excited by visible light, and appeared dark red through the Chelsea color filter. When we examined it with the handheld spectroscope, we noted absorption bands at approximately 590 and 635 nm, as in the greenish blue spinel described above. There were also broad absorptions from about 530 to 590 nm and 660 to 690 nm, and a sharp line at approximately 690 nm. EDXRF analysis revealed the presence of Ni, Fe, and Cr, as well as traces of V, Zn, and Ga. The color is due to the combination of  $Cr^{3+}$  and  $Ni^{2+}$  absorptions.

The pale pink crystal fluoresced a weak to moderate, slightly chalky orange to long-wave U.V. radiation, with a yellower reaction of the same intensity to short-wave U.V. It showed no lines in the handheld spectroscope, but an absorption spectrum obtained with a spectrophotometer showed one very weak broad band centered at about 560 nm, very similar to that seen for Cr in the red flux synthetic spinels, but considerably weaker in intensity. EDXRF analysis revealed V, Mn, Fe, Ni, Zn, Ga, and possibly Cu as impurities.

Because of their unusual coloring agents, such as Ni and Mn, these other colors of Russian flux synthetic spinels do not duplicate spinels found in nature. In particular, even these experimental crystals do not reproduce the blue component that iron causes in the color of many natural spinels. It would appear that doping synthetic spinels with unusual impurities may produce crystals with attractive colors, but generally these colors would not correspond to those of natural spinels.

red crystals ranged from 6.19 to 45.14 ct, with the largest one (to our knowledge, the largest crystal of its kind reported so far) measuring 23.76 × 20.86 × 12.88 mm. The blue crystals ranged from 1.06 to 14.30 ct, with the largest one measuring 13.10 × 12.81 × 11.83 mm.

We also examined nine red and 12 blue faceted Russian flux synthetic spinels (see, e.g., figures 1 and 2), which ranged from 0.19 to 8.58 ct. Included as well were two (one rough and one faceted) blue flux synthetic spinels from Russia, loaned by Dr. Henry Hänni, that were known to have a higher iron content than our samples.

In addition to the Russian flux-grown synthetic samples, we examined the following gemologically and/or chemically for comparison: (1) 28 red-to-pink or purple and eight blue natural spinels (including four "cobalt blue" samples from Sri Lanka and four grayish blue spinels—one from Sri Lanka and three of uncertain origin); (2) one flux synthetic blue spinel, two flux synthetic red spinels, and five flux synthetic blue and red-to-pink gahnites ( $\text{ZnAl}_2\text{O}_4$ ) grown on an experimental basis at Bell Laboratories in New Jersey; and (3) one red and three blue flame-fusion synthetic spinels. The natural red-to-pink or purple spinels reportedly came from the following localities: Africa—2, Myanmar (Burma)—16, Sri Lanka—3, Tajikistan (Pamir Mountains)—2, Tanzania—3, and Thailand—2. The range of color was chosen to determine if any identification criteria established would be valid for other colors of spinel with a distinct red component. The natural and synthetic blue spinels include some of those examined by Shigley and Stockton in 1984.

The gemological properties of all the Russian flux-grown synthetic spinels were determined using the following instruments and methods. Refractive-index readings were taken with a Duplex II refractometer and a near-monochromatic, sodium-equivalent light source. The specific gravity was determined hydrostatically (average of three separate measurements). We also used pure methylene iodide, with a room-temperature specific gravity of 3.32, to estimate specific gravity and determine the usefulness of standard sink-float testing. Ultraviolet luminescence was examined under darkroom conditions, using both long-wave and short-wave ultraviolet radiation, with the sample placed against a nonfluorescent black background. Contrast control goggles were worn during the testing procedure to help eliminate secondary reflections.

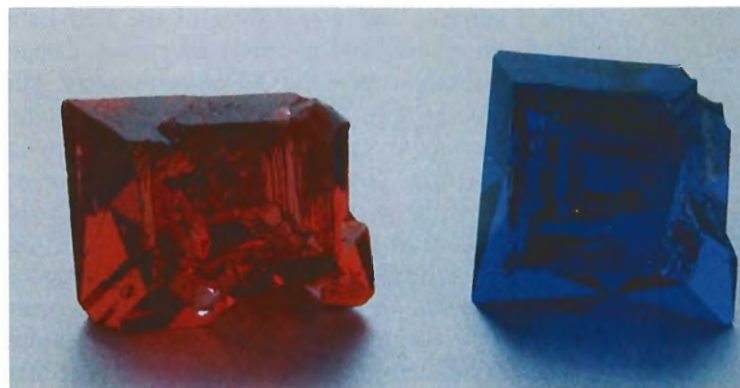


Figure 3. The irregular surface at the base of each Russian flux synthetic spinel crystal (red = 17.19 ct; blue = 14.30 ct) appears to be the point of attachment or growth nucleation. Photo by Maha DeMaggio.

A Beck prism spectroscope and a GIA GEM "DISCAN" digital-scanning diffraction-grating spectroscope were used to observe the visible absorption spectra. The synthetic spinels were also examined spectroscopically with light passed through a flask of copper sulfate solution so that any emission (fluorescence) lines might be seen.

Two methods were used to test the samples for luminescence to visible light, a property referred to in gemology as "transmission luminescence." In the case of the blue spinels, where the visible-light luminescence color differs from the body color of the stone, each sample was placed on the end of a 150-watt tungsten-halogen fiber-optic light wand. This method, however, is not effective when the body and transmission luminescence colors are the same, as is the case for red spinels. For these samples, then, we used the crossed-filters technique (see, e.g., Webster, 1983; Hodgkinson, 1991), with a saturated copper sulfate solution and a red no. 25A photographic filter.

A gemological microscope was used with a variety of illumination techniques, including dark-field, transmitted light, polarized light, shadowing, and oblique illumination. A Zeiss research microscope was used to examine the surface features of the rough crystals, and to compare them to surface characteristics found on natural spinel crystals. Visible absorption spectra were recorded over the range of 350 to 750 nm using a Hitachi model U4001 spectrophotometer, at a scan speed of 120 nm/minute and a slit width of 2.00 nm.

We determined the chemical composition of 12 red and six blue flux-grown synthetic spinels, 28

natural spinels, and a sampling of the Bell Labs flux-grown spinels and gahnites by energy dispersive X-ray fluorescence (EDXRF) spectrometry. The EDXRF spectrometer used was a Tracor X-ray (currently Spectrace Instruments) Spectrace 5000 with a rhodium-target X-ray tube. Typical excitation conditions were: a tube voltage of 30 kV, a tube current of 0.35 mA, a 0.5-mm-thick rhodium filter, and a vacuum atmosphere. These excitation conditions were chosen because they were appropriate for detecting elements between potassium (K) and molybdenum (Mo) in general, and zinc (Zn) in particular (Jenkins, 1980), which are known to occur in natural and synthetic spinels. With EDXRF analysis, we both determined the elements present in each sample tested and compared the relative peak areas of an element from one sample to the next. To confirm the EDXRF results, a quantitative analysis of three flux synthetic red spinel crystals and three faceted natural pink or red spinels was carried out using a Jeol model 733 electron microprobe at the California Institute of Technology.

#### GEMOLOGICAL CHARACTERISTICS OF THE FLUX SYNTHETIC SPINELS

Tables 1 and 2 summarize the gemological properties of the Russian flux-grown synthetic red and blue spinels we examined during this study, as well as those of natural and flame-fusion synthetic spinels previously reported in the literature (see, e.g., *GIA Gem Property Chart A*, 1985; Hurlbut and Kammerling, 1991) and confirmed by the authors' experience. Specific features are discussed below.

**Color.** The body color in daylight of the red flux synthetic spinels (both rough and faceted) examined was a vivid, medium dark, slightly purplish red (figures 1 and 3). In incandescent light, the two largest crystals and all but the largest faceted stone showed a very slight orange to brown component. With fluorescent lighting, this orange to brown component was absent, and the purple secondary hue appeared more pronounced.

The body color in daylight of all but one of the rough crystals and all of the faceted samples of blue flux synthetic spinel was a saturated, medium dark to dark, very slightly violetish blue (figures 2 and 3). The exception, a 1.85-ct crystal, was a significantly more saturated blue. In incandescent light, all of the rough crystals and faceted blue stones

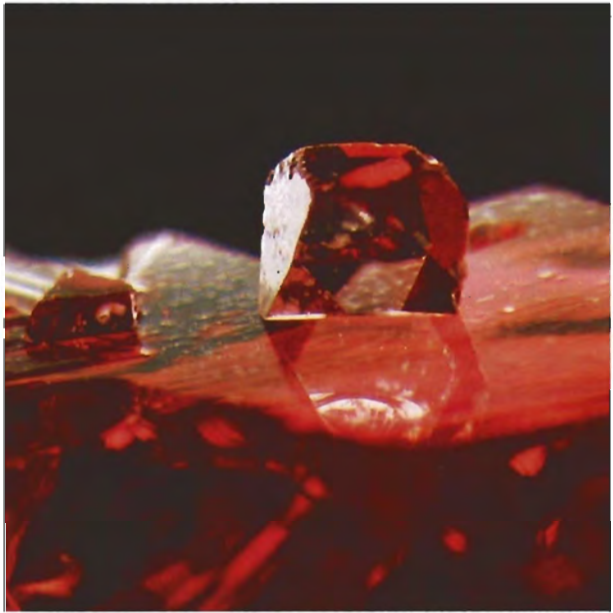


Figure 4. Two small synthetic red spinel crystals are attached to an octahedral face of this crystal. The largest of these small crystals measures 1.2 mm on a side. Photomicrograph by John I. Koivula.

appeared evenly colored with slight red flashes noted when they were rocked in the light. With fluorescent lighting, we observed a slight gray color component.

**Index of Refraction.** The R.I.'s of the red flux synthetic spinels we examined agree with published values (see, e.g., Brown et al., 1990; Henn and Bank, 1992), and are within the range of R.I. values for natural red spinel.

The R.I.'s of the blue flux synthetic spinels we examined are somewhat lower than the 1.719 value reported for a Russian blue flux synthetic crystal by Henn and Bank (1991, 1992), and are within the R.I. range (1.710–1.720) previously determined for natural "cobalt blue" spinels (Shigley and Stockton, 1984). The faceted blue flux synthetic spinel from Dr. Hänni had an R.I. of 1.717—higher than that of our other blue flux synthetic spinels—probably because of its high iron content.

**Specific Gravity.** The range of S.G. values for all the flux synthetic spinels tested was within the range for natural spinels. If a hydrostatic balance is not available, a gemologist can estimate the S.G.

using heavy liquids. All of the samples readily sank in methylene iodide (S.G. 3.32) when they were submerged just below the liquid's surface and released.

**Ultraviolet Luminescence.** In general, we observed a strong purplish red to slightly orangy red reaction to long-wave U.V. radiation—with a weaker, slightly orangy red reaction to short-wave U.V.—in the flux synthetic red spinels examined. With short-wave U.V., some edges between faces on the rough crystals appeared superficially chalky and, in certain directions, more yellowish orange. No phosphorescence was detected following exposure to either source.

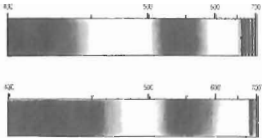
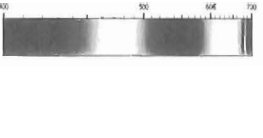
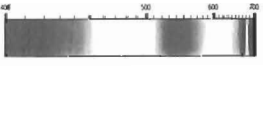
With the exception of the slight chalkiness to short-wave U.V. shown by some of the crystal edges, the ultraviolet luminescence of these flux red spinels is essentially identical to that of natural red-to-pink spinels from Burma and Sri Lanka

(Webster, 1983; Liddicoat, 1990), and is consistent with information previously reported on these flux synthetics (see, e.g., Henn and Bank, 1992).

For the blue flux synthetic spinels we examined, the long-wave U.V. fluorescence varied from weak to moderate, slightly chalky, red to reddish purple. The short-wave U.V. fluorescence was slightly stronger, but the same color. Again, no phosphorescence was detected. The long-wave U.V. behavior is similar to that of "cobalt blue" natural spinels we have tested (but which are inert to short-wave U.V.). In contrast, flame-fusion synthetic spinels of the same bright blue color exhibit strong red fluorescence to long-wave U.V., but mottled blue to bluish white fluorescence to short-wave U.V. (see table 2; also, Schwarz, 1981; Webster, 1983).

**Visible-Light Spectroscopy.** When examined with a handheld spectroscope, all of the red synthetic

**TABLE 1.** Gemological characteristics of natural, flame-fusion synthetic, and Russian flux-grown synthetic red spinels.<sup>a</sup>

Property	Natural red	Flame-fusion synthetic red	Flux-grown synthetic red
Index of refraction	1.718 (+0.017)(-0.008)	1.722 (±0.003)	1.719 (±0.003)
Specific gravity	3.60 (+0.10)(-0.03)	3.59 (±0.01)	3.61 (±0.03)
Polariscope reaction	Singly refractive (SR); possible weak to moderate anomalous double refraction (ADR)	Singly refractive (SR); strong anomalous double refraction (ADR); "cross hatch" pattern	Singly refractive (SR); possible weak to moderate anomalous double refraction (ADR)
Chelsea filter reaction	Red	Red	Red to orangy red
Fluorescence <sup>b</sup>			
Long-wave	Weak to strong, red or orange	Strong red	Strong, purplish red to slightly orangy red
Short-wave	Inert to weak, red or orange-red	Inert to moderate red	Moderate to strong slightly orangy red
Transmission luminescence	Red	Red	Red to orangy red
Inclusions	Most commonly octahedra either singly or in a fingerprint pattern; other inclusions might consist of apatite and dolomite	Curved color banding and curved striae; gas bubbles that occasionally contain a secondary phase	Orangy brown to black flux inclusions occurring singly or in a fingerprint pattern; also metallic platelets
Spectra			

<sup>a</sup> Properties for natural and flame-fusion synthetic red spinels are as reported in GIA Gem Property Chart A (1985) and Hurlbut and Kammerling (1991), and as determined by the authors' experience. Properties for the Russian flux-grown synthetic spinels are based on the examination of four crystals and nine faceted red samples.

<sup>b</sup> No phosphorescence was observed to either wavelength.

spinel showed general absorption in the violet and blue from the ultraviolet to about 450 nm, and a broad absorption band between approximately 510 and 580 nm. We also noted a fluorescent line in the red between 680 and 685 nm. These absorption features are similar to those observed in a natural red Burmese spinel (see table 1—lower spectrum).

Note that none of the flux synthetic red spinels examined exhibited the “organ-pipe” fluorescence emission spectrum of sharp lines (as seen in the red portion of the top spectrum for natural red spinel in table 1) reported for a number of natural red spinels when viewed with a handheld spectroscope (Webster, 1983, p. 134).

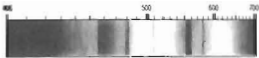
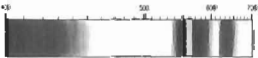
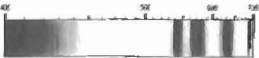
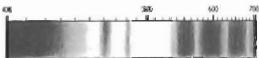
All of the flux synthetic blue spinels examined displayed strong absorption bands between approximately 535 and 550, 560 and 590, and 615 and 635 nm. In some of the larger samples, we saw a very weak sharp line at about 690 nm. There was also a weak absorption below about 430 that increased toward the ultraviolet (see table 2).

**Transmission Luminescence/Filter Reactions.** Both the red and blue flux synthetic spinels exhibited a red to orangy red “transmission” luminescence to visible light. The intensity of this luminescence appears to be directly proportional to that of the ultraviolet fluorescence. This is the same reaction we have seen with “cobalt blue” natural spinels.

Both the red and blue flux synthetic spinels displayed a red to orangy red color when exposed to an intense incandescent light source and viewed with a Chelsea color filter. This is almost identical to the reaction of natural red spinels. Natural “cobalt blue” spinels exhibit a weak orange-to-red reaction, while natural blue spinels colored by iron do not show any color when tested by this method, presumably because luminescence is quenched by the iron present.

**Magnification.** Many of the red and blue crystals and faceted flux synthetic spinels contained metal-

**TABLE 2.** Gemological characteristics of natural, flame-fusion synthetic, and Russian flux-grown synthetic blue spinels.<sup>a</sup>

Property	Natural blue	Flame-fusion synthetic blue	Flux-grown synthetic blue
Index of refraction	1.718 (+0.017)(-0.008)	1.728 (+0.012)(-0.008)	1.714 (±0.002)
Specific gravity	3.60 (+0.10)(-0.03)	3.64 (+0.02)(-0.12)	3.62 (±0.04)
Polariscope reaction	Singly refractive (SR); possible weak to moderate anomalous double refraction (ADR)	Singly refractive (SR); strong anomalous double refraction (ADR); “cross hatch” pattern	Singly refractive (SR); possible weak to moderate anomalous double refraction (ADR)
Chelsea filter reaction	Fe: Inert Co: Weak orange-to-red	Red	Red to orangy red
Fluorescence <sup>b</sup>			
Long-wave	Fe: Inert Co: Weak to moderate red	Strong red	Weak to moderate, slightly chalky red to reddish purple
Short-wave	Fe: Inert Co: Inert	Mottled blue to bluish white	Same color as long-wave U.V. but slightly stronger
Transmission luminescence	Fe: Inert Co: Red	Red	Red to orangy red
Inclusions	Octahedra either singly or in a fingerprint pattern; other crystal inclusions might include graphite, dolomite, and sphen	Tiny “bread-crumbs” inclusions; gas bubbles	Orangy brown to black flux inclusions occurring singly or in a fingerprint pattern; also metallic platelets
Spectra			
Fe type:			
Co type:			

<sup>a</sup> Properties for natural and flame-fusion synthetic blue spinels are as reported in GIA Gem Property Chart A (1985) and Hurlbut and Kammerling (1991), and as determined by the authors' experience. Properties for the Russian flux-grown synthetic spinels are based on the examination of 16 crystals and 12 faceted blue samples.

<sup>b</sup> No phosphorescence was observed to either wavelength.





Figure 5. Dark reddish to orangy brown, jagged-edged flux inclusions (with gas bubbles), such as this 3-mm-long example, provide proof that the host stone is synthetic. Note how the inclusions taper to a point. Photomicrograph by John I. Koivula.

lic or flux inclusions that were deep orangy brown to almost black. These inclusions exhibited sharply angular to jagged profiles, which were sometimes slightly rounded and tapered to points; some contained gas bubbles (figures 5 and 6). These bubbles presumably were caused by contraction of the flux as it cooled, as described in Kashan synthetic ruby by Burch (1984). The flux inclusions could be seen as colorless to white to slightly yellowish or orangy brown net- or fingerprint-like patterns (figures 7 and 8), similar to those observed in some flux-grown synthetic rubies (see, e.g., Burch, 1984).

Some of the flux particles noted were very small and, though still distinctly orangy brown (fig-

Figure 7. Flux inclusions formed net- or fingerprint-like patterns in some of the flux synthetic red spinels. Photomicrograph by John I. Koivula; magnified 20 $\times$ .

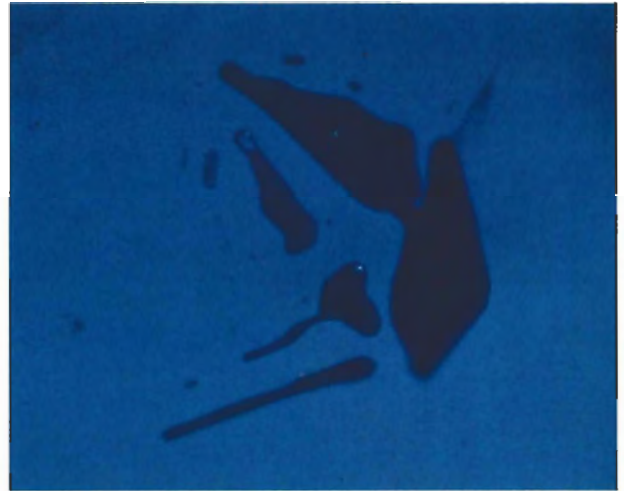
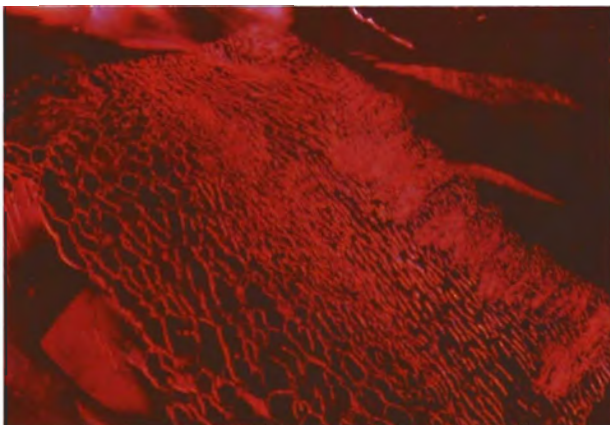
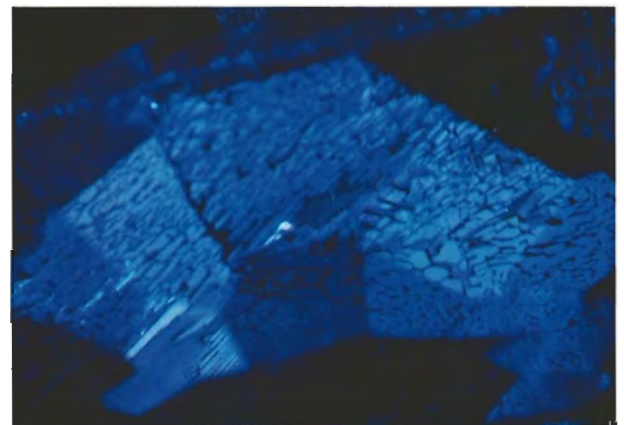


Figure 6. Gas bubbles were also evident in the flux inclusions seen in some of the blue synthetic spinels. Photomicrograph by John I. Koivula; magnified 40 $\times$ .

ure 9), these might be mistaken for natural inclusions by those not familiar with this new synthetic.

A few of the faceted stones contained minute triangular grayish silver inclusions, which exhibited a distinctly metallic luster when observed with oblique surface-incident light (figure 10). Because they were located deep within the host material, they could not be analyzed by X-ray diffraction. From their general appearance and the results of EDXRF chemical analysis on the host stones, we believe that they consist of platinum or iridium derived from the crucibles in which the synthetic spinels were grown.

Figure 8. A distinctive net-like pattern of flux inclusions was also typical of the flux synthetic blue spinels. Photomicrograph by John I. Koivula; magnified 15 $\times$ .



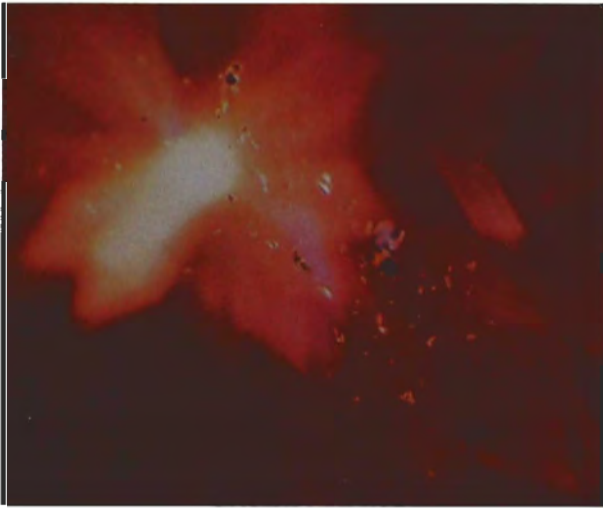


Figure 9. Tiny flux particles such as these might be mistaken for natural inclusions by those not familiar with this flux synthetic spinel. Photomicrograph by John I. Koivula; magnified 25 $\times$ .

A specific crystallographic orientation of the flux inclusions could not be determined in any of the faceted stones. In some of the crystals, however, the larger flux inclusions formed pyramid-shaped phantoms in near-perfect alignment with the external faces and edges of the octahedra. This

Figure 10. Minute, triangular solid inclusions with distinct metallic luster—probably platinum or iridium—were observed in a few stones. Photomicrograph by John I. Koivula; magnified 20 $\times$ .

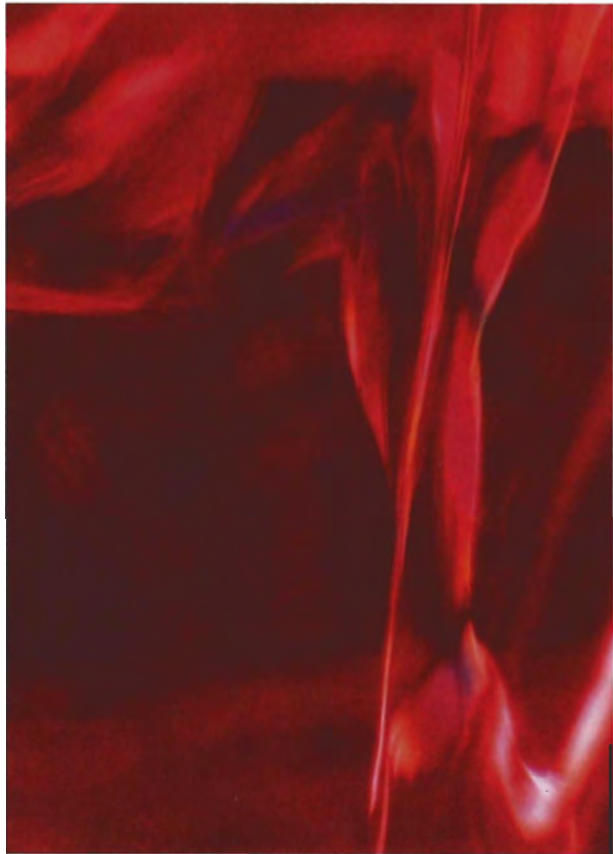


Figure 11. In several of the samples, iridescence was noted in air-filled fractures. Photomicrograph by John I. Koivula; magnified 25 $\times$ .

orientation is consistent with the growth of the synthetic spinel crystal along octahedral planes. Some of these inclusions were centered just under the flat surfaces (again, see figure 3) that appear to form the plane of crucible attachment of the crystal during growth.

In some of the samples, we observed mirror-like air-filled fractures that appeared iridescent when viewed in certain directions (figure 11). As expected, polarized light revealed an anomalous birefringence ("strain") pattern in association with these fractures (as well as with some of the flux inclusions).

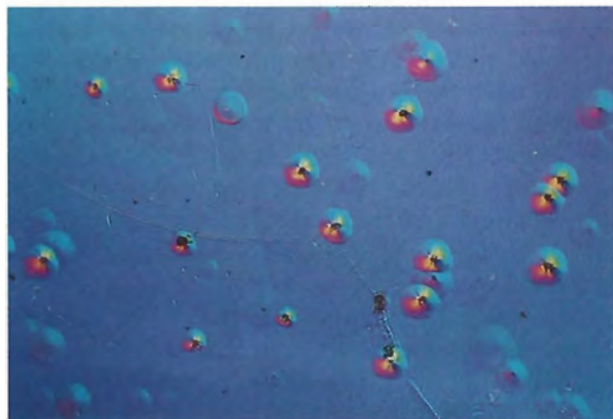
We examined the synthetic spinel crystals by means of Nomarski differential interference contrast microscopy to compare their surface features to those of natural spinel crystals. Most natural crystals that have not been subjected to some form of erosion or abrasion show either very smooth surfaces or slight signs of chemical dissolution in

Figure 12. Natural spinel crystals like this one commonly have triangular etch features. Photomicrograph by John I. Koivula; magnified 80×



the form of minute triangular "etch pits" on their octahedral faces (figure 12). Although the octahedral surfaces of the three red synthetic crystals appeared relatively smooth to the unaided eye, on closer inspection they were found to be decorated with roughly circular to semicircular growth hillocks (figure 13) of a type not yet observed by the authors on the surfaces of natural spinel crystals. Their appearance suggests that they represent slightly triangular growth spirals around a screw-type dislocation (I. Sunagawa, pers. comm., 1993).

Figure 13. In contrast to the triangular etch features noted on the surface of natural spinels (figure 12), circular to semicircular growth hillocks were noted on the octahedral faces of the three Russian flux-grown synthetic crystals. Photomicrograph by John I. Koivula; magnified 80×



One feature that seems to be relatively rare and was only seen in the blue flux synthetic spinels is an unusual "dendritic" inclusion that forms distinctly shaped, extremely thin, delicate fans of varying sizes (figure 14). These "fans" appear opaque in darkfield or transmitted light, and have an obvious metallic luster when observed in reflected light. Because destructive testing would have been necessary and results could not be guaranteed, we could not establish the nature of these dendritic inclusions.

We did not observe any color zoning in either the crystals or the faceted samples.

#### CHEMICAL COMPOSITION

EDXRF chemical analysis of the Russian flux synthetic spinels revealed differences in their compositions from those of natural spinels of similar colors (figures 15 and 16). Due to the excitation conditions used, the magnesium (Mg) and aluminum (Al) present as intrinsic components in spinels do not produce well-defined peaks, but they also have no diagnostic value in this context. Other elements, present as impurities in spinel, can be divided into "major" and "minor." The former have relatively large X-ray peak areas, whereas the latter always have smaller peak areas.

In the Russian flux synthetic red spinels we tested (e.g., figure 15A-B), chromium (Cr) and iron (Fe) were major impurities, with Cr content being relatively constant but Fe varying from one sample to the next. When they were present, nickel (Ni),

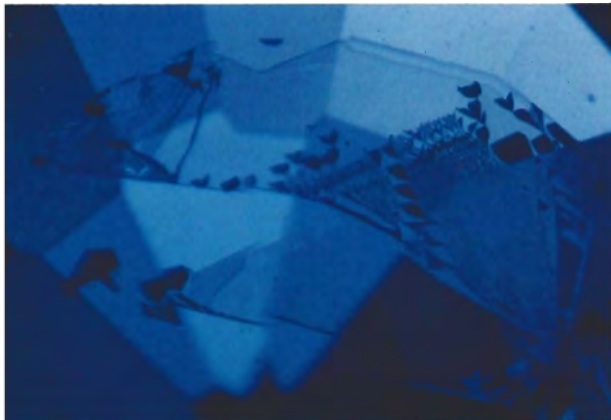


Figure 14. Dendritic inclusions, such as this one, appear to be rare; among the flux synthetic spinels we examined, they were only seen in the blue material. Photomicrograph by John I. Koivula; magnified 15 $\times$ .

vanadium (V), zinc (Zn), gallium (Ga), and lead (Pb) were all minor impurities, with the exception of one sample in which Ni was a major impurity. We did not detect Pb in any of the natural spinels. Two flux synthetic red spinels grown at Bell Laboratories, although both similar in color to one another, as well as to the Russian samples, contained Cr and Fe in one instance and Mn in the other.

In contrast, all 28 natural red-to-pink or purple spinels we analyzed had more Zn than the flux synthetics (compare spectra 15A–B to 15C–E). Cr and Fe varied in content, with generally more Cr than Fe in red spinels from Myanmar, and more Fe than Cr in pink spinels from Myanmar and other localities. The minor impurities titanium (Ti), V, Ga, Ni, and copper (Cu) varied in content in natural spinels from one locality to the next, but generally V was greater than Ti. The Ga content differed from one natural spinel to the next, even when they were from the same locality. Ni and Cu were the least abundant impurities we detected. Cu was not detected in either of the samples for which spectra are illustrated in figure 15A–B.

In the nine flux synthetic blue spinels we analyzed (figure 15A–B), we always found cobalt (Co) and Fe, with Co greater than Fe. The minor impurities V, Cr, manganese (Mn), Pb, Ni, Zn, and Ga occurred in most samples but in varying contents. Fe, Co, Ga, and Pb were present in the one flux synthetic blue spinel from Bell Laboratories that

we analyzed. In contrast, the four Sri Lankan “cobalt blue” natural spinels examined contained Fe and Zn as major impurities, Ga as a minor impurity, and Ni, V, Cr, Mn, and Cu as trace impurities in varying amounts (figure 16C–E). Cu was detected in samples 1791 and 1807 but is not visible in the spectra illustrated. Note that the peak for Co cannot be distinguished from other element peaks in the EDXRF spectra of these natural blue spinels due to the low concentration of Co and the overlap of its characteristic peaks with those of other elements (Koivula et al., 1990b). Nonetheless, there is a sufficient amount (as shown by the spectral data discussed below) to give rise to the saturated blue color.

Finally, iridium (Ir) was found only in the red flux synthetic spinels, and platinum (Pt) occurred only in the blue flux synthetic spinels.

For comparison with these qualitative EDXRF results, table 3 presents quantitative microprobe analyses of three natural faceted pink-to-red spinels and three flux synthetic red spinel crystals. These samples were chosen to represent the lowest Zn concentration detected among the natural spinels and the highest Zn levels among the flux synthetic spinels. The EDXRF and microprobe results are consistent. Furthermore, these microprobe data confirm the similarity in MgO:Al<sub>2</sub>O<sub>3</sub> ratios of natural and flux synthetic spinels. We did not do microprobe analysis on the blue spinels, since chemical analysis is not necessary to separate natural from synthetic “cobalt blue” spinels.

#### VISIBLE ABSORPTION SPECTROPHOTOMETRY

Figure 17 compares the visible absorption spectra (labeled A through F) for three natural, one flame-fusion synthetic, and two flux synthetic (one each Russian and Bell Laboratories) blue spinels, both as recorded with GIA’s Hitachi spectrophotometer and as seen with a handheld spectroscope. We recorded similar spectra for natural and synthetic red spinels (flux and flame-fusion), but these are not shown because the spectral curves were virtually identical, and therefore, are not diagnostic (see the comparison of the spectra obtained with a handheld spectroscope in table 1).

Examination of the six spectral curves in figure 17 reveals differences between the “iron blue” and “cobalt blue” natural spinels mentioned above. Spectra A and B (for grayish blue natural spinels)

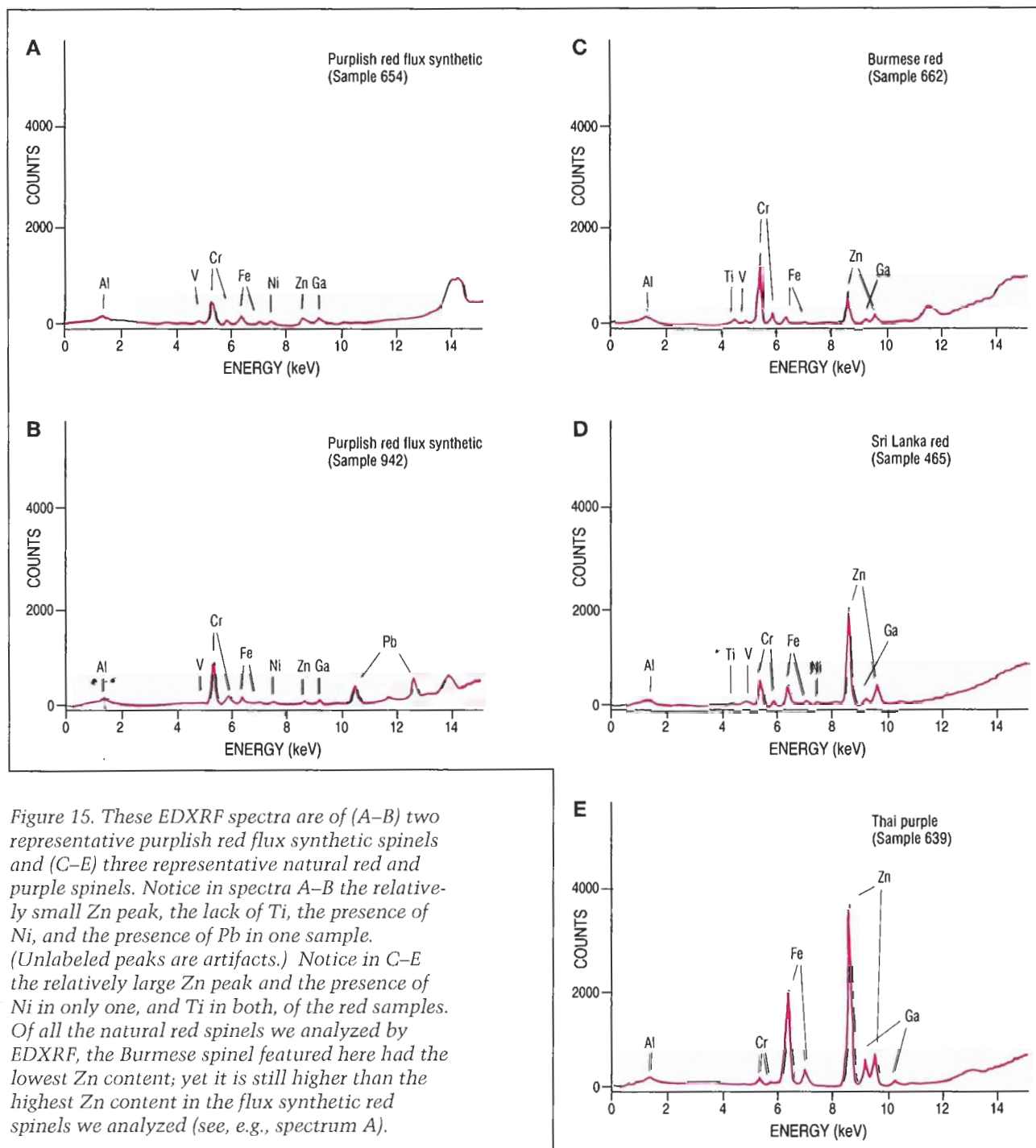


Figure 15. These EDXRF spectra are of (A–B) two representative purplish red flux synthetic spinels and (C–E) three representative natural red and purple spinels. Notice in spectra A–B the relatively small Zn peak, the lack of Ti, the presence of Ni, and the presence of Pb in one sample. (Unlabeled peaks are artifacts.) Notice in C–E the relatively large Zn peak and the presence of Ni in only one, and Ti in both, of the red samples. Of all the natural red spinels we analyzed by EDXRF, the Burmese spinel featured here had the lowest Zn content; yet it is still higher than the highest Zn content in the flux synthetic red spinels we analyzed (see, e.g., spectrum A).

exhibit absorption bands throughout the visible range and increasing absorption below about 430 nm that have been attributed to iron (Schmetzer et al., 1989, p. 166). With increasing Fe content, all of these absorption bands become more pronounced, so much so that those between 550 and 670 nm can begin to be seen with a handheld spectroscope (spectrum B).

Spectrum C is for a natural “cobalt blue” spinel from Sri Lanka in the GIA reference collection. This particular spinel was used to prepare the spectrum labeled as “type 1” in the article on “cobalt blue” natural spinels by Shigley and Stockton (1984). The spectrum shows the weaker bands between 350 and 500 nm due to Fe, as well as a group of three broad, more intense bands (at

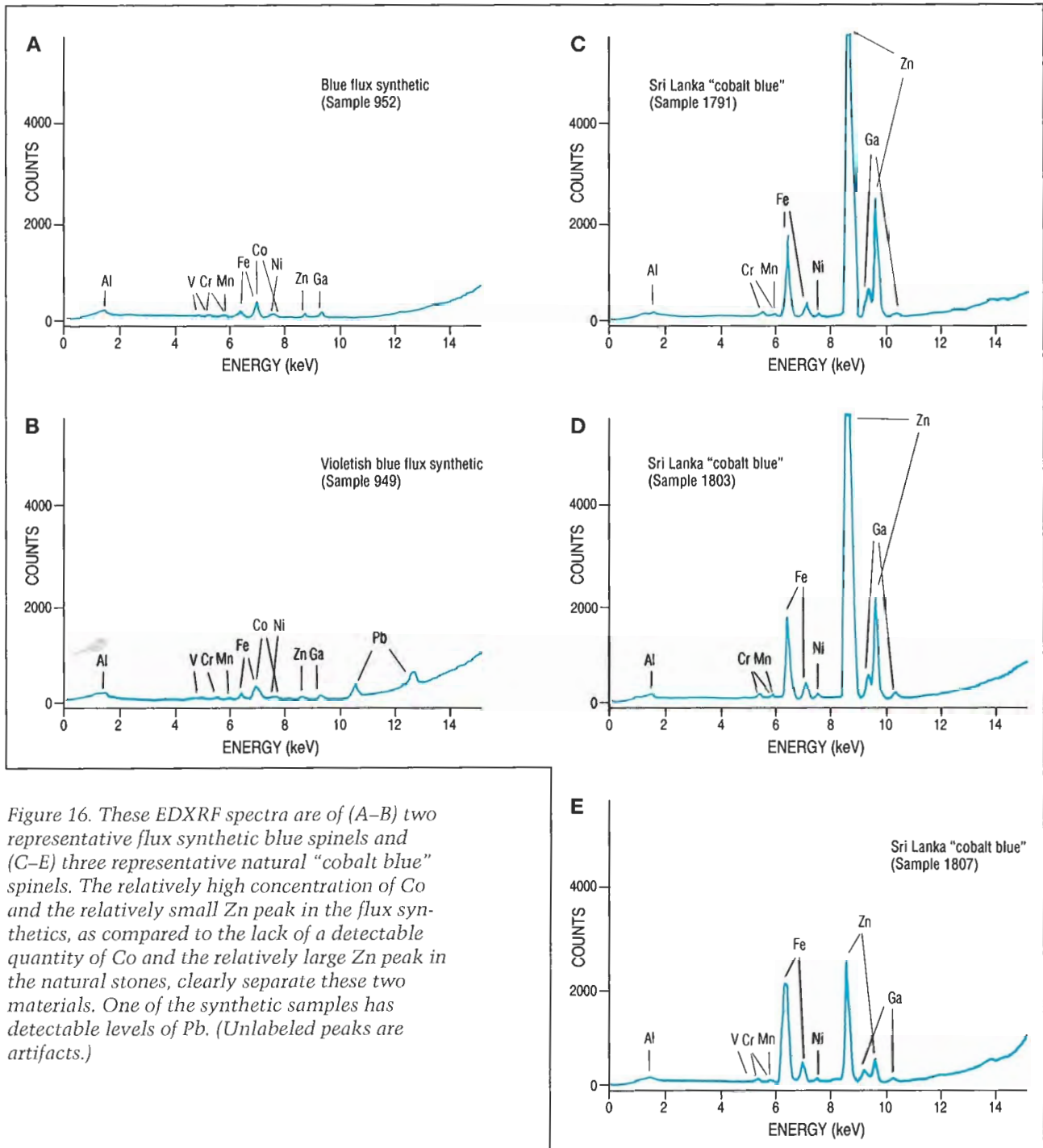


Figure 16. These EDXRF spectra are of (A–B) two representative flux synthetic blue spinels and (C–E) three representative natural “cobalt blue” spinels. The relatively high concentration of Co and the relatively small Zn peak in the flux synthetics, as compared to the lack of a detectable quantity of Co and the relatively large Zn peak in the natural stones, clearly separate these two materials. One of the synthetic samples has detectable levels of Pb. (Unlabeled peaks are artifacts.)

about 550, 585, and 625 nm) that are all attributed to cobalt (Schmetzer et al., 1989). Note that these cobalt features completely overlap and obscure the weaker Fe features between 500 and 700 nm that can be seen in spectra A and B. Three spectral features, when seen in combination, establish these “cobalt blue” spinels as natural: (1) the presence of the Co absorption bands between 500 and 600 nm,

(2) the weak absorption bands due to Fe below 500 nm, and (3) the increasing absorption below about 430 nm also due to Fe.

Spectra D, E, and F are for a Russian flux-grown synthetic, a flame-fusion synthetic, and a Bell Laboratories flux synthetic blue spinel, respectively. All three spectra show the series of stronger absorption bands from 500 to 650 nm due to cobalt

(again, see Schmetzer et al., 1989). The three spectra are very similar (in respect to the location of features) to that of the natural "cobalt blue" spinel (spectrum C) in the region between 500 and 700 nm, but they lack the iron-related spectral features, most notably below 500 nm (even though Fe is detected in them by EDXRF; see figure 16A).

## DISCUSSION

Because of the similarities in chemical composition between flux synthetic and natural spinels, their indices of refraction and specific gravity are nearly identical, thus providing no means of separation. In the case of red flux synthetic spinels, flux or metallic inclusions, when present, are the only diagnostic gemological properties; in the case of red natural spinels, only the "organ pipe" luminescence lines in the visible absorption spectrum, when present, are diagnostic (note that the presence of only one fluorescent line or a doublet would be of no help in making a separation). In a stone that lacks characteristic inclusions or a characteristic absorption spectrum, chemical analysis is critical to the separation of natural from flux synthetic red spinels.

All of the natural red spinels we analyzed by EDXRF showed a more intense Zn peak than their

flux synthetic counterparts. Microprobe analyses confirmed that there is no overlap (and that, in fact, there is a significant gap) between the ranges of Zn concentration detected in natural (0.05 to 0.10 wt.% ZnO) and flux synthetic spinels (no more than 0.01 wt.% ZnO). Therefore, the presence of a comparatively large amount of Zn is proof of natural origin. However, there is a complete series within the spinel group to a Zn end member, gahnite, which has also been grown in the laboratory (see box B). The differences in Zn concentration between natural and flux synthetic spinels are large enough that this separation can be done solely using EDXRF analysis; there is no need to use the electron microprobe or other quantitative procedures. Using a more sensitive, quantitative analytical technique known as optical emission spectroscopy, Schwarz (1981) studied the differences in chemistry between flame-fusion synthetic spinels of various colors (none of which were pink to red) and natural pink-to-red spinels from Myanmar and Sri Lanka. He, too, found significantly more Zn in natural spinels than in the flame-fusion synthetics.

We also found Ti only in the natural red spinels. Therefore, the presence of Ti indicates a natural origin. Fe was more abundant in the natural

**TABLE 3.** Electron microprobe analyses of representative pink-to-red natural spinels and Russian flux-grown synthetic spinels<sup>a</sup>.

Oxide	Natural spinels (wt.%)			Russian flux-grown synthetic spinels (wt.%)		
	No. 646 <sup>b</sup> (Pink)	No. 647 <sup>b</sup> (Pink)	No. 662 <sup>c</sup> (Red)	No. 656 (Purplish red)	No. 695 (Purplish red)	No. 654 (Purplish red)
MgO	27.72	27.81	28.17	27.70	27.38	27.59
Al <sub>2</sub> O <sub>3</sub>	69.46	69.62	67.24	70.64	70.31	71.07
TiO <sub>2</sub>	0.01	0.02	0.41	BDL <sup>d</sup>	BDL	BDL
V <sub>2</sub> O <sub>3</sub>	0.05	0.04	0.38	0.05	0.04	0.03
Cr <sub>2</sub> O <sub>3</sub>	0.06	0.05	3.09	0.47	0.49	0.34
MnO	BDL	0.01	0.01	BDL	0.02	BDL
FeO	0.48	0.31	BDL	BDL	0.05	0.04
NiO	0.01	BDL	BDL	BDL	BDL	BDL
ZnO	0.07	0.10	0.05	0.01	0.01	BDL
Ga <sub>2</sub> O <sub>3</sub>	0.04	0.02	BDL	0.02	BDL	0.03
Total	97.90	97.98	99.35	98.89	98.30	99.10

<sup>a</sup> Electron microprobe analyses were performed on an automated, five-crystal JEOL 733 spectrometer operating at a beam-accelerating potential of 15 kV and a current of 40 nA. K-alpha lines were analyzed for each element. Standards include: (Mg, Al)—spinel, (Si, Ca)—anorthite, (K)—microcline, (Ti)—TiO<sub>2</sub>, (V)—V<sub>2</sub>O<sub>5</sub>, (Cr)—Cr<sub>2</sub>O<sub>3</sub>, (Mn)—Mn olivine, (Fe)—fayalite, (Ni)—Ni olivine, (Zn)—ZnO, and (Ga)—GaAs. Two analyses at different locations were performed on each sample. Total iron is shown as FeO; total manganese as MnO. The microprobe data were corrected using the program CITZAF (Armstrong, 1988) employing the absorption correction of Armstrong (1982), the atomic number correction of Love et al. (1978), and the fluorescence correction of Reed (1965; as modified by Armstrong, 1988). Analyses performed by Paul Carpenter.

<sup>b</sup> From Tajikistan.

<sup>c</sup> From Myanmar.

<sup>d</sup> BDL = below the detection limits of the instrument (less than 0.01 wt.% oxide).

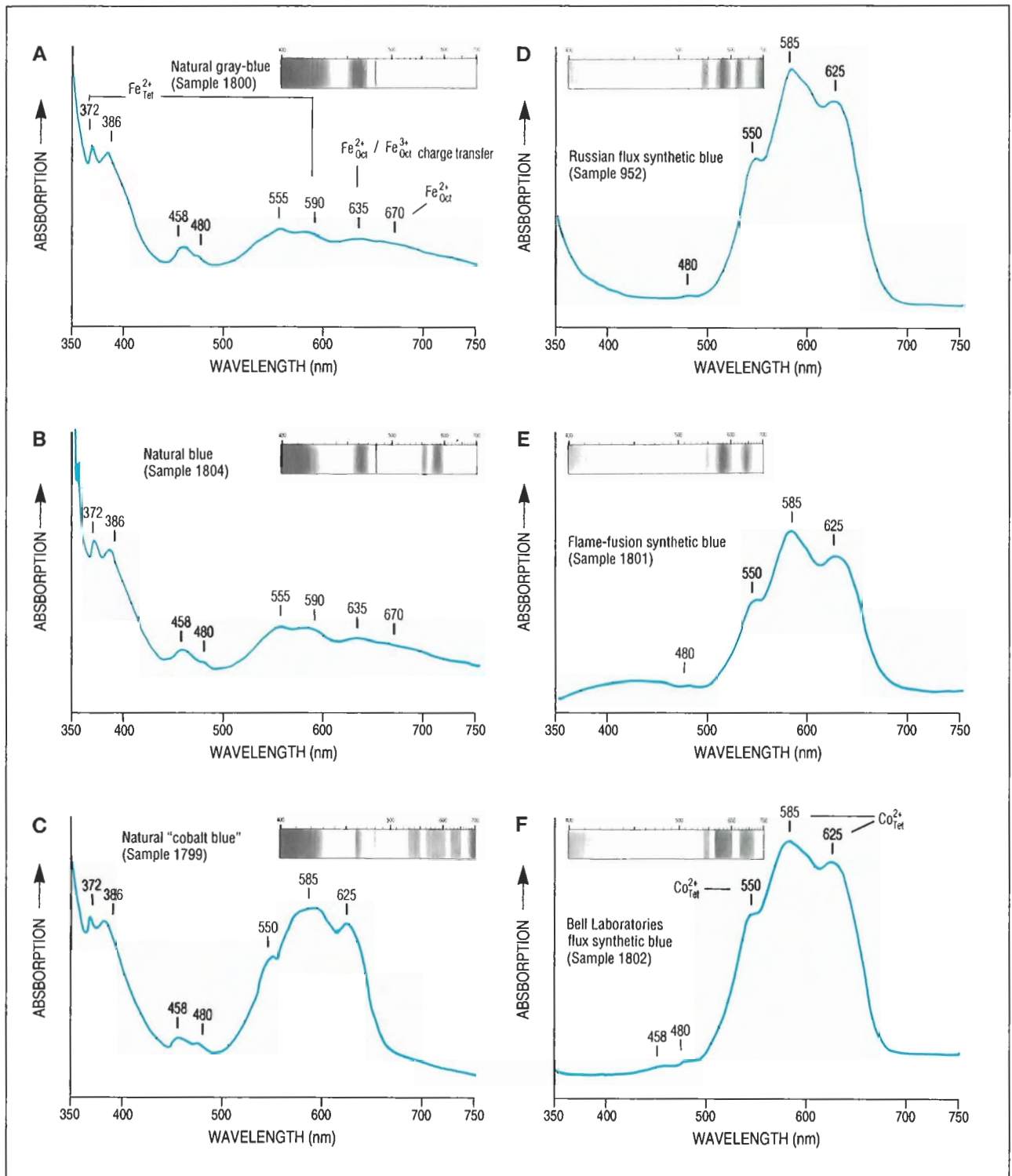


Figure 17. These visible absorption spectra for three natural and three synthetic blue spinels, as recorded with a Hitachi spectrophotometer and seen with a handheld spectroscope, illustrate the evolution from Fe-related features to Co-related features. (For details see text.) Spectrum A is of a 2.11-ct natural gray-blue spinel; spectrum B is of a 2.88-ct natural blue spinel; and spectrum C is of a 1.92-ct natural "cobalt blue" spinel. Spectrum D is of a 0.83-ct faceted Russian flux synthetic blue spinel; spectrum E is of a flame-fusion synthetic blue spinel fragment; and spectrum F is of a 0.15-ct flux synthetic blue spinel crystal grown at Bell Laboratories. Spectra A, C, E, and F were labeled as "spectra types" II, I, III, and IV, respectively, in Shigley and Stockton (1984).



## BOX B: SYNTHETIC GAHNITE

Gahnite,  $ZnAl_2O_4$ , the zinc equivalent of spinel ( $MgAl_2O_4$ ), has been grown in various colors by the flux method, but only on an experimental basis (Nassau, 1980). This rare synthetic was mentioned in the gemological literature as early as 1967 by Liddicoat. As part of our study, we analyzed several pink-to-red flux synthetic gahnites grown in the 1970s at Bell Laboratories (figure B-1). Not surprisingly, the colors result from doping this material with Cr.

Since both synthetic spinel and gahnite crystals can be grown by the flux method, in similar pink-to-red colors, it appears that one could possibly grow a synthetic spinel crystal containing an amount of zinc similar to that detected in natural spinels (see, e.g., Wood and White, 1968). However, it is uncertain whether crystal growers would spend the time and money that would undoubtedly be required to alter their current growth methods simply to circumvent a particular gem identification method. In addition, the new product might have other distinctive gemological properties. We have no evidence that such pink-to-red spinel containing abundant Zn has been synthesized.



Figure B-1. These flux synthetic gahnites (0.47–23.25 ct) were grown on an experimental basis at Bell Laboratories. Courtesy of Dr. Kurt Nassau; photo by Robert Weldon.

red spinels (except for those from Myanmar), and Ga was sometimes more abundant (but with significant overlap in concentration level) in the natural than in the flux synthetic red spinels. Ni was found as a trace impurity in both groups. Cr and V were recorded in both the natural and the flux synthetic red spinels, but in varying relative quantities. Finally, the presence of either Ir (from the crucible) or Pb (from the flux) proves synthetic origin.

Magnification is the key gemological test in separating blue flux synthetic from similar-colored natural spinels, both Fe- and Co-containing. If characteristic inclusions are not present, Fe bands in the visible-light spectrum and an inert reaction to short-wave U.V. radiation will identify both Fe- and Co-containing spinels as natural (table 2). The more common Fe-containing natural blue spinels can also be separated on the basis of their absence of transmission luminescence, of fluorescence to long-wave U.V. radiation, or of a reaction to the Chelsea color filter. Natural blue spinels contain more Zn, and generally more Fe and Ga, whereas the flux synthetic spinels contain more Co and, in some cases, they contain Pb or Pt (with the presence of either of the latter two elements constituting proof of synthetic origin).

### CONCLUSION

In this article, we have described the gemological properties and chemical characteristics of the new flux synthetic red and blue spinels from Russia. For blue flux synthetic spinels, microscopy, visible-light spectroscopy, and short-wave U.V. fluorescence will suffice for separation from both Fe-containing and Co-containing natural spinels. Red flux synthetic spinels can be identified gemologically only if flux or metallic inclusions are present. In either case, qualitative chemical analysis by EDXRF appears to provide definitive proof, as it did for all the spinels examined for this study.

The commercial availability of Russian flux synthetic spinels in a range of colors and significant faceted sizes will require that gemologists consider a variety of tests to identify this material. For some stones, they will need to use a combination of both standard gem-testing methods and advanced chemical analysis. This situation has already been demonstrated in the case of natural and synthetic ruby (see, e.g., Muhlmeister and Devouard, 1991). In the absence of definitive gemological tests, this article points out the growing importance of rapid, nondestructive, EDXRF chemical analysis to modern gem testing.

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Laboratories in New Jersey. Dr. Henry Hänni loaned two blue flux synthetic spinels. Patricia Maddison of the GIA Gem Trade Laboratory gemologically tested many of the faceted stones, while Mike Moon and Meredith Mercer of GIA Research prepared some of the initial visible absorption spectra. Paul Carpenter carried out the electron microprobe analysis at the California Institute of Technology in Pasadena, California. This study was made possible in part by funds from the Dr. Byron C. Butler Fund for Inclusion Research.

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