
NOTES • AND • NEW TECHNIQUES

'COBALT-BLUE' GEM SPINELS

By James E. Shigley and Carol M. Stockton

The traditional gemological technique for distinguishing natural from synthetic blue spinel has involved the use of refractive index and absorption spectra. Recently, however, the standard interpretation of these tests has proved troublesome in the identification of several intensely colored blue stones that have R.I.'s in the range of natural blue spinels but that exhibit spectral features generally associated with synthetic cobalt-colored spinels. To establish the origin of these specimens, a detailed investigation of natural, flame-fusion, and flux blue spinels was carried out. Our results indicate that, while spectral features in the longer wavelengths are unreliable for separating these spinels, an iron-related absorption band at about 460 nm was seen only in our natural specimens. Flame-fusion synthetics may still be distinguished by their lower R.I.'s.

Several natural spinels with the intense blue color and so-called "cobalt" absorption bands generally associated with synthetic blue spinels have recently appeared on the gem market (figure 1). Such similarities to the synthetic material have led to difficulties in the recognition of these unusual natural stones by traditional gemological methods (Fryer, 1982). The present study establishes compositional and spectral means for the identification of these intensely colored natural blue spinels and discusses the occurrence of cobalt in them as a possible coloring agent.

DATA COLLECTION

Blue spinels included in our study consist of 18 natural and 10 synthetic (8 flame-fusion and 2

flux) stones (figure 2) that range from slightly grayish to vivid in saturation, light to dark in tone, and violetish to greenish blue in hue (as defined in GIA's colored stone grading course). The natural blue spinels include both cut stones and rough gem material acquired from several sources. While we cannot be certain of the exact origins of these specimens, they probably came from Sri Lanka. The flame-fusion synthetics consist of cut stones and boule fragments typical of the material that has long been produced by the Verneuil process. For the flux-grown specimens, we used two small (2–3 mm) octahedral crystals. We are unaware of the existence of any flux blue spinel crystals of sufficient size for faceting; nor have we encountered any of this material in already cut form. Moreover, flux blue spinel does not appear to be readily available in quantity in the gem marketplace, although Webster (1983) noted that clusters of the octahedral crystals have occasionally been used in jewelry.

Several types of data were gathered for each spinel studied: refractive index, specific gravity, inclusions, visible light absorption spectra (spectrophotometer and hand spectroscope), and chemical composition (microprobe, X-ray fluorescence, and neutron activation). A complete tabulation of these data and a comparison of our results with those reported by other investigators will be provided in a detailed account to be published elsewhere (Shigley and Stockton, in preparation).

DISCUSSION OF DATA

Physical and Optical Properties. The measured refractive indices of the natural and synthetic spi-



Figure 1. Two natural spinels (5.30 ct and 1.37 ct, respectively) that have the intense blue color normally associated with cobalt-doped synthetic spinel. Photo by Michael Havstad.

nels in our study agree with the values previously reported for similar material (Liddicoat, 1981; Webster, 1983). Those of the flame-fusion synthetics are slightly higher than those of the natural stones. The specific gravity ranges, however, overlap almost completely and thus appear to be unreliable indicators of origin. The refractive index and specific gravity values of the two flux synthetics lie well within the ranges for natural spinels (see figure 3).

The observation of strain patterns in our specimens through crossed polarizing filters revealed generally more strain in the flame-fusion synthetics than in either the flux synthetics or the natural spinels. However, all three groups displayed a variety of strain patterns that provided no clear indication of stone origin.

Inclusions. When present, inclusions can be excellent indicators of spinel origin (Gübelin, 1974; Liddicoat, 1981; Webster, 1983). Most of the natural specimens in this study contain one or more of the common inclusions considered diagnostic of natural spinel, including stringers of minute octahedra, either in straight lines or as "fingerprints" (figure 4), individual octahedra of spinel group minerals or negative octahedra filled with other minerals (figures 5 and 6), and iron-stained healing planes (figure 7). One of the more intense blue specimens from our study collection also contains octahedra with lily-pad inclusions around them (figure 8), and another contains natural-appearing intersecting needles (figure 9).

The synthetic flame-fusion specimens that we examined were remarkably inclusion-free. One stone contains stringers of minute gas bubbles (figure 10) accompanied by thread-like gas inclusions, both of which are typical of synthetic spinel (*op. cit.*). In addition, flame-fusion synthetic spinel may include gas bubbles with negative crystal faces (figure 11) that appear deceptively natural.

No typical or diagnostic inclusions have heretofore been observed in flux synthetic blue spinels (Fryer, 1982), but we did note the presence of cross-hatched growth lines parallel to the crystal faces of both samples that we studied. Considerably more material of this type must be examined, however,

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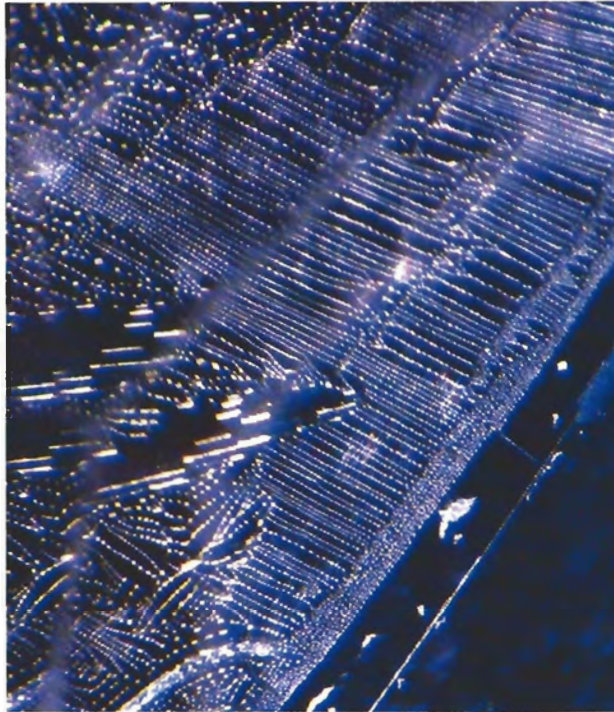


Figure 4. Stringers of minute spinel octahedra such as these are probably the most common type of inclusion seen in natural spinels. Magnified 35x.

somewhat to form a single region of absorption. Type II stones have a strong H band, but less frequently display the other bands above 500 nm. Type III spectra (flame-fusion synthetics) invariably have strong F, I, J, and K bands, but no others that can be resolved with a hand spectroscope. Type IV spectra (flux synthetics) differ from type III spectra principally in that the D band is of sufficient intensity that it is sometimes visible in the hand spectroscope. Moreover, the F, I, J, and K bands are so strong in the flux spinel spectra that they usually cannot be resolved into separate bands.

Figure 6. A distorted negative octahedron (left) in one of the intense-blue natural spinels loaned to us for this study. Microprobe analysis of the mineral contained in this inclusion revealed a composition primarily of calcium, aluminum, and silicon, and confirmed the natural origin of the host spinel. Magnified 40x.

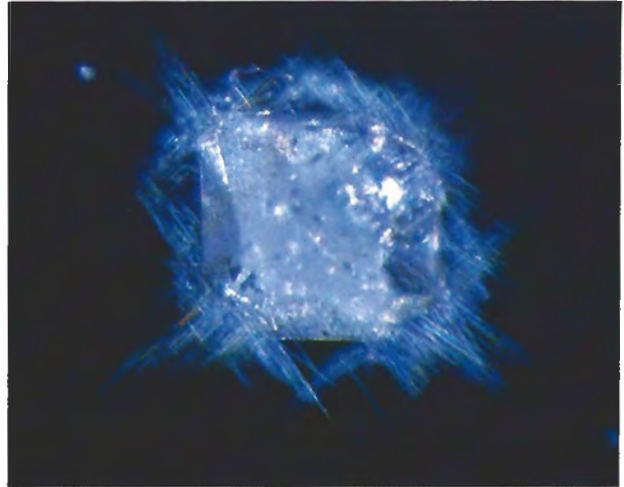
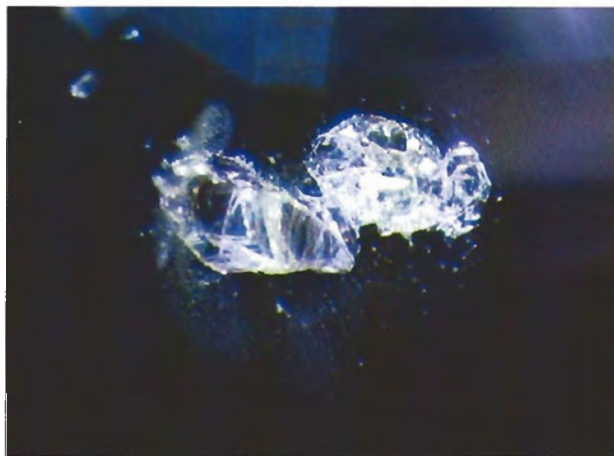
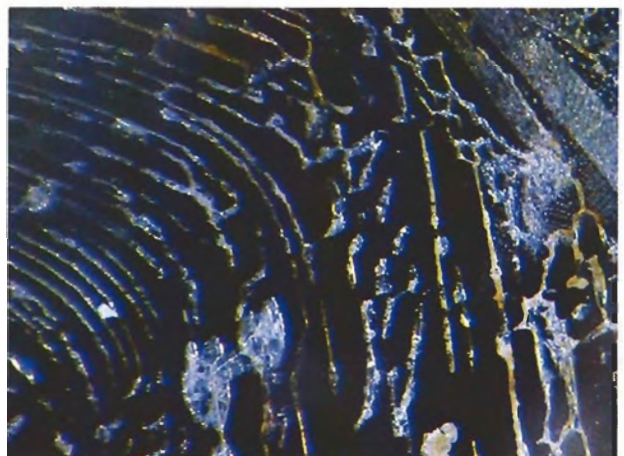


Figure 5. Negative octahedron filled with calcite in a natural blue spinel. Magnified 55x.

Chemistry. The mineralogical species spinel (ideal formula $MgAl_2O_4$) is a member of a chemically interrelated group of minerals and thus can have other elements (such as Fe, Zn, or Cr) that substitute for Mg or Al (Lindsley, 1976). These sub-

Figure 7. Thin films, some stained by iron, along a healing plane are also diagnostic of the natural origin of a blue spinel. Magnified 30x.



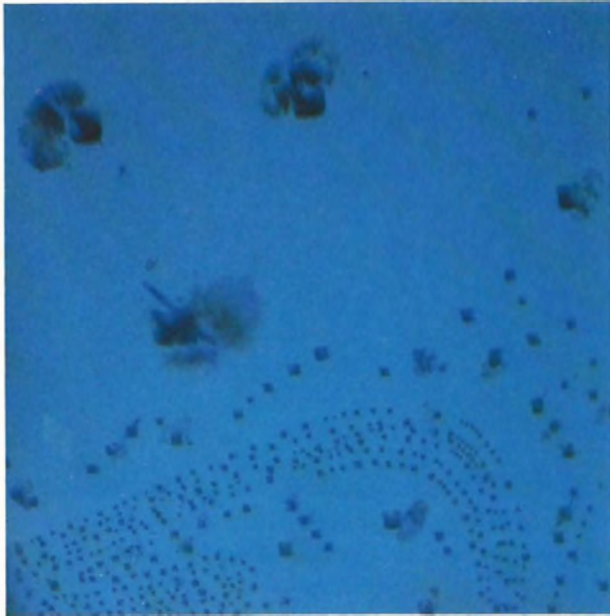


Figure 8. One of the intense-blue natural spinels studied contains numerous octahedra, some of which are surrounded by lily pads that probably contain a thin film of liquid. Magnified 50 \times .

stitutions are responsible for much of the variability that can be observed in the physical properties of this gem mineral (Winchell, 1941).

Table 1 summarizes our chemical data, from which compositional differences between natural and synthetic blue spinels are apparent. Flame-fusion synthetic stones have excess alumina and thus can easily be distinguished chemically from natural spinels on the basis of the ratio Al:(Mg+Fe+Zn) (Rinne, 1928; Tromnau, 1934).

Figure 10. These stringers of minute gas bubbles are characteristic of flame-fusion synthetic spinel. Magnified 45 \times .



Figure 9. Another of the intense-blue natural spinels contains these intersecting needles. Magnified 45 \times .

Flux spinels, however, resemble the natural gem material more closely in this respect.

The iron content in the natural blue spinels studied considerably exceeds that in the synthetics, and trace levels of both gallium and zinc were always present in the former but never in the latter. Nickel and vanadium was found to occur in some of the natural stones, but in none of the synthetics; conversely, titanium was found in most of the flame-fusion synthetics but in none of the natural stones. Small amounts of cobalt were found by microprobe and/or XRF in spinels of all three groups. However, we confirmed the presence of cobalt in several of our spinels (including samples

Figure 11. Gas bubbles with crystal forms, such as this cuboctahedral one, are occasionally seen in flame-fusion synthetic blue spinel. Such negative crystals can be very deceptive and should not be regarded as diagnostic of natural or synthetic origin. Magnified 50 \times .



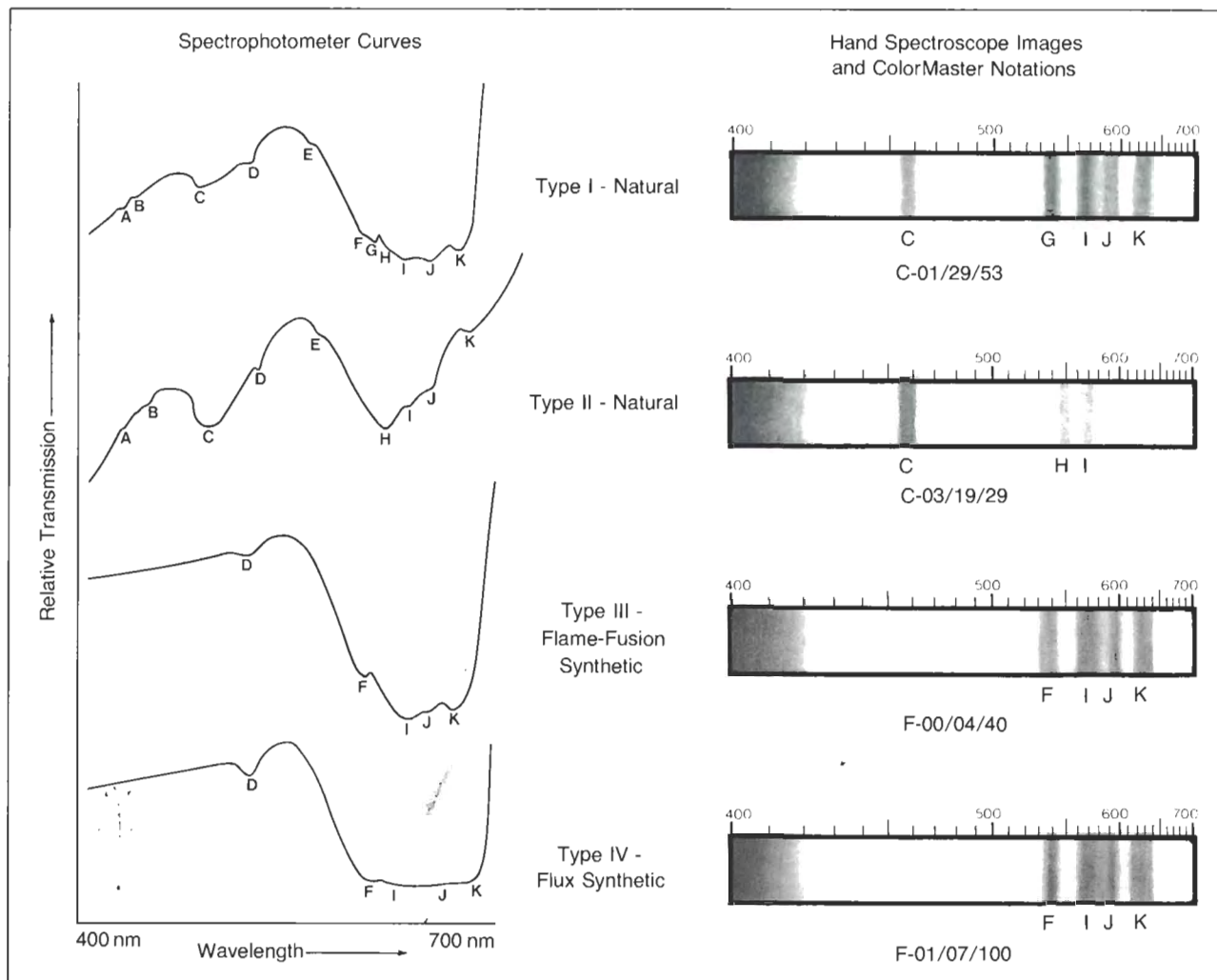


Figure 12. Illustrations of representative spectral curves and hand spectroscope images of the four types of spectra noted in the natural and synthetic blue spinels studied. The ColorMaster notations for each type are given below the hand spectroscope images.

of flux, flame-fusion, and natural intense-blue stones) by infrared spectrophotometry. Furthermore, a light, slightly gray-blue natural spinel was submitted for trace analysis of cobalt by instrumental neutron activation analysis (INAA) and proved to contain 5.3 ppm of cobalt.

INTERPRETATION

Several of the natural spinels we examined are the very intense blue commonly associated with synthetic spinels (figure 13). A case of mistaken identification could easily result in such instances. However, the spectral features and chemistry of spinel are closely interrelated. Thus, absorption bands may provide clues to chemical composition that will serve to distinguish natural and synthetic spinels of this color.

From a comparison of our data with the work of other investigators on spinel absorption spectra (Shigley and Stockton, in preparation), we suggest that bands A, B, C, E, G, and H are due to iron. Almost all of these bands were observed in the spectra of all our natural blue spinels, but none was evident in the spectra of any of the synthetics. Of the six bands, the C band at about 460 nm is perhaps the most useful for the gemologist working with a hand spectroscope because it is distinct in terms of its relative intensity and its isolation from other strong absorption features.

Cobalt is the primary coloring agent in synthetic blue spinels (Rinne, 1928; Tromnau, 1934), while the blue in natural spinels has been attributed solely to iron (Anderson and Payne, 1956). However, our data suggest that cobalt may con-



Figure 13. Two spinels of a similar, intense blue. The 1.88-ct stone on the left is a flame-fusion synthetic, while the 1.40-ct one on the right is natural. The spectral curves for these stones (types III and I, respectively; see figure 12) show similarity in the positions and strengths of their absorption bands in the region above 500 nm. However, recognition of the A, B, and particularly the C bands at shorter wavelengths in the natural stone provides a means for distinguishing it from its synthetic counterpart. Photo by Michael Havstad.

tribute to the color of natural blue spinels as well. With one exception (Mitchell, 1977), cobalt has not been considered a coloring agent in natural blue spinels. In fact, it has generally been accepted in gemology that cobalt cannot cause a blue coloration in any natural gem mineral, and thus that cobalt-related spectral features are proof of a synthetic origin (Anderson and Payne, 1956; Webster, 1983). However, cobalt has been found in other blue-colored minerals (Shannon, 1923), and both it and iron are capable of producing a blue color in materials, although considerably less cobalt than iron is required to produce an equally intense blue (Marfunin, 1979).

The D, F, I, J, and K bands are clearly due to cobalt in synthetic blue spinels; yet in natural blue stones, bands that appear in about the same locations as the I+J and K bands have traditionally been associated with iron. All five bands are strongest in intensity in the flux synthetics, which contain more cobalt than any of the other samples, and are present as well in all of our flame-fusion samples. We suggest, however, that these bands are due to cobalt in both natural and synthetic blue spinels.

The grayish blue natural spinel found to contain 5.3 ppm (0.00053%) cobalt when analyzed by INAA has the nine absorption bands from C through K that can be detected by the spectrophotometer (only C, H, and I can be seen with a hand spectroscope). According to our correlations, then, both iron (present at 1.43 wt. % FeO) and cobalt are represented in the spectrum of this stone, although bands associated with the latter are generally weaker than those attributed to the former. It would thus be reasonable to assume that natural intense-

blue spinels that display even stronger cobalt-associated bands would contain even more of this element. In fact, a number of our natural specimens have amounts of cobalt detectable by microprobe (Shigley and Stockton, in preparation), and all of these exhibit stronger D, F, I, J, and K bands than does the stone with 5.3 ppm cobalt.

Other minor or trace elements found in our specimens do not appear to have a significant influence on the spectra of either the natural or the synthetic blue spinels examined in this study.

CONCLUSIONS

The presence of the iron-induced C band (about 460 nm) in the spectrum of a blue spinel is positive proof of natural origin, since neither flux nor flame-fusion synthetic spinels have sufficient iron to produce a detectable band at this wavelength. This spectral band will be especially useful to the gemologist if at some future date flux-grown synthetic spinels (indistinguishable from natural blue spinels by refractive index) become commercially available. Separation of natural from flame-fusion blue spinels can still be achieved by the use of refractive index: below 1.720 in all the natural stones we examined, and above that in all our flame-fusion synthetics. It is theoretically possible that, since additional iron raises the refractive index of spinel, a natural stone could contain enough of that element to produce a refractive index over 1.720 (i.e., within the range of the flame-fusion synthetics), but in this event the corresponding C band would be even stronger.

We know of no natural blue spinels without an observable C band, and thus it seems likely that this band will be present in the spectra of all

TABLE 1. Summary of chemical data for the 18 natural and 10 synthetic (8 flame-fusion and 2 flux-grown) blue spinels studied (ranges of oxide components in wt. %).

Oxide composition	Natural	Flame-fusion	Flux
MgO	25.45–27.88	9.55–11.87	26.35–26.76
Al ₂ O ₃	70.20–71.61	87.99–90.41	72.67–73.37
TiO ₂	n.d. ^a	n.d.– ^{ab}	n.d.
V ₂ O ₃	n.d.–0.06	n.d.	n.d.
Cr ₂ O ₃	n.d.– [*]	n.d.–0.07	n.d.
Ga ₂ O ₃	[*]	n.d.	n.d.
MnO	n.d.–0.07	n.d.– [*]	n.d.
FeO	0.69–3.53	[*]	[*]
CoO	n.d.–0.05	n.d.–0.06	0.18–0.19
NiO	n.d.–0.14	n.d.	n.d.
ZnO	[*] –0.44	n.d.	n.d.
Total	99.19–100.73	99.86–100.59	99.20–100.32
Refractive index	1.711–1.719	1.723–1.729	1.714–1.716
Specific gravity	3.59–3.67	3.63–3.67	3.63

^an.d. = below the detection limits of X-ray fluorescence (as low as 0.002 wt. %, depending on elements present).
^b* = detected by nonquantitative X-ray fluorescence, but below the reliable detection limits of the microprobe (about 0.04 wt. %).

natural blue gem spinels. The virtual absence of iron in synthetic spinels is evident in the lack of a C band in their spectra (see table 1). While iron-doped flux synthetic blue spinels could quite possibly be grown at some future date, our data show that other features of their chemical composition would still provide a positive means of identifying them as distinct from natural blue spinels (Shigley and Stockton, in preparation).

Our data establish the presence of cobalt in natural blue gem spinels and its role as a coloring agent in some of them. It thus becomes unreasonable to consider the use of anything termed

cobalt absorption bands as a criterion for the separation of natural from synthetic blue spinels. Our observations suggest that both iron and cobalt can give rise to absorption bands in the 500–650 nm region of the visible spectrum. Since we have been able to distinguish only very slight differences in the locations of some of these bands with the use of the spectrophotometer, it would be hopeless to expect to do so with a hand spectroscope. With careful and judicious use, however, the hand spectroscope can be of value, as with the detection of the C and D bands to identify, respectively, natural and flux-grown synthetic blue spinels.

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