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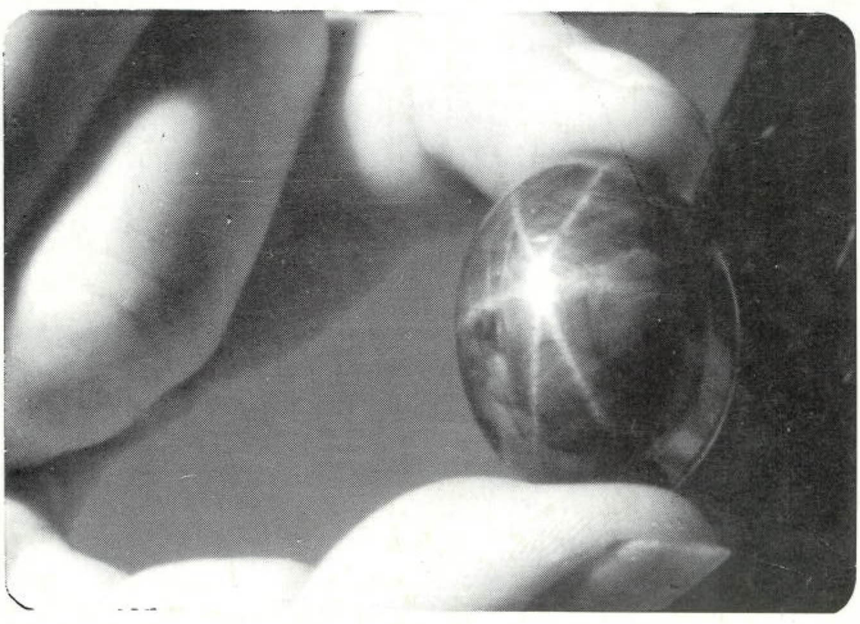

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# A New Type of Synthetic Ruby on the Market: Offered as Hydrothermal Rubies from Novosibirsk*

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## INTRODUCTION

Until now the commercial production of synthetic ruby has consisted of two major types of synthesis, the flame-fusion and flux-growth processes, even though the techniques for a third type involving the hydrothermal growth of synthetic rubies have been known since the late 1950's. The early hydrothermal ruby production was reported as consisting of thin overgrowths on natural ruby seeds (Gubelin, 1961[1]). The authors first became aware of the recent production of hydrothermal synthetic rubies in Novosibirsk during the Fall of 1991. In January 1993, synthetic rubies described as "hydrothermal" synthetic rubies produced at Novosibirsk first began appearing on the market in Bangkok (including the samples in this study, weighing 1.69, 0.69 and 0.62 ct).

The hydrothermal growth process is often responsible for the formation of ruby in natural deposits worldwide, excluding those resulting from magmatic melts. Therefore, it can be expected that the internal characteristics for hydrothermally grown synthetic rubies will include the presence of fluid inclusions comparable to those of their natural counterparts as opposed to the flux remnants present in the healed fracture systems of other synthetic rubies. This could create potential problems in the separation between natural and synthetic rubies. The aim of this study is to provide the identification characteristics and results of standard gemmological as well as more sophisticated testing.

## GEMMOLOGICAL PROPERTIES

The standard gemmological properties of refractive index, pleochroism, specific gravity, UV-fluorescence and visible spectral characteristics were determined to be consistent with other natural and synthetic rubies from different localities and producers from around the world. All of the gemmological properties determined for these "hydrothermal" synthetic rubies are listed in Table 1.

## VISUAL APPEARANCE

The three sample stones in this study, possessed colours reminiscent of natural rubies coming from Thailand and the Mogok stone-tract in Burma (Myanmar). These are the two typical "colour-types" which are most often duplicated by the various manufacturers of synthetic rubies. In all three cases, the red hue consisted of very high saturations, with tones ranging from medium to dark (Fig. 1). One visual feature was quite apparent and involved a very slight reduction in the transparency of the synthetic rubies creating a certain "sleepiness" which was imparted to the stones when viewed with the unaided eye (due to the nature of the graining features, to be discussed later). This had the effect of making the sharp facet edges of the pavilion diffused when viewing the stones face-up (this "sleepiness" is a property which the authors have noticed as well in certain natural rubies exposed to high temperature heat treatment).

## MICROSCOPIC EXAMINATION

The microscopic examination of the Russian hydrothermal synthetic rubies showed several very interesting primary and secondary internal features and characteristics which have never been observed before in either natural or synthetic rubies.

### Graining

The most obvious and striking feature observed in these stones consisted of very pronounced graining, which was present throughout. The term "graining" is used here to describe the growth features, which can provide useful identification characteristics and clues to the conditions surrounding the growth of the original crystal. As mentioned previously, these graining features were so strongly present as to have an effect on the overall transparency of the stones, not reducing them to semi-transparent, but giving them an overall "sleepy" general appearance. These graining features are quite distinctive and rather reminiscent of the graining features observed in the Russian production of hydrothermal synthetic emeralds. In most viewing directions this graining is observed as a striated pattern (Fig. 2), although one direction is characterised by a strongly "roiled" appearance ( Fig. 3). When viewed immersed using horizontal microscopes, using the methods described by Kiefert and Schmetzer, 1991[2], these growth features were determined to be located at 90 degrees to the optic axis direction placing them parallel to the basal growth plane. An additional growth

* Novosobirsk is some 2500 km east of Moscow.

*Fig.1. The new "hydrothermal" synthetic rubies reportedly from Novosibirsk. The colours observed are comparable to natural rubies from Thailand or Burma. Weights range from 1.69 ct to 0.62 ct.*

characteristic which was observed in one of the synthetic rubies examined, consisting of an unusual combination of growth features creating a "christmas tree" pattern (Fig. 4). This "christmas tree" pattern was also only visible in one direction located at 90 degrees to the optic axis. At this point however, it is uncertain if this pattern is a result of twinning or some other irregularity in the growth of the original crystal. The information learned from these graining features indicates that the original crystals from which these stones came, consisted of poorly aggregated single crystals which did not form, dominated by a planar growth process like those found in both natural and flux-grown synthetic rubies but rather by some form of highly disturbed "undulating" growth process (numerous lattice defects). Further research on this topic, including the analysis of rough crystals is necessary to properly detail the information surrounding the growth characteristics of these synthetic rubies.

**Colour Zoning**

When these stones were observed with the unaided eye, their colour appears very homogenous. Upon viewing the stones with a microscope over a diffused light source or immersed in a heavy liquid such as di-iodo methane, certain fluctuations in colour-zoning could be observed interwoven with the strong graining characteristics (Fig. 5) Colour zoning is often observed in both natural and synthetic rubies of all kinds, and can be due to slight variations of colour-

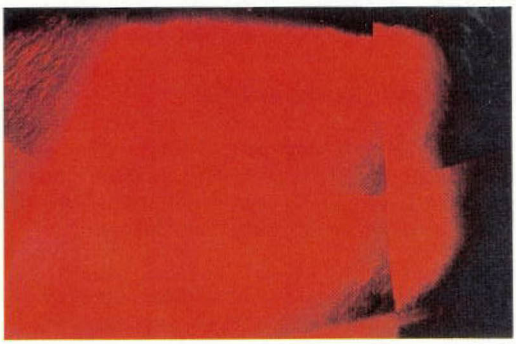


*Fig.2. The most prominent internal characteristic observed in the hydrothermal synthetic rubies are the very strong graining features which in most directions displayed a striated pattern. (x35)*

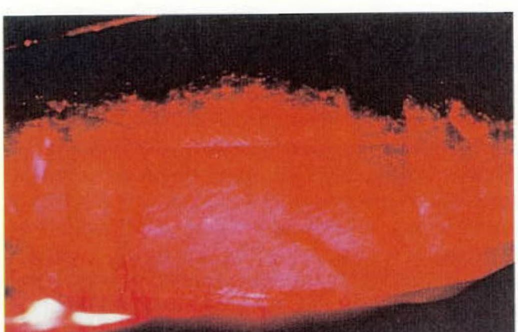


*Fig.3. In one direction parallel to the basal growth plane, these prominent graining features display a strongly "roiled" character. (x35)*

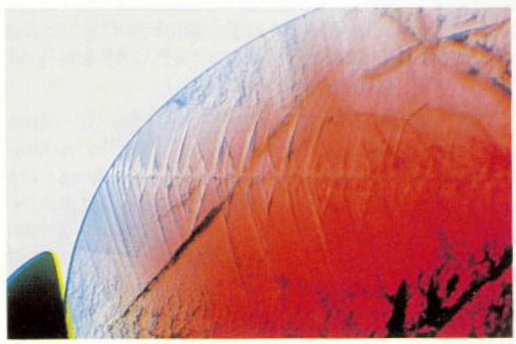


*Fig.4. Unusual graining pattern in one of the "hydrothermal" synthetic rubies (0.62 ct), showing a "christmas tree" like image. The cause of this linear lattice disturbance is unknown. (x40)*

*Fig.5. Fluctuations in colour concentrations in a "hydrothermal" synthetic ruby interwoven with the strong graining features. (x30)*

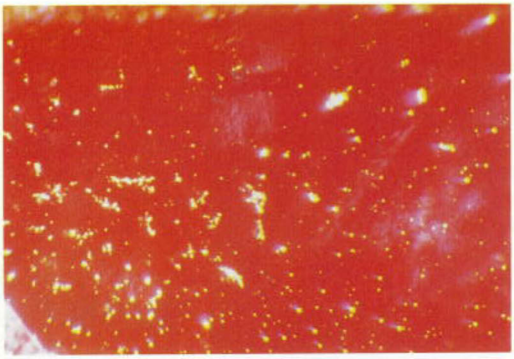


***Fig.6. Numerous small, highly reflective "golden" coloured inclusions consisting of two types of copper-rich alloys, occurring either isolated or in small groups. (x30)***

***Fig.7. The highly reflective "golden" appearance of the copper alloy inclusions reaching the surface in a hydrothermal synthetic ruby is shown. (x45)***

causing trace element concentrations in the growing solution or from changes in the oxidizing conditions of the fluid. However, the type of colour zoning observed in these stones, is quite unique and unlike the "swirled" or planer colour-zoning visible in natural and other synthetic rubies.

**Solid Inclusions**

Numerous solid inclusions were observed in these synthetic rubies, consisting of small, highly reflective, "golden" coloured inclusions occurring in small collective groups or sparsely located individually (Fig. 6). A much larger, similar appearing tabular inclusion came to the surface of the crown in one of the stones, which also displayed a highly reflective "golden" appearance (Fig. 7).

To date, two different types of solid inclusions have been identified, these consist of well crystallized, isometrical thin to thick platelets of opaque metallic alloys. Electron microscope EDX analysis of surface reaching inclusions identified two different types of copper alloys; a) homogenous compositions of predominantly copper (Cu) with minor amounts of iron (Fe), nickel (Ni) and titanium (Ti) (Fig. 10a and b) a more brittle alloy consisting of again predominantly copper (Cu), but with minor amounts of iodine (I) and sulphur (S) (Fig. 11). The typical size range of the platelets could occur in small groups of a single type, or consisting of a combination of the two different types (Fig. 12). As a special note; there were no evidence of noble metals such as gold or platinum detected, even with an analytical penetration depth reaching a few tenths of a millimetre (non-destructive X-ray fluorescent analysis).

**Needle-like Inclusions**

It was long believed that needle inclusions did not occur in synthetic rubies, although more recently it has been accepted that such inclusions can occasionally occur. Observed in one of the hydrothermal synthetic rubies was a long slender needle-like inclusion (Fig. 8). The linear direction of this inclusion is parallel to the striated direction of the strong graining features. The needle appeared to be transparent and colourless but it could not be conclusively determined whether it is the result of a negative crystal or solid inclusion.

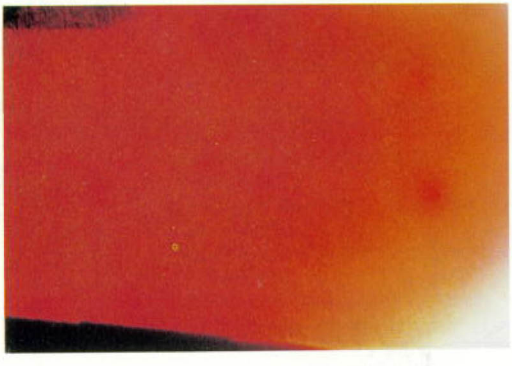


***Fig.8. Needle like inclusion in a "hydrothermal" synthetic ruby following the striated direction of the graining pattern. (immersion, x40)***

***Fig.9. Healed fracture systems present in a "hydrothermal" synthetic ruby. These fingerprint like inclusions occasionally contain gas phases. They are transparent and colourless and may potentially be confused with healed fracture systems of natural rubies. (x35)***

Fig. 10

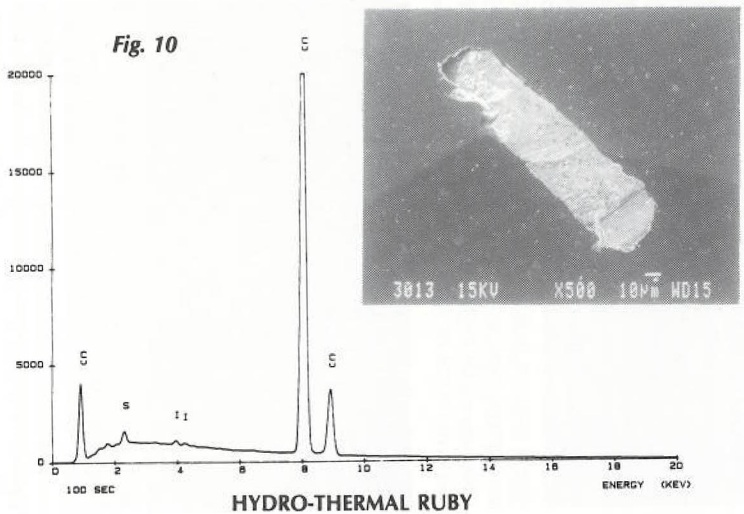



*Fig.10. Two types of metallic inclusions are identified by electron microscopic analysis of surface-reaching inclusions. The chemical composition of the first type consisted predominantly of copper, iodine and sulphur as shown on a SEM image (inclusion length 160 microns) and shown graphically. Analytical details: Joel JSM 840 electron microscope in connection with a TN 2000-EDX, beam current 15kV, 1nA, samples carbon coated). Analysts: R. Wessikon and P. Wagli, Laboratory of Solid State Physics, Electron Microscopy, ETH Zurich, Switzerland.*

*Fig.11. Electron microscopic study of a second type of metallic inclusion in "hydrothermal" synthetic ruby. SEM image shows a well-crystallized and twinned metallic inclusion (6 microns in diameter) consisting of copper, chromium, titanium, iron and nickel as shown graphically by ED analysis.*

*Fig.12. Electron microscopic study of metallic inclusions reaching the surface in "hydrothermal" synthetic ruby. SEM image showing a group consisting of two types of metallic inclusions: Cu-S-I alloys (broken out during cut) and Cu-Cr-Fe-Ti-Ni alloys. The size of individual inclusions is approximately 5 microns. EDX analyses from the Cu-S-I alloys is shown.*

Fig. 11

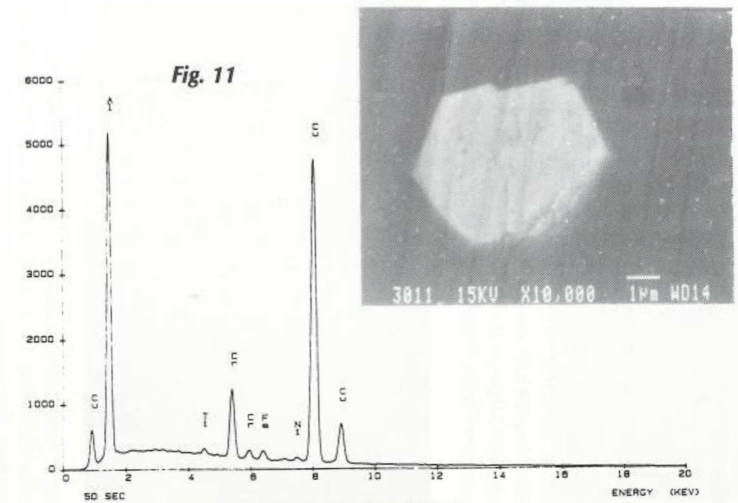
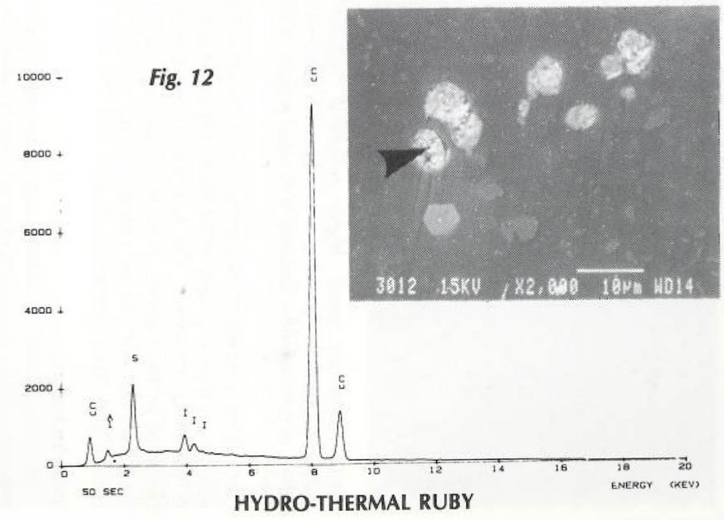



Fig. 12



**Fingerprint Inclusions**

Healed fracture systems forming fingerprint inclusions were also observed in the synthetic rubies (Fig. 9), similar to fingerprints in natural rubies, these were transparent and generally curved and irregular in character, occasionally containing a secondary gas phase. In contrast to the healed fracture systems observed in flux grown synthetic rubies, which are generally not transparent, x-ray fluorescence analysis was performed on one healed fracture system where it reached the surface, with no detection of lead (Pb), molybdenum (Mo), bismuth (Bi) or tungsten (W), as would be expected if flux residues were filling the communication tubes. Future analyses with Raman spectroscopy may help to explain the exact nature of these inclusions.

***Table 1. Gemmological properties of "hydrothermal" synthetic rubies showing typical characteristics. Notice the slightly variable properties of the synthetic rubies with variation in Fe-concentration (colour, UV luminescence, absorption and emission).***

| | |
|---|---|
| Colour | A high saturation of red with tones of medium (a) to dark (b) |
| General appearance | A general "sleepiness" due to a slightly reduced transparency |
| Refractive Index | a = 1.760-1.762<br>o = 1.768-1.770 |
| Birefringence | 0.008 |
| Optic character | uniaxial negative |
| Specific gravity | 3.99-4.00 |
| Pleochroism | strong dichroism:<br>saturated orange-red perpendicular to c-axis<br>saturated purple-red parallel to c-axis |
| UV luminescence | long wave: weak (b) to medium (a) red<br>short wave: inert (b) to weak (a) red |
| Visible absorption spectrum (perpendicular to c-axis) | 400-465 nm (general absorption band)<br>469,475,477 nm (sharp lines)<br>525-595 nm absorption band (a)<br>495-610 nm absorption band (b)<br>659, 668, 675, 692*, 694* nm (sharp lines)<br>* appear as a moderate (b) to strong (a) emission line |
| Internal features | strong, striated and heavily "roiled" graining patterns<br>"golden" coloured metallic inclusions:<br>two types have been identified so far including<br>Cu-Ni-Fe-Ti-alloys and Cu-I-S materials<br>Fingerprint inclusions occasionally containing gas bubbles |

(a) comparatively Fe-poor type "hydrothermal" synthetic ruby
(b) comparatively Fe-rich type "hydrothermal" synthetic ruby

## UV-VIS-NIR SPECTRAL CHARACTERISTICS

The polarized spectral characteristics through the ultraviolet, visible and near-infrared regions, were recorded on a Perkin-Einer Lambda 9 spectrophotometer. The resulting spectra showed features which have been recorded for certain natural rubies containing relatively high amounts of chromium and iron (see section on chemical analysis).

The "hydrothermal" synthetic ruby which possessed comparatively higher amounts of iron (4300 ppm), displayed spectral characteristics which have been observed more commonly in natural rubies originating from Thailand than other world deposits. These features consist of no detectable absorption minimum in the UV region and a shift of the absorption minimum in the blue to green-blue region of the visible spectrum to 480 and 485 nm (Fig. 13a). The two "hydrothermal" synthetic rubies possessing comparatively lower amounts of iron (1680 and 1910 ppm respectively, table 2), displayed spectral characteristics which were slightly different. There is an absorption minimum shift observed in the visible as well, but in contrast, these samples showed UV absorption characteristics which are unlike those reported for rubies originating from Thailand, including the shape and location of the absorption minimum (Bosshard, 1982). Also present were a series of peaks located between 330 and 345 nm. These peaks have been seen in natural rubies from various localities, but they have not been reported before as occurring with the prominence observed here (Fig. 13b). The special characteristics of these samples is unlike those recorded for other types of synthetic rubies.

## CHEMICAL ANALYSIS

A chemical analysis by means of energy dispersive x-ray fluorescence (ED-XRA), was performed with a SPECTRAC TN5000. Using a special measuring routine of Prof. W. Stern (Institute of Mineralogy and Petrography, University of Basel) including low, medium and high x-ray energies, a special colimator designed for x-ray focusing, standards including corundum, rutile and hematite as well as a fundamental parameter correction computer program. The resulting trace element concentrations are provided in percentages after the recorded data is adjusted and normalized, equating a standard of 100% total element concentration.

The chemical compositons of the "hydrothermal" synthetic rubies are shown in table 2. The samples contained mainly alumina without additional light

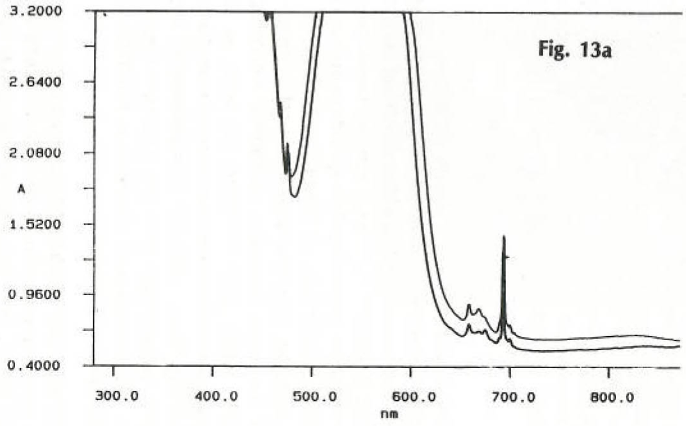
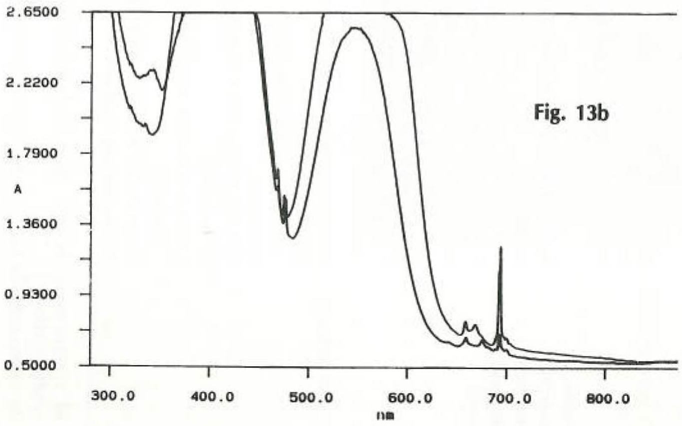


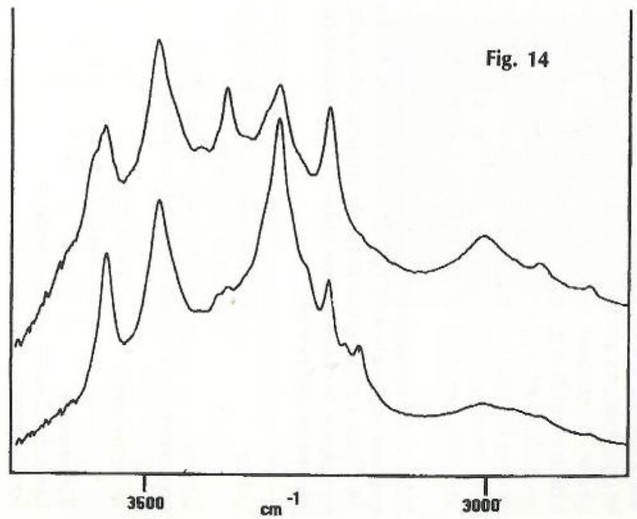

*Fig.13. The absorption spectra of the "hydrothermal" synthetic rubies were measured through the UV to NIR ranges. The spectras were recorded in polarized light for the ordinary ray (upper curve) and extraordinary ray (lower curve).*

*(a) The spectra recorded for the "hydrothermal" synthetic ruby richest in Fe (1.69 ct), showed similar absorption characteristics to natural rubies originating from Thailand (due to the similar chromium and iron concentrations; see text). Note the total absorbence in the UV region and the absorbence characteristics in the visible region around 480 to 485 nm.*

*(b) The spectra recorded for the "hydrothermal" synthetic ruby containing lower concentrations of Fe (0.82 ct), showed similar absorption characteristics in the visible range to natural rubies from Thailand, but dissimilarities were noted in the ultraviolet region, including a series of prominent peaks located between 330 and 345 nm.*

*Fig.14. Infrared spectrum of two "hydrothermal" synthetic rubies recorded in absorbence from 2800 to 3700 cm$^{-1}$ (0.89 ct and 1.89 ct). Note presence of sharp absorption peaks and variable intensities probably due to sample orientation. (Analysis by G. Bosshart)*



| | R0.62 | R0.69 | R1.69 | |
|---|---|---|---|---|
| $Al_2O_3$ | 99.5 | 98.8 | 98.8 | |
| $P_2O_5$ | 0.000 | 0.000 | 0.000 | bd |
| MgO | 0.000 | 0.000 | 0.000 | bd |
| $SiO_2$ | 0.000 | 0.000 | 0.000 | bd |
| CaO | 0.006 | 0.004 | 0.002 | bd |
| $K_2O$ | 0.010 | 0.008 | 0.007 | bd |
| $Cr_2O_3$ | 0.191 | 0.893 | 0.703 | |
| $Fe_2O_3$ | 0.137 | 0.166 | 0.430 | |
| MnO | 0.023 | 0.066 | 0.039 | |
| $TiO_2$ | 0.011 | 0.005 | 0.028 | |
| CuO | *0.084 | *0.005 | *0.008 | |
| NiO | 0.009 | 0.007 | 0.018 | |
| $V_2O_5$ | 0.001 | 0.004 | 0.002 | bd |
| $Ga_2O_3$ | 0.000 | 0.000 | 0.001 | bd |

* = due to metallic inclusions

bd = below or at detection limit

***Table 2. Chemical Analysis by ED-XFA of "hydrothermal" synthetic rubies claimed to be produced in Novosibirsk (expressed in oxide-weight percent, analytical details see text). Note absence or irrelevant concentrations of $V_2O_5$ and $Ga_2O_3$ as typical for synthetic rubies. Analysis by University of Basel, IMP, Geochemical Laboratory, Basel, Switzerland).***

elements in detectable or relevant concentrations. Trace elements of chromium (Cr), iron (Fe), titanium (Ti), copper (Cu) and nickel (Ni) were detected, with zero to extremely minor concentrations of vanadium (V) and gallium (Ga). The Cu-concentrations are the result of the contributions by the metallic inclusions, which is possibly true for the Ni and Ti as well.

Compared to natural rubies (Tang et al, 1988)[4] the concentrations of Cr are within the normal values. In most of the natural rubies, however, Ga and V are present in much higher concentrations. This is also true for Thai rubies which contain the lowest V and Ga concentrations among the natural rubies. The Fe concentrations are within the range observed for Fe-rich rubies originating from magmatic deposits such as Thailand or Cambodia but they are much higher than in most of the other world deposits of natural rubies.

In comparison to the chemical composition of other synthetic rubies the low V concentrations (Tang et al, 1989[5], Muhlmeister, 1991[6]) and Ga concentrations (Hanni and Stern, 1982[7]) are typical of many different types of synthetic rubies. The Fe concentrations, however, are much higher than in any of the other synthetic rubies observed to date. No concentrations of Pb, Mo, Bi, W, Pt were detected as are occasionally found in flux grown synthetic rubies due to the presence of flux or metal inclusions.

## INFRARED SPECTROSCOPY

Infrared analysis was applied by using FTIR PU 9600. The samples were measured in reflection mode using a diffusing reflection unit. In comparison to the normal infrared spectrum of corundum in the area between 800 to 400 wavenumbers, additional sharp lines occurred between 3000 and 3800 with the strongest peaks located at 3238, 3310, 3389, 3498 and 3575 $cm^{-1}$ (see Fig. 14). The intensities of the absorption peaks were variable in the three samples probably as a result of orientation effects. These lines occurred independently of the presence or lack of fingerprint inclusions. Very sharp absorption peaks whose strength seem to be dependent on the orientation of the samples in the infrared spectrum around 3500 are most likely due to hydroxyl-anions present in the corundum.

## DISCUSSION OF POSSIBLE GROWTH METHOD

A hydrothermal growth process for synthetic ruby was patented by Bell Telephone Laboratories, U.S. Patent 2,979,413;1961 (see Yaverbaum, 1980)[8]. In this process the following main components are described: A furnace and an autoclave consisting of a bomb tube with one or two internal liners. The inner liner can be divided by a baffle to separate it into two chambers. One chamber (the growing chamber) may contain a seed crystal cut perpendicular to the c-axis. The other chamber (nutrition chamber) contains solid nutrients as either aluminium oxide, aluminium hydroxide or even crystalline corundum. Aqueous solutions with dissolved sodium carbonate are described as being the most effective transporting media for dissolved alumina. The furnace produces the necessary heat and heat gradients between the two chambers in order to create a convection current for the transportation of dissolved alumina to the crystal seed located in the lower temperature chamber. Critical parameters for the growth of hydrothermal rubies include the nature of the nutrient, the crystallographic orientation of the seed, the composition of the aqueous solutions, the temperature gradients, the absolute maximum temperatures and pressures reached in the autoclave as well as other technical details such as the permeability of the baffle. The chemical composition of those parts exposed to the aggressive solutions is a critical factor as well. It may be necessary to cover them with noble metals such as silver, platinum or gold. Because the nutrient solutions are corrosive to iron, plating the interiors may be preferred if iron contamination of the growing crystal is to be minimized. Hydrothermal rubies have also been produced experimentally by Carroll Chatham, consisting of a thin overgrowth on natural seeds (Gubelin, 1961)[1].

The internal features and inclusions present in these "hydrothermal" rubies reflected the formation conditions and materials used in the production process. Assuming the production techniques for the hydrothermal rubies in Novosibirsk is a modification of those described previously, certain theories can be applied to account for the observed internal features for the samples tested here. The habit formations of all synthetic rubies are heavily influenced by the formation conditions, the presence of trace elements can also have an influence. The homogeneous metal inclusions consisting of copper, nickel, iron and titanium can be present for a variety of reasons, relating to the dissolution of those portions of the autoclave exposed to corrosive solutions, to impurities in the nutrients or playing a role in the complexing and precipitation processes during hydrothermal ruby growth; copper wires may be used to fix seeds in the autoclave. The use of metal alloys involving noble metals as well as Cu and Ni or the use of steel containing Ni is also possible. The presence of iodine and sulphur in one type of the metal inclusions, points to the use of iodine and sulphur for complexing agents, most likely involving others as well, to transport metals. These can easily be responsible for very corrosive conditions (metal-iodine complexes or metal-sulphur complexes) under elevated temperatures and pressures. The high Fe-concentration present in the synthetic rubies may be produced intentionally or as a result of corrosion occurring to the exposed portions of the autoclave. The effect of such additional trace elements on the habit of the growing crystals and whether they are added to the hydrothermal solutions for the purpose of habit variation and/or appearance modification, is unknown. In one of the synthetic rubies described here the comparatively higher Fe-concentrations resulted in a much darker appearing stone. This elevated concentration could have been intentional or a result of undesired corrosion adding iron to the growing crystal.

No remnants of seed crystals were identified, however, the use of seed crystals seems more likely than spontaneous nucleation as the method of crystal growth. This is evidenced by the presence of dominated crystal growth parallel to the basal plane and the absence of twinning characteristics. As rough crystals become available, a more detailed analysis will be necessary to settle these questions.

## CONCLUSIONS

The synthetic rubies described in this report, were represented as a new hydrothermal production of synthetic ruby coming from Novosibirsk. The properties and characteristics (including the infrared characteristics) observed do not seem to contradict this claim, however, this information still needs to be verified. Speculation on the growth environment surrounding these synthetic rubies during their formation was possible assuming the methods used do not drastically differ from those utilized for earlier production of hydrothermal synthetic ruby. Further studies of fluid inclusion compositions by means of Raman spectroscopy will provide insightful information concerning the hydrothermal nature of the synthetics. Additonal information can also be collected from a detailed study of the rough crystals, including the potential use of seeds, as soon as they become available.

Even though these synthetic rubies represent a completely new type of synthetic which can be encountered in the market today, their identification should not prove to be difficult. Their overall appearance is characterized by a "sleepiness" as a result of a slightly reduced transparency, however, this is a feature which has been observed in some natural rubies exposed to high temperature heat-treatment. The most striking characteristic found was the presence of strong irregular growth features. They are readily observed using a microscope or 10x loupe and consist of striated and heavily "roiled" graining patterns. These patterns are unlike any of the "swirled" or planar growth characteristics observed in natural rubies from various localites or the different types of flame fusion and flux grown synthetic rubies from various manufacturers. The presence of highly reflective "golden" metallic inclusions can also be considered quite distinctive, however, these inclusions could possibly be misinterpreted as naturally occurring sulphides such as pyrite, chalcopyrite and pyrrotite which are occasionally found in natural rubies from various localities including Burma, Vietnam, Afghanistan and certain areas in East Africa. In cases where the inclusion features do not provide sufficient proof of the natural or synthetic origin for a ruby in question, high-tech instrumentation such as x-ray fluorescence, infrared and electron microscope analysis can identify the chemical composition of the ruby as well as inclusions, providing a conclusive means of separation.

## ACKNOWLEDGEMENTS

We would like to thank R. Wessiken and P. Wagli for electron microscope analysis, Mr. G. Bosshart for infra-red analysis and Prof. W. Stern for X-ray fluorescence analysis. These new synthetic rubies were brought to the attention of one of the authors by Mr. T. Tumey from Thai Gem Exchange to whom we wish to express our thanks.

## UPDATE

**Dr Peretti has advised (mid-February) from Bangkok that he has obtained samples of rough, and that seed crystals have been used. Details will appear in a further article in due course.**

**Ed.**