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*Synthetic emerald crystal. Courtesy of D. Fursenko*

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# A new type of Tairus hydrothermally-grown synthetic emerald, coloured by vanadium and copper

Dr Karl Schmetzer<sup>1</sup>, Dr Dietmar Schwarz<sup>2</sup>,  
Dr Heinz-Jürgen Bernhardt<sup>3</sup> and Dr Tobias Häger<sup>4</sup>

1. Taubenweg 16, D-85238 Petershausen, Germany

2. Gübelin Gem Lab, Maihofstr. 102, CH-6006 Lucerne, Switzerland

3. Central Microprobe Facility, Ruhr-University, D-44780 Bochum, Germany

4. Institute of Gemstone Research, University of Mainz, D-55099 Mainz, Germany

**Abstract:** *Gemmological, chemical and spectroscopic properties of a new type of hydrothermally-grown synthetic emerald produced commercially by the Tairus company in Novosibirsk, Russia, are described. The results of chemical and spectroscopic examination in the UV-Vis range indicate that the samples are coloured by a combination of vanadium and copper; chromium contents are negligible. Infrared spectra show the presence of different types of water molecules and/or hydroxyl ions. Two major types of isomorphic replacement are present, octahedral substitution of aluminium by vanadium and tetrahedral substitution of silicon by aluminium with charge compensation by lithium on channel sites. Distinction of this new type of synthetic emerald from natural emerald can be made on the basis of distinct growth features visible through the microscope, and chemical and/or spectroscopic features may also be helpful.*

**Keywords:** *content of Cr, Cu, V; gemmological properties; IR spectra; synthetic emerald; Tairus; UV-Vis spectra*

## Introduction

Since 1989, the year of its foundation, the Tairus company has become one of the world's largest producers of synthetic gem materials, mainly differently coloured varieties of the corundum and beryl families. Tairus is a Joint Venture between the Russian Academy of Sciences (Siberian Branch) of Novosibirsk and Tairus (Thailand) Co. Ltd of Bangkok.

In the past, a number of different types of synthetic emerald have been grown hydrothermally by Tairus. Emeralds coloured by a combination of chromium, iron, nickel and copper were produced by Tairus and elsewhere in Russia (see Granadchikova *et al.*, 1983; Schmetzer, 1988) in steel autoclaves without noble metal liners, and synthetic emeralds

coloured mainly by chromium were grown in autoclaves with noble metal insets or with teflon coating. A product which was marketed as 'internally clean' synthetic emerald was grown using specially oriented seed crystals (Koivula *et al.*, 1996; Schmetzer, 1996). With this special orientation of the seed, the Russian researchers tried to avoid the formation of easily detectable growth features.

In 2001, the Tairus company purchased Biron's growth technology (intellectual know-how and technical equipment) from Australia which was developed to produce synthetic emeralds whose colour is due to almost equal amounts of chromium and vanadium – in an attempt to resemble Colombian emeralds as closely as possible. After an intermediate production period in Thailand 2002, Biron type synthetic emerald is now produced by Tairus in Russia (W. Barshai, *pers. comm.* 2004).



**Figure 1:** Faceted samples of the new type of Tairus hydrothermally-grown synthetic emerald coloured by vanadium and copper; samples from 0.91 ct (centre, 5.0 × 7.0 mm) to 1.17 ct (right, 6.1 × 8.1 mm). Photo by M. Glas.

In 2004, a new type of synthetic emerald (Figure 1) was introduced by Tairus to the international market as 'Colombian Color Emerald'. The new development in synthetic emerald growth is attributed to Dr Dimitry Fursenko and his team, who worked on this project since 1999 and which culminated in September 2004 when the first rough crystals were cut (see <http://www.tairus.com/>). It is the purpose of the present paper to characterise this new type of hydrothermally-grown variety of synthetic beryl.

## Crystal growth

The following section was produced using the information given and the photos submitted by the Russian scientists involved in the production of the new type of synthetic emerald in the laboratories of Tairus in Novosibirsk. Fursenko and his team are pictured in Figure 2a, and all research and development as well as commercial production is performed in the Tairus building in Novosibirsk (Figure 2b).



**Figure 2a:** The technology for the growth of the new type of synthetic emerald has been developed by Dr. Dimitry Fursenko (centre) and his team, Dr. Victor Thomas (right) and Ivan Fursenko (left). Courtesy of D. Fursenko.

**Figure 2b:** The commercial production as well as the scientific research is performed in the Tairus building in Novosibirsk, Russia. Courtesy of D. Fursenko.



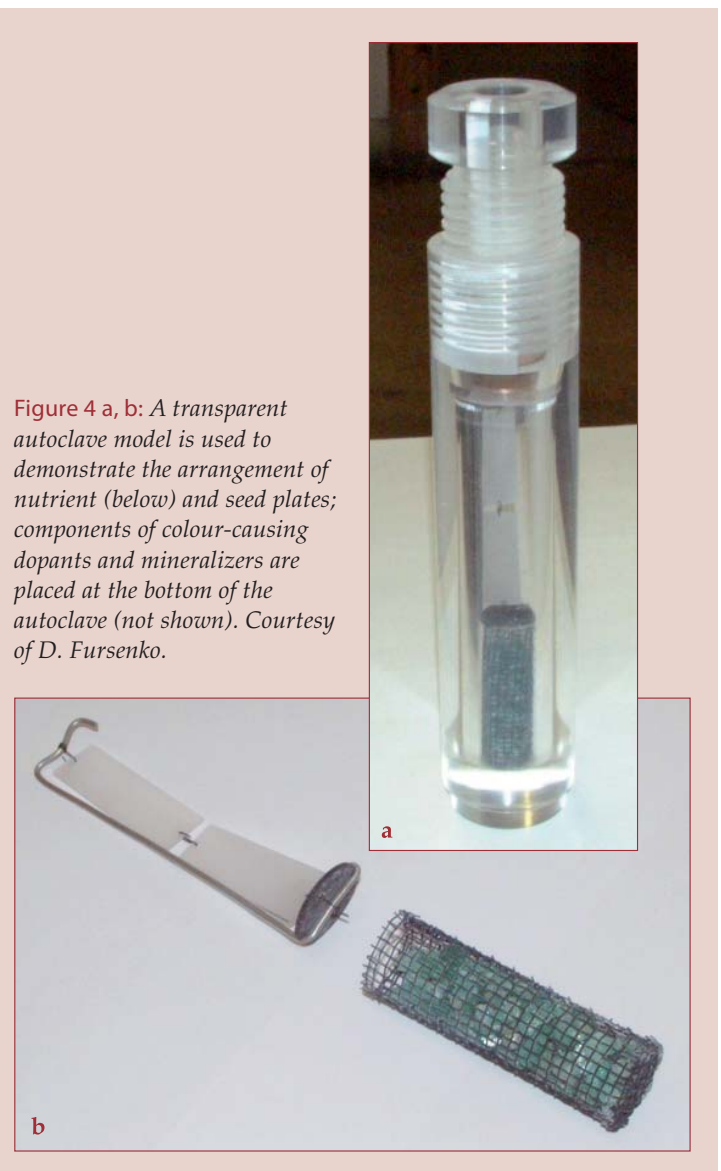


**Figure 3 a, b:** The commercial production of the new type of Tairus synthetic emerald is performed in steel autoclaves with noble metal lining; height of the autoclaves about 50 cm, external diameter about 9 cm. Courtesy of D. Fursenko.

Commercial growth is performed in steel autoclaves (Figure 3 a, b) with a working chamber of 250 to 300 ml. A transparent model for demonstration (Figure 4a) shows the arrangement of seed plates and nutrient (Figure 4b). Colourless or very pale green natural beryl from the Ural mountains (cracked and purified) is used as the initial charge for crystal growth. The beryl nutrient, colour-causing dopants and components of the mineraliser (not shown) are placed into the lower part of the working chamber. Typical sizes of seed plates located in the upper part of the autoclave are 80 × 18 mm. Crystals are grown at a temperature near 600 °C and a pressure near 1.5 kbar. The temperature gradient in the autoclave is in the range of 50 to 100 °C. With these growth parameters, a growth rate of 0.3 mm per day is obtained. Typically, a synthetic emerald crystal (Figure 5) measures 80 × 18 × 14 mm, indicating a growth period of about 20 days.

## Materials and methods

For this study, we examined ten hydrothermally-grown synthetic emeralds of the new type (Figure 6), which were purchased by one of the authors (DS) at Tairus, Bangkok, in 2004. They comprised four faceted stones (0.91 to 1.64 ct) and six platy rough crystals (2.86 to 10.70 ct). The rough crystals (thickness between 4 and 5 mm) had been sawn by the producer along the boundary of the seed and the grown emerald, in this way removing all residual parts of the seed plate. We were informed that our samples represent the commercial production after the final development of the growth technique.



**Figure 4 a, b:** A transparent autoclave model is used to demonstrate the arrangement of nutrient (below) and seed plates; components of colour-causing dopants and mineralizers are placed at the bottom of the autoclave (not shown). Courtesy of D. Fursenko.



**Figure 5:** A typical synthetic emerald crystal measures about  $80 \times 18 \times 14$  mm. Courtesy of D. Fursenko.



**Figure 6:** Faceted and rough samples of the new type of Tairus hydrothermally-grown synthetic emerald coloured by vanadium and copper; rough crystal plate of 3.23 ct ( $12.7 \times 6.6$  mm), faceted stone of 1.16 ct ( $6.1 \times 8.1$  mm). Photo by M. Glas.

Standard gemmological methods were used to determine refractive indices (RI), optical character, specific gravity (SG) and fluorescence under long- and short-wave ultraviolet (UV) radiation. Standard microscopic techniques were used to examine the internal features under different lighting conditions, both with and without immersion liquids. The orientation of growth planes and colour zoning was performed with a horizontal (immersion) microscope with a specially designed sample holder and specially designed eye pieces (to measure angles).

For chemical characterisation, we first submitted all ten samples for qualitative energy-dispersive X-ray fluorescence (EDXRF) analysis using a Tracor Northern Spectrace 5000 system. Quantitative chemical data for the four faceted samples were determined by electron microprobe using a Cameca Camebax SX 50 instrument. Traverses with 10 point analyses each were performed across

the table facets of the four faceted gemstones. To obtain quantitative data for water and light elements (lithium and beryllium), slices were cut from two rough crystal plates and the powder obtained from these slices was used for wet chemical analyses. Lithium and beryllium contents were determined by atomic absorption spectroscopy (AAS), and the water content of the sample was analysed by Karl-Fischer titration.

Polarized UV-Vis absorption spectra (280 to 800 nm) from all ten samples were recorded with a Perkin Elmer Lambda 19 spectrophotometer. For the two samples for which the best orientation was obtainable (according to the determination of the optic axis by an immersion microscope combined with the results of UV-Vis spectroscopy), we also measured polarized absorption spectra in the near infrared (800 to 2500 nm;  $12500$  to  $4000$   $\text{cm}^{-1}$ ) with the Perkin-Elmer Lambda 19. Infrared spectroscopy in the mid-infrared range ( $4000$  to  $400$   $\text{cm}^{-1}$ ) was performed using two different methods. For an overview of the complete range, a limited amount of powder was scraped from two rough samples for the preparation of KBr pressed pellets. For the measurement of polarized spectra in the mid-infrared, thin slices were sawn from two rough crystal plates with appropriate orientation (determined from immersion microscopy). These thin slices were polished to a thickness of about 0.3 mm to enable polarized measurement in the  $4000$  to  $2000$   $\text{cm}^{-1}$  range (below  $2000$   $\text{cm}^{-1}$  the thickness of these slices did not allow any reliable measurements). Both types of mid-infrared spectra were recorded using a Perkin Elmer FT-IR 1725X infrared spectrometer.

Solid particles on the rough surfaces of two synthetic-emerald crystals were analysed using an electron microprobe. For the identification of similar-appearing inclusions in one rough sample, this crystal was cut and polished in several steps until one of these inclusions was sufficiently exposed at the surface to enable an examination by electron microprobe and optical microscopy.

## Results

### Visual appearance and gemmological properties

All rough crystals had uneven, undulating surfaces parallel to the sawn plane (Figure 7), i.e. parallel to the original surface of the seed. This step-like surface consists of numerous faces of polycentrically growing synthetic emerald subindividuals. When examined with the unaided eye, all samples showed an intense, homogeneous, slightly bluish green colouration without any prominent colour zoning. The variation of colour within our ten samples was limited, indicating that these products came from an established production line.

Standard gemmological properties (Table I) show only small variation, and overlap those of natural emeralds from various localities, especially those of low alkali-bearing stones from Colombia. They are in the range commonly observed also for low iron-bearing or iron-free hydrothermally-grown synthetic emeralds.



**Figure 7:** Rough crystal plate of 7.52 ct the new type of Tairus hydrothermally-grown synthetic emerald coloured by vanadium and copper showing an uneven, undulating surface formed by numerous faces of subindividuals of synthetic emerald; size of plate about 16.5 × 7.5 mm, weight 7.52 ct. Photo by M. Glas.

The results of microprobe analyses of four faceted samples are presented in Table II. In addition to the major components of beryl,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , there are distinct amounts of vanadium and smaller percentages of chromium and copper. Traces of other transition metals and alkali elements are also present, while caesium, chlorine and fluorine were below the detection limit of the electron microprobe. Only a small variation within the three colour-causing trace elements, vanadium, chromium, and copper, was detected on traverses across the table facets of the cut synthetic emeralds (Table III).

Wet chemical analyses of powdered material from two samples showed the presence of distinct amounts of water and minor amounts of lithium (Table II). The values of  $\text{Li}_2\text{O}$ ,  $\text{BeO}$  and  $\text{H}_2\text{O}$  did not show significant variation between the duplicate samples, so average values were used for the calculation of cation proportions and the crystal chemical formula, based on 36 oxygens, according to the general formula  $\text{Be}_6\text{Al}_4\text{Si}_{12}\text{O}_{36}$  (see Deer *et al.*, 1986).

Isomorphic replacement of Be, Al, and Si in the beryl structure has been discussed in numerous papers, and summaries are given by Shatskiy *et al.* (1981), Aurisicchio *et al.* (1988), Lebedev *et al.* (1988), and Sherriff *et al.* (1991). According to these authors, beryls are subdivided into two groups, one with predominant octahedral aluminium substitution and the other with predominant tetrahedral beryllium substitution.

**Table I.** Gemmological properties of V-Cu-bearing Tairus synthetic emeralds

Colour	Homogeneous, very slightly bluish green
Pleochroism	Parallel c: bluish green Perpendicular c: yellowish green
RI	$n_o$ 1.576 – 1.578 $n_e$ 1.570 – 1.571
Birefringence	0.006 – 0.007
SG	2.68 – 2.69
UV fluorescence	Short wave: inert Long wave: inert

### Chemical composition and formula

The results of qualitative X-ray fluorescence analysis indicate that there are no major differences between rough crystal plates and faceted synthetic emeralds.

Table II: Chemical composition of V-Cu-bearing Tairus synthetic emeralds

Microprobe analyses (average of 10 points on each emerald)				
Wt.%	A	B	C	D
SiO <sub>2</sub>	64.91	64.62	63.81	64.45
TiO <sub>2</sub>	0.01	0.01	0.01	0.01
Al <sub>2</sub> O <sub>3</sub>	18.22	18.03	18.11	18.30
V <sub>2</sub> O <sub>3</sub>	1.14	1.33	1.34	1.36
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.04	0.04	0.04
Fe <sub>2</sub> O <sub>3</sub> *	0.01	0.03	0.01	0.01
MnO	0.01	0.01	0.01	0.02
NiO	0.01	0.02	0.01	0.01
MgO	0.01	0.01	0.01	0.01
CuO	0.13	0.10	0.09	0.12
Na <sub>2</sub> O	0.02	0.02	0.03	0.02
K <sub>2</sub> O	0.01	0.02	0.02	0.02
Cs <sub>2</sub> O	bdl	bdl	bdl	bdl
F	bdl	bdl	bdl	bdl
Cl	bdl	bdl	bdl	bdl
Wet chemical analyses (average of two powder samples)				
Li <sub>2</sub> O	0.26	0.26	0.26	0.26
BeO	13.50	13.50	13.50	13.50
H <sub>2</sub> O	1.48	1.48	1.48	1.48
Sum microprobe and wet chemical analyses	99.74	99.49	98.74	99.60

\*Total iron as Fe<sub>2</sub>O<sub>3</sub>, bdl = below detection limit

Number of ions based on 36 oxygens (excluding H <sub>2</sub> O)				
Specimen	A	B	C	D
Si	11.888	11.875	11.816	11.834
Ti	0.002	0.002	0.002	0.001
Al	3.932	3.905	3.952	3.960
V	0.167	0.196	0.200	0.201
Cr	0.004	0.007	0.006	0.006
Fe	0.002	0.004	0.002	0.002
Mn	0.002	0.003	0.002	0.003
Ni	0.002	0.003	0.001	0.001
Mg	0.002	0.002	0.003	0.002
Sum Al octahedron	4.113	4.122	4.168	4.176
Cu	0.017	0.014	0.013	0.016
Be	5.941	5.960	6.006	5.955
Sum Be tetrahedron	5.956	5.974	6.019	5.971
Li	0.190	0.191	0.192	0.191
Na	0.005	0.008	0.009	0.007
K	0.003	0.005	0.005	0.005
Sum alkalis	0.198	0.204	0.206	0.203
H <sub>2</sub> O	0.901	0.904	0.911	0.903

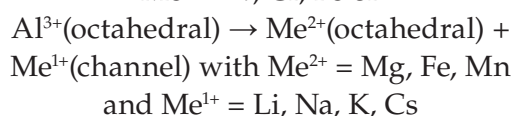
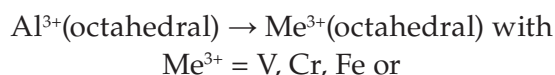
Average formula: (Be<sub>5.96</sub>Cu<sub>0.02</sub>Li<sub>0.02</sub>)<sup>tet</sup>(Al<sub>3.79</sub>V<sub>0.21</sub>)<sup>oct</sup>(Si<sub>11.85</sub>Al<sub>0.15</sub>)<sub>12</sub><sup>tet</sup>O<sub>36</sub>(Li<sub>0.18</sub>H<sub>2</sub>O<sub>0.91</sub>)<sup>channel</sup>



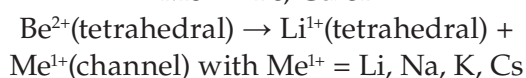
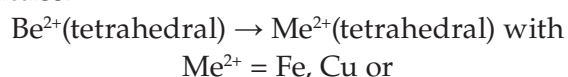
Table III: Chemical variation of colour-causing trace elements in V-Cu-bearing Tairus synthetic emeralds

Microprobe analyses (ranges of 10 point analyses each, data in wt.%)				
Specimen	A	B	C	D
V <sub>2</sub> O <sub>3</sub>	1.09 - 1.21	1.24 - 1.41	1.30 - 1.40	1.30 - 1.43
Cr <sub>2</sub> O <sub>3</sub>	0.01 - 0.05	0.02 - 0.08	0.02 - 0.06	0.02 - 0.07
CuO	0.09 - 0.17	0.07 - 0.014	0.06 - 0.14	0.07 - 0.15

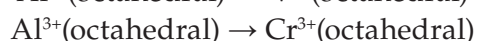
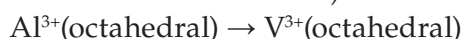
In octahedral sites in beryl, aluminium can be replaced by trivalent transition metals such as chromium, vanadium, and iron. Heterovalent isomorphic substitution is characterised by replacement of aluminium by divalent transition metals such as iron, manganese or by magnesium. For charge balance, alkalis enter channel sites of the beryl lattice and these substitutions can be summarised as follows:



In tetrahedral sites, beryllium can be replaced by divalent transition metals such as iron or copper. Heterovalent isomorphic substitution is characterised by replacement of beryllium by lithium. For charge balance, alkalis enter channel sites of the beryl lattice:

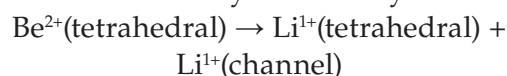


In the new type of Tairus synthetic emeralds, the major colour-causing trace elements are vanadium, chromium and copper, replacing aluminium on octahedral and beryllium on tetrahedral sites according to the following scheme (see spectroscopic properties and cause of colour):

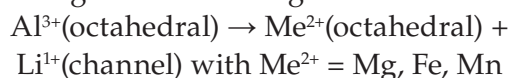


The results of chemical analyses show also a limited heterovalent isomorphic replacement of beryllium by lithium, because the sum of Be + Cu (sum Be tetrahedron

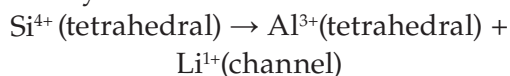
in Table II) is slightly smaller than the theoretical value of 6 apfu (atoms per formula unit). For charge balance, lithium also enters channel sites of the synthetic beryls:



In addition, the traces of bivalent magnesium, iron or manganese on aluminium sites need charge compensation according to the following scheme:



The analyses of the Tairus synthetic emeralds also show a small but distinct silicon deficiency (Si apfu smaller than 12) and some excess aluminium (sum Al octahedron in Table II larger than 4 apfu). An isomorphic replacement of Al and Si has been discussed in several papers (see, for example, Shatskiy *et al.*, 1981; Schmetzer and Bernhardt, 1994). Considering the different possibilities discussed and the necessity of charge balance, the following coupled isomorphic replacement scheme is consistent with analytical data:

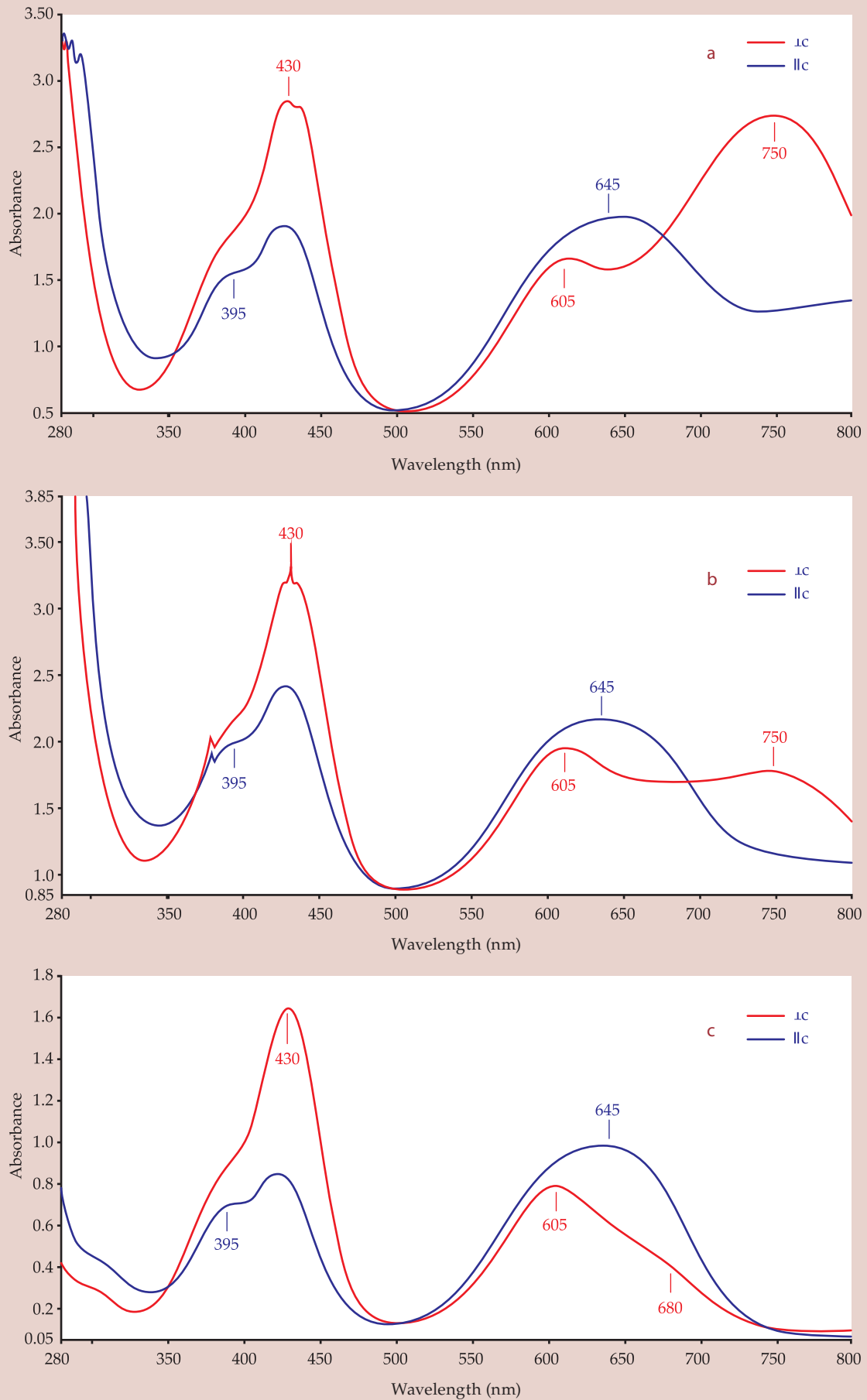


Lithium has a complex function:

- a) it replaces beryllium in tetrahedral sites and
- b) it enters channel sites as charge compensator
  - b1) for bivalent magnesium, iron or manganese on aluminium sites,
  - b2) for lithium on beryllium sites and
  - b3) for aluminium on silicon sites, which is the major fraction of the three.

The amount of lithium determined experimentally is in good agreement with this complex function.





**Figure 8:** Polarized absorption spectra of two samples of the new type of Tairus hydrothermally-grown synthetic emerald coloured by vanadium and copper (a,b) compared with the spectra of a vanadium-bearing hydrothermally-grown Biron synthetic emerald (c).

**Table IV:** Spectral features related to transition metals in Tairus synthetic emerald

Absorption maximum (nm)	Polarisation E	Assignment
1180	⊥c	Cu <sup>2+</sup> on tetrahedral Be <sup>2+</sup> sites
920	∥c	
750	⊥c	
680 sh	⊥c *	Vanadium (?)
645	∥c	V <sup>3+</sup> on octahedral Al <sup>3+</sup> sites
605	⊥c	
430	⊥c > ∥c	
395	∥c > ⊥c	

sh = shoulder

\* hidden by the Cu<sup>2+</sup> band at 750 nm

As a result, the average crystal chemical formula for the four samples is calculated as given in Table II. The dominant isomorphous substitution in our Tairus synthetic emeralds is a replacement of aluminium by vanadium on octahedral sites. A heterovalent substitution of silicon by aluminium on tetrahedral sites with charge compensation by lithium on channel sites is also present.

### Spectroscopic features of transition metals in beryl and cause of colour

Absorption spectra of samples of the new type of Tairus synthetic emerald (Figure 8 a,b) show numerous broad absorption bands in the UV-Vis-NIR range (Table IV). For an assignment of these absorption maxima, we have to consider the results of chemical analyses which indicate that the only significant colour-causing transition metals are vanadium and copper.

The position of absorption maxima at 1180, 920 and 750 nm is consistent with the spectra of copper-bearing hydrothermally-grown synthetic beryls (Solntsev *et al.*, 1976; Solntsev, 1981 a,b; Lebedev *et al.*, 1983, 1986; Rodionov *et al.*, 1987) and, consequently, these three broad absorption bands are assigned to Cu<sup>2+</sup> on tetrahedral beryllium sites.

Absorption spectra of natural vanadium- and iron-bearing beryls from Brazil and Kenya (Wood and Nassau, 1968;

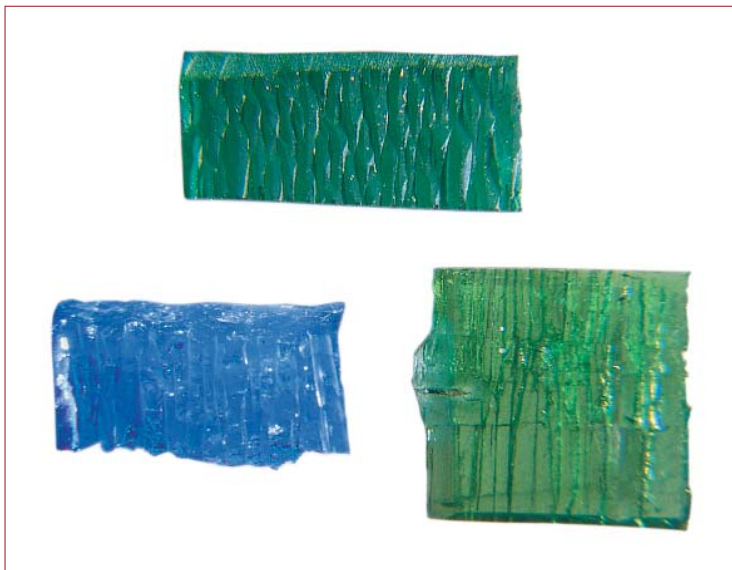
Schmetzer, 1978, 1982) are similar, but not completely identical to absorption spectra of hydrothermally-grown synthetic vanadium- and iron-bearing or to synthetic vanadium-bearing, iron-free beryls (Beckwith and Troup, 1973; Solntsev, 1981 a,b; Lebedev *et al.*, 1983, 1986). The differences in the 350 to 450 nm range are partly understandable by an overlap of the absorption bands due to vanadium and those due to iron, mostly in natural samples. Differences in the 600 to 700 nm range, on the other hand, are not completely understood at present.

If we focus only on the vanadium-related absorption bands of the spectra of the new type of Tairus synthetic emerald, these are identical with the spectra of vanadium-doped beryl crystals grown through gas-transport reactions (Rodionov *et al.*, 1987) as well as with the spectra of a vanadium-bearing, chromium- and iron-free sample grown by the Biron company in Australia for research purposes (Figure 8c; note: samples of the commercial production of Biron normally contained similar amounts of both, chromium and vanadium, see, for example, analyses by Mashkovtsev and Smirnov, 2004).

Comparing the pure vanadium spectrum of the Biron sample, it is evident that our spectra of the Tairus synthetic emerald samples are due to a superimposition of a 'pure' vanadium and a 'pure' copper spectrum. Thus, the absorption bands at 645, 605, 430 and 395 nm (Table IV) are assigned to V<sup>3+</sup> on octahedral aluminium sites. The assignment of an additional shoulder at 680 nm (see Figure 8c), which is seen in the spectra of various natural and synthetic vanadium-bearing samples (Wood and Nassau, 1968; Beckwith and Troup, 1973; Schmetzer, 1978, 1982; Rodionov *et al.*, 1987) is rather uncertain. This shoulder might be due to vanadium cations which are not in the trivalent state.

Compared to vanadium, the relative amounts of chromium are small. Under these circumstances, the absorption bands of chromium are hidden by the much stronger absorption bands of vanadium (see Schmetzer, 1978, 1982; Schwarz and Schmetzer, 2002).

The bluish-green colour of the new Tairus samples is consistent with a combination of the yellowish-green colouration of a vanadium-bearing synthetic beryl sample and the blue colour of a copper-bearing hydrothermally-grown beryl (Figure 9). It is evident, that the colour of the pure vanadium-bearing yellowish-green sample is shifted to the desired bluish-green 'emerald' colour by the influence of the copper dopant of the synthetic beryl.



**Figure 9:** The slightly bluish green coloration of the new type of Tairus synthetic emerald (top, 7.52 ct, 16.5 × 7.5 mm) is caused by superimposition of the light blue colouration of a synthetic copper-bearing beryl (below left) and the yellowish-green colouration of a synthetic vanadium-bearing beryl (below right); the copper- and vanadium-doped samples are Russian research samples obtained by one of the authors in the early 1990s. Photo by M. Glas.

### Infrared spectroscopy

#### Mid-infrared range (from 4000 to 400 cm<sup>-1</sup>)

The spectra of the KBr pellets prepared with the emerald powder (Figure 10) show two absorption bands at 3697 and 3595 cm<sup>-1</sup>. These spectra are consistent with infrared powder spectra of chromium-, iron-, nickel- and copper-bearing Russian hydrothermally-grown synthetic emeralds as described by Schmetzer (1988; see also the references cited therein). This general type of spectrum is identical for both lithium- and sodium-bearing synthetic beryl crystals (Shatskiy *et*

*al.*, 1981; Vladimirova *et al.*, 1987).

In the mid-infrared the fundamental vibrations of molecules in the channels of the beryl structure as well as lattice vibrations are present. In our samples, no absorption bands related to chlorine (in the 2500 to 3100 cm<sup>-1</sup> range, Schmetzer *et al.*, 1997; Mashkovtsev and Solntsev, 2002; Mashkovtsev and Smirnov, 2004), to ammonium (in the 2500 to 3300 cm<sup>-1</sup> range, Mashkovtsev and Solntsev, 2002; Mashkovtsev and Smirnov, 2004; Mashkovtsev *et al.*, 2004) or to CO<sub>2</sub> (at 2360 cm<sup>-1</sup>, Wood and Nassau, 1967, 1968; Charoy *et al.*, 1996; Mashkovtsev and Smirnov, 2004) were observed.

Polarized spectra (Figure 11) show two strong absorption bands at 3695 and 3596 cm<sup>-1</sup> and one weaker band at 3505 cm<sup>-1</sup> (polarization parallel to *c*) as well as two doublets at 3684, 3675 cm<sup>-1</sup> and 3605, 3593 cm<sup>-1</sup>, a broad band at 3873 cm<sup>-1</sup> and two weak bands at 3558 and 3505 cm<sup>-1</sup> (polarization perpendicular to *c*). These spectra are identical with the spectra of chromium-, iron-, nickel- and copper-bearing Russian hydrothermally-grown synthetic emeralds grown for research purposes (Mashkovtsev and Lebedev, 1993) and with chromium-, iron-, nickel- and copper-bearing hydrothermally-grown synthetic emeralds of commercial Tairus production (Mashkovtsev and Solntsev, 2002; Mashkovtsev and Smirnov, 2004).

Using polarized infrared absorption spectra of alkali-bearing natural and alkali-free synthetic beryls and emeralds, two types of water molecules were characterized in channel sites of the beryl structure (Flanigen *et al.*, 1967; Wood and Nassau, 1967, 1968; Aines and Rossman, 1984). Type-I water molecules have their two-fold symmetry axis perpendicular to the *c*-axis of the beryl crystal and are not adjacent to alkali ions. Type-II water molecules have their two-fold symmetry axis parallel to the *c*-axis of the beryl crystal and are adjacent to alkali ions. Furthermore, comparing intensity ratios of the three main water absorption bands in the 3500 cm<sup>-1</sup> to 3800 cm<sup>-1</sup> range, it was concluded that one or more additional types of water

or hydroxyl group are present in beryl (Schmetzer, 1989; Schmetzer and Kiefert, 1990).

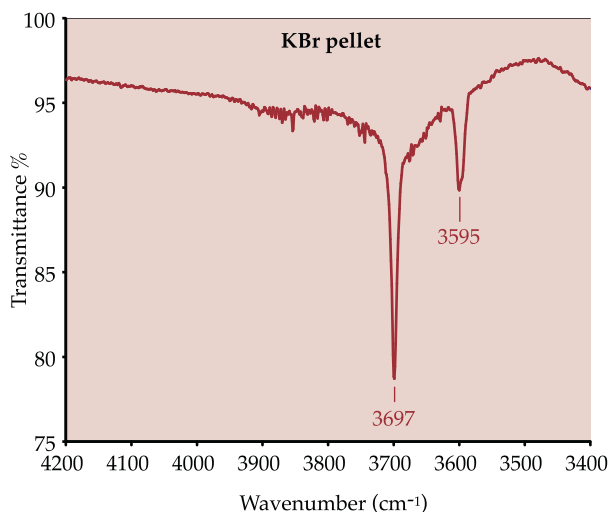
Subsequently, this general statement was confirmed by numerous researchers, but different assignments of various absorption bands in natural and synthetic alkali-bearing beryl and emerald samples have been given (Mashkovtsev and Lebedev, 1993; Aurisicchio *et al.*, 1994; Charoy *et al.*, 1996; Mathew *et al.*, 1997; Mashkovtsev and Solntsev, 2002; Mashkovtsev and Smirnov, 2004; Mashkovtsev *et al.*, 2004). In most cases, the doublets in the 3670 and in the 3600  $\text{cm}^{-1}$  range are considered as overlaps of two different types of water maxima or as overlaps of water and hydroxyl bands.

In summary, we can conclude that the mid-infrared spectra of the new type of lithium-bearing hydrothermally-grown Tairus synthetic emeralds are due to three different types of water molecules or to two different types of water molecules and hydroxyl ions. The spectra are identical with those of older hydrothermally-grown synthetic beryls and emeralds (research samples and early commercial production) as well as with the spectra of previously produced types of synthetic emeralds grown by Tairus in Novosibirsk.

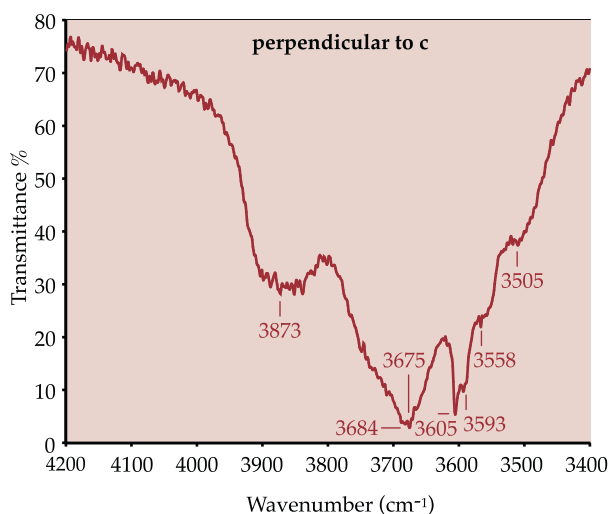
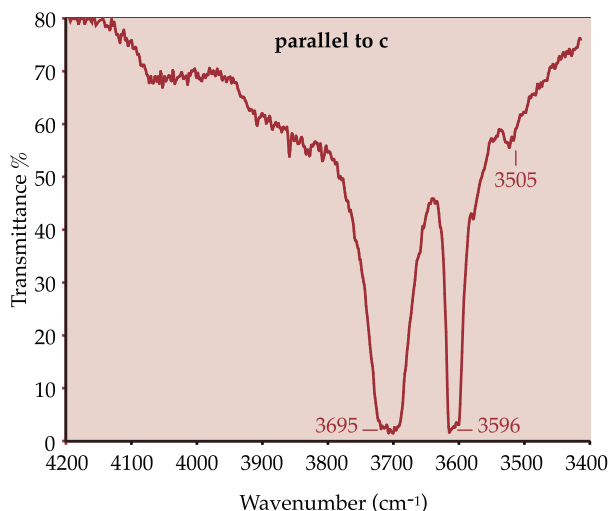
#### **Near-infrared range (from 800 to 2500 nm; i.e. from 12500 to 4000 $\text{cm}^{-1}$ )**

In the near-infrared numerous relatively broad to small absorption bands (Figure 12) are present in our samples. The two broad bands at 1180 and 920 nm have already been assigned to  $\text{Cu}^{2+}$  replacing  $\text{Be}^{2+}$  on tetrahedral lattice sites (see above).

In the spectrum with polarization E parallel *c* we observed absorption maxima at 1150, 1400, 1413, 1468, 1768, 1897, 2152 and 2460 nm; in the spectrum with E perpendicular to *c*, the absorption bands were found at 1366, 1410, 1420, 1430, 1835, 1898, 1961 and 2207 nm. Using the references cited above, all absorption bands are assigned to overtone and combination frequencies of both types of water and hydroxyl groups.

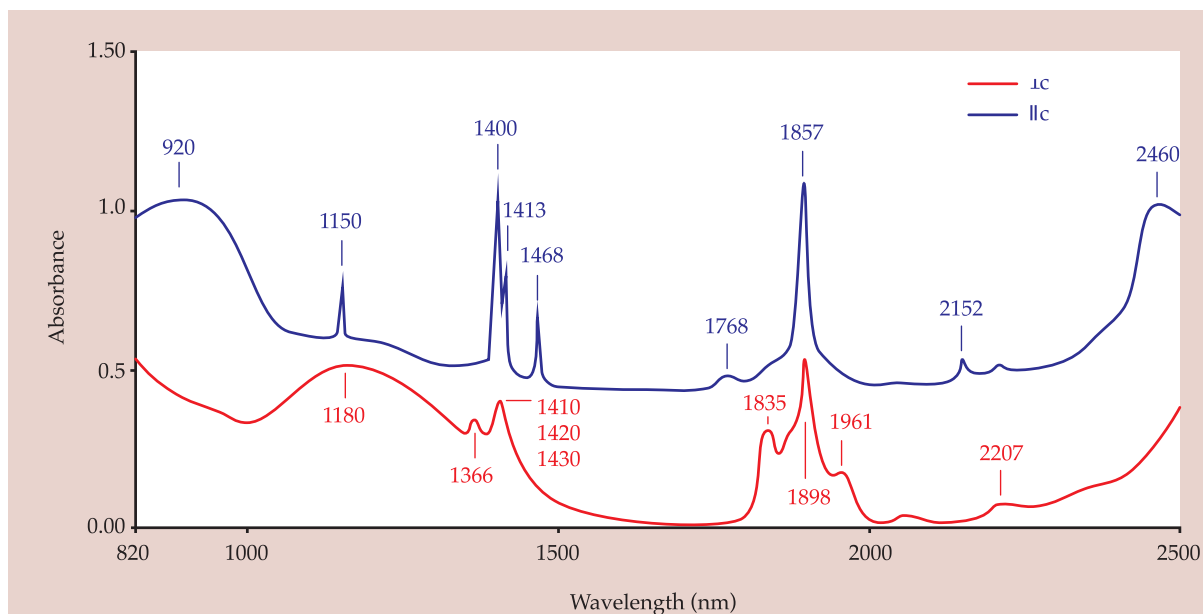


**Figure 10:** Mid-infrared absorption spectra of synthetic emerald powder (KBr pellet technique) in the range of fundamental water vibrations show two dominant absorption bands at 3697 and 3595  $\text{cm}^{-1}$  which were assigned to two different types of water molecules in the beryl structure.



**Figure 11:** Polarized absorption spectra of a 0.3 mm thick oriented crystal plate in the mid-infrared range showing numerous absorption bands of different types of water molecules and/or hydroxyl ions.





**Figure 12:** Polarized absorption spectra in the near infrared showing two broad absorption bands due to copper at 1180 and 920 nm and numerous absorption bands of different types of water molecules and/or hydroxyl ions; the upper spectrum is vertically displaced for clarity.

## Microscopic characteristics

### Structural properties

Neither rough nor faceted samples of the new type of Tairus hydrothermally-grown synthetic emerald showed residues of seed plates. All samples, however, contain step-like growth lines related to a weak colour zoning (*Figure 13*). In the rough samples, the sizes of the numerous steps within the growth lines increased from the sawn plane, which was next to the seed plate, towards the distant as-grown surface of the synthetic emerald crystal (*Figure 14*).

In both the rough and faceted samples, the angle between the step-like growth planes and the *c*-axis (representing the angle between seed plate and *c*-axis) was found to lie in a limited range between 28° and 30°. These results indicate that the synthetic emeralds were grown with seed plates cut with an angle to the *c*-axis slightly smaller than the characteristic angle of about 30°-32° which was for a long time used in growing synthetic emeralds in Russia (Schmetzer, 1988, 1996).

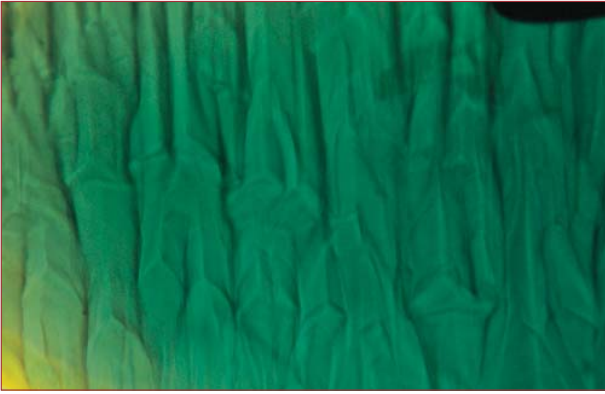
Almost perpendicular to the step-like growth lines, subgrain boundaries which are irregular and with a variety of orientations are present (*Figure 13, 14*). In one direction oblique to the step-like growth planes,



**Figure 13:** Faceted Tairus hydrothermally-grown synthetic emerald coloured by vanadium and copper; with step-like growth lines and colour zoning, and irregular subgrain boundaries almost perpendicular to the growth and colour zoning. Immersion, 40×. Photo by K. Schmetzer.



**Figure 14:** Rough crystal plate with step-like growth lines and colour zoning, irregular subgrain boundaries almost perpendicular to the growth and colour zoning. Immersion, 40×. Photo by K. Schmetzer.

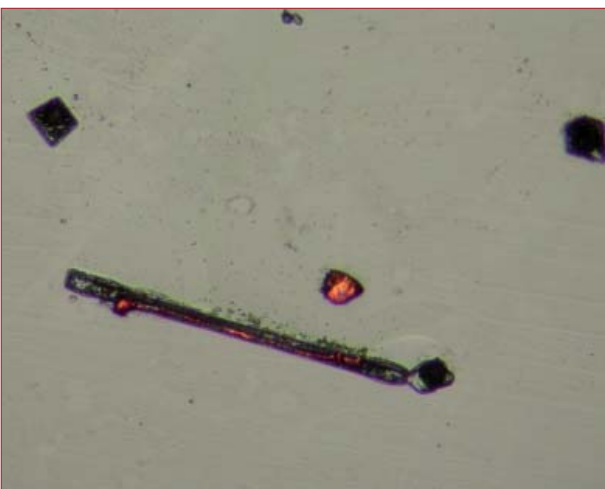


**Figure 15:** Faceted Tairus synthetic emerald showing block structure between subparallel oriented subindividuals. Immersion, 60 $\times$ . Photo by K. Schmetzer.

a characteristic block structure between subparallel oriented subindividuals is present (Figure 15). These microscopic features are characteristic for synthetic beryl and synthetic emerald, which is grown hydrothermally from seed plates cut oblique to the *c*-axis of the beryl crystal and non-parallel to possible natural faces of beryl (Klyakhin *et al.*, 1981; Granadchikova *et al.*, 1983; Lebedev and Askhabov, 1984; Lebedev *et al.*, 1986; Schmetzer, 1988).

### Inclusions

Most of our Tairus synthetic emeralds were extremely clean. In one crystal and on the surface of two rough synthetic emerald plates, there are tiny opaque crystals or lamellae with a metallic lustre (Figure 16a).



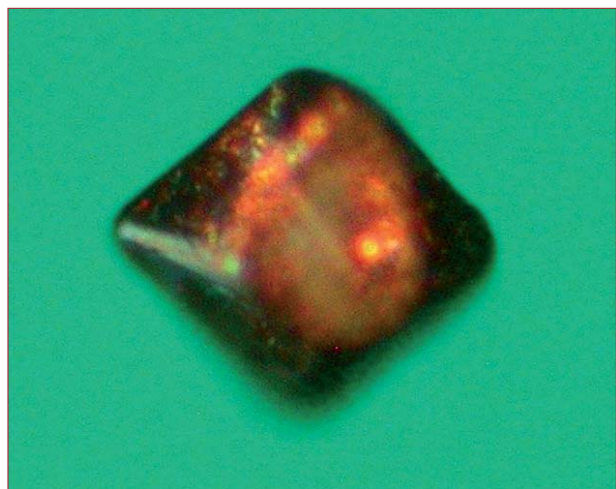
**Figure 16a:** On the surface of two Tairus hydrothermally-grown synthetic emerald plates we observed several crystals or lamellae of metallic copper. Reflected light, size of the lamella about 300  $\mu\text{m}$ . Photo by H.-J. Bernhardt.

The solids on the surface of the rough crystal plates were identified using the electron microprobe as native copper. For the identification of the solid inclusions within a synthetic emerald plate, the sample was cut and polished until an octahedral crystal with metallic appearance (Figure 16b) was exposed at the surface; this inclusion was also identified as native copper. Only a few synthetic emerald samples contain small feathers consisting of liquid and two-phase inclusions.

## Discussion

The ten samples of the new synthetic hydrothermally-grown beryl variety marketed by Tairus as 'Colombian Color Emerald' examined in the present study, reveal only small variability in their gemmological, chemical and spectroscopic properties. These data indicate – as announced by the producer – that our research material comprised samples of a commercial product grown by a finally developed technical process (see crystal growth).

According to the orientation of step-like growth structures and colour zoning, the orientation of the seed (about 28 -30° inclined to the *c*-axis) is only slightly different from the 'traditional' orientation used in Russia for commercial crystal growth of various types of synthetic emerald (about 30 -32°). A more



**Figure 16b:** This octahedral copper crystal inclusion in a Tairus synthetic emerald was exposed at the surface after cutting and polishing of the sample. Reflected light, diameter of the crystal about 55  $\mu\text{m}$ . Photo by H.-J. Bernhardt.



**Figure 17:** Different types of hydrothermally-grown synthetic emeralds; upper line left: Biron (Australia) synthetic emerald coloured by chromium and vanadium (1.49 ct, 7.9 × 6.4 mm), centre: Russian synthetic emerald coloured by chromium (grown in an autoclave with noble metal liner), right: Russian synthetic emerald coloured by chromium, iron, copper, and nickel (grown in an autoclave without noble metal liner); lower line: two samples of the new type grown by Tairus coloured by vanadium and copper. Photo by M. Glas.

significant difference and the new scientific development in Novosibirsk is the formation and establishment of a growth medium in which both colour-causing trace elements, vanadium and copper, are incorporated in the required concentration as well as in the required valence state (mainly as  $V^{3+}$  and  $Cu^{2+}$ ) into the beryl lattice. This suggests careful control of oxygen partial pressure in the autoclave, but, towards the end of the growth period, the partial pressure may change and enable the formation of native copper crystals both as inclusions and on the surfaces of crystals.

Gemmological properties of the material are in the range commonly observed for natural and hydrothermally-grown synthetic emeralds. Chemical and spectroscopic properties indicate that the synthetic beryls are coloured by a combination of vanadium and copper; chromium, which may derive from the natural colourless or slightly green beryl from the Ural mountains used as nutrient, is a very minor component. Infrared spectroscopy shows the presence of various types of water molecules and hydroxyl

groups, partly related to lithium in channel sites in the beryl structure.

Although experimental samples coloured by vanadium (yellowish green) or by copper (light blue) have been known for several decades, the new product is the first example of a synthetic bluish green 'emerald colour' synthetic beryl whose colour is caused by a combination of vanadium and copper, i.e. without any significant influence of chromium. The desired 'Colombian type' colouration of the new material closely matches the colour of other hydrothermally-grown synthetic emeralds on the market, for example synthetic emeralds coloured by:

- chromium,
- vanadium and chromium, or
- a combination of chromium, iron, copper and nickel (Figure 17).

The causes of colour and the definition of variously coloured natural and synthetic green beryls as 'emerald' was recently discussed by Schwarz and Schmetzer (2002). Considering that a practical definition of the term 'emerald' should include all materials accepted in general by the trade as emerald



without any need of a quantitative, time consuming chemical analysis (for example of chromium and/or vanadium contents in Colombian emeralds which show a great variability of chromium to vanadium ratios), the following suggestion was made: “Emeralds are yellowish green, green or bluish green, natural or synthetic beryls, which reveal distinct chromium and/or vanadium absorption bands in the red and blue-violet ranges of their absorption spectra.” Using this practical suggestion, the new material from Tairus is designated as synthetic emerald. The colour of the material underlines this designation, even if no distinct amounts of chromium are present in the synthetic beryls.

The distinguishing of the new type of Tairus synthetic emeralds from other emeralds can be carried out by microscopic examination on the basis of typical growth features such as step-like growth lines confined to colour zoning, irregular subgrain boundaries, and block structures between subparallel oriented subindividuals. In certain circumstances, spectroscopic and/or chemical data might also be helpful.

## References

- Aines, R.D., and Rossman, G.R., 1984. The high temperature behaviour of water and carbon dioxide in cordierite and beryl. *American Mineralogist*, 69, 319-27
- Aurischio, C., Fioravanti, G., Grubessi, O., and Zanazzi, P.F., 1988. Reappraisal of the crystal chemistry of beryl. *American Mineralogist*, 73, 826-37
- Aurischio, C., Grubessi, O., and Zecchini, P., 1994. Infrared spectroscopy and crystal chemistry of the beryl group. *Canadian Mineralogist*, 32, 55-68
- Beckwith, P.J., and Troup, G.J., 1973. The optical and infrared absorption of  $V^{3+}$  in beryl ( $Be_3Al_2Si_6O_{18}$ ). *Physica Status Solidi (a)*, 16, 181-6
- Charoy, B., De Donato, P., Barres, O., and Pinto-Coelho, C., 1996. Channel occupancy in an alkali-poor beryl from Serra Branca (Goias, Brazil): Spectroscopic characterisation. *American Mineralogist*, 81, 395-403
- Deer, W.A., Howie, R.A., and Zussman, J., 1986. *Rock-forming minerals. Vol. 1B, Second Edition, Disilicates and Ring Silicates*. Longman Scientific & Technical, Harlow, England
- Flanigen, E.M., Breck, D.W., Mumbach, N.R., and Taylor, A.M., 1967. Characteristics of synthetic emeralds. *American Mineralogist*, 52, 744-72
- Granadchikova, B.G., Andreenko, E.D., Solodova, Yu.P., Bukin, G.V., and Klyakhin, V.A., 1983. Diagnostics of natural and synthetic emeralds. *Izv. Vyssh. Uchebn. Zaved., Geol. Razved.*, 26(10) 87-93 [in Russian]
- Koivula, J.I., Kammerling, R.C., DeGhionno, D., Reinitz, I., Fritsch, E., and Johnson, M.L., 1996. Gemological investigation of a new type of Russian hydrothermal synthetic emerald. *Gems & Gemology*, 32(1), 32-9
- Klyakhin, V.A., Lebedev, A.S., Il'in, A.G., and Solntsev, V.P., 1981. Growing of hydrothermal beryl. *Sintez i Vyrashchivanie Optich. Kristallov i Yuvelir. Kamnei, Novosibirsk 1981*, 45-66 [in Russian]
- Lebedev, A.S., and Askhabov, A.M., 1984. Regeneration of beryl crystals. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, 113(5), 618-28 [in Russian]
- Lebedev, A.S., Ilyin, A.G., and Klyakhin, V.A., 1983. Variétés de beryl “gemme” hydrothermal. *Revue de Gemmologie a.f.g.*, No. 76, 4-5
- Lebedev, A.S., Il'in, A.G., and Klyakhin, V.A., 1986. *Hydrothermally grown beryls of gem quality. In: Morphology and phase equilibria of minerals. Proceedings of the 13<sup>th</sup> General Meeting of the International Mineralogical Association, Varna 1982, Sofia 1986*, 403-11 [in Russian]
- Lebedev, A.S., Klyakhin, V.A., and Solntsev, V.P., 1988. Crystal-chemical characteristics of hydrothermal beryls. *Trudy Instituta Geologii i Geofiziki (Novosibirsk)*, 708, 75-94 [in Russian]
- Mashkovtsev, R.I., and Lebedev, A.S., 1993. Infrared spectroscopy of water in beryl. *Journal of Structural Chemistry* 33, 930-3
- Mashkovtsev, R.I., and Smirnov, S.Z., 2004. The nature of channel constituents in hydrothermal synthetic emerald. *Journal of Gemmology*, 29(4), 215-27
- Mashkovtsev, R.I., and Solntsev, V.P., 2002. Channel constituents in synthetic beryl: ammonium. *Physics and Chemistry of Minerals*, 29(1), 65-71
- Mashkovtsev, R.I., Stoyanov, E.S., and Thomas, V.G., 2004. State of molecules and ions in the structural channels of synthetic beryl with an ammonium impurity. *Journal of Structural Chemistry* 45(1), 56-63
- Mathew, G., Karanth, R.V., Gundu Rao, T.K., and Deshpande, R.S., 1997. Channel constituents of alkali-poor Orissan beryls: An FT-IR spectroscopic study. *Current Science*, 73(11), 1004-11
- Rodionov, A.Ya., Solntsev, V.P., and Weis, N.S., 1987. Crystallisation and properties of colored varieties of gas-transport beryl. *Trudy Instituta Geologii i Geofiziki (Novosibirsk)*, 679, 41-53 [in Russian]
- Schmetzer, K., 1978. *Vanadium III als Farbträger bei natürlichen Silikaten und Oxiden – ein Beitrag zur Kristallchemie des Vanadiums*. Dissertation, Universität Heidelberg, 277 pp
- Schmetzer, K., 1982. Absorptionsspektroskopie und Farbe von  $V^{3+}$ -haltigen natürlichen Oxiden und Silikaten – ein Beitrag zur Kristallchemie des Vanadiums. *Neues Jahrbuch für Mineralogie Abhandlungen*, 144(1), 73-106
- Schmetzer, K., 1988. Characterisation of Russian hydrothermally-grown synthetic emeralds. *Journal of Gemmology*, 21(3), 145-64



- Schmetzer, K., 1989. Types of water in natural and synthetic emerald. *Neues Jahrbuch für Mineralogie Monatshefte*, 1983(1), 15-26
- Schmetzer, K., 1996. Growth method and growth-related properties of a new type of Russian hydrothermal synthetic emerald. *Gems & Gemology*, 32(1), 40-3
- Schmetzer, K., and Bernhardt, H.-J., 1994. Isomorphic replacement of Al and Si in tetrahedral Be and Si sites of beryl from Torrington, NSW, Australia. *Neues Jahrbuch für Mineralogie Monatshefte*, 1994(3), 121-9
- Schmetzer, K., and Kiefert, L., 1990. Water in beryl – a contribution to the separability of natural and synthetic emeralds by infrared spectroscopy. *Journal of Gemmology*, 22(4), 215-23
- Schmetzer, K., Kiefert, L., Bernhardt, H.-J., and Zhang, B.L., 1997. Characterisation of Chinese hydrothermal synthetic emerald. *Gems & Gemology*, 33(4), 276-91
- Schwarz, D., and Schmetzer, K., 2002. *The definition of emerald – the green variety of beryl colored by chromium and/or vanadium*. Emeralds of the World, extraLapis English, No. 2, 74-8
- Shatskiy, V.S., Lebedev, A.S., Pavlyuchenko, V.S., Kovaleva, L.T., Koz'menko, O.A., Yudin, A.N., and Belov, N.V., 1981. Conditions for entry of alkali cations into beryl. *Geochemistry International*, 18(2), 7-17
- Sherriff, B.L., Grundy, H.D., Hartman, J.S., Hawthorne, F.C., and Fern, P., 1991. The incorporation of alkalis in beryl: Multi-nuclear MAS NMR and crystal-structure study. *Canadian Mineralogist*, 29, 271-85
- Solntsev, V.P., 1981a. Nature of color centers and EPR in beryl and chrysoberyl. *Trudy Instituta Geologii i Geofiziki (Novosibirsk)*, 499, 92-140 [in Russian]
- Solntsev, V.P., 1981b. Absorption spectra and EPR of trace impurities in beryllium-containing minerals and their relation to specimen color. *Issled. Fiz. Svoistv i Sostova Sintet. Mineralov i Monokristallov, Novosibirsk 1981*, 37-47 [in Russian]
- Solntsev, V.P., Lebedev, A.S., Pavlyuchenko, V.S., and Klyakhin, V.A., 1976. Copper centers in synthetic beryl. *Sov. Phys. Solid State*, 18(5), 805-6
- Vladimirova, M.V., Lebedev, A.S., and Gevork'yan, S.V., 1987. IR spectroscopic study of water in synthetic crystals of beryl. *Mineralogicheskii Zhurnal*, 9(6) 57-63 [in Russian]
- Wood, D.L., and Nassau, K., 1967. Infrared spectra of foreign molecules in beryl. *Journal of Chemical Physics*, 47(7), 2220-8
- Wood, D.L., and Nassau, K., 1968. The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *American Mineralogist*, 53, 777-800