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Contributions to Gemology

No.11 January 2012 (Updated September 2015)

World of Magnificent Spinels
Provenance and Identification

Burma

Vietnam

Cornflower-Blue Spinel over 10ct from Vietnam

Inclusions in Spinel

GRS GEMRESEARCH SWISSLAB

NEW GENERATION OF PULLED SYNTHETIC SPINEL FROM RUSSIA IMITATING NATURAL "LAVENDER"-COLORED AND NATURAL "COBALT"-SPINEL FROM VIETNAM

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INTRODUCTION

In May 2015, the author (AP) was made aware that a company in Thailand (Tairus Co. LTD, Bangkok) had commissioned to a laboratory in Russia the production of new types of synthetic spinel of "lavender" colors by the method of crystal pulling from flux. This technique is the same used at the Institute of Monocrystals in Novosibirsk. The author (AP) had previously inspected this institute in Siberia. From this visit, AP made an educational video about the methods used in Novosibirsk and 2 still snapshots are shown in this report Fig. 318a-b. Spinel produced by pulling from a Flux is also known as Czochralski method and this method can be modified to produce stochiometric spinel (Grabmaier et al., 1968 and Wyon et al., 1986).

The new synthetic spinels are produced by a private laboratory outside the Russian capital Moscow and not in Siberia. The producers confirmed, however, that a similar setup is being used. GRS was informed that a series of these spinels had been certified as "natural spinels" by a recognized gemological laboratory. Some copies of gemological reports were produced to underline this point. We did not have the possibility to verify this claim but alerted the concerned laboratory that remains anonymous here.

This early indication of possible misidentifications in the trade convinced us that the material may create some danger to the gem industry and that an alert to the industry is required.

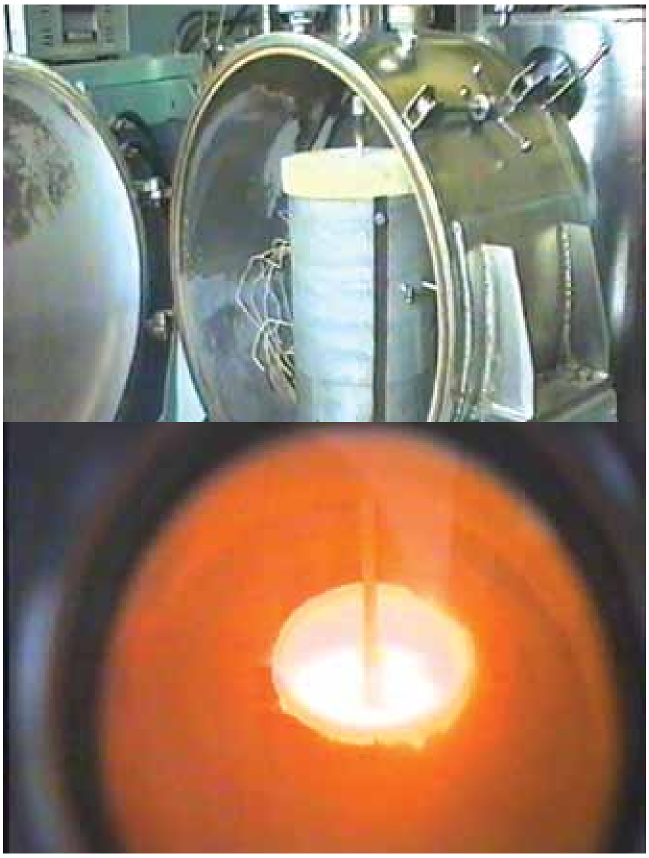

Fig. 318a-b *Flux synthetic production facility in Novosibirsk at the Institute of Monocrystals. Fig. 318b View through the observation window to a solid material pulled from a flux. Photos taken in 1994 by AP.*

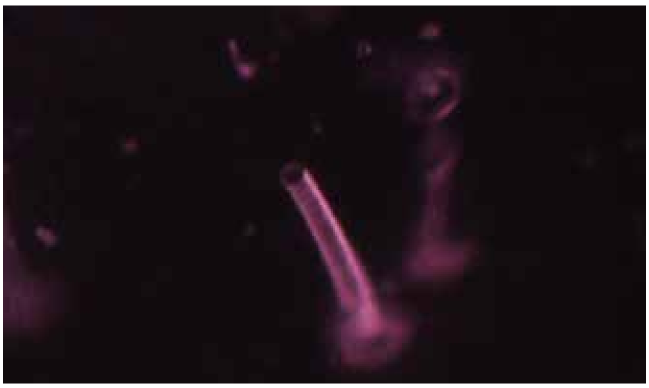

Fig. 319 *Tube inclusion in synthetic spinel of purple color. The tube shows a screw-like mark at the surface indicating that the spinel was produced by turning from a flux.*

MATERIAL, COLOR VARIETIES AND INCLUSION FEATURES

During a visit to the Tairus office in Bangkok, a new production was lying on the table due to increased demand after a test run in the market (Fig. 320). A series of different products labeled with numbers were in the process of being cut and divided into different color varieties. Approximately 11 color types with all shade varieties ranging between pinkish-red and blue are being produced. The different tones include very

Fig. 320 *Spinels commercially produced by the pulled method from flux. Note the approximate 5cm diameter of the cylinders and the different color varieties. The rough is about 250ct in size. Photo by AP at Tairus, Bangkok.*

classic vibrant pinkish-red color, imitating the most expensive spinel varieties in the world, with all transitions to an almost pure "neon" blue (cobalt-spinel). Pastel violet and pastel purple or "lavender" colors (Fig. 322a-d) as well as color-changing violet spinels with color-change to pink when viewed in incandescent light (Fig. 323) are also available. Whereas the pinkish-red and blue synthetic spinel produced by flux are already known in the market since almost 2 decades, the "lavender" colors and color-changing varieties are a new addition for spinels produced by flux method. Such colors have so far only been produced by flame fusion. GRS acquired cut-offs of the different products, including samples containing inclusions that were rejected as well as one larger piece of rough (see Fig. 321a-b).

Four pieces were cut at the GRS research cutting facility in Bangkok to almost completely inclusion free samples, perfectly imitating natural spinel from Vietnam (Fig. 322a-d). Some of the rejected pieces contained interesting overgrowths at the surface (Fig. 339-340) and inclusion features (Fig. 327-328). These inclusion features included occasionally myriads of pinpoint-bubbles (Fig. 327), clusters of opaque cubic solids (Fig. 340a) as well as rounded transparent

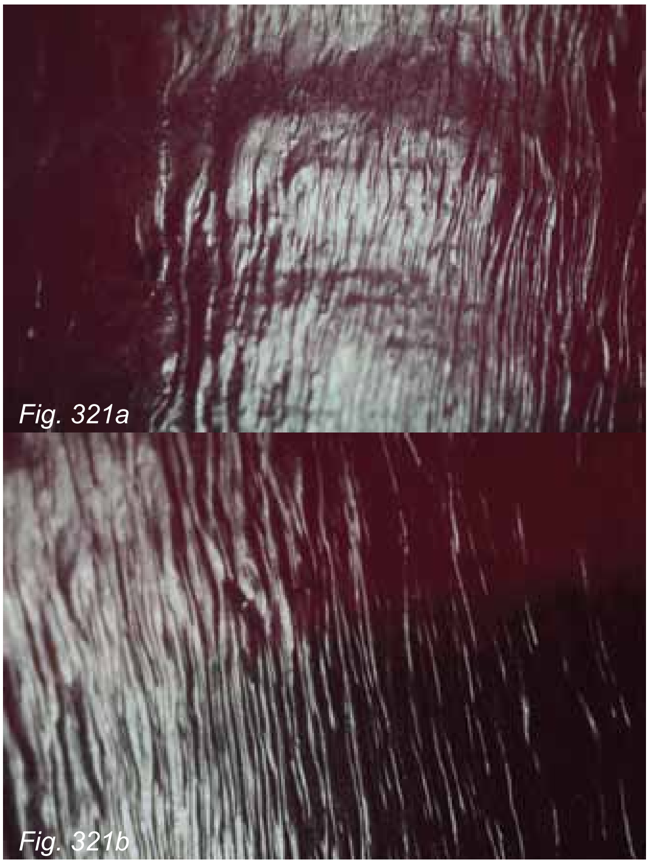

Fig. 321a

Fig. 321b

Fig. 321a-b *Details of the striae on the rough of synthetic spinel indicates that the spinels were pulled in the process when they were synthesized from a flux. Rings perpendicular to it also indicate that they were rotated.*

Fig. 322a-d Spinels produced by flux (pulled method) of different colors, including pinkish-red, lavender, color-changing and violetish-blue color varieties. Synthetic spinels cut by GRS from the rough, over 1ct each in size.

Fig. 323 Color-changing synthetic spinels produced by flux (pulled method), with color-change from violet (in daylight) to purplish-pink (in incandescent light). Approximately 1ct, cut by GRS from the rough.

crystals (Fig. 335-337). Large curved tubes were seen in the rough materials but may not be found in cut stones (Fig. 328b-c).

One of these tubes resembled a screw (Fig. 319) and can be taken as indicator that this spinel was indeed produced by rotation in a flux. The pulling mechanism is corroborated by the striae found on the surface of the rough cylinder-shaped spinels, in direction of the long axis of the cylinder (Fig. 321a-b).

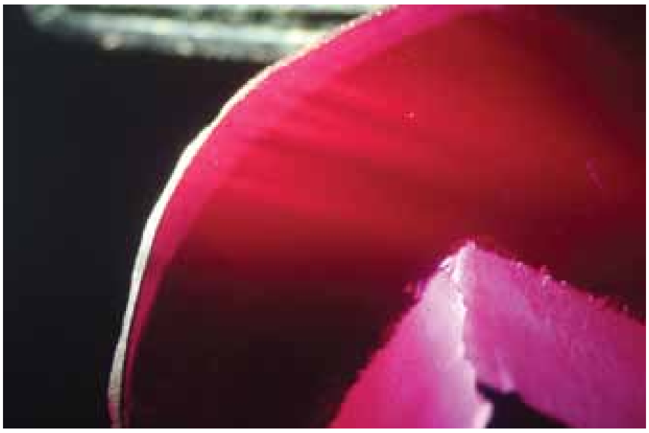

Fig. 324 Microphotograph of a synthetic spinel cylinder showing diffuse color-zoning of pink and violetish bands.

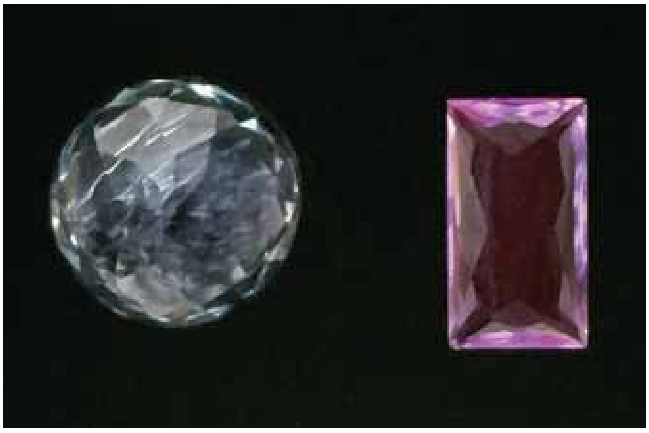

Fig. 325 Two synthetic spinels as seen trough a polariscope with crossed polarizers. Left a Verneuil synthetic spinel and on the right the new type of synthetic spinel produced from flux. Note only the Verneuil spinel shows cross-hatched anomalous interference patterns.

COLOR ZONING AND UV FLUORESCENCE

With fiber optic illumination, diffuse cloudy color zoning was visible in some samples (Fig. 324). All samples showed a strong red UV fluorescence at shortwave (254nm) and longwave (366nm) UV excitation. Corresponding color varieties of natural spinel from Vietnam, Burma and Tanzania did not show this fluorescence under UV light. This is a good screening test for natural parcels of fancy colored spinels.

STANDARD GEMOLOGICAL TESTS

The new synthetic spinels have RI's ranging from 1.714 - 1.715. These are typical RI's for natural or synthetic flux spinels but different than RI's found in Verneuil spinel (RI 1.725-1.730). Also the density is within the range of natural and flux spinel ($\rho = 3.5$). No anomaly in birefringence was observed (see comparison to Verneuil spinel Fig. 325). These synthetic spinels under crossed polarizing filters, they remained dark (isotropic). The absence of anomalous birefringence is often considered a critical test to distinguish natural spinel from their synthetic counterparts produced by the Verneuil process. It has to be remembered though that synthetic spinels produced by flux methods are indistinguishable by only using the polariscope as testing tool (lit. 3 & lit. 4).

Fig. 327 Inclusion in a rough synthetic spinel of pinkish-red color. Myriads of pinpoint bubbles may be seen in concentrated areas.

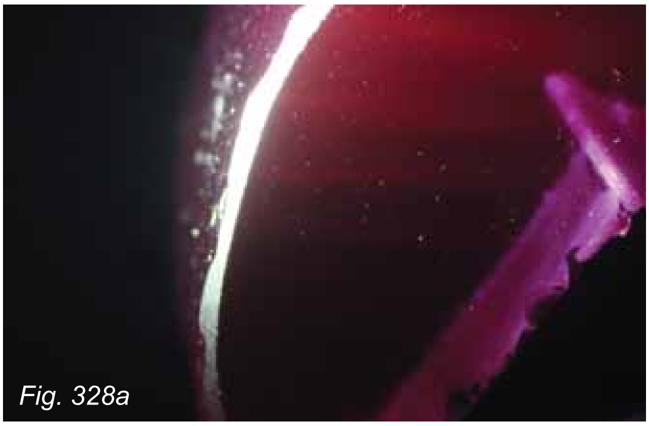

Fig. 328a

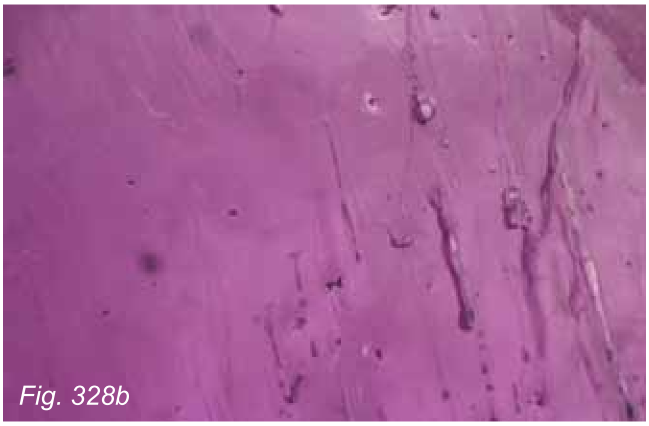

Fig. 328b

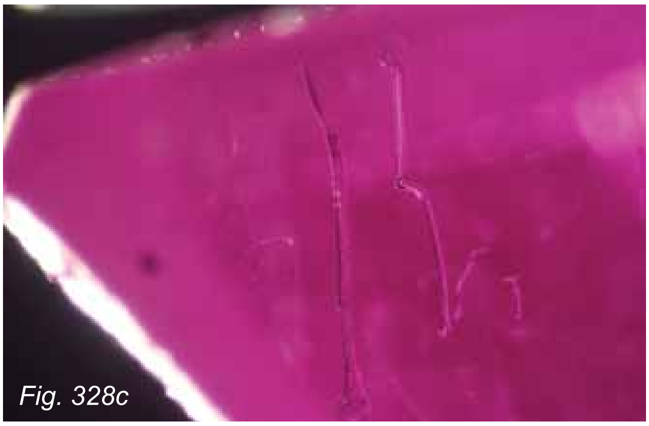

Fig. 328c

Fig. 328a-c These types of irregular tubes with 2-phase inclusions (solid and gas phases) are occasionally found in these pulled synthetic spinels. They may only be found in rejected rough materials and it may well be that they are not present in the faceted stones that appear on the market.

ADVANCED INVESTIGATIONS

In order to characterize this material with advanced methods, we have studied the samples by ED-XRF (Fischerscope XUV773, with vacuum, quantitative) and LIBS-analysis (Laser induced breakdown spectroscopy at 30 mJ frequency, 266nm Nd:YAG laser (Continuum, USA) with a pulse width of 6 ns, coupled to an in-house built ICCD/Echelle spectrometer with a working range of 190-900nm, qualitative) for chemical composition, by SEM-EDX (FEI XL30 Sirion FEG, EDAX) for inclusion analysis, by photoluminescence (custom-built, PL405nm and PL535nm, using a Avantes quadruple-channel Czerny-Turner spectrometer) and by UV-VIS-NIR spectroscopy (custom-built, UV-VIS-NIR using a Avantes quadruple-channel Czerny-Turner spectrometer and two broadband light sources) for the analysis of the color origin.

RESULTS

ABSORPTION SPECTROSCOPY

The UV-VIS results revealed classic spectra of Cr- and Co-bearing spinels (Fig. 329) lacking Fe concentrations.

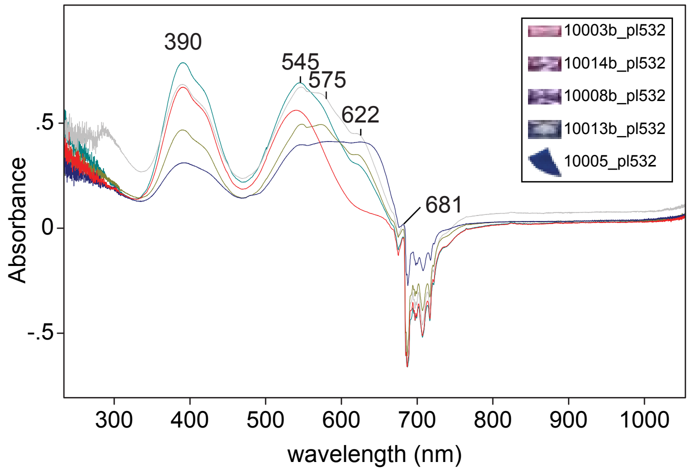

Fig. 329 UV-VIS-NIR absorption spectra recorded at liquid nitrogen temperature (LNT) for the respective groups: Russian synthetic spinel (pulled from flux) of different colors (pastel pink, purple, violet and blue) from Russia. Important features are highlighted. The ordinate shows the absorbance in arbitrary units. Note the typical absorption characteristics of Co in spinel structure in the range 550nm to 650nm, superimposed to those of Cr. Increase in Co concentration for pink to blue colors. Measured with GRS UV-VIS-NIR analysis system using Avantes AvaSpec with a quadruple-channel Czerny-Turner spectrometer.

CHEMICAL COMPOSITION

ED-XRF analysis confirmed that the chemical composition contains typical stoichiometric Mg and Al concentrations found in natural and synthetic flux spinel (Tab. 9). The Co concentrations of these synthetic spinels are in the same order of magnitude as other natural spinels of same color but higher in Cr and lower in Fe and Zn.

Surface spot analyses by ED-XRF focusing on opaque particles revealed the presence of platinum (Pt), iridium (Ir) and bismuth (Bi) (Fig. 330-331). The analyses by SEM-EDX confirmed the presence of Ir particles and in addition xenomorphic Mg-Al-Si-solids that were detected on the surface of the spinels. During LIBS-analyses we focused on the presence of Li and Be concentrations in these new spinels. Natural and synthetic spinels have similar concentrations of Li. Be is detected in all the natural spinels tested. None of the synthetic spinels tested showed any detectable quantities of Be, except on the unpolished rim of the boule.

INTERPRETATION

The blackish solid clusters seen in the microscope could be identified as predominantly Ir particles, which are coming from the crucible (Lit.1). Only one Pt particle could be detected (by ED-XRF spot analysis) whereas all the other particles were identified during SEM-EDX as Ir particles (size see Fig. 339-340). The presence of Si in the chemical analyses (Tab. 9) can be explained by the presence of silicate particles that were found during SEM-EDX analyses (Fig. 338) and are not part of the chemical composition of these synthetic spinels. Bi concentrations are localized by ED-XRF in the area of the filled tubes and are most likely part of the flux used. Ir and Pt may be part of the crucible or corrosive products of other parts used in the production process. The role of Si in the process and the nature of these Si-bearing solids are not yet understood. The light element test by LIBS for distinction of natural and synthetic spinels (e.g. presence of Be in natural spinels only versus no Be in synthetic spinels except on unpolished surfaces of the outer rim of the boule), can also be applied to identify this new synthetic type of spinel (Lit. 1).

	Color	Origin	Raman 785nm	LIBS Be	LIBS Li	Density (ρ)	ED-XRF	MgO wt%	Al_2O_3 wt%	SiO_2 ppm	TiO_2 ppm	V_2O_3 ppm	Cr_2O_3 ppm	Fe_2O_3 ppm	Co_3O_4 ppm	ZnO ppm	Ga_2O_3 ppm
Tab. 9: ED-XRF analyses of synthetic and natural spinels																	
Synthetic	purple	Russia	no peaks, fluorescence	(-)*	X	3.57	avg(3)	26	73	3770	bdl	bdl	2513	69	77	bdl	bdl
Synthetic	purple-pink	Russia	no peaks, fluorescence	(-)*	X	3.59	avg(3)	26	73	9274	bdl	bdl	2276	141	51	bdl	bdl
Synthetic	purple	Russia	no peaks, fluorescence	(-)*	X	3.60	avg(3)	26	73	6489	bdl	bdl	1511	134	60	bdl	bdl
Synthetic	purple-pink	Russia	no peaks, fluorescence	(-)*	X	3.64	avg(3)	27	72	5603	bdl	bdl	3250	155	73	bdl	bdl
Natural	purple-pink	Burma	peaks present	X	X	3.63	avg(2)	27	72	322	207	248	99	5764	bdl	731	143
Natural	violet	Burma	peaks present	X	X	3.61	avg(2)	27	72	390	bdl	53	37	7476	bdl	643	130
Natural	greyish purple	Burma	peaks present	X	X	3.63	avg(2)	26	73	266	bdl	92	bdl	6211	bdl	748	280
Natural	purplish pink	Vietnam, Luc Yen	peaks present	X	X	3.62	avg(2)	25	73	365	bdl	bdl	bdl	11601	bdl	2624	271
Natural	purplish pink	Tanzania	peaks present	X	X	3.58	avg(2)	25	74	bdl	bdl	bdl	55	4595	bdl	717	79
Natural	purplish pink	Tanzania	peaks present	X	X	3.59	avg(2)	26	74	351	115	211	113	2336	bdl	1396	186
	*Be on rough surface only X= was detected						approx. detection limits	1	1	250	100	50	30	30	30	20	20

Tab. 9 ED-XRF analyses of selected synthetic and natural spinels of corresponding colors. Note the presence of higher Cr and absence of Fe in the synthetic spinels. Natural spinels are characterized by higher Fe, Zn, V, Ti and Ga concentrations. Si concentrations in synthetic spinels are due to inclusions (see text).

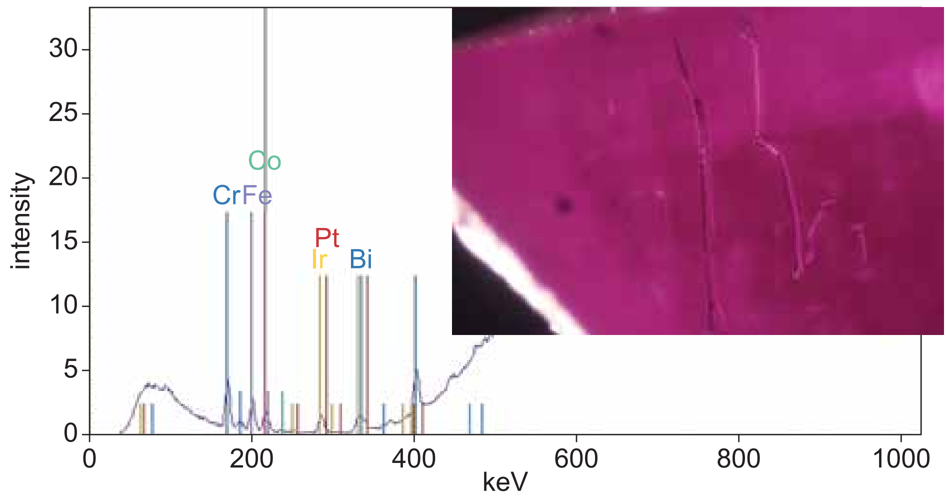

Fig. 330 ED-XRF analyses of an area in the synthetic spinel with presence of tubes revealed concentrations of Bi (Pt and Ir is due to black particles present as overgrowth on the surface and as inclusions). A microphotograph of the tubes is shown.

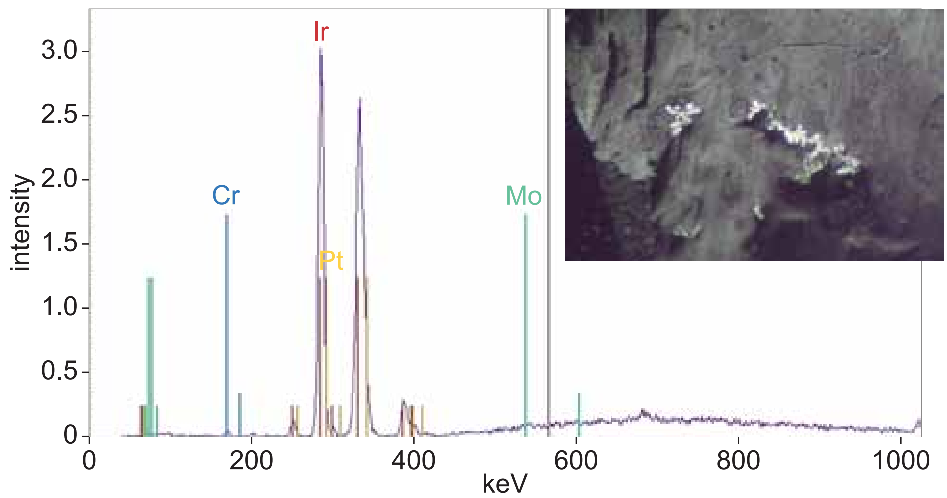

Fig. 331 ED-XRF analyses of the surface of the new synthetic spinel in an area of 2 different type of opaque particles (inserted picture in reflected light). The analyses revealed Pt and Ir concentrations.

PHOTOLUMINESCENCE

During PL analysis we found that the new material produced prominent emission spectra when analyzed with 2 different lasers at room temperature as well as at low temperature using liquid nitrogen (Fig. 332). The peaks around 680 to 730 nm are due to the Cr concentrations in these synthetic spinels and the position of Cr in the crystallographic lattice. These spectra have not been observed in other synthetic spinels produced by flux or Verneuil and are also different than those found in heated spinels (Fig. 303-304) and all other natural spinels tested so far in this book. However, they are similar to the PL of cobalt diffused natural spinels that we reported earlier (Fig. 310).

INTERPRETATION PHOTOLUMINESCENE

The PL-results seem to indicate that this new type of synthetic spinel is produced by a new process so far unknown to the gemological world. They have characteristics of "normal spinel" with some slight Mg-Al disorder. Mg-Al ordering is strongly influenced by the rate of quenching (Widmer et al. 2014). Therefore, a multi-step process in the production of these new spinels (pulled from flux and tempered) can also not be excluded.

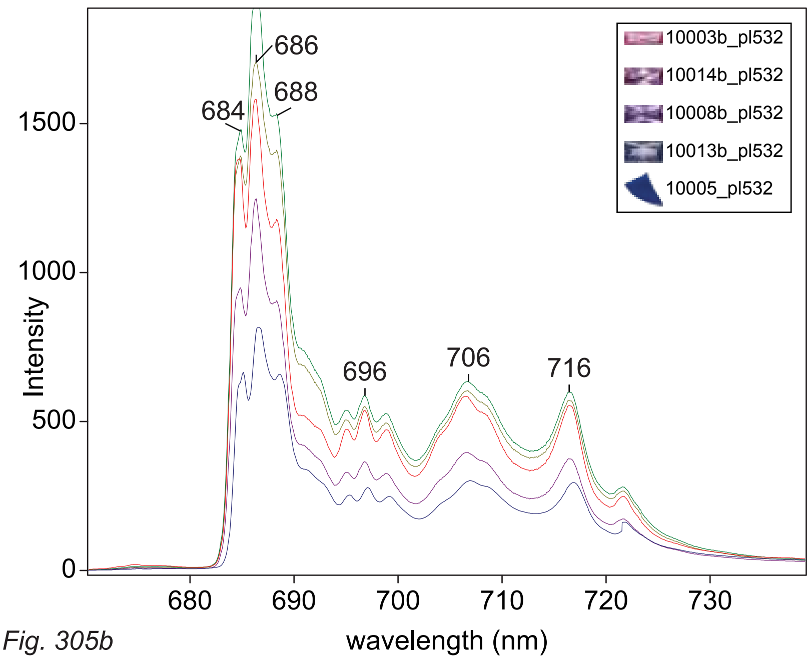

Fig. 305b

Fig. 332 *PL spectra (excitation 405nm) of synthetic spinel recorded at liquid nitrogen temperature (LNT) for the respective groups: Synthetic spinel (pulled from flux) of different colors from Russia. The ordinate shows the intensity (counts) in arbitrary units. Note the PL lines and their position are found in either normal or inverse spinel. The synthetic spinel is interpreted as normal spinel with slight Mg-Al disorder. Measured with GRS' photoluminescence analysis system using Avantes AvaSpec with a quadruple-channel Czerny-Turner spectrometer.*

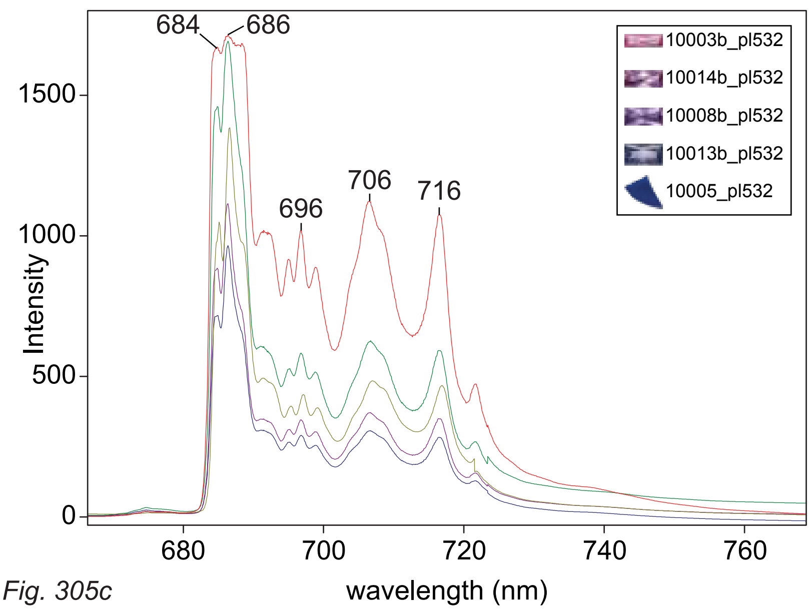

Fig. 305c

Fig. 333 *PL spectra (excitation 532nm) of synthetic spinel recorded at liquid nitrogen temperature (LNT) for the respective groups (see Fig. 333)*

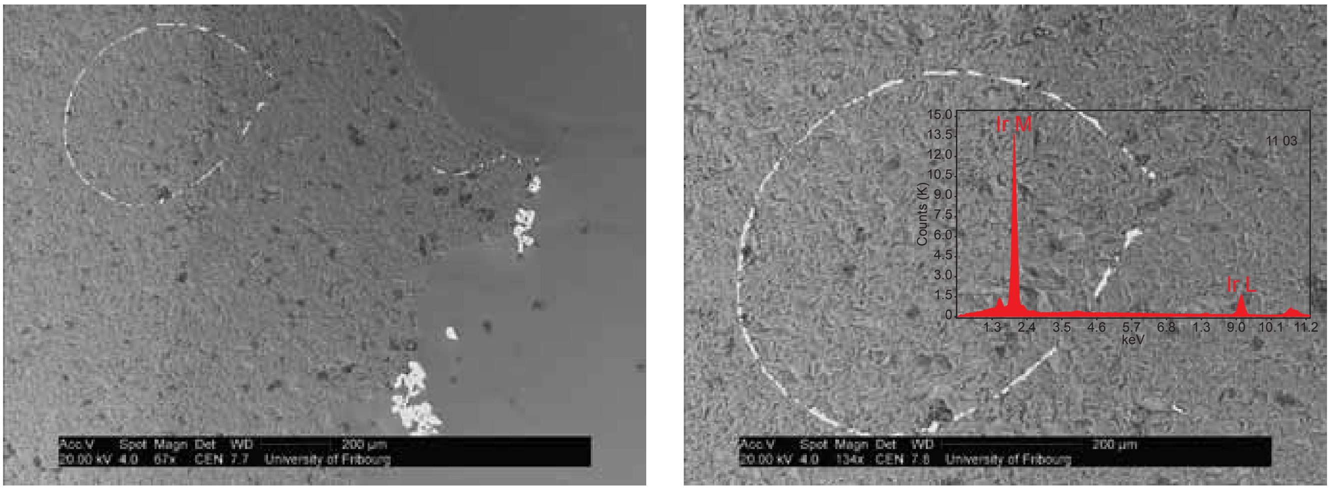

Fig. 334a-b SEM-BSE image of synthetic spinel with a rough surface and surrounding overgrowing particles. Note that the series of small Ir particles are found as clusters as well as in a circle bordering an isolated round spinel area. SEM-EDX spectrum of Ir particles measured at 20kV acceleration voltage is inserted (Fig. 334b).

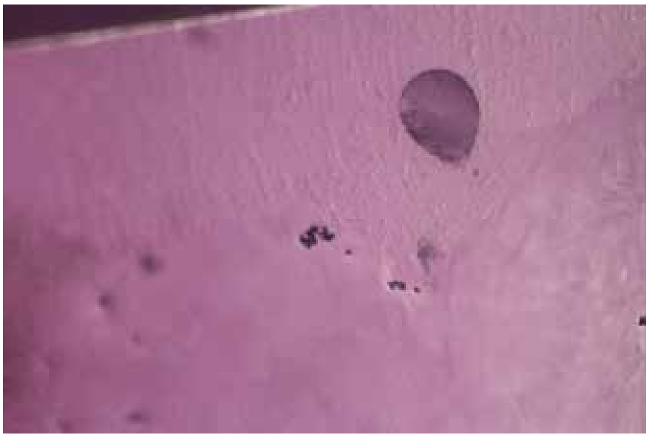

Fig. 335 Pear-shaped round inclusion in synthetic spinel was identified as spinel.

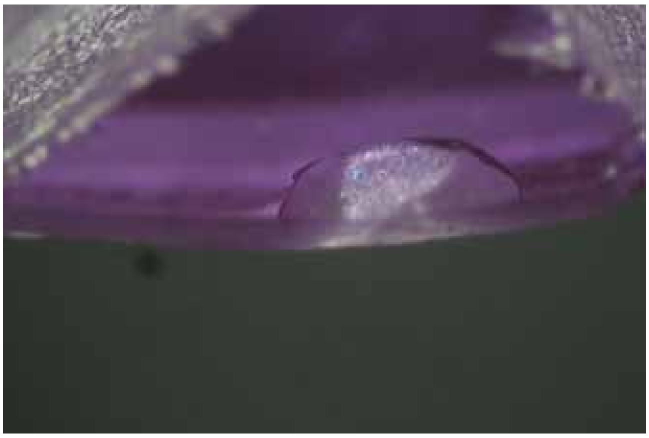

Fig. 336 Round spinel inclusion inside the synthetic spinel reaches the surface of the rough and is bordered by a rim consisting of Ir (see Fig. 334b).

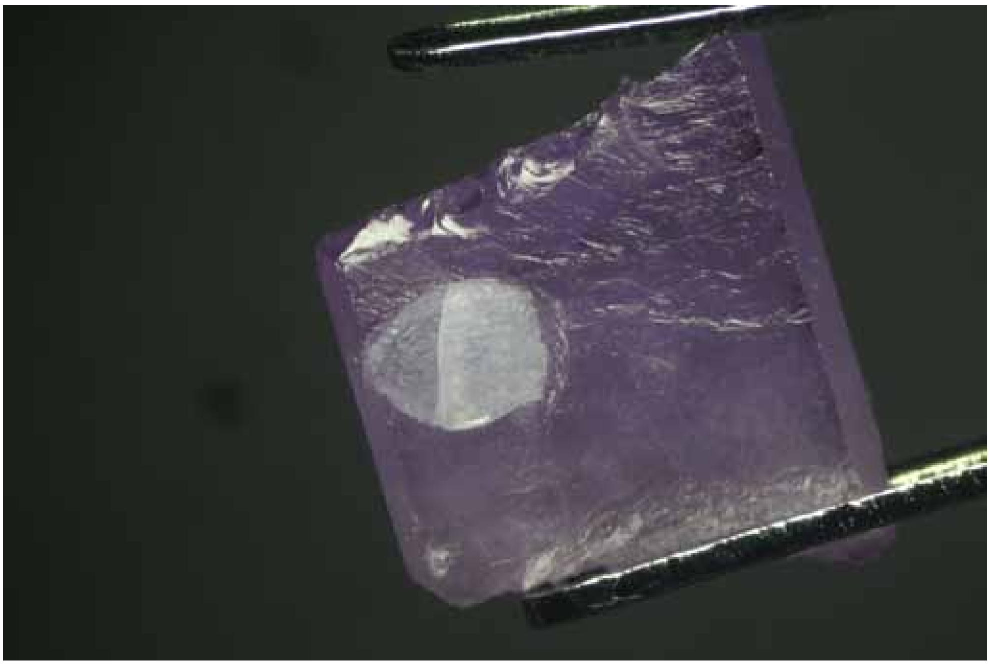

Fig. 337 A bicolored area of the rough reveals an isolated round spinel material that it is not an inclusion of a different material. It may be misinterpreted as an inclusion supporting natural origin of the synthetic material.

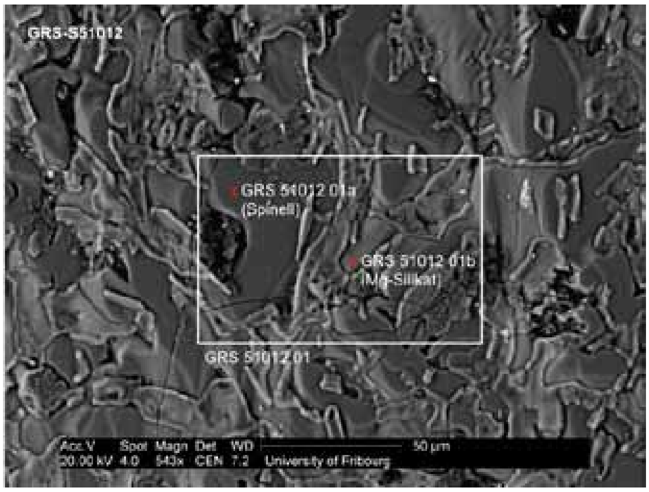

Fig. 338a

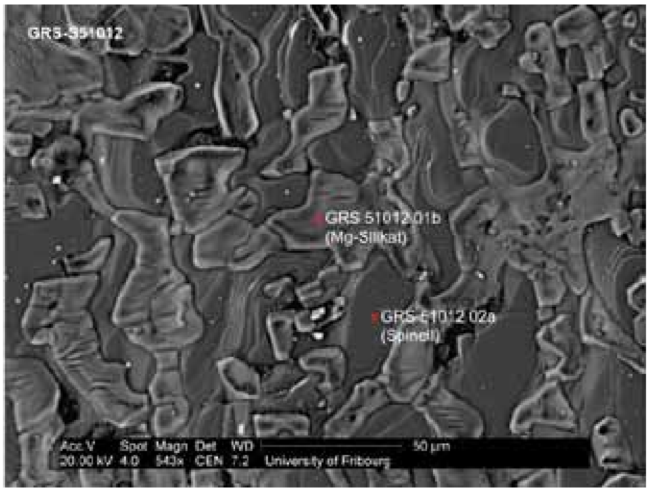

Fig. 338b

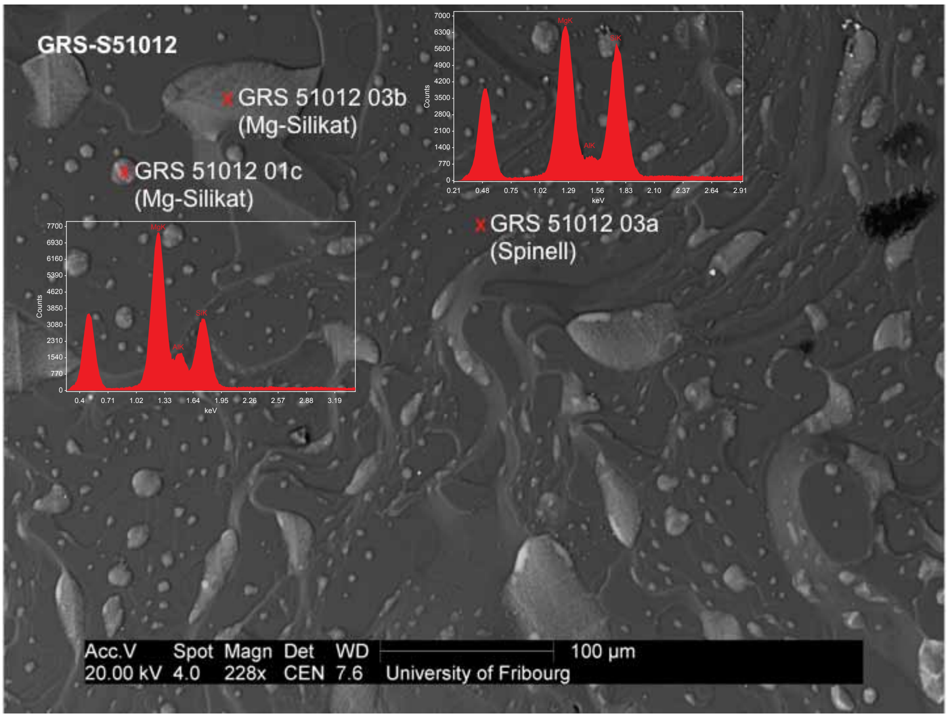

Fig. 338a-c SEM-SE image of the surface of the synthetic rough material allowed to analyse overgrowing substances. It is seen that the surface contains swirled solid substances filling cavities of the rough surface. EDX spectra of the material confirms that the particles are composed of Mg-silicates and Mg-Al-silicates (see inserted spectra).

CONCLUSION

A new synthetic spinel appeared on the market that is produced by the crystal pulling method from flux. Standard gemological tests are not conclusive (RI in the range of natural counterparts). A first indication for synthetic origin is the intense red UV fluorescence that is stronger than in the color varieties of natural counterparts. This is due to the high Cr concentrations in this synthetic cobalt-spinel and the absence of Fe concentrations. Typical inclusions are often absent in these new spinels. If they are present, they include opaque clusters of solids (Ir particles from the crucible), curved tubes filled with flux (containing Bi) as well as myriad pinpoints. A diffuse color zoning may be observed as well. The new synthetic materials can be distinguished by ED-XRF analyses by their absence or lower concentrations of Zn, Fe and Ga. Higher Si concentrations are due to Mg-Al-Si solid inclusions. Bi concentrations are located in areas with Flux inclusions; Ir and Pt is due to opaque inclusions. PL analyses identifies these spinels as “normal” with slight Mg, Al disorder. The light element test is of limited use due to Lithium concentrations in the stone and Beryllium concentrations on the surface. These new synthetic spinels may appear in the market as imitations mixed into lots of lavender to pastel blue spinel originating from Vietnam or other origins.

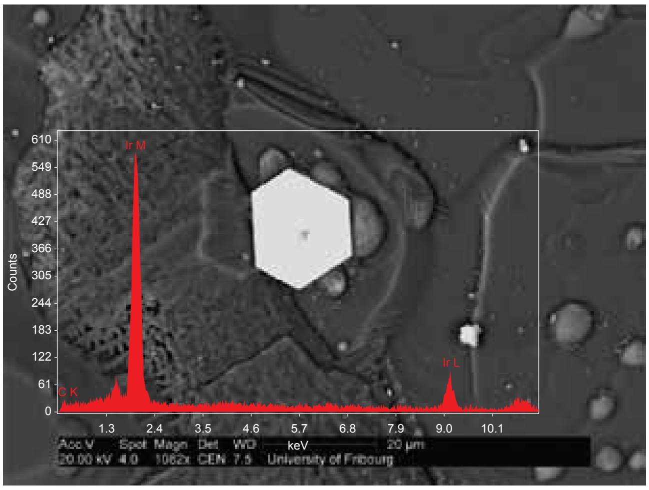

Fig. 339a

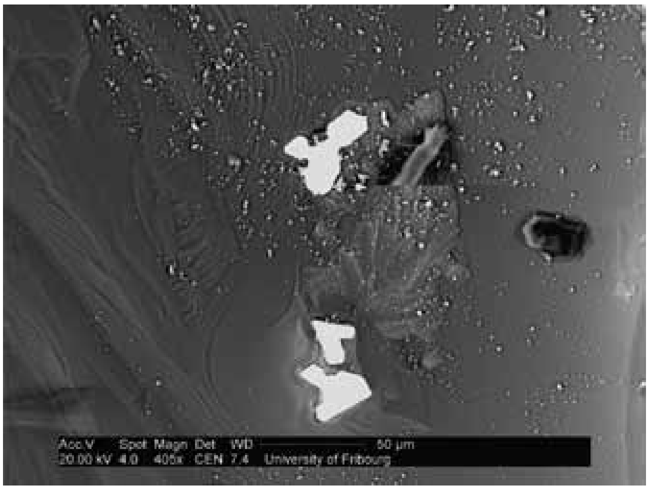

Fig. 339b

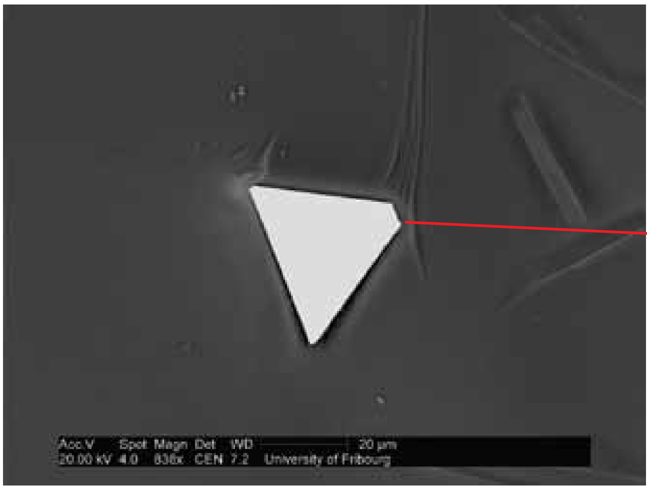

Fig. 339c

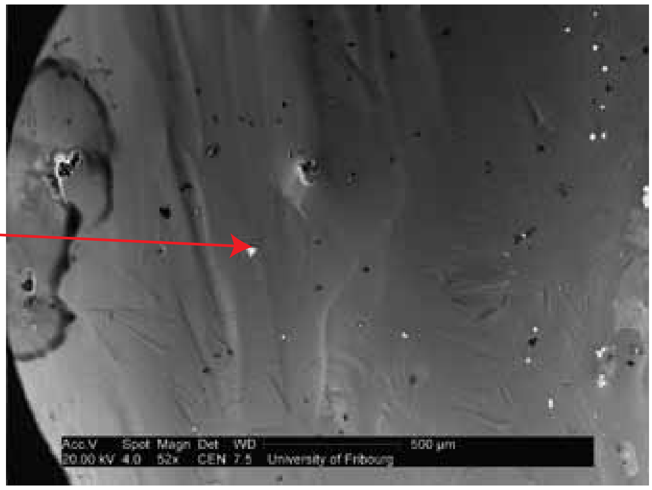

Fig. 339b

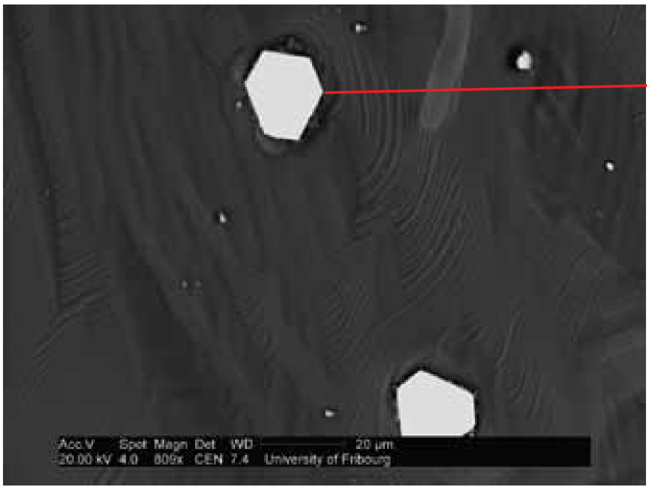

Fig. 339e

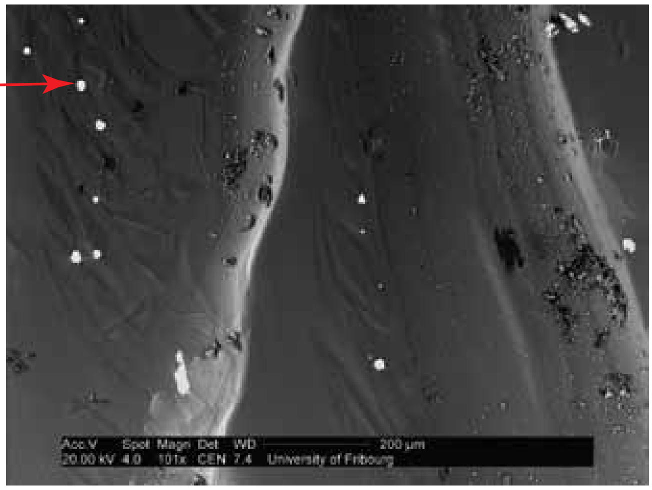

Fig. 339f

Fig. 339a-f *SEM-BSE image of the surface of the new synthetic spinel produced by flux (pulled method). Numerous particles composed of Ir were identified in the shape of triangles (Fig. 339c) or hexagons (Fig. 339a and e). The particles may also form clusters (Fig. 339b) and can be misinterpreted as opaque inclusions suggesting natural origin. All particles were identified by SEM-EDX as Ir alloy.*

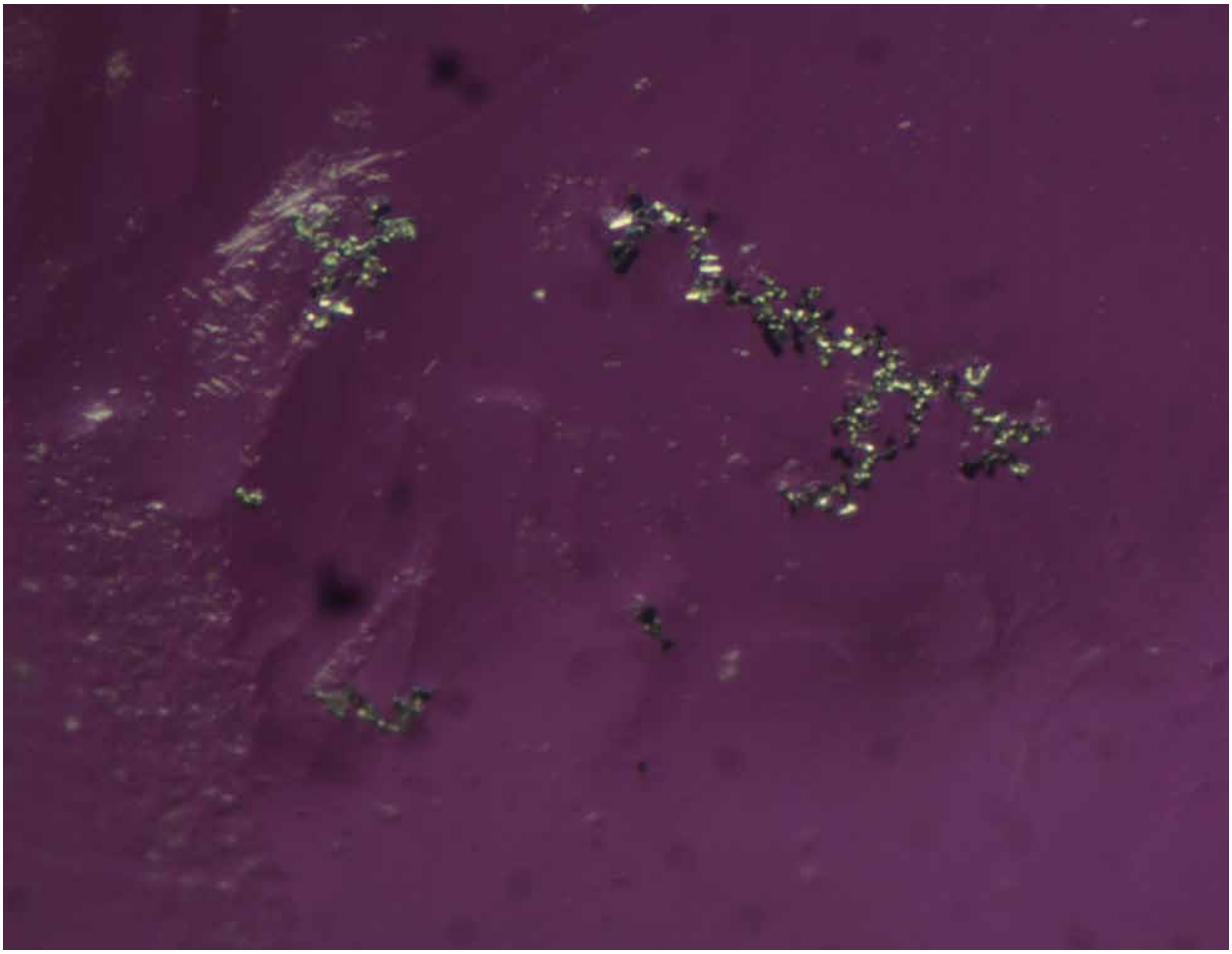

Fig. 340a *Microphotograph of clusters of solid black inclusions occasionally present in the new synthetic spinels. Attention: May be misinterpreted as a natural phenomenon.*

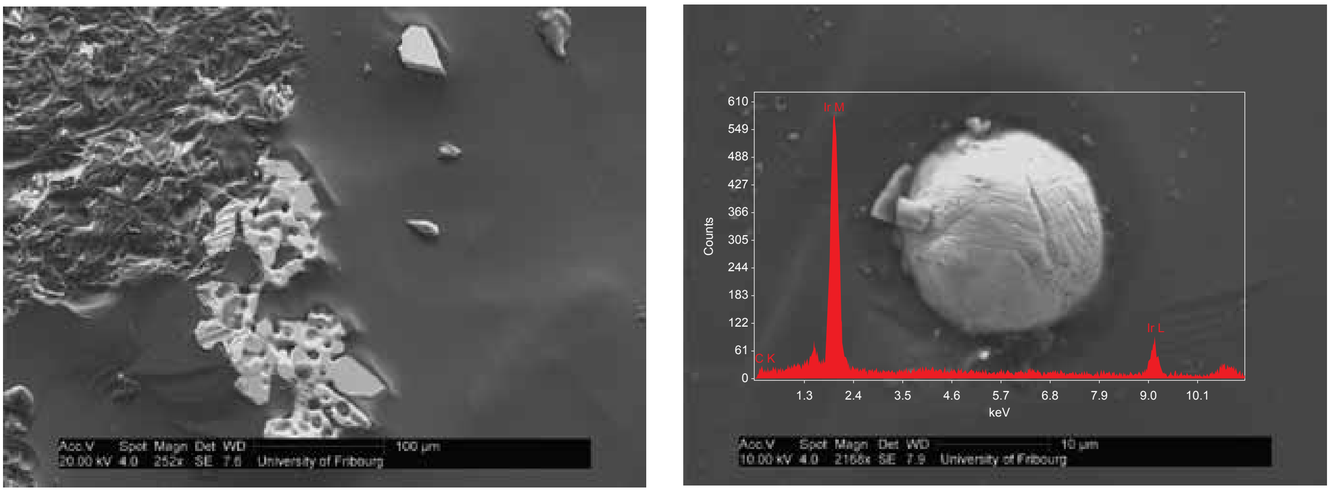

Fig. 340b-c *SEM-BSE image details of particles found on the surface of the new synthetic spinels. They are composed of Ir. A round inclusion turned out to be of Ir particle as well (see inserted SEM-EDX spectrum).*

LITERATURE

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