



GRS Alert: New spinel treatment discovered involving heat and cobalt-diffusion

Introduction

Cobalt-spinels are considered one of the most precious spinel and are rarely colored blue with or without grey to black tones. Blue "cobalt spinel" are at least 10-100x more expensive per carat than grayish-blue colored spinel. Cobalt intensifies the blue color in spinel, considerably enhancing its beauty. Cobalt-spinel over 5 ct can be US\$ 10,000 to 30,000 per carat depending on beauty, while grayish-blue over-dark stones are only US\$ 250 to 500 per carat depending on size (see Fig. 307b).

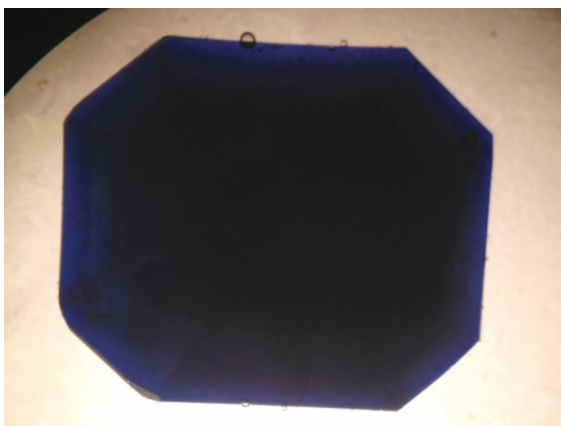


Fig. 1a

Therefore, the incentives for color-enhancement by cobalt diffusion treatment of spinel are high and it should appear sooner or later in the market. Although we have not seen much of this new treatment yet, its appearance in the market is now a reality. Fig. 307a The new type of blue spinel appeared in Sri Lanka in a local market in Beruwala and was brought to our attention by local gemologist MTM Haris.

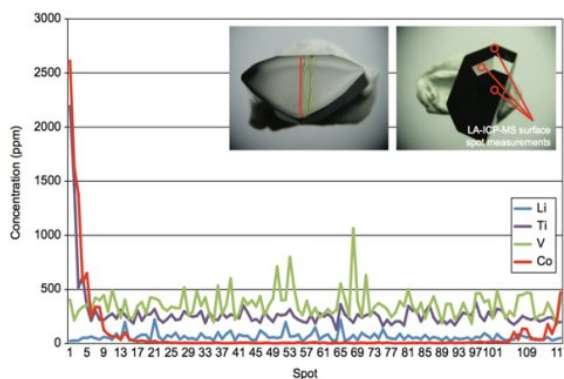


Fig. 2b Surface staining in a Co-diffusion treated spinel. It is located at feathers and cracks on the surface. The spinel was repolished after diffusion-treatment but these features were not removed.

He had seen an unusual spinel of dark blue colour, RI near 1.720 with diffused line and not sharp for a faceted spinel. The spectroscope shows a cobalt spectrum, but cobalt line somewhere near 650 nm rather than 630 nm for natural cobalt spinel. He initially thought that it might be a new synthetic spinel but iron spectrum, RI and inclusions proved it otherwise as a natural spinel. When immersed, this stone shows purple colour concentration around cracks and edges. Some purple colour patches were also seen. No umbrella effect, such as in surface diffusion treated blue sapphires. A tension crack suggested that heat treatment was involved. However, its color was more similar to a dark natural Cobalt-spinel from the origin of Sri Lanka, unlike Cobalt spinel from Vietnam or synthetic counterparts. Under the immersion microscope, a blue rim was noticed that was seen following the outline of the cut stone (Fig. 307a) and this suggested a diffusion-treatment.

The sample was sent to and analysed by GRS with advanced analytical techniques in order to provide proof of this new diffusion-treatment that was previously unreported in the literature. GRS contacted a cooperating laboratory at the ETH Zurich for LA-ICP-MS analyses. A visual inspection of the sample in the GRS laboratory showed that in addition to the observations described above, irregular blue patches can be found on the surface of the sample that are normally considered indications of diffusion treatment.

For the purpose of studying the sample further, it was cut into 2 pieces (Fig. 309). It allowed us to investigate the sample in a profile across the rim and core. The special testing with ED-XRF confirmed unusually high Cobalt concentrations along with low iron-concentrations in the rim (Fig. 312). LA-ICP-MS analysis confirmed high cobalt and titanium-concentrations in the rim as well as underlying concentrations of Zn, Fe and Li (Fig. 309 and Tab Diff1), suggesting a natural spinel material was subjected to diffusion treatment. The results of photoluminescence spectroscopy showed that the spinel was heat-treated (Fig. 310 and Fig. 311). LA-ICP-MS analysis in a profile across the sample finally proved that the sample was surface-diffused to a depth of 300 microns with cobalt and titanium. The base material used was confirmed as a natural spinel of light grayish-blue color. It can be concluded that a new cobalt diffusion-treatment of spinel exists in the market and that blackish-blue Cobalt spinel, with colors and refractive index similar to natural counterparts, must be carefully investigated for the possibility of diffusion treatment using special analysis such as PL and LA-ICP-MS in combination with microscopic analyses.



Tab 1: LA-ICP-MS analyses						
	Surface		Outer Rim		Center	
	avg (6)	stdev	avg (4)	stdev	avg (6)	stdev
Li	44.8	5.9	33.8	13.3	69.4	45.3
B	1.83	0.91	2.57	0.71	1.66	0.62
Ti	200	12	1201	787	230	40
V	241	17	316	79	295	58
Mn	154	10	172	80	185	57
Fe	9561	792	8208	1624	12626	4920
Co	12719	2273	1550	842	7.72	3.59
Ni	120	85	8.33	7.74	3.20	1.23
Cu	17.2	3.1	7.69	8.82	1.80	0.94
Zn	1666	167	2071	131	2810	915
Ga	282	29	303	78	503	253

Fig. 4 Chemical profile analysis across a diffusion-treated spinel. The diffusion-treated spinel has been cut in half and measured with 117 measuring points. It can be seen that Ti and Co increase toward the rim (from diffusion), while Li concentrations remain constant ("natural fingerprint"). Tab. 1 LA-ICP-MS analyses by Prof. Detlef Günther from the ETH ZH (Hoenggerberg) for some elements present in the spinel, in ppm (Cr and Be concentrations not measured. Cr is present, see PL analysis, Fig. 4 and ED-XRF Fig. 6)

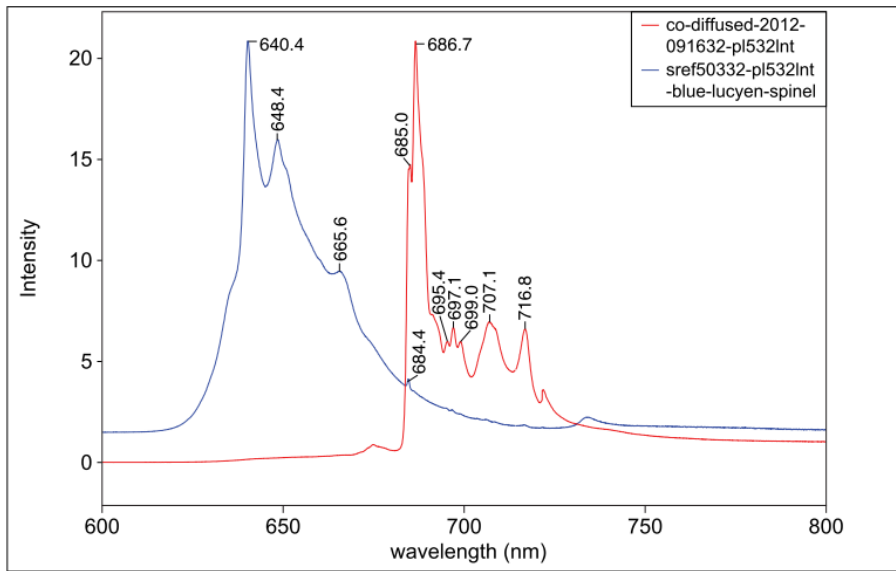


Fig. 310 Photoluminescence spectra of unheated Vietnamese Cobalt-spinel (left) and Co-diffused natural spinel (right). The spectra of the Co-diffused spinel is indicative of thermal enhancement. As can be seen, the diffusion-treated spinel was only partially transformed from a normal spinel into an inverse spinel (compare to Fig. 311).

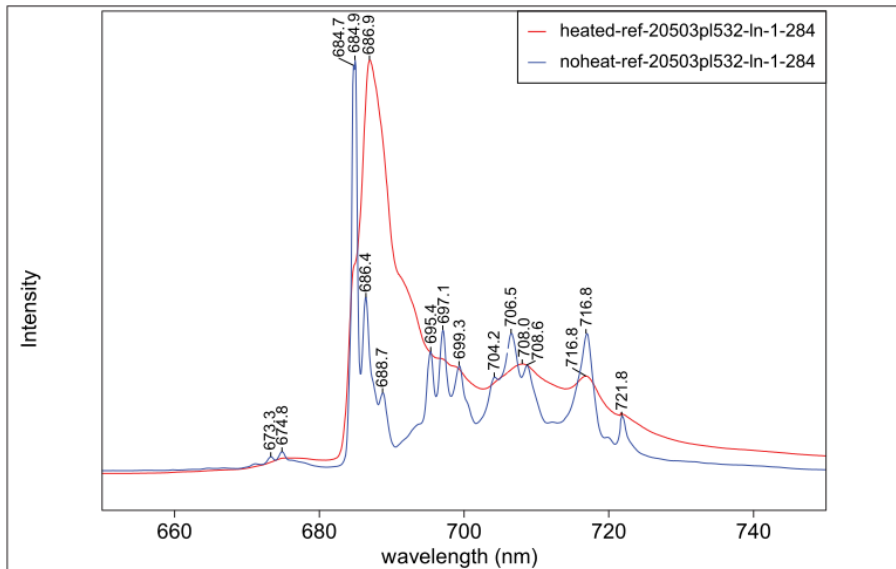


Fig. 311 Photoluminescence spectra (PL 532) of same spinel before and after heat-treatment (spinel heated at GRS experimental heat-treatment facility in Mogok). Note the significant shift of lines and disappearance of lines (Blue is unheated and Red after heat treatment). This is attributed to the spinel's transformation of normal to inverse spinel crystal structure and heat-treatment above 700 °C.

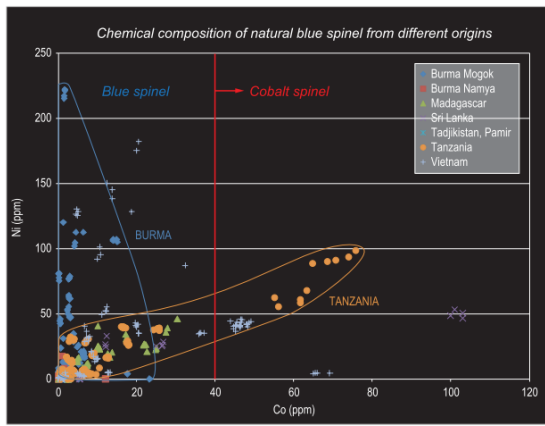


Fig. 313 The Ni-Co-origin diagram: High Co-concentrations are found Tanzanian, Vietnamese and Sri Lankan spinels. Burmese spinels contain high Ni/Co-ratios in comparison to certain spinels from Tanzania (blackish-blue colors). Spinel of highest Co-concentrations from Vietnam did also contain some Ni-concentrations. Above 40-60ppm Co (at low Fe-concentrations) spinels can be called Cobalt spinels.

Authors

Dr. Adolf Peretti¹, Prof. Detlef Günther² and MTM Haris³

¹ GRS Gemresearch Swisslab Ltd, Sempacherstr.1, CH-6003 Lucerne, Switzerland

² Laboratory of Inorganic Chemistry, ETH Zurich, HCI, G113, CH-8093 Zurich, Switzerland

³ EG Lab, Emteem Gem Laboratory, Chinafort, Beruwala, Sri Lanka

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