A Rare Bicoloured Spinel

Recently, the GIT Gem Testing Laboratory (GIT-GTL) received for identification a bicoloured purple and greenish blue stone that weighed 0.57 ct and measured 7.02 × 3.32 × 2.27 mm (Figure 27). The stone was singly refractive with an RI of 1.718 and a hydrostatic SG value of 3.60. Observation with a gemmological microscope revealed oriented arrays of slender, short to elongate iridescent silk inclusions and minute particles in the purple colour zone (Figure 28), but no inclusions in the greenish blue portion. It was inert to both long- and short-wave UV radiation. The stone's RI and SG values, as well as its inclusion features, are typical for natural spinel.

UV-Vis-NIR spectroscopy, recorded with a Perkin-Elmer Lambda 950 spectrophotometer in the range of 300–1500 nm, showed absorption features at 371, 386, 458 and 555 nm for the purple zone, while the greenish blue portion displayed the same characteristics along with additional broad bands at 656 and 917 nm (Figure 29). These features were assigned by D'Ippolito *et al.* (2015) to Fe^{2+}, Fe^{3+} and Fe^{2+}-Fe^{3+} intervalence charge transfer (IVCT). In the spectrum of the purple zone, the absorptions at 371, 386 and 555 nm (all due to Fe^{2+}) create a transmission window in the blue-violet region which, combined with decreasing absorption in the red region, give rise to the purple colouration. The spectrum of the other colour zone, by contrast, shows stronger Fe^{2+} absorption at 371 and 386 nm, and the presence of a broad band at around 656 nm (due to Fe^{2+}-Fe^{3+} IVCT) combines to create a transmission window in the blue-green region, thus giving rise to the greenish blue colouration. We therefore infer that the greenish blue zone contains somewhat more Fe^{2+} and Fe^{3+} than the purple area, in agreement with a

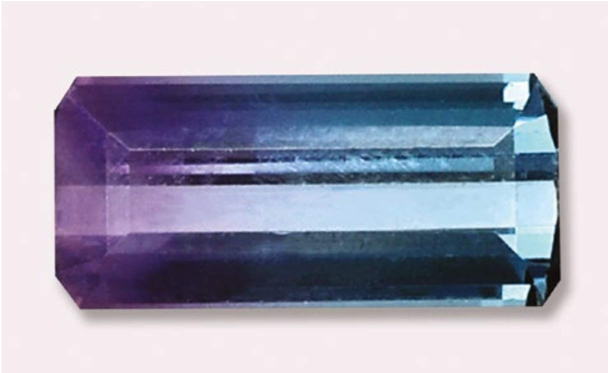

Figure 27: This 0.57 ct bicoloured purple and greenish blue stone was identified as spinel. Photo by A. Buathong.

relatively higher total iron content in that portion of the sample (see below).

PL spectroscopy of both the purple and greenish blue zones of the spinel, measured by a Renishaw inVia Raman microspectrometer using 532 nm laser excitation at room temperature, showed a series of emission centres at 671, 673, 675, 685, 686, 695, 697, 699, 704, 706, 708, 718 and 722 nm (Figure 30). This emission series perfectly matched the reference PL spectrum for spinel in the RRUFF database, and is known to be due to Cr^{3+} substituting for Al^{3+} in the octahedral site (e.g. Gaft *et al.* 2005; Skvortsova *et al.* 2011). Furthermore, the rather sharp peaks associated with the Cr-related emission centres in the PL spectra also indicate this stone has not been subjected to heat treatment (Saeseaw *et al.* 2009; Smith 2012).

Semi-quantitative chemical analysis of the stone's purple and greenish blue zones by EDXRF spectroscopy (using an Eagle III instrument) revealed the expected major amounts of Mg and Al, along with minor Fe, Si and Zn, and traces of V, Cr and Ga (Table I). Overall, the chemical data, when normalised to 100 wt.%, are

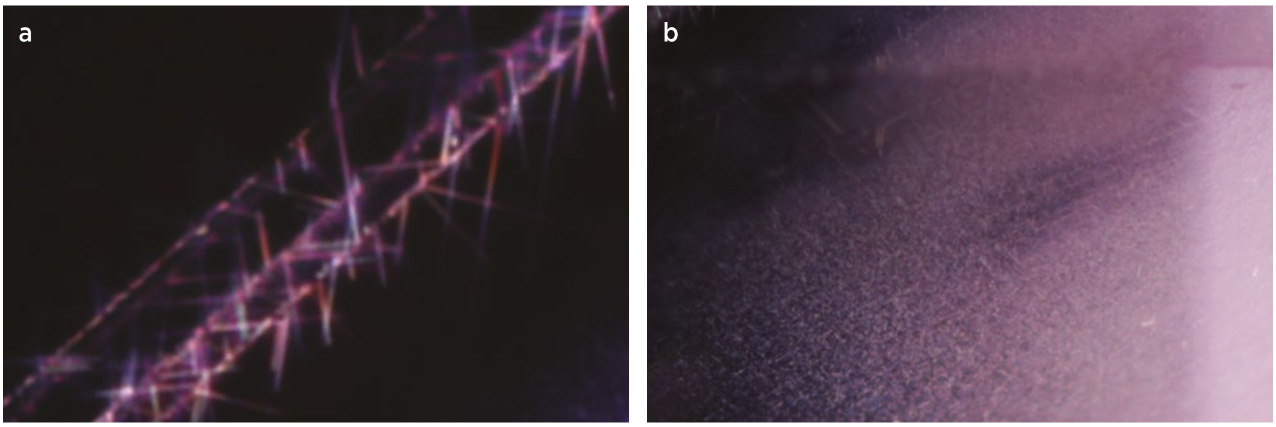

Figure 28: (**a**) Networks of iridescent silk and (**b**) minute particles were observed in the purple zone of the bicoloured spinel. Photomicrographs by A. Buathong; image widths 1.3 mm.

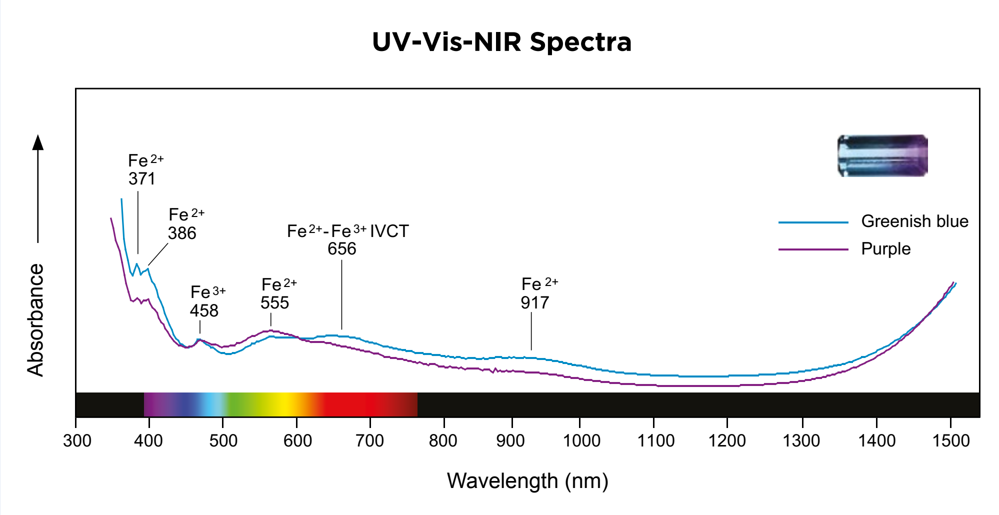

Figure 29: UV-Vis-NIR spectra of the purple and greenish blue zones of the spinel show absorption features related to Fe^{2+} and Fe^{3+}. The path length of the beam was about 2.3 mm.

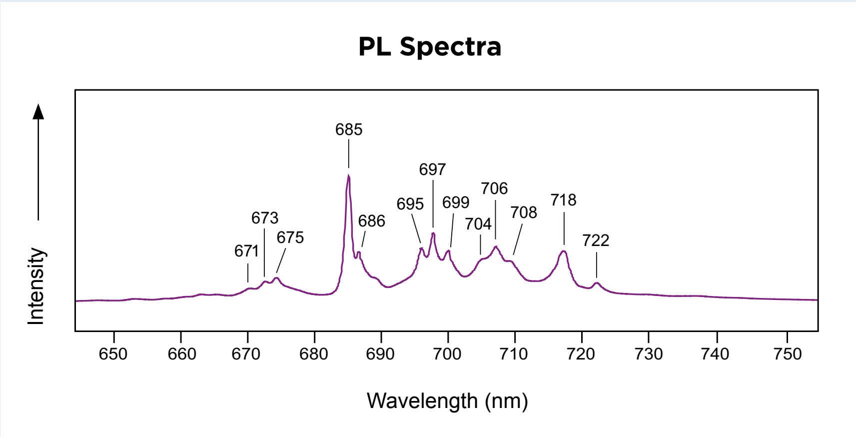

Figure 30: Time-resolved PL spectra of both colour zones of the spinel show a series of sharp Cr^{3+}-related emission centres, as illustrated by this spectrum of the purple zone.

Table I: Minor- and trace-element composition of the bicoloured spinel by EDXRF spectroscopy.

Oxides (wt.%)	Purple zone	Greenish blue zone
SiO_2	1.64	1.33
V_2O_5	0.05	0.06
Cr_2O_3	0.03	0.03
Fe_2O_3 (total)	2.56	2.77
ZnO	1.01	0.69
Ga_2O_3	0.04	0.06

consistent with the spinel composition ($MgAl_2O_4$)—wherein minor Zn^{2+} and, probably, Fe^{2+} substitute for Mg^{2+} in the tetrahedral sites and traces of Fe^{3+}, Si^{4+}, Cr^{3+}, V^{3+} and Ga^{3+} replace Al^{3+} in the octahedral sites.

The chemical composition of this stone, with significant Zn content (Muhlmeister *et al.* 1993) and the series of sharp Cr-related emission features in the PL spectra, indicates that it is a natural, unheated spinel. Even though spinel has commonly been found in a rather wide colour range—including colourless, red, blue, violet, green, brown, pink and black—bicoloured specimens such as this stone are very scarce (cf. DuToit 2012).

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Purple Tourmaline from Zambia

Tourmaline is not commonly encountered in the violet-to-purple colour range, so these authors were interested to see some new purple material that reportedly came from Zambia in 2019. A rough parcel of this tourmaline was obtained by Farooq Hashmi (Intimate Gems, Glen Cove, New York, USA) during the February 2020 Tucson gem shows. His supplier had about 100–150 g of rough material and Hashmi obtained several pieces that he kindly loaned for examination.

The crystals consisted of striated prisms with sharp edges and no evidence of alluvial transport (e.g. Figure 31). The ends of the prisms were formed by broken surfaces except for one that showed evidence of chemical resorption in the form of parallelogram-shaped etch pits. Most of the crystals had surface residues of rust-coloured material, as would be expected from lateritic soil. Their body colour was a fairly homogeneous medium-to-dark slightly greyish purple, and they showed strong dichroism in pale purple (lavender) and vivid purple. Internal features consisted of planar and irregular thin films, partially healed fractures marked by the presence of fluid inclusions ('trichites'), fissures, tubes and elongate colourless birefringent crystals; the last two features were oriented parallel to the *c*-axis.

Figure 31: This purple tourmaline (8.03 g) reportedly came from a new find in Zambia. Photo by B. M. Laurs.