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Blumentritt F., Zuber G., Caplan C., Notari F. (2025). *Diffusion-induced blue spinel-like layer on natural sapphire*. Gems & Gemology, Gem News International. 61(2), pp. 221-223.

TREATMENTS

Diffusion-induced blue spinel-like layer on natural sapphire. Recently, the GGTL laboratory in Geneva received three gems for identification weighing 1.43, 1.55, and 2.65 ct and exhibiting a blue coloration fairly typical of cobalt-bearing gems such as spinel (figure 25, left). Microscopic observation revealed the presence of inclusions, some

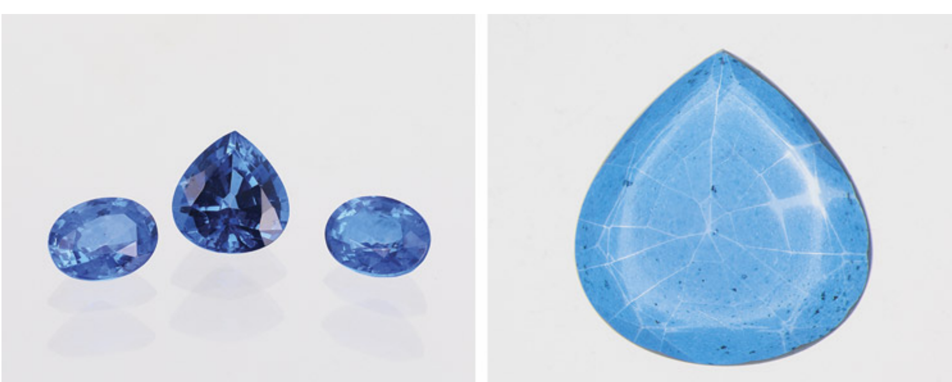

Figure 25. Left: Sapphires, weighing 1.43, 1.55, and 2.65 ct, diffused with cobalt and zinc, which formed a surface layer of blue spinel. Right: The 2.65 ct sample in immersion with brightfield illumination showing the typical spiderweb effect of diffused stones. Photos by Féodor Blumentritt.

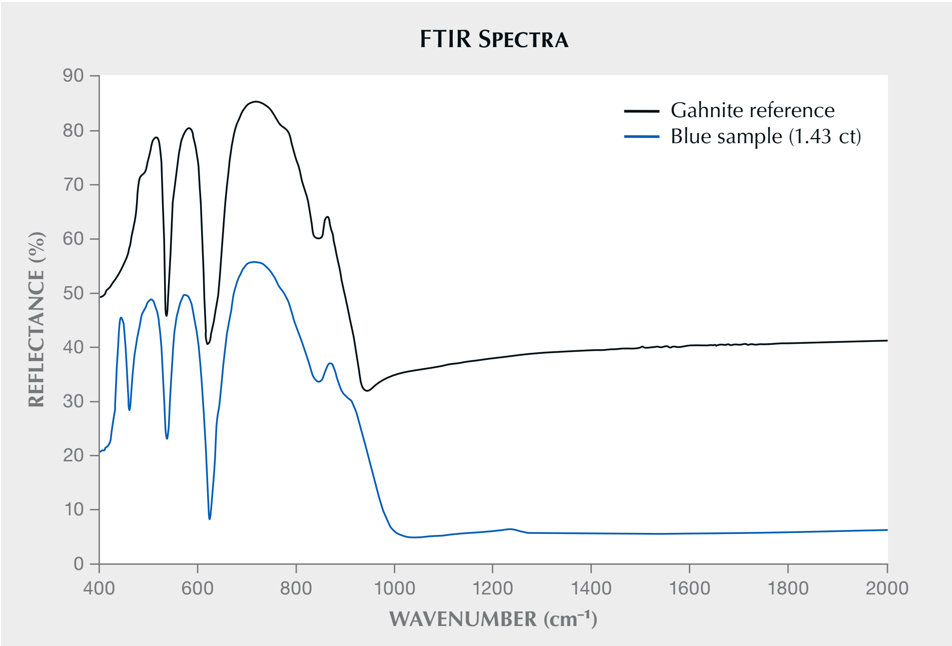

Figure 26. Infrared spectra in specular reflectance mode of a natural gahnite reference sample from Madagascar and the 1.43 ct blue sapphire sample. Spectra are offset vertically for clarity.

altered, such as rutile needles, mineral inclusions surrounded by discoidal fractures, and Rose channels. However, the surface condition and color zonation indicated the presence of diffusion. Some facets that were visibly unpolished following treatment displayed a granular appearance. In immersion fluid, it was observed that some of the edges and facets underwent repolishing, resulting in colorless surfaces (figure 25, right). On one of the stones, the color zonation was clearly visible on the surface of the facets and appeared as a cloudy pattern.

The identification of these stones by means of specular reflectance infrared spectroscopy demonstrated a clear correlation with gahnite ($ZnAl_2O_4$; figure 26). However, analysis of the stones' luminescence under long-wave

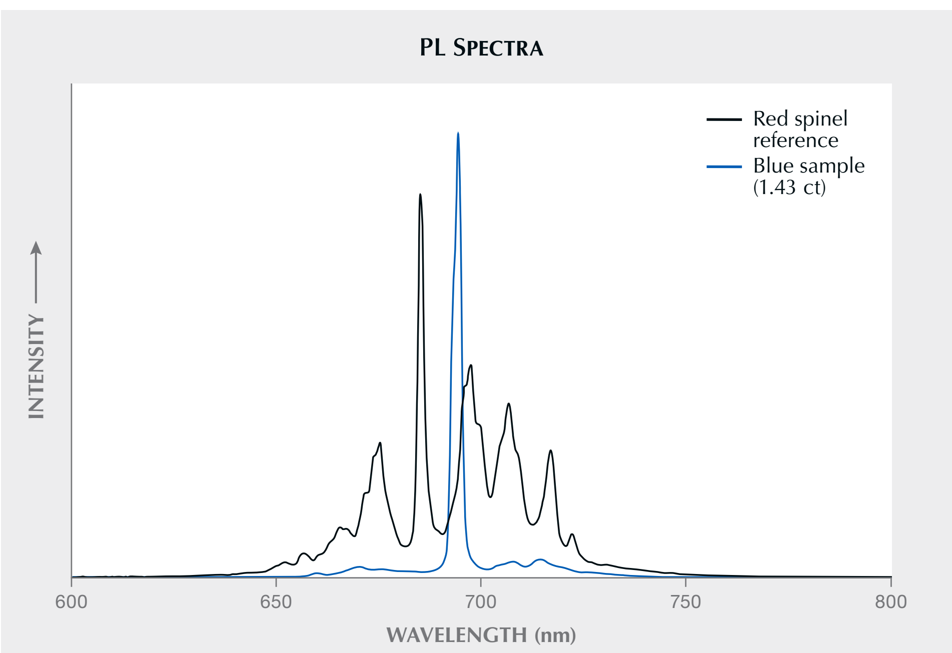

Figure 27. Typical luminescence spectrum of a red spinel reference sample compared with the luminescence spectrum of the 1.43 ct blue sapphire sample that matched the usual luminescence of Cr^{3+} in corundum. Note that the resolution of the spectrometer was not high enough to distinguish the two R1 and R2 transitions at about 694 nm.

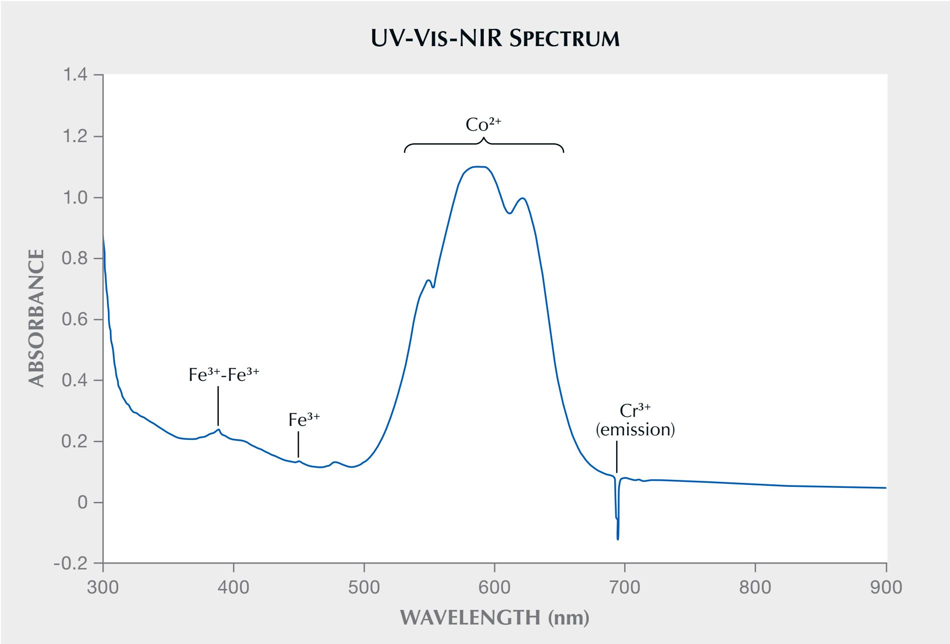

Figure 28. Absorption spectrum of the 1.43 ct sample showing characteristic features of Co^{2+} usually measured in spinel, superimposed to usual iron absorption features of sapphire.

ultraviolet (365 nm) light revealed a Cr^{3+} luminescence spectrum, characteristic of an octahedral environment in corundum (T. Kushida and Y. Tanaka, "Direct optical excitation into excited states of Cr^{3+} pairs in ruby," *Solid State Communications*, Vol. 11, No. 10, 1972, pp. 1341–1344), rather than in spinel structure (figure 27; see e.g., I. Malíčková et al., "Optical and luminescence spectroscopy of varicolored gem spinel from Mogok, Myanmar and Lục Yên, Vietnam," *Minerals*, Vol. 11, No. 2, 2021, article no. 169). This luminescence was homogeneous across the stones, and it was confirmed that it did not emanate solely from the surface by illuminating the colorless zonation of the stones. The results of an energy-dispersive X-ray fluorescence semi-quantitative chemical analysis provided evidence to support the inconsistency between the infrared spectrum and luminescence, with a majority proportion of aluminum (~89.9 wt.% of Al_2O_3) and, to a lesser extent, zinc (~6.5 wt.% of ZnO). The proportions of the two elements do not correspond to a spinel structural formula. Instead, they were consistent with the hypothesis of the coexistence of spinel and corundum structures.

Moreover, the detection of large quantities of cobalt (~3.4 wt.% of Co_3O_4) was consistent with the ultraviolet/visible/near-infrared (UV-Vis-NIR) absorption spectrum, supporting cobalt as the main cause of color (figure 28; D.K. Sardar et al., "Spectroscopic properties of Co^{2+} in related spinels," *Journal of Applied Physics*, Vol. 91, No. 8, 2002, pp. 4846–4852). A previous publication already documented "cobalt-diffused sapphires" (R.E. Kane et al., "The identification of blue diffusion-treated sapphires," Summer 1990 *G&G*, pp. 115–133), but the presence of Co^{2+} in a corundum structure remained unclear despite a parallel made with the color of cobalt-blue synthetic spinel. One later article (Summer 2002 Gem Trade Lab Notes, p. 167) discussed a possible interaction of cobalt with the corundum surface without being more specific.

The aforementioned analyses led to the identification of these stones as natural sapphire partly owing to the typical Cr^{3+} luminescence. These sapphires likely underwent an attempt at diffusion of zinc and cobalt, resulting in the crystallization of a layer of blue spinel structure (gahnite) on the surface, which was identified by reflectance infrared spectroscopy. This treatment serves to demonstrate the considerable inventiveness required to induce a cobalt-bearing spinel color in corundum.

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