Unheated Pink Sapphire from Madagascar with OH-related 3232 and 3185 cm^{-1} FTIR Bands

The alluvial gem deposits of Ilakaka in south-western Madagascar have been known for more than two decades as an important source of corundum, mainly producing pink to purple stones, but also blue, yellow and padparadscha varieties. Some of this material, especially purple to slightly purplish pink hues, is commonly heat treated (mostly in oxidising conditions) to shift the colour to a more attractive and vivid 'hot' pink.

For experienced gemmologists, the detection of heat treatment of corundum performed at high temperatures (1400°C and above) is relatively straightforward, often relying on the presence of heat-related microscopic features, as well as Raman spectroscopy (of inclusions) and FTIR spectroscopy. More challenging, however, is the detection of corundum heated at lower temperatures—around 800–1200°C—partly because microscopic features that indicate low-temperature heating are often absent (Pardieu *et al*. 2015; Krzemnicki *et al*. 2023; Soonthorntantikul & Palke 2025). In such cases, detection relies entirely on careful spectroscopic analyses.

FTIR spectroscopy has long been used to detect heat treatment of corundum via the presence of specific absorption bands related to structurally bonded hydroxyl (OH) groups in the corundum (α-Al_2O_3) structure. Typically, sharp peaks of the 3309 cm^{-1} series are observed, caused by structural OH defects combining with aluminium vacancies and tetravalent cation Ti^{4+} substitutions for Al (Moon & Phillips 1991). Nominal band positions of this series include 3309, 3232 and 3185 cm^{-1}. Unheated metamorphic pink and blue sapphires and rubies generally display only the 3309 cm^{-1} peak, reflecting two Ti^{4+} substitutions + Al vacancy + OH defect clusters. Heating causes the dissociation of these clusters, producing single Ti^{4+} substitution + Al vacancy + OH defect clusters and a corresponding increase in the 3232 and 3185 cm^{-1} peaks, with a decrease in the one at 3309 cm^{-1} (Moon & Phillips 1991). Consequently, the presence of the 3232 and 3185 cm^{-1} peaks has been widely interpreted as a robust indicator of heat treatment in metamorphic corundum (Pardieu *et al*. 2015; Krzemnicki 2018; Saeseaw *et al*. 2020; Soonthorntantikul & Palke 2025).

On the other hand, the presence of goethite (α-FeO[OH]) inclusions is considered robust evidence for unheated corundum (Koivula 1987, 2013; Sripoonjan *et al*. 2016; Krzemnicki *et al*. 2023). Goethite has low thermal stability and dehydrates to hematite (α-Fe_2O_3) at temperatures between 300°C and 325°C, a range far below conventional and low-temperature heat treatments of corundum. Thus, the identification of goethite inclusions through microscopic observations and Raman analysis provides proof that a stone has not been subjected to a heat-treatment process.

Figure 29: The 0.71 ct slab on the lower right was polished from this parcel of pink to purplish pink sapphires that was recently mined from Ilakaka, Madagascar. Photos by H. A. O. Wang; digitally arranged by M. S. Krzemnicki.

This note describes a pink sapphire from a parcel of untreated rough material (Figure 29) that was recently mined from Ilakaka. The parcel was kindly donated to SSEF for research by A. Leuenberger (ALine GmbH, Switzerland) and Nirina Rakotosaona (Madagascar). The pink sapphire described here was cut at SSEF into a 0.71 ct parallel-polished slab, with the *c*-axis inclined to the flat faces due to the shape of the rough. Microscopic observation revealed the presence of numerous tiny zircon inclusions (mostly in clusters) together with several hollow channels filled with a brown to orangey brown epigenetic material, with no evident features indicating heat treatment (Figure 30).

Figure 30: The 0.71 ct pink sapphire contains numerous tiny zircon inclusions and several deep channels (parallel to the *c*-axis) containing epigenetic goethite (identified by Raman analysis). Photomicrograph by M. S. Krzemnicki; magnified 50×.

Careful spectroscopic investigation of this sample revealed a paradox. Its FTIR spectrum exhibited peaks at 3231.3 and 3183.6 cm^{-1} (Figure 31), which are considered indicators of heat treatment as described above. However, Raman analyses of the deep-channel structures confirmed that they were filled with goethite (Figure 32), providing evidence that the sample had not been heated.

This result is consistent with additional samples (pink to purple and blue sapphires, as well as rubies) analysed by the authors in recent months in which both the 3232 and 3185 cm^{-1} peaks were present

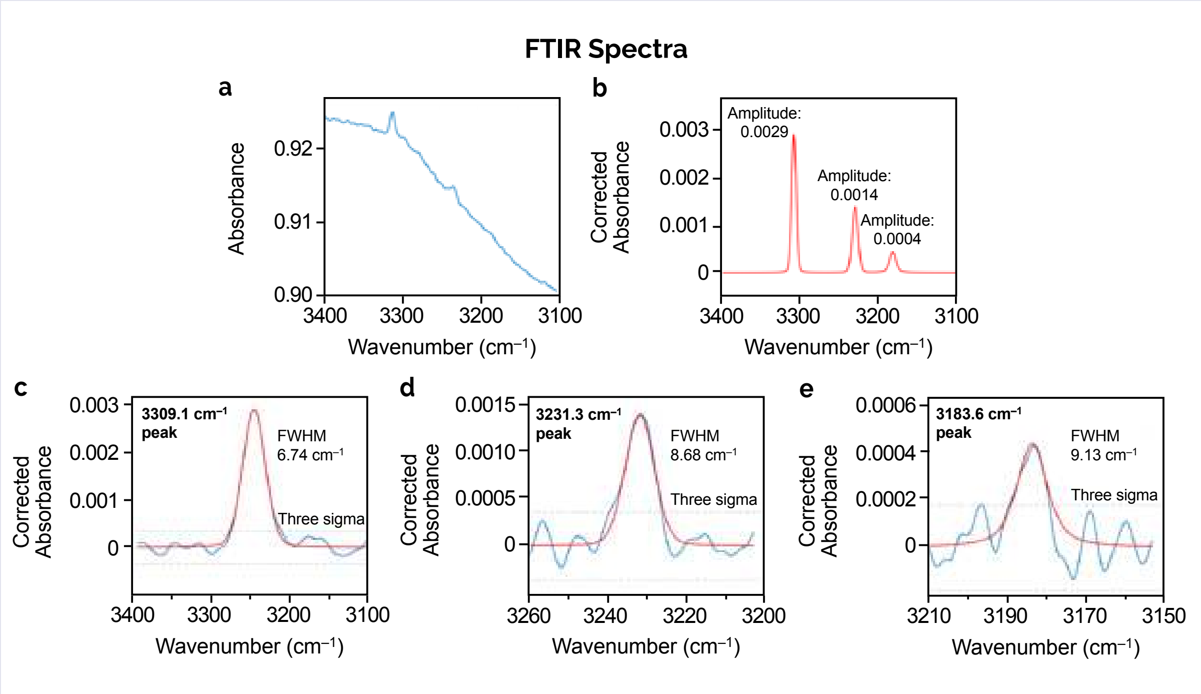

Figure 31: (**a**) An unpolarised diffuse reflectance FTIR spectrum of the pink sapphire is shown (**b**) after peak fitting in order to reveal the presence of the 3309 cm^{-1} series, with peaks at (**c**) 3309.1, (**d**) 3231.3 and (**e**) 3183.6 cm^{-1}. In c–e, the blue trace is the original spectrum before fitting, and the horizontal dashed lines mark the three-sigma boundaries calculated from the nearby baseline signal.

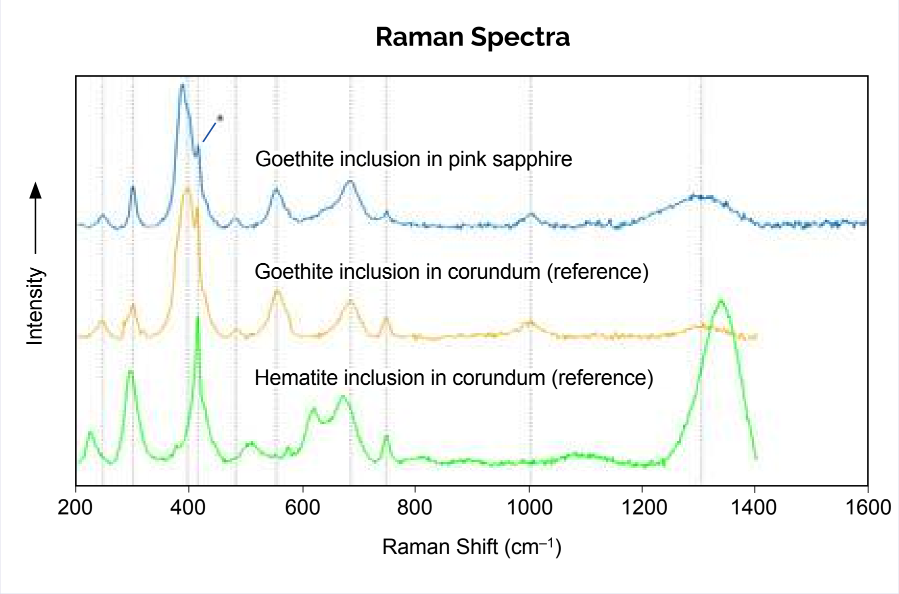

Figure 32: The Raman spectrum of goethite present in hollow channels within the pink sapphire is shown together with SSEF reference spectra for goethite and hematite inclusions in corundum. The Raman peak from the host corundum is marked with an asterisk.

together with metamict zircon inclusions and/or hydroxides such as goethite in deep surface-reaching fissures and hollow channels, along with diaspore in fluid inclusions. These features clearly indicated that the stones had not been heated (Krzemnicki *et al*. 2025), as both hydroxides would have dehydrated to Fe- and Al-oxides, respectively, at temperatures as low as 325°C (goethite to hematite) and 550°C (diaspore to corundum) during heat treatment.

Based on these findings, it is apparent that the 3232 and 3185 cm^{-1} FTIR peaks are not always the result of heat treatment but may also be present in unheated corundum of metamorphic origin. As such, the 3309 cm^{-1} peak series, together with other OH-related peaks which are not yet fully understood (e.g. the peak at 3180 cm^{-1} described by Soonthorntantikul & Palke 2025), are caused by a complex interplay of Al vacancies coupled with Ti^{4+} substitutions and OH defects in the corundum structure that may be an expression of the complicated formation process of corundum, and thus is not always a criterion for heat treatment.

Therefore, we suggest that careful Raman analyses of inclusions (such as goethite, diaspore and zircon) are mandatory when identifying the heat treatment of corundum, as temperature-dependent phase transformations such as the dehydration of goethite and diaspore can provide conclusive evidence for whether a ruby or sapphire (of any colour) has been heat treated.

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A Pink Sapphire with Questionable Heat Treatment

A pink sapphire weighing over 20 ct was recently submitted to Guild Gem Laboratories, and it presented a particularly challenging case for the determination of heat treatment. According to the client, the stone had previously received four reports from three different laboratories, with inconsistent conclusions. One laboratory initially classified the stone as unheated four years ago but later revised their assessment to heated. Subsequently, two additional laboratories issued contradictory opinions—one concluding