Zircon inclusions in unheated pink sapphires from Ilakaka, Madagascar: A Raman spectroscopic study

M.S. Krzemnicki, P. Lefèvre, W. Zhou, H.A.O. Wang
Swiss Gemmological Institute SSEF
gemlab@ssef.ch

Since its discovery in 1998, the secondary gem deposit of Ilakaka, southwestern Madagascar has produced a large number of outstanding stones for the gem trade, notably sapphires and fancy sapphires in a wide range of colours (Milisenda et al. 2001). Until today, pink sapphires from Ilakaka are found in great numbers in the trade, often characterised by an outstanding quality and a pastel pink to vivid pink ("hot pink") colour.

Interestingly, pink sapphires from Ilakaka commonly contain numerous rounded zircon inclusions, sometimes even clustered in aggregates (Figure 1). Zircon is found in corundum from many different geological settings and geographic origins and may provide crucial information for gem testing, both, regarding heat treatment (Wang et al. 2006, Krzemnicki 2010, Saeseaw et al. 2020) and origin determination (Xu & Krzemnicki 2021).

The Raman analysis of zircon inclusions in pink sapphires from Ilakaka (Madagascar) is widely used in gem labs as a routine test as it may provide supporting analytical evidence of a heat treatment. In this study, we focus on Raman spectra of zircon inclusions in unheated pink to purplish pink sapphires from Ilakaka to better characterise and understand the range and variability of the SiO_4-related bandwidths. More than 100 zircon inclusions in 28 samples (rough and cut) from the SSEF research collection were analysed using an InVia Renishaw Raman microprobe coupled with a 514 nm argon-ion laser. In accordance with literature (Nasdala et al. 1995, Wang et al. 2006, Saeseaw et al. 2020) we focussed on the main Raman peak υ3 (SiO_4 anti-symmetrical stretching mode) of zircon at about 1010 cm^{-1} as a measure of its crystallinity (or degree of metamictization). From these spectra we determined the υ3 bandwidth (FWHM: Full-Width-Half-Maximum) by fitting into a software-integrated Gaussian-Lorentzian function after baseline correction.

Our results of all analysed zircon inclusions in unheated samples show a large variation of υ3 peak position and bandwidth not only in different pink to purple sapphires, but even in neighbouring zircon inclusions within the same specimen (Figure 2). Interestingly, we also found peak variations when measuring several different positions of selected single zircon inclusions. The FWHM of υ3 in our unheated samples range between 7.5 to 17.6 cm^{-1}, with a median value of below 10. Similar results have been described by Wanthanachaisaeng (2006, 2007). Our analyses in unheated rough and cut pink sapphires from Ilakaka, however, reveal bandwidth values distinctly lower than those reported by Wang et al. (2006) and Saeseaw et al. (2020) in their samples. Our results show, that heat treatment detection of pink sapphires from Madagascar based on Raman spectra of zircon inclusions alone needs to be applied cautiously to avoid misinterpretations.

Figure 1: Pink sapphire of 7.9 ct from Ilakaka, Madagascar and photomicrograph of zircon inclusions (magnification 50x).

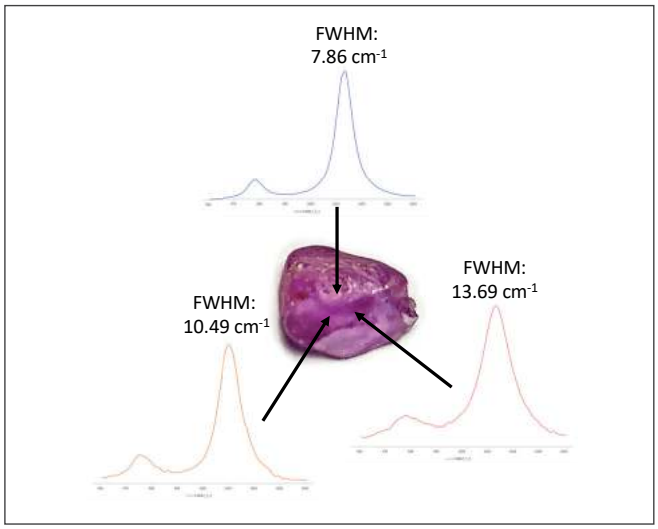

Figure 2: Variability of the bandwidth (FWHM) of the main zircon Raman peak at about 1010 cm^{-1} in three different zircon inclusions in an unheated rough pink sapphire from Ilakaka, Madagascar.

References

Krzemnicki M.S. (2010) How to get the "blues" out of the pink: Detection of low-temperature heating of pink sapphires. SSEF Facette, No. 17, p 12

Milisenda, C.C., Henn, U., and Henn, J. (2001). New gemstone occurrences in the south-west of Madagascar. Journal of Gemmology, 27(7), 385-94

Nasdala L., Irmer G., Wolf D. (1995) The degree of metamictization in zircon: A Raman spectroscopic study. European Journal of Mineralogy, 7(3), 471-478

Saeseaw S., Khowpong C., & Vertriest W. (2020). Low-temperature heat treatment of pink sapphires from Ilakaka, Madagascar. Gems & Gemology, 56(4), 448-457

Wang W., Scarratt K., Emmett J.L., Breeding C.M., Douthit T.R. (2006) The effects of heat treatment on zircon inclusions in Madagascar sapphires. Gems & Gemology, 42(2), 134-150

Wanthanachaisaeng, B., Häger, T., Hofmeister, W., and Nasdal, L. (2006). Raman- und fluoreszenz-spexktroskopische Eigenschaften von Zirkon-Einschlüssen in chrom-haltigen Korundum aus Ilakaka und deren Veränderung durch Hitzebehandlung. Zeitschr. Deutschen Gemmol. Gesell., 55, 119-132.

Wanthanachaisaeng B. (2007). The influence of heat treatment on the phase relations in mineral growth systems. PhD thesis, J. Gutenberg University Mainz, Germany, 79 pp.

Xu W., Krzemnicki M.S. (2021). Raman spectroscopic investigation of zircon in gem-quality sapphire: Application in origin determination. Journal of Raman Spectroscopy, 52 (5), 1011–1021