HFSE-enriched sapphires of gem quality: A combined FTIR and trace element study and implications for heat treatment detection

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Gem-quality sapphires containing 'exotic' elements such as Sn, Nb, Zr, Ta, W, are of special interest in gemmological research, as the concentration of these so-called high-field-strength-elements (HFSE) often correlate with detectable traces of naturally incorporated beryllium (Whatanakul *et al*. 2004, Pardieu 2007, Shen 2007, Zhou *et al*. 2022 & 2024). It is this correlation, which enables gemmologists in most cases to safely separate them from Be-diffusion treated sapphires which show no such correlation when analysed with LAICPMS. In addition, some of these sapphires may also contain thorium and lead traces, which enable us to carry out direct radiometric dating on such sapphires (Wälle & Wang 2023).

Interestingly, such 'exotic' trace elements are found in both, basaltic sapphires (e.g. Nigeria, Tasmania, N-Madagascar) and metamorphic sapphires (e.g. Madagascar, Sri Lanka, Afghanistan) and are commonly related to metasomatic processes during crystal growth. How these incompatible elements and beryllium were incorporated into sapphires has been investigated in several studies, with models explaining the presence of these elements either by primary integration of nano-inclusions during growth of the sapphire or by direct incorporation of these elements into the corundum structure with a possible epigenetic segregation into nanoclusters or precipitates as nanoparticles of separate phases (Shen & Wirth 2012, Emori et al 2019; Oto *et al*. 2023, Jin *et al*. 2024 and references therein).

This study focuses mainly on FTIR spectroscopy of HFSE-enriched sapphires of metamorphic origin from Madagascar and Sri Lanka. We analysed 18 untreated but gem-quality sapphires ranging in weight from 0.45 ct to 50 ct, partly from the SSEF research collection and from reliable trade members (Figure 1). All samples contained either goethite (e.g. in deep hollow tubes) or diaspore in fluid inclusions,

Figure 1: Selection of investigated sapphires (5.7 ct to 50 ct) from Madagascar and Sri Lanka.

thus confirming them to be unheated samples (Sripoonjan *et al.* 2016; Krzemnicki *et al.* 2023). Interestingly, most of the investigated samples were of very fine quality with a velvety blue colour generally related to a certain amount of turbidity and occasionally dense growth structures and thin laces of very dark ink-blue colour.

Most of these HFSE-sapphires showed a broad absorption band at about 3300 cm^{-1}, partly accompanied by peaks at 3182, 3232, and 3308 cm^{-1} related to OH- groups associated with Al vacancies (Moon & Phillips 1991; Beran & Rossman 2006; Jollands *et al.* 2023 and references therein). By comparing their trace element content, we found best correlation with the tantalum concentration in these samples, although contribution by other HFSE-elements including Sn cannot be fully excluded. In general, HFSE-bearing sapphires with a low Ta concentration exhibited none to a small band, whereas stones with higher Ta were characterised by an increasingly strong band at 3300 cm^{-1}. As a special case, we found in sample 032 a similar but slightly shifted broad band centred at about 3385 cm^{-1} with two small side peaks at 3254 and 3310 cm^{-1}. Although high in tantalum (Ta_{mean} 67 ppm), the reason for this 'shift' and the side peak at 3254 cm^{-1} is not yet fully understood and needs further research.

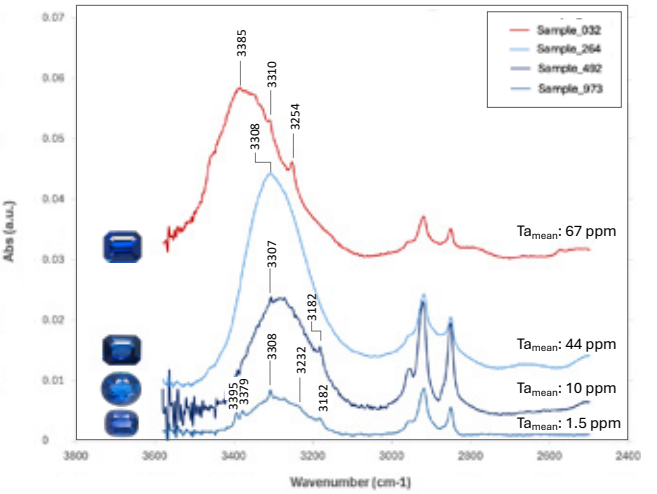

Figure 2: FTIR spectra of selected HFSE-sapphires characterised by a broad band centred at 3300 or 3385 cm^{-1}. Sample 973 generally has a mean Ta concentration of 1.5 ppm, but contains a micro-zonation enriched up to 345 ppm Ta, which may have a certain (small) influence on the observed FTIR spectrum.

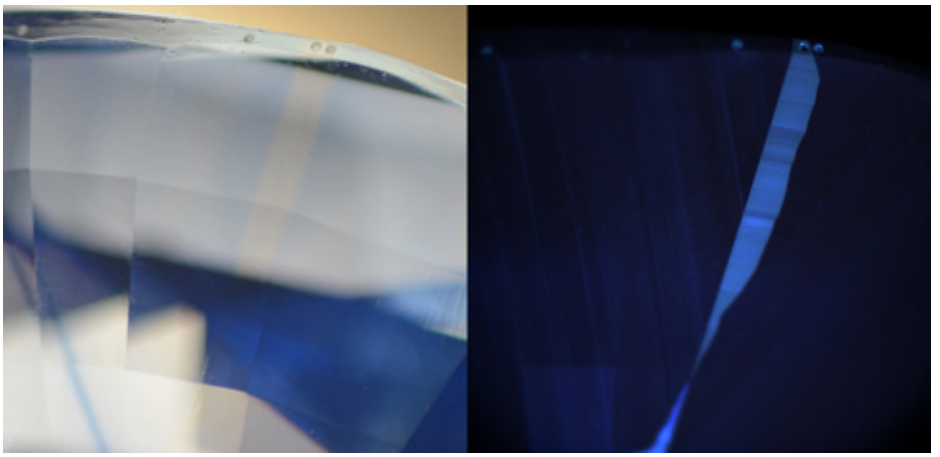

Figure 3: Thin Ta-rich (and HFSE-rich) zone in HFSE-sapphire sample 973 seen under microscope as colourless band and as chalky white zone in deep UV (DiamondView™).

Conclusions:

This study on unheated sapphires enriched in HFSE-elements reveals the presence of a broad absorption band at about 3300 cm^{-1}, seemingly best correlated with the Ta-concentration in these sapphires. The 'shift' of this band to 3385 cm^{-1} observed in one sample (Sample 032) is yet not fully understood, although assumed to be also related to some extent to tantalum.

Notably, some of these unheated sapphires show small OH- related peaks (3182, 3232, and 3308 cm^{-1}). In addition, these unheated sapphires also exhibit varying intensities of chalky white reactions. Although both features (OH- peaks in FTIR and chalky reaction in SWUV) are well known and described in heat treated metamorphic sapphires, this study reveals that such features may also be encountered in unheated stones. As such this study further underlines, that a simplistic approach for no-heat/heated distinction can be erroneous specifically for metamorphic sapphires with velvety appearance and turbidity. Only a full characterisation of these sapphires including Raman spectroscopy on inclusions (diaspore, goethite, zircon) and detailed trace element analyses (LAICPMS) may provide the answer whether such a sapphire had been heated or not.

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