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Pink to Purple Sapphires from Ilakaka, Madagascar: Insights to Separate Unheated from Heated Samples

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Abstract: The present study is focused on the analysis of zircon inclusions found in pink to purple sapphires from Ilakaka (Madagascar) with an optical microscope, Fourier-transform infrared (FTIR), and micro-Raman spectroscopy in order to update previous knowledge and find insights to separate heated from unheated samples. In total, 157 zircon inclusions in 15 unheated samples and 74 zircon inclusions in 6 heated samples are analysed using micro-Raman spectroscopy with standardised parameters. The full width at half maximum (FWHM) of the main Raman band due to anti-symmetric stretching vibration ν_3 of the SiO_4 tetrahedron in the zircon structure has been carefully measured. In the unheated samples, it ranges from 6.26 to 21.73 cm^{-1} with an average of 10.74 cm^{-1}, a median of 10.04 cm^{-1}, and a standard deviation of 2.84 cm^{-1}. On the other hand, it is lower in the heated samples, ranging from 4.83 to 14.97 cm^{-1} with an average of 7.23 cm^{-1}, median of 7.06 cm^{-1}, and standard deviation of 1.63 cm^{-1}. In our unheated samples, the FWHM was rarely below 7 cm^{-1}. In our heated samples, the FWHM was rarely above 12 cm^{-1} but mostly below 8 cm^{-1}, with a variation restricted to less than 3 cm^{-1} in the same sample. The present work will hopefully further contribute to more accurately identifying the low-temperature heat treatment of pink sapphires from Ilakaka, Madagascar.

Keywords: pink sapphire; Ilakaka (Madagascar); zircon inclusions; "low" temperature heat treatment; micro-Raman spectroscopy

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1. Introduction

Pink sapphire is corundum (Al_2O_3) with pink as the main colour. It is principally coloured by Cr^{3+}, with minor influences from the Fe^{2+}-Ti^{4+} charge transfer or V^{3+} (both giving a purplish component), or Fe^{3+} and colour centres (giving a brownish component) [1–3]. Separation of rubies and pink sapphires is performed visually using master stones (Figure 1) or sometimes colour charts [4].

Pink sapphires of gem quality can be found in various mines around the globe, for example, in Myanmar (Burma), Vietnam, Sri Lanka (Ceylon), Mozambique, and Madagascar [5–7]. Most gem-quality pink sapphires on the market today come from Ilakaka, Madagascar, from a secondary gem deposit discovered at the end of the 1990s [8,9]. Faceted stones from Ilakaka rarely exceed 10 ct. Many of those present the characteristic of numerous rounded zircons measuring from several to more than 100 μm in dimension (Figure 2a,b). They may form clusters or "nests" (Figure 2c), are less often shaped as elongated prisms (Figure 2d), and are less frequently accompanied by coloured monazites (see again Figure 2a).

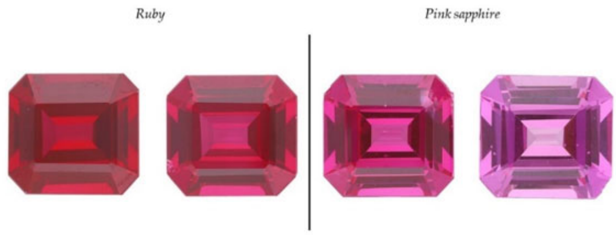


Figure 1. Four synthetic-coloured corundum used as master stones in LFG to separate rubies from pink sapphires. The two samples on the left are synthetic rubies, and the two on the right are pink sapphires. The left samples are about 14.10 × 12.06 × 7.19 mm and weigh about 2.54 ct each. Photo: Aurélien Delaunay; © LFG.

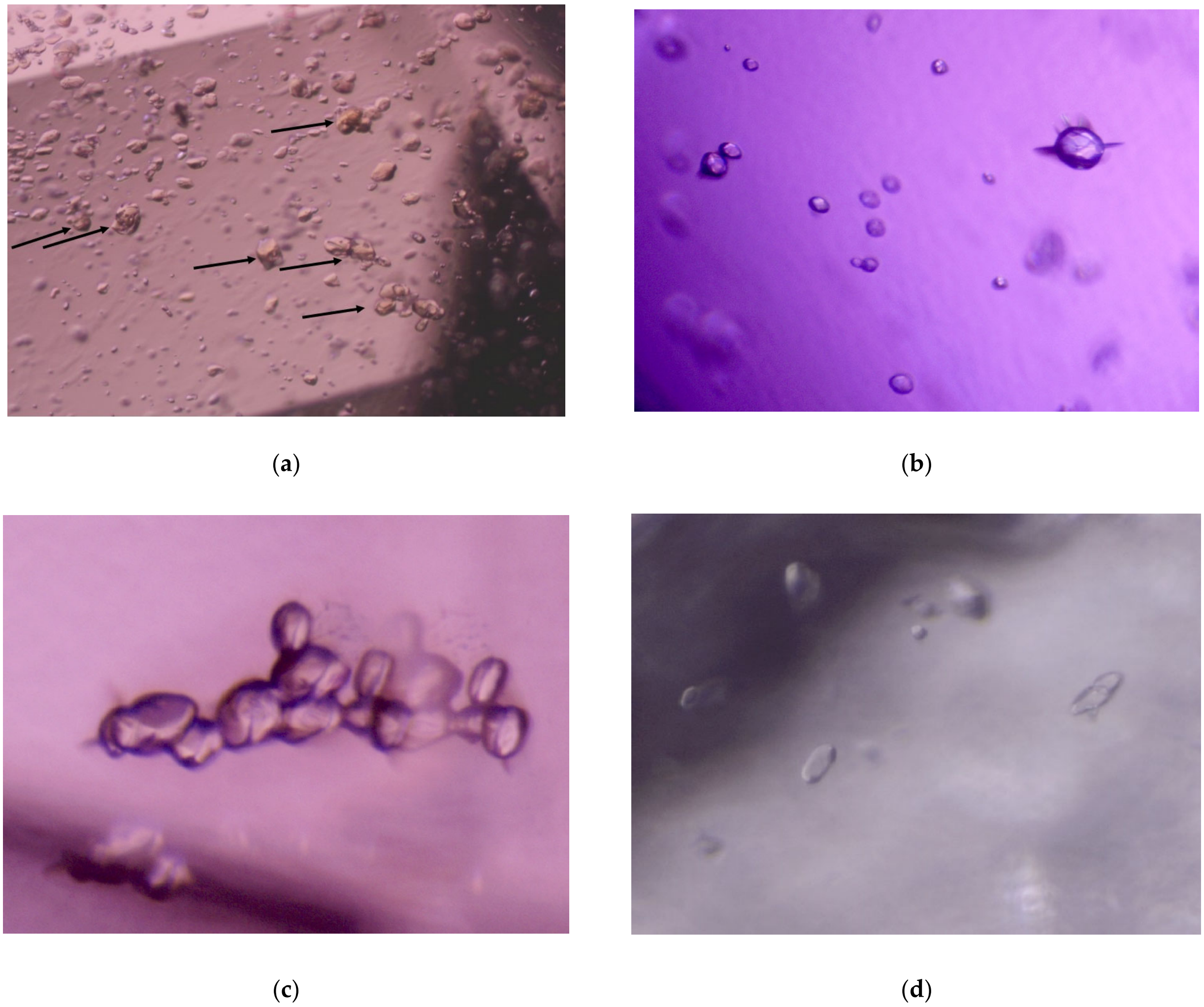
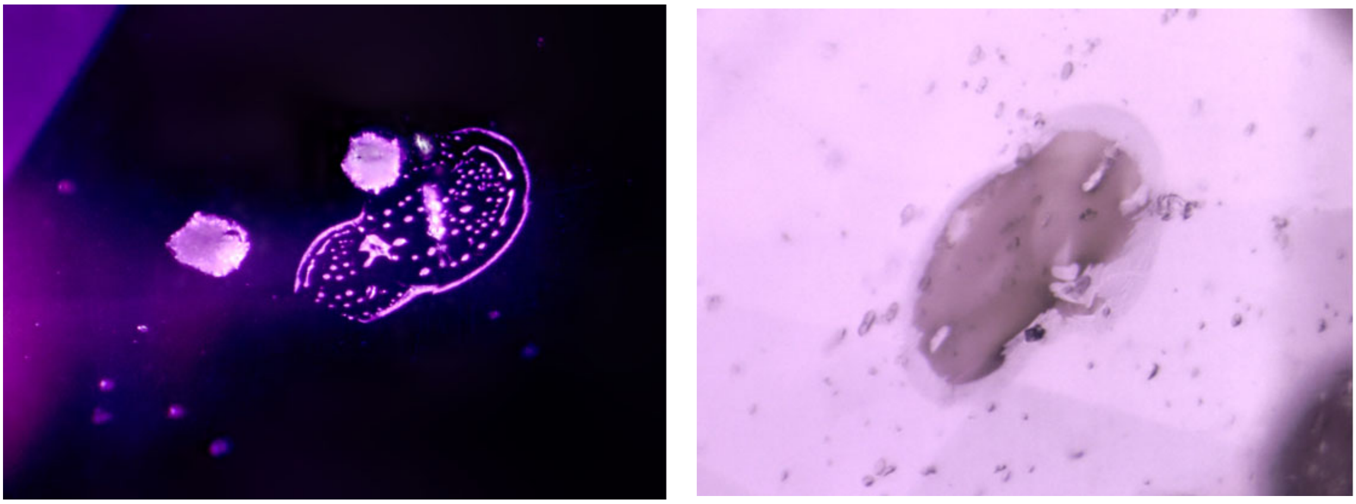


Figure 2. Inclusion scene observed frequently in unheated pink sapphires from Ilakaka, Madagascar. The photomicrographs are not colour calibrated, and their colours might not be accurate. (**a**) Numerous transparent colourless zircons of rounded shapes and brown coloured monazites indicated by black arrows, field of view (FOV): 2 mm; (**b**) Zircons of rounded shapes with tension halos and fractures in the host pink sapphire, FOV: 3 mm; (**c**) Clustered transparent rounded colourless zircons, FOV: 2 mm; (**d**) Elongated prismatic (euhedral) colourless zircon inclusions, FOV: 1 mm. Microphotos by Ugo Hennebois; © LFG.

Heat treatment under various conditions has been used to improve their colour by decreasing or removing their violet-to-purple (and sometimes brown) component and enhancing their pink appearance [9–16]. This treatment to improve corundum's colour has been known for more than 1500 years [17]. Heat treatment at temperatures above

1200 °C visibly alters the appearance of some inclusions in corundum. It is considered that the boundary between heat treatment at "low" and "high" temperatures is from 1200 to 1350 °C [13,18–20]. Unheated gems fetch higher prices than heated ones; thus, separating unheated from heated gems is one of the main issues of gemological laboratories today [9–22].

In pink sapphires, heat treatment at "high" temperatures can be identified by a variety of criteria and technologies. First, simple observation with a binocular microscope reveals the alteration of the zircon, such as a "frosty" appearance of slightly melted zircon inclusions (Figure 3a) and altered fissures (Figure 3b) [10,21]. Under a short-wave ultraviolet (SWUV) lamp, some heated sapphires (including pink ones) present a chalky blue luminescence due to the high-temperature internal diffusion of titanate groups in the mineral [23]. FTIR spectroscopy reveals the presence of absorption bands at around 3309 and 3232 cm^{-1}, with sometimes a band at 3185 cm^{-1} [12,13,16]. These infrared bands are due to different complexes of titanium associated with hydroxyl defects in corundum [24] and present strong polarisation [25]. The band at 3232 cm^{-1} is especially considered proof of heat treatment. On the contrary, FTIR bands from 2900 to 3700 cm^{-1}, linked with hydrous minerals inclusions, indicate that the sample is unheated [25], as these inclusions would lose their structural water during heat treatment [26].



(**a**) (**b**)

Figure 3. Inclusion scene observed in "high" temperature heated pink sapphires from Ilakaka, Madagascar. The photomicrographs are not colour calibrated, and their colours might not be accurate. (**a**) Altered zircon inclusions with "frosty" appearances and melt aureoles, FOV: 1.5 mm; (**b**) Fissure traces of alteration and numerous zircons, FOV: 3 mm. Microphotos by Ugo Hennebois; © LFG.

One newer criterion is related to micro-Raman spectroscopy of zircon inclusions, specifically in pink sapphires from Ilalaka, Madagascar. Many of those zircons are disordered because of self-irradiation (radiation-damaged, also known as metamictisation) with broadened bands compared to perfectly crystallised references. Thus, heating reduces disorder in those zircons and, consequently, the FWHM of all bands [9,10,13]. The easiest band on which to measure this effect is the strongest one, at around 1010 cm^{-1}. This feature will be called from here on the main Raman band. It is the anti-symmetric stretching vibration ν_3 of the SiO_4 in the zircon structure. In well-crystalised zircons, the FWHM of this feature is below 5 cm^{-1}, whereas in highly radiation-damaged zircons, it may reach more than 30 cm^{-1} [27]. The degree of radiation damage in the zircon inclusions of gem-quality corundum, as well as their age determined by isotopic methods, may be used in some cases for corundum's origin determination [28–32].

Unlike its high-temperature counterpart, heat treatment of pink sapphires at relatively "low" temperatures, below 1200 °C and sometimes 800 °C, is challenging to identify [11–13,16,20]. One rare possibility concerned coloured monazite inclusions in pink sapphires from Ilakaka, Madagascar. They keep their colour after being heated up to 600 °C; thus, the presence of colourless monazite inclusions can be used as one of the rare microscopic indications of low-temperature heat treatment [13]. On the other hand, the presence of coloured monazite inclusions cannot be used as an indication that the sample is unheated [13,33]. As the treatment only subtly affects the inclusions, one turns to spectroscopic methods. To this day, none of the series of FTIR bands indicating heat treatment at 3309 and 3232 cm^{-1}, sometimes along with a band at 3185 cm^{-1}, have been observed in an unheated pink sapphire [12,13]. Yet, the absence of these bands does not indicate that the sample is unheated.

In view of this lack of adequate criteria to identify unheated pink sapphires from Ilakaka, measuring with precision the full width at half maximum (FWHM) of the main Raman band around 1010 cm^{-1} in zircon inclusions could be potentially very useful for gemological laboratories. Values reported in the literature vary considerably (see Table 1). In unheated samples, it spans from 10.1 to 13.5 cm^{-1} (average of 11.5 cm^{-1} [10]) to 8.8–13.8 cm^{-1} [13], from 7.5 to 17.6 cm^{-1} (median value below 10 cm^{-1} [9]), and from 7.1 to 21.7 cm^{-1} with a median value of 11.3 cm^{-1} and an average of 11.6 cm^{-1} [14,15]. By comparison, the FWHM reported in heat-treated pink sapphires from Ilakaka averages 8.7 cm^{-1} for samples heated to 1400 °C [10] and from 6.6 to 12.7 cm^{-1} for samples heated to 1000 °C [13]. The importance of the spatial and spectral resolutions, as well as of the instrument used, was recently revealed [14,15]. Additionally, samples' reliability is very important [34]; one of the authors (VP) observed that most of the samples were heated before being faceted in the mining area. In the present study, updated Raman data measured to minimise the influence of spectroscopic and instrumental parameters in zircon inclusions in pink to purple sapphires from Ilakaka, themselves carefully selected, are presented to gauge the usefulness of this approach.

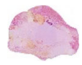
Table 1. FWHM, median, and mean values, when mentioned (na*: not available), of the main Raman band at around 1010 cm^{-1} of zircon inclusions found in (unheated and heated) pink sapphires from Ilakaka, Madagascar, with the reference from which they are extracted. Spatial and spectral resolutions were mentioned only in articles [13,14], and these are similar to those used in the present study.

Treatment	FWHM (cm^{-1})	Median Value (cm^{-1})	Average Value (cm^{-1})	Reference
Unheated	10.1–13.5	na*	11.5	[9]
Unheated	8.8–13.8	na*	na*	[12]
Unheated	7.5–17.6	<10	na*	[8]
Unheated	7.1–21.7	11.3	11.6	[13,14]
Heated to 1000 °C	6.6–12.7	na*	na*	[12]
Heated to 1400 °C	na*	na*	8.7	[9]

2. Materials and Methods

We studied zircon inclusions of fifteen unheated pink sapphires from Ilakaka, Madagascar (Table 2). All the samples are reliable as they were collected by one of the authors (VP) in 2005, where gravels were washed; i.e., they represent B-Type samples according to a recently published degree of confidence [34]. All samples were obtained rough (not faceted), and one side was polished so their inclusions are easier to observe via optical microscope.

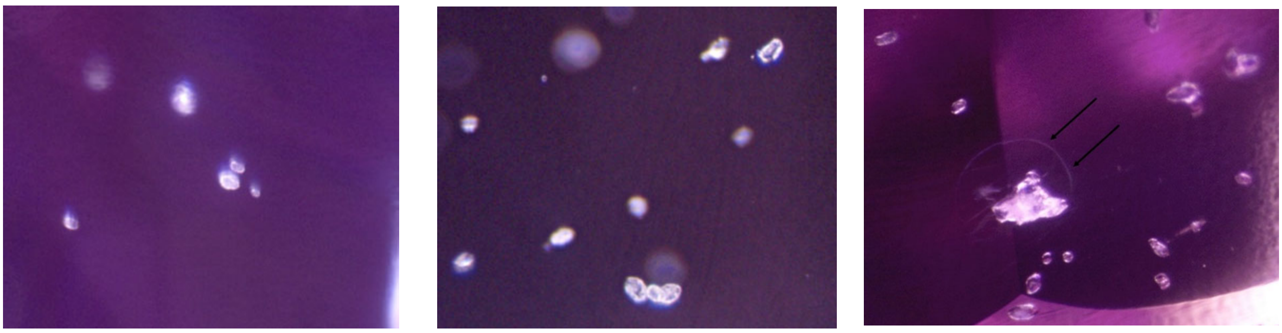
Table 2. Characteristics of the fifteen studied unheated pink sapphires from Ilakaka, Madagascar (1 ct = 0.2 g).

Sample Number	Mass (ct)	Dimensions (mm)	Colour	Photo
SK-007	0.373	4.43 × 4.15 × 2.02	Light pink	
SK-008	0.412	5.09 × 4.64 × 1.86	Light pink	
SK-009	0.525	6.44 × 4.13 × 2.04	Pink	
SK-010	0.566	6.83 × 5.31 × 1.63	Pink	
SK-011	0.346	5.12 × 4.07 × 2.00	Purplish-pink	
SK-012	0.328	5.13 × 3.50 × 2.16	Light pink	
SK-013	0.307	3.96 × 3.03 × 2.04	Light pink	
SK-014	0.337	4.71 × 3.75 × 2.19	Pink	
SK-015	0.599	5.01 × 4.49 × 2.51	Pinkish-purple	
SK-016	0.460	4.76 × 3.59 × 2.29	Purple-pink	
SK-017	0.346	4.28 × 3.23 × 2.44	Pinkish-purple	
SK-018	0.319	4.15 × 3.49 × 2.06	Light pink	
SK-023	0.255	4.98 × 3.77 × 1.65	Pink	
SK-024	0.550	5.37 × 4.16 × 2.62	Pink	
SK-025	0.357	4.35 × 3.70 × 2.29	Pink	

Six faceted heated pink sapphires from Ilakaka, Madagascar, from the LFG collection (Z-Type [34]) were also studied (Table 3). Two of the samples (LFG101 and LFG102) presented indications of heating under the microscope (Figure 4a,b) and might be considered as heated at "high" temperature. The four other samples (LFG103, LFG 104, LFG105, and LFG106) presented FTIR absorption bands at 3232 and 3309 cm^{-1}, observed to this day only in pink sapphires from Ilakaka, Madagascar, if they have been heated [12,13]. One of these four samples (LFG103) also presented indications of heating under the microscope (Figure 4c) and might thus be considered as heated at "high" temperature, but the other three samples presented no indications of heating under the microscope and might be considered as heated at "low" temperature (Figure 5a–c).

Table 3. Characteristics of the six heated pink sapphires from Ilakaka, Madagascar.

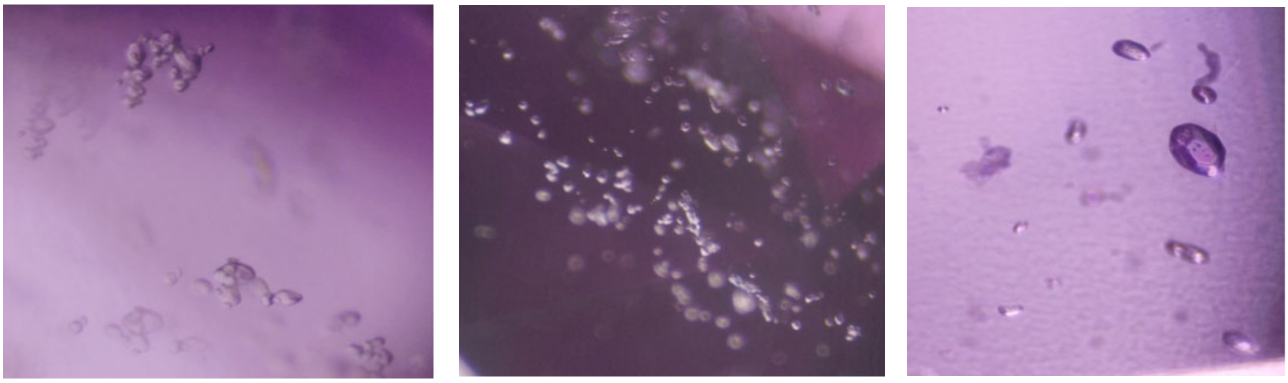
Sample Number	Mass (ct)	Dimensions (mm)	Colour	Photo
LFG101	1.797	9.02 × 6.22 × 4.28	Purplish pink	
LFG102	1.893	8.94 × 6.52 × 4.02	Purplish pink	
LFG103	2.038	7.78 × 6.30 × 4.86	Purplish pink	
LFG104	3.022	9.57 × 7.74 × 4.55	Purplish pink	
LFG105	3.214	10.27 × 8.39 × 4.57	Purplish pink	
LFG106	3.027	9.22 × 7.93 × 4.87	Purplish pink	



(**a**) (**b**) (**c**)

Figure 4. Inclusion scene observed in three of our heated pink sapphires from Ilakaka, Madagascar. Indications of heating under microscope are observed in these samples. The photomicrographs are not colour calibrated, and their colours might not be accurate. (**a**) Altered zircons with turbid/frosty appearance in the sample LFG101, FOV: 2 mm; (**b**) altered zircons with turbid/frosty appearance in the sample LFG102, FOV: 1.5 mm; (**c**) altered zircons with Toll-like structures by black arrows in the sample LFG103, FOV: 2 mm. Microphotos by Ugo Hennebois; © LFG.

All samples were examined under a Zeiss Stemi 508 binocular microscope (Oberkochen, Germany). FTIR spectra (400–8000 cm^{-1}) were obtained using the Nicolet iS5 spectrometer (Thermo Fischer Scientific, Waltham, MA, USA) with a 4 cm^{-1} resolution and averaging 200 scans. Raman spectra were acquired using identical instrumentation and conditions to those detailed in previous publications [15,16]; Raman spectra were acquired on a Renishaw inVia spectrometer (Renishaw plc, Wotton-under-Edge, Gloucestershire, UK) coupled with an optical microscope (always using 50× long-working-distance objective lens) with a 514 nm laser excitation (diode-pumped solid-state laser of about 10 mW laser power on the sample), a confocal mode (20 µm entrance slit), a grating of 1800 grooves/mm, and about 1.5 cm^{-1} spectral resolution. The acquired spectra are from 600 to 1200 cm^{-1}, with 5 accumulation and 20 s exposure time. The FWHM of the main Raman band was calculated using the instrument software, choosing a fit with a Lorentzian function after baseline correction. A diamond was used for the calibration of Raman spectrometer using the 1331.80 cm^{-1} Raman band. When the sample geometry allowed it, several zircon inclusions were measured (up to twenty). However, in one sample (SK-016), no zircon inclusions could be analysed. When zircon inclusions are near the surface, and due to relaxation effects, the exact position of the Raman bands may be affected [32]. Whenever possible, zircon inclusions in the sample, and not at the proximity of the surface, were analysed. This was, however, not possible for one sample (e.g., sample SK-018), as the two inclusions accessible are situated near the surface. In some large enough (i.e., ca. 100 microns) zircon inclusions, more than one spot was analysed in order to check for possible zoning.



(**a**) (**b**) (**c**)

Figure 5. Inclusion scene observed in three studied heated pink sapphires from Ilakaka, Madagascar. No indications of heating under microscope are observed in these samples. The photomicrographs are not colour calibrated, and their colours might not be accurate. (**a**) Clustered transparent rounded colourless zircons of various sizes in the sample LFG104, FOV: 1 mm; (**b**) transparent colourless zircons of different shapes and sizes in the sample LFG105, FOV: 2.5 mm; (**c**) transparent colourless prismatic (euhedral) colourless zircon with other zircons of different shape in the sample LFG106, FOV: 0.5 mm. Microphotos by Ugo Hennebois; © LFG.

3. Results and Discussion

Table 4 lists the ranges in position and FWHM of the main Raman band of zircon measured on 157 zircon inclusions found in 15 unheated pink to purple sapphires from Ilakaka (Madagascar). In Figure 6a (black traces), the main Raman zircon band is presented on an expanded scale from 980 to 1050 cm^{-1} so that differences in width can be better appreciated in the spectra of two different zircon inclusions in two unheated pink to purple sapphires. As previously observed [9,10,13–16], a large variation of the FWHM and position of the zircon inclusion's ν_3 Raman band can be observed (Table 4) from sample to sample, and even within the same unheated sample [14]. The exact position of the maximum of the main Raman band ranged from 1003.76 cm^{-1} to 1021.61 cm^{-1} with an average of 1015.70 cm^{-1}, median of 1016.26 cm^{-1}, and standard deviation of 2.82 cm^{-1}. The FWHM of this band ranged from 6.26 to 21.73 cm^{-1} with an average of 10.75 cm^{-1}, median value of 10.04 cm^{-1}, and standard deviation of 2.84 cm^{-1}. In accordance with the previous studies [10,21], zircon inclusions in pink to purple sapphires from Ilakaka, Madagascar, are radiation-damaged.

Table 4. Range of position and FWHM of Raman main band observed in zircon inclusions of unheated pink to purple sapphires from Ilakaka, Madagascar.

Sample	Range of Peak Position (cm^{-1})	Range of FWHM (cm^{-1})	Number of Analysed Zircon Inclusions	Total Number of Raman Analyses
SK-007	1013.86–1019.02	7.87–17.70	20	28
SK-008	1017.56–1020.65	15.07–18.42	5	7
SK-009	1018.81–1019.73	9.47–21.73	7	7
SK-010	1005.10–1017.21	7.06–13.14	10	10
SK-011	1011.87–1019.01	9.60–13.39	10	10
SK-012	1011.13–1015.32	8.11–12.09	5	5
SK-013	1014.12–1017.22	7.11–11.65	8	8
SK-014	1011.20–1016.63	7.87–13.80	10	10
SK-015	1012.74–1021.11	7.55–14.21	7	7
SK-016	-	-	-	-
SK-017	1012.37–1018.22	7.25–16.15	13	17
SK-018	1003.76–1005.25	14.48–15.85	2	2
SK-023	1014.14–1021.61	6.26–15.39	20	26
SK-024	1014.55–1018.21	6.83–13	20	26
SK-025	1010.00–1016.14	6.81–10.31	20	26

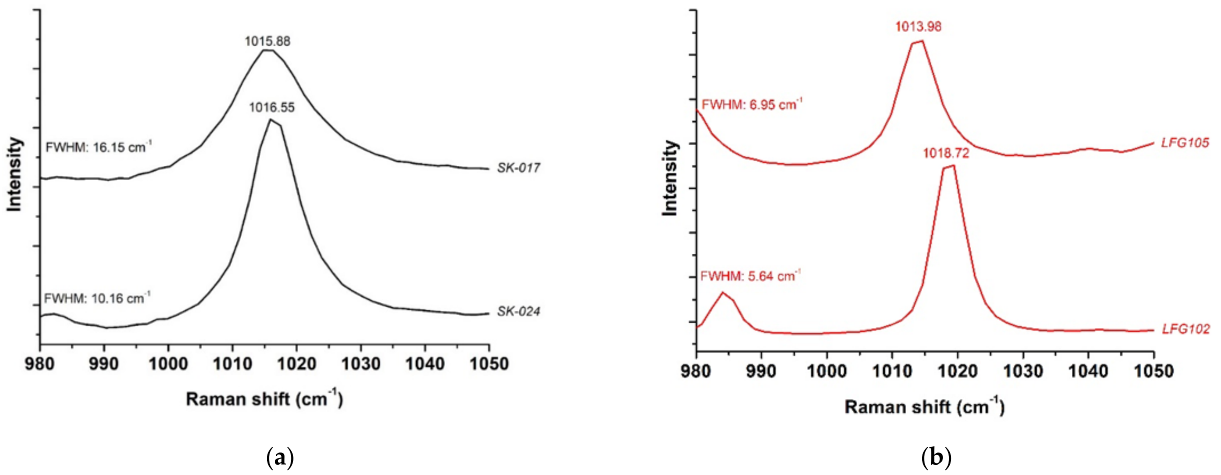


Figure 6. FWHM and exact position of the main zircon band measured in two zircon inclusions in two pink to purple sapphires from Ilakaka, Madagascar: (**a**) unheated (black traces) and (**b**) heated (red traces). Spectra are shifted vertically for clarity.

In Table 5, the ranges in position and FWHM of 74 analysed zircons found in six heated pink to purple sapphires from Ilakaka (Madagascar) are listed. In Figure 6b (red traces), examples of Raman spectra are presented. The exact position of the maximum of the main Raman band ranged from 1007.29 cm^{-1} to 1020.23 cm^{-1} with an average of 1014.38 cm^{-1}, median of 1013.78 cm^{-1}, and standard deviation of 2.96 cm^{-1}. The FWHM of this band ranged from 4.83 to 14.97 cm^{-1} with an average of 7.23 cm^{-1}, median value of 7.06 cm^{-1}, and standard deviation of 1.63 cm^{-1}. These values, taken as a whole, are relatively lower than those observed in unheated samples (see again Table 4). This is because heat treatment leads to structural reconstitution and better crystalline order in zircon inclusions, thus leading to a decrease in the FWHM. It confirms what was observed previously in pink sapphires from Madagascar [10,13] as well as other radiation-damaged zircons [21,35–38].

Table 5. Range of position and FWHM of Raman main band observed in zircon inclusions of heated pink to purple sapphires from Ilakaka, Madagascar.

Sample	Range of Peak Position (cm^{-1})	Range of FWHM (cm^{-1})	Number of Analysed Zircon Inclusions	Total Number of Raman Analyses
LFG101	1018.34–1020.23	5.47–5.91	6	6
LFG102	1017.95–1019.57	4.83–6.86	10	10
LFG103	1007.29–1013.24	6.56–9.32	11	11
LFG104	1009.75–1013.82	6.36–7.79	10	10
LFG105	1010.58–1014.12	6.19–11.38	17	22
LFG106	1018.34–1020.23	5.16–14.97	20	34

In Figure 7, the position and FWHM of the main band obtained on zircon inclusions in all unheated (black squares) and heated (red circles) pink sapphires from Ilakaka, Madagascar, from this study are shown. Unheated and heated samples presented comparable main Raman band positions, with the vast majority of these situated above 1010 cm^{-1}. It has been presented that this band shifts towards the highest wavenumbers due to compressive strain; thus, as in previous studies, the band positions indicate pressure around the zircon inclusion [10,21,31,32,39,40]. It has been suggested that in some cases (e.g., for diamonds' inclusions), compressive strain (also referred to as "fossilised pressure" or "overpressure") on the inclusion can be up to 2–3 GPa (see [21,40–42] and references therein). Free-standing radiation-damaged zircons present a significantly lower Raman peak maximum position (see isobar line in Figure 7). The inclusions situated by samples' surfaces present lower peak maximum positions, sometimes below 1010 cm^{-1}, possibly due to pressure relaxation [31]. Suggested calculations of the compressive stress of zircon inclusions using Raman spectroscopy [42] indicate a large variation from below 1 GPa to above 4 GPa. It has been suggested that calculated stress accuracy might be affected due to partial non-hydrostatic stress or inhomogeneous damage within the analysed sample volume (see [42] and references therein). Moreover, compressive strain affects the zircon inclusions' main Raman position change during heat treatment; during a heat treatment up to 1000 °C, the band shifts towards lower wavenumbers, and on the other hand, when it is heated above 1000 °C it shifts towards higher wavenumbers [21,37,42].

Table 6 presents the frequency of a given FWHM range by a step of 1 cm^{-1} observed for the main Raman band in zircon inclusions and the corresponding statistics for both non-heated and heated samples. Unheated samples presented zircon inclusions with a broadened main Raman band, having a FWHM sometimes over 20 cm^{-1} (see Figure 7 and sample SK-009 in Table 4). Heated samples presented zircon inclusions with a sharper main Raman band, and the FWHM may sometimes be below 6 cm^{-1} (see also Table 5, samples LFG101, LFG102, LFG103, and LFG 104). A FWHM of $<$7 cm^{-1} for the main Raman zircon band was observed in 34 out of 74 inclusions of heated samples. On the other hand, for the unheated samples, no zircon inclusions with a FWHM $<$ 6 cm^{-1} were observed in the studied samples, and only 3 out of 157 had a low FWHM between 6 and 7 cm^{-1}. The majority (68 out of 74, i.e., ca. 92%) of the studied zircon inclusions in the heated samples present a FWHM ranging below 9 cm^{-1}. Moreover, a FWHM $>$ 12 cm^{-1} was observed in only 1 of 74 studied zircon inclusions in heated samples, but in 47 out of 157 in unheated samples. One might think that zircon inclusions with a relatively high FWHM (e.g., above 17 cm^{-1}) before heating would present a relatively high FWHM after heat treatment at low temperatures because of partial structural reconstitution of the inclusion. This is possibly the reason why we measured a FWHM of 14.97 cm^{-1} in one sample, a FWHM from 9 to 12 cm^{-1} (5 out of 74), and otherwise a FWHM below 9 cm^{-1} in the heated samples (see again Tables 5 and 6).

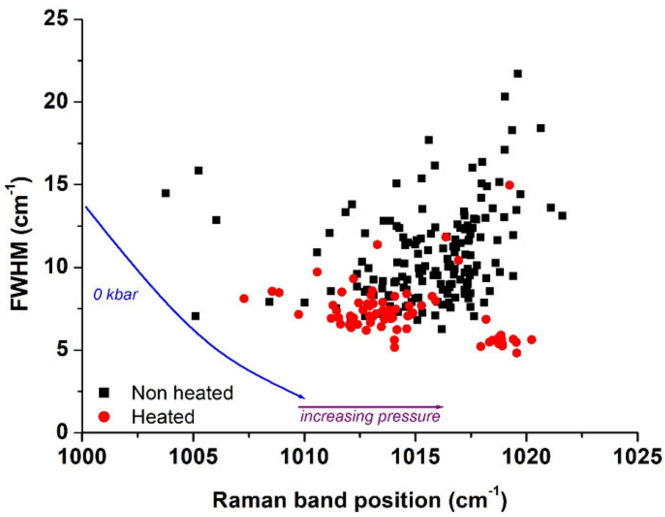


Figure 7. FWHM and exact position of the main zircon band measured in zircon inclusions of unheated (black squares) and heated (red circles) samples from Ilakaka, Madagascar. Due to compressive strain, the exact position of the main Raman band of the zircon inclusions is shifted towards higher wavenumbers compared to those expected for the free-standing radiation-damaged zircons (0 kbar isobar blue line) [21].

Table 6. Frequency of observation of a specific range of FWHM observed in 157 zircon inclusions in 15 unheated, and 74 zircon inclusions in 6 heated, pink to purple sapphires from Ilakaka, Madagascar.

Range of FWHM (cm^{-1})	Non-Heated	Heated
<6	0/157	17/74 (ca. 23%)
6–7	3/157 (ca. 1.9%)	17/74 (ca. 23%)
7–8	21/157 (ca. 13.4%)	25/74 (ca. 34%)
8–9	25/157 (ca. 15.9%)	9/74 (ca. 12%)
9–10	28/157 (ca. 17.8%)	2/74 (ca. 2.7%)
10–11	15/157 (ca. 9.6%)	1/74 (ca. 1.3%)
11–12	18/157 (ca. 11.5%)	2/74 (ca. 2.7%)
12–13	19/157 (ca. 12.1%)	0/74
13–14	10/157 (ca. 6.4%)	0/74
14–15	4/157 (ca. 2.5%)	1/74 (ca. 1.3%)
15–16	5/157 (ca. 3.1%)	0/74
16–17	3/157 (ca. 1.9%)	0/74
17–18	2/157 (ca. 1.3%)	0/74
18–19	2/157 (ca. 1.3%)	0/74
>20	2/157 (ca. 1.3%)	0/74

Heat treatment of pink to purple sapphires at temperatures above 1400 °C can partially (or entirely) decompose zircon inclusions to baddeleyite (ZrO_2) and a SiO_2-rich phase; these can be identified via micro-Raman spectroscopy [10,21]. Only one inclusion in the heated sample LFG102 presented such characteristics reflected in the Raman spectrum. Moreover, photoluminescence bands linked to REE are observed in Raman spectra of zircon; using a 514 nm laser excitation, these bands can affect the signal of the main zircon Raman band [10,21,37]. These bands were observed after heat treatment accompanied by an FHWM below 7 cm^{-1} for the main zircon Raman band [10]; however, in our case, these were also observed in a zircon inclusion in an unheated sample (SK-025).

When several zircon inclusions can be measured in the same sample, the variation of the FWHM and position of the zircon inclusion main Raman band can be checked. In several cases, variations of the FWHM are large in unheated samples and less important in heated ones [16]. Again, this is because heat treatment leads to structural reconstitution of zircon inclusions and a decrease in the FWHM and its ranges. Comparing the minimum and the maximum value of the FWHM observed in Tables 4 and 5, a more important variation is observed in our unheated samples than in heated gems. For instance, four heated (LFG101, LFG102, LFG103, and LFG 104) samples out of the six present a variation between the maximum and the minimum FWHM of less than 3 cm^{-1}. For the studied unheated samples, the difference can be over 10 cm^{-1} (see SK-009 in Table 4), larger than those previously reported for a single sample [9,14]. However, heated samples LFG105 and LFG 106 also present relatively large variations of the FWHM, and unheated samples SK-012, SK-013, and SK-025 present a smaller variation. In our sampling, a range of variation of less than 3 cm^{-1} for the FWHM combined with a FWHM below 8 cm^{-1} is only observed for the heated samples. This provides a criterion applicable to our limited population of Ilakaka gems.

When the inclusion was large enough, several micro-Raman analyses were acquired in a single zircon inclusion. This was performed for 16 zircons in six unheated samples and 7 zircons in two heated samples. The FWHM in one unheated zircon (SK-017) varied over 7.88 cm^{-1}, from 8.27 to 16.15 cm^{-1} [14]. In other unheated samples, the FWHM varied less than 4.5 cm^{-1}, and in some zircon inclusions, the FWHM did not vary much (<1 cm^{-1}). In the heated samples, two zircon inclusions in the sample LFG106 present a variation of slightly above 4 cm^{-1}, with the other measurements having a variation being less than 2.5 cm^{-1} and sometimes below 1 cm^{-1}. Differences in the FWHM in the same zircon inclusion reveal heterogeneous radiation damage [42]. In cathodoluminescence (CL) images, zoning was observed for zircon inclusions in sapphires from the same region [28,29]. The fact that relatively large variations of the FWHM in the same zircon inclusion could also be observed in heated samples further confirms that low-temperature heating leads only to partial structural reconstruction of zircons.

Zircon inclusions can be found in several gem-quality sapphires of various colours and from different mining areas [7,21,28–32,43]. The characteristics presented here are for pink to purple sapphires from Ilakaka, Madagascar. Preliminary studies on unheated similar coloured sapphires from Myanmar (Burma) and Sri Lanka (Ceylon) showed that these present zircon inclusions with narrower FWHMs. Additionally, rubies and sapphires from Madagascar might present different Raman spectroscopic characteristics; data on such stones need to be acquired so they can be used for similar applications.

If another instrument is used instead of the one described for the present study, the criteria should be used with caution as, apart from the spectral and spatial resolution, different parameters linked to the instrument could play a role in the exact shape of the bands, and thus, on the measured FWHM. In order to compare studies using another instrument with the results presented here, instrument profile functions should also be taken into consideration [44].

4. Conclusions

Determining whether a pink to purple sapphire from Ilakaka, Madagascar, is heat-treated at low temperatures or not is vital to gemological laboratories around the world. This is because this locality has produced most of the pink to purple sapphires in the market today. Under the microscope, samples heated at low temperatures are challenging to identify. Thus, identification of such treatment can be accurately performed only using spectroscopy. FTIR spectroscopy is in some cases useful as the presence of the series of FTIR bands at 3309 and 3232 cm^{-1}, sometimes along with a band at 3185 cm^{-1}, in pink to purple sapphires, indicates heat treatment [12,13]. Frequently, those pink to purple sapphires present numerous zircon inclusions of various shapes, often over 100 μm in maximum dimension. These are radiation damaged, and even low-temperature heat treatment may lead to structural reconstitution of zircon inclusions. Micro-Raman spectroscopy can also give valuable clues to the identification with careful measurement of the peak position and FWHM of the main Raman band, that is, the anti-symmetric stretching vibration ν_3 of the SiO_4 at about 1010 cm^{-1} [9,10,13–16]. In this study, unheated samples and heated samples of reliable geographic and thermal history present a large variation of the FWHM and position of this band, always using the same spectroscopic parameters. For unheated samples, the FWHM was rarely observed below 7 cm^{-1}, and for heated samples, the FWHM was rarely above 12 cm^{-1} but mostly below 8 cm^{-1}.

Analyses by micro-Raman spectroscopy of various zircon inclusions within one single sample provide useful indications as to the band position and FWHM. Only in heated samples does the FWHM have a value below 8 cm^{-1}, with a variation range limited to 3 cm^{-1}, indicating relatively good crystallinity. This might be used as an additional criterion for the identification of heated pink to purple sapphires from Ilakaka, Madagascar. The criteria proposed here apply strictly to zircon that can be easily analysed by micro-Raman in pink to purple sapphires from the Ilakaka mining area in Madagascar. These criteria cannot work in the case where no such inclusions are present, or if they are present but difficult to access with the Raman spectrometer. Zircon inclusions might be found in pink to purple sapphires from other countries, such as Myanmar (Burma) and Sri Lanka (Ceylon). Additionally, other coloured sapphires from Madagascar containing zircon inclusions might not present similar spectroscopic characteristics.

Further studies on reliable samples will improve the statistics presented here. Additionally, results on the same samples before and after heat treatment, and also by performing line scans or even better maps using micro-Raman spectroscopy, will help understand the exact effect of low-temperature heat treatment on the zircon inclusions of pink to purple sapphires from Ilakaka, Madagascar. Moreover, as zircon inclusions of different shapes are documented in the studied samples, it might be useful to look for possible relations between the FWHM and the inclusions' shape (e.g., check whether sharper bands are linked with specific zircon shapes). Similar extended studies with micro-Raman spectroscopy, for example, on monazite inclusions as well as epigenetic iron staining (e.g., goethite, which changes form in relatively low temperature), might give additional clues for more accurate identification of this challenging treatment.

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References

1. Fritsch, E.; Rossman, G.R. An update on color in gems. Part I. Introduction and colors caused by dispersed metal ions. *Gems Gemol.* **1987**, *23*, 126–139. [CrossRef]
2. Emmett, J.L.; Dubinsky, E.V.; Hughes, R.W.; Scarratt, K. Color, Spectra & Luminescence. In *Ruby & Sapphire: A Gemmologist's Guide*; Hughes, R., Ed.; RWH Publishing: Bangkok, Thailand, 2017; pp. 90–148.
3. Dubinsky, E.V.; Stone-Sundberg, J.; Emmett, J.L. A quantitative description of the causes of color in corundum. *Gems Gemol.* **2020**, *56*, 2–28. [CrossRef]
4. Krzemnicki, M.; Cartier, L.E.; Lefèvre, P.; Zhou, W. Colour varieties of gems—Where to set the boundary? *InColor* **2020**, *45*, 92–95.

5. Giuliani, G.; Ohnenstetter, D.; Fallick, A.E.; Groat, L.; Fagan, A.J. The geology and genesis of gem corundum deposits. In *Geology of Gem Deposits*, 2nd ed.; Mineralogical Association of Canada Short Course Series; Groat, L.A., Ed.; Mineralogical Association of Canada: Tucson, AZ, USA, 2014; Volume 44, pp. 113–134, ISBN 9780921294375.
6. Giuliani, G.; Groat, L. Geology of corundum and emerald deposits: A review. *Gems Gemol.* **2019**, *55*, 464–489. [CrossRef]
7. Palke, A.C.; Saeseaw, S.; Renfro, N.D.; Sun, Z.; McClure, S.F. Geographic origin determination of ruby. *Gems Gemol.* **2019**, *55*, 580–612. [CrossRef]
8. Milisenda, C.C.; Henn, U.; Henn, J. New gemstone occurrences in the south-west of Madagascar. *J. Gemmol.* **2001**, *27*, 385–394. [CrossRef]
9. Krzemnicki, M.S.; Lefèvre, P.; Zhou, W.; Wang, H.A.O. Zircon inclusions in unheated pink sapphires from Ilakaka, Madagascar: A Raman spectroscopic study. In Proceedings of the International Gemmological Conference, Online, 20–21 November 2021.
10. Wang, W.; Scarratt, K.; Emmett, J.L.; Breeding, C.M.; Douthit, T.R. The effects of heat treatment on zircon inclusions in Madagascar sapphires. *Gems Gemol.* **2006**, *42*, 134–150. [CrossRef]
11. Krzemnicki, M.S. How to get the "blues" out of the pink: Detection of low-temperature heating of pink sapphires. *Facette* **2010**, *17*, 12.
12. Saeseaw, S.; Khowpong, C. The effect of low-temperature heat treatment on pink sapphire. *Gems Gemol.* **2019**, *56*, 290–291.
13. Saeseaw, S.; Khowpong, C.; Vertriest, W. Low-temperature heat treatment of pink sapphires from Ilakaka, Madagascar. *Gems Gemol.* **2020**, *56*, 448–457. [CrossRef]
14. Karampelas, S.; Hennebois, U.; Delaunay, A.; Pardieu, V.; Mevellec, J.-Y.; Fritsch, E. Raman spectroscopy of zircon inclusions in unheated pink sapphires from Ilakaka, Madagascar: Opening new perspectives. *J. Gemmol.* **2022**, *38*, 16–18. [CrossRef]
15. Karampelas, S.; Hennebois, U.; Mevellec, J.-Y.; Pardieu, V.; Delaunay, A.; Fritsch, E. Identification of heated pink sapphires from Ilakaka (Madagascar). In Proceedings of the 7th International Gem & Jewelry Conference (GIT2021), Chanthaburi, Thailand, 2–3 February 2022; p. 212.
16. Karampelas, S.; Hennebois, U.; Delaunay, A. Détection du traitement thermique à basse température des corindons. *Rev. Gemmol. A.F.G.* **2022**, *217*, 4–5.
17. Notari, F.; Hainschwang, T.; Caplan, C.; Ho, K. The heat treatment of corundum at moderate temperature. *InColor* **2019**, *42*, 14–23.
18. Emmett, J.L.; Hughes, R.W.; Douthit, T.R. Treatments. In *Ruby & Sapphire: A Gemmologist's Guide*; Hughes, R., Ed.; RWH Publishing: Bangkok, Thailand, 2017; pp. 196–248.
19. McClure, S.F.; Smith, C.P.; Wang, W.; Hall, M. Identification and durability of lead glass-filled rubies. *Gems Gemol.* **2006**, *42*, 22–34. [CrossRef]
20. Hughes, E.B.; Vertriest, W. A canary in the ruby mine: Low-temperature heat treatment experiments on Burmese rubies. *Gems Gemol.* **2022**, *58*, 400–423. [CrossRef]
21. Wanthanachaisaeng, B. The Influence of Heat Treatment on the Phase Relations in Mineral Growth Systems. Ph.D. Thesis, Johannes Gutenberg University of Mainz, Mainz, Germany, 2007; 79p.
22. Sripoonjan, T.; Wanthanachaisaeng, B.; Leelawatanasuk, T. Phase Transformation of Epigenetic Iron Staining: Indication of Low-Temperature Heat Treatment in Mozambique Ruby. *J. Gemmol.* **2016**, *35*, 156–161. [CrossRef]
23. Vigier, M.; Fritsch, E.; Cavignac, T.; Latouche, C.; Jobic, S. Shortwave UV Blue Luminescence of Some Minerals and Gems due to Titanate Groups. *Minerals* **2023**, *13*, 104. [CrossRef]
24. Balan, E. Theoretical infrared spectra of OH defects in corundum (α-Al_2O_3). *Eur. J. Mineral.* **2020**, *32*, 457–467. [CrossRef]
25. Beran, A.; Rossman, G.R. OH in natural occurring corundum. *Eur. J. Mineral.* **2006**, *18*, 441–447. [CrossRef]
26. Smith, C.P. A contribution to understanding the infrared spectra of rubies from Mong Hsu, Myanmar. *J. Gemmol.* **1995**, *24*, 321–335. [CrossRef]
27. Nasdala, L.; Irmer, G.; Wolf, D. The degree of metamictization in zircon: A Raman spectroscopic study. *Eur. J. Mineral.* **1995**, *7*, 471–478. [CrossRef]
28. Elmaleh, E. Blue Sapphires from Madagascar, Sri Lanka, Tanzania and Burma (Myanmar): Gemological, Chemical, Spectroscopic Characterization and Dating of Zircon Inclusions. Master's Thesis, University of Geneva, Geneva, Switzerland, 2015; 425p.
29. Elmaleh, E.; Karampelas, S.; Schmidt, S.T.; Galster, F. Zircon inclusions in blue sapphire. In Proceedings of the 34th International Gemmological Conference, Vilnius, Lithuania, 26–30 August 2015; pp. 51–52.
30. Link, K. Age determinations of zircon inclusions in faceted sapphires. *J. Gemmol.* **2015**, *34*, 692–700. [CrossRef]
31. Elmaleh, E.; Schmidt, S.T.; Karampelas, S.; Link, K.; Kiefert, L.; Süssenberger, A.; Paul, A. U-Pb Ages of Zircon Inclusions in Sapphires from Ratnapura and Balangoda (Sri Lanka) and Implications for Geographic Origin. *Gems Gemol.* **2019**, *55*, 18–28. [CrossRef]
32. Xu, W.; Krzemnicki, M.S. Raman spectroscopic investigation of zircon in gem-quality sapphire: Application in origin determination. *J. Raman Spectrosc.* **2021**, *52*, 1011–1021. [CrossRef]
33. Hennebois, U.; Delaunay, A.; Karampelas, S. Heated purplish pink sapphire from Ilakaka (Madagascar) with colored monazite inclusions. *Gems Gemol.* **2023**, *59*, 159–160.
34. Vertriest, W.; Palke, A.C.; Renfro, N.D. Field gemology: Building a research collection and understanding the development of gem deposits. *Gems Gemol.* **2019**, *55*, 490–511. [CrossRef]
35. Zhang, M.; Salje, E.K.H.; Capitani, G.C.; Leroux, H.; Clark, A.M.; Schlüter, J.; Ewing, R.C. Annealing of O-decay damage in zircon: A Raman spectroscopy study. *J. Phys. Condens. Matter* **2000**, *12*, 3131–3148. [CrossRef]

36. Nasdala, L.; Lengauer, C.; Hanchar, J.; Kronz, A.; Wirth, R.; Blanc, P.; Kennedy, A.; Seydoux-Guillaume, A.M. Annealing radiation damage and the recovery of cathodoluminescence. *Chem. Geol.* **2002**, *191*, 121–140. [CrossRef]
37. Váczi, T.; Nasdala, L.; Wirth, R.; Mehofer, M.; Libowitzky, E.; Häger, T. On the breakdown of zircon upon "dry" thermal annealing. *Mineral. Petrol.* **2009**, *97*, 129–138. [CrossRef]
38. Marsellos, A.E.; Garver, J.I. Radiation damage and uranium concentration in zircon as assessed by Raman spectroscopy and neutron irradiation. *Am. Mineral.* **2010**, *95*, 1192–1201. [CrossRef]
39. Knittle, E.; Williams, Q. High-pressure Raman spectroscopy of $ZrSiO_4$: Observation of the zircon to scheelite transition at 300 K. *Am. Mineral.* **1993**, *78*, 245–252.
40. Nasdala, L.; Miletich, R.; Ruschel, K.; Váczi, T. Raman study of radiation-damaged zircon under hydrostatic compression. *Phys. Chem. Miner.* **2008**, *35*, 597–602. [CrossRef]
41. Noguchi, N.; Abduriyim, A.; Shimizu, I.; Kamegata, N.; Odake, S.; Kagi, H. Imaging of internal stress around a mineral inclusion in a sapphire crystal: Application of micro-Raman and photoluminescence spectroscopy. *J. Raman Spectrosc.* **2013**, *44*, 147–154. [CrossRef]
42. Zeug, M.; Rodríguez Vargas, A.I.; Nasdala, L. Spectroscopic study of inclusions in gem corundum from Mercaderes, Cauca, Colombia. *Phys. Chem. Miner.* **2017**, *44*, 221–233. [CrossRef]
43. Palke, A.C.; Saeseaw, S.; Renfro, N.D.; Sun, Z.; McClure, S.F. Geographic origin determination of blue sapphire. *Gems Gemol.* **2019**, *55*, 536–579. [CrossRef]
44. Váczi, T. A New, Simple Approximation for the Deconvolution of Instrumental Broadening in Spectroscopic Band Profiles. *Appl. Spectrosc.* **2014**, *68*, 1274–1278. [CrossRef]