Phase Transformation of Epigenetic Iron Staining: Indication of Low-Temperature Heat Treatment in Mozambique Ruby

Tasnara Sripoonjan, Bhuwadol Wanthanachaisaeng and Thanong Leelawatanasuk

In the past several years, Mozambique has emerged as one of the world's most important sources of ruby, and unheated stones from this country are in particularly strong demand. Nevertheless, it is common for these rubies to undergo low-temperature heating (~1,000 °C or below) to slightly improve their colour. The treated stones may show very subtle or no alteration of internal features (e.g. mineral inclusions, 'fingerprints', needles, 'silk', etc.). However, 'iron-stained' surface-reaching fractures in the rubies commonly display a noticeably more intense colour after heating. Raman and FTIR spectroscopy were used to document a transition from goethite to hematite within stained fractures in samples heated to 500 °C and 600 °C. The identification of hematite within such fractures provides key evidence for the low-temperature heat treatment of Mozambique ruby.

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Introduction

Mozambique is currently a globally important source of gem-quality ruby (e.g. Figure 1). Since the late 2000s, various ruby deposits have been discovered in the country, particularly around the Montepuez district (e.g. GIT-GTL, 2010). The stones show a range of colours and qualities, from pinkish red to purplish red with low-to-high clarity. The red colour is commonly inhomogeneous, with bluish zoning being commonly visible. Heat treatment is the most commonly used method to improve the colour so that it is acceptable to the gem trade. In late 2014, the Gem and Jewelry Institute of Thailand's Gem Testing Laboratory (GIT-GTL) learned about the low-temperature heat treatment of corundum, particularly of ruby from Mozambique. Low-temperature heating was subsequently documented as effective for improving the appearance of this material and removing bluish overtones (Pardieu et al., 2015). Typically the treatment process involves heating in air to at least 550°C, and then the temperature is increased by 100°C to a maximum of 750°C; however, the temperature at which the colour change occurs is not known to the present authors.

Heat treatment of corundum has been performed for centuries, and initially gem burners used firewood or charcoal as a heat source, sometimes with a blowpipe. Such treatments were performed

Figure 1: Mozambique has emerged as an important ruby source, as shown by these untreated stones (1.02–5.93 ct). Photo by T. Sripoonjan.

at relatively low temperatures compared to some current heating methods, although more recently these low-temperature conditions have been applied using modern electric furnaces. The identification of such treatments by gem laboratories is problematic—particularly for labs that rely only on the appearance of inclusions—resulting in inconsistencies in identification reports. While in some cases careful microscopic observation of inclusions may indicate that a ruby underwent low-temperature heating, the application of Fourier-transform infrared (FTIR) spectroscopy may provide additional proof by detecting the alteration of inclusions such as diaspore (Smith, 1995, 2010). Furthermore, the effects of heating may be detected in weathering-related minerals such as kaolinite (C. Smith, pers. comm., 2016). The systematic study of samples before and after heating is necessary to understand the temperatures under which transformations may occur.

One of the most prominent internal features in both rough and faceted rubies from Mozambique is iron-oxide staining, seen as yellow-to-orange epigenetic residues along surface-reaching fractures. The colour saturation of the iron staining tends to be intensified by heating (Kammerling and Koivula, 1989; de Faria and Lopes, 2007; Koivula, 2013; Pardieu et al., 2015). This study further investigates the changes that occur in iron-stained fractures within Mozambique rubies, and provides criteria for detecting their low-temperature treatment.

Materials and Methods

Ten representative unheated rough samples of ruby from Mozambique (0.11–0.41 g) were used in this study, and all work was carried out at GIT-GTL. Each sample was cut in half, and one piece was used for heating experiments while the other was retained for reference (Figure 2). All

Figure 2: Ten rough ruby samples from Mozambique were sliced in half, and the right-hand portion of each sample was subjected to heating experiments (to 500 °C, and then to 600 °C), while the other half was kept for reference and colour comparison. Photo by T. Sripoonjan.

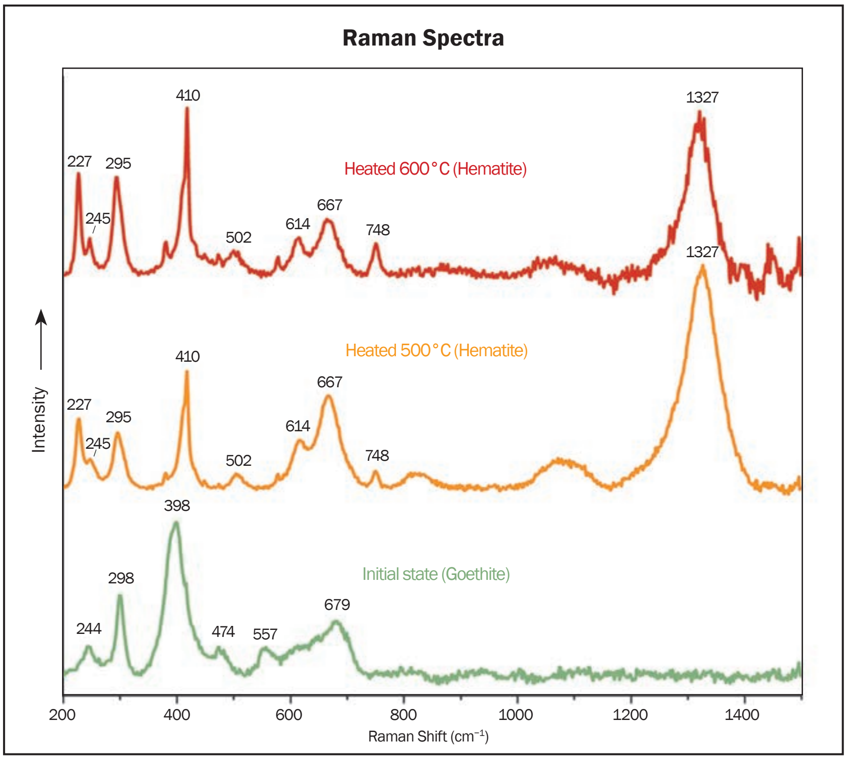


Figure 3: Raman spectra of iron-stained residues within fractures in the Mozambique rubies indicated the presence of goethite in the unheated stones and hematite in samples that were heated to 500 °C and 600 °C.

of the rubies contained prominent iron-stained fractures. The test samples were placed within an alumina crucible in an electric resistance furnace and thermally treated in air for a dwell time of two hours. The samples were initially heated to 500°C and allowed to cool slowly before being analysed. Then they were heated again, to 600°C, and more data were collected.

The iron-stained residues in the unheated reference samples and in the treated rubies were analysed with a Renishaw inVia Raman microscope, and the spectra were compared to GIT-GTL's gemstone and mineral databases and Renishaw's minerals and inorganic material database. In addition, FTIR spectroscopy of all samples was performed with a Thermo Scientific Nicolet 6700 instrument (128 scans, 4 cm^{-1} resolution and 4000-400 cm^{-1} range, using a DTGS detector and KBr beam splitter). The beam was directed through areas of the samples containing iron-stained fractures.

Results and Discussion

Raman spectroscopy of the unheated ruby samples (e.g. Figure 3, bottom) identified the epigenetic iron-stained residues as goethite, α-$Fe^{3+}O(OH)$. This compound precipitated in surface-reaching fractures after iron-bearing groundwater dried out under oxidizing conditions (Kennedy, 1990; Koivula, 2013).

After the samples were heated to 500°C and 600°C, the colour of the iron stains appeared more saturated, as shown in Figures 4 and 5. Raman

Figure 4: The iron-stained fractures in this representative sample of Mozambique ruby display a noticeable increase in orangey red coloration in the heated half (right side) compared to the untreated portion (left side). Photos by Y. Lhongsomboon.

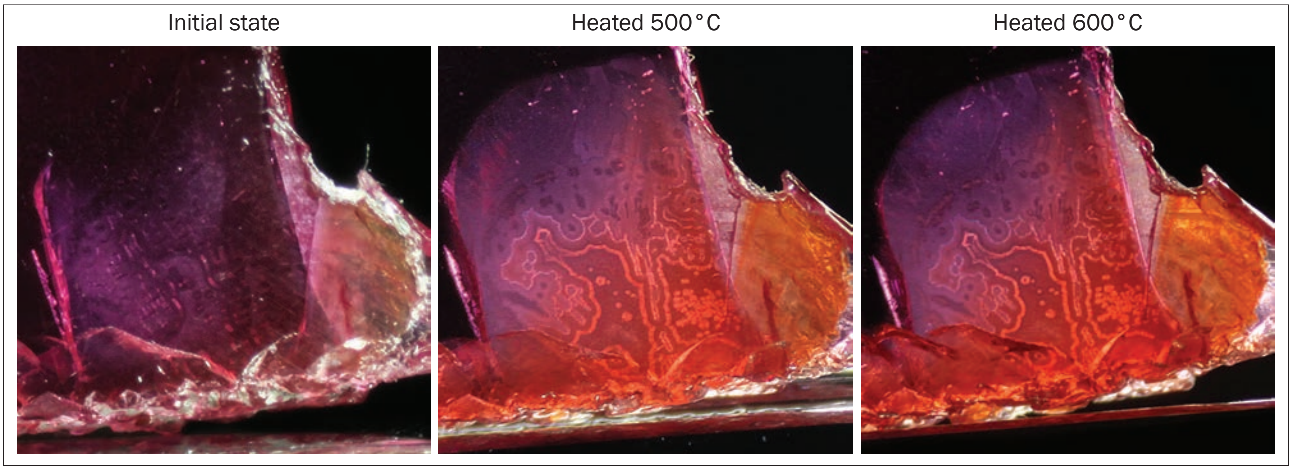
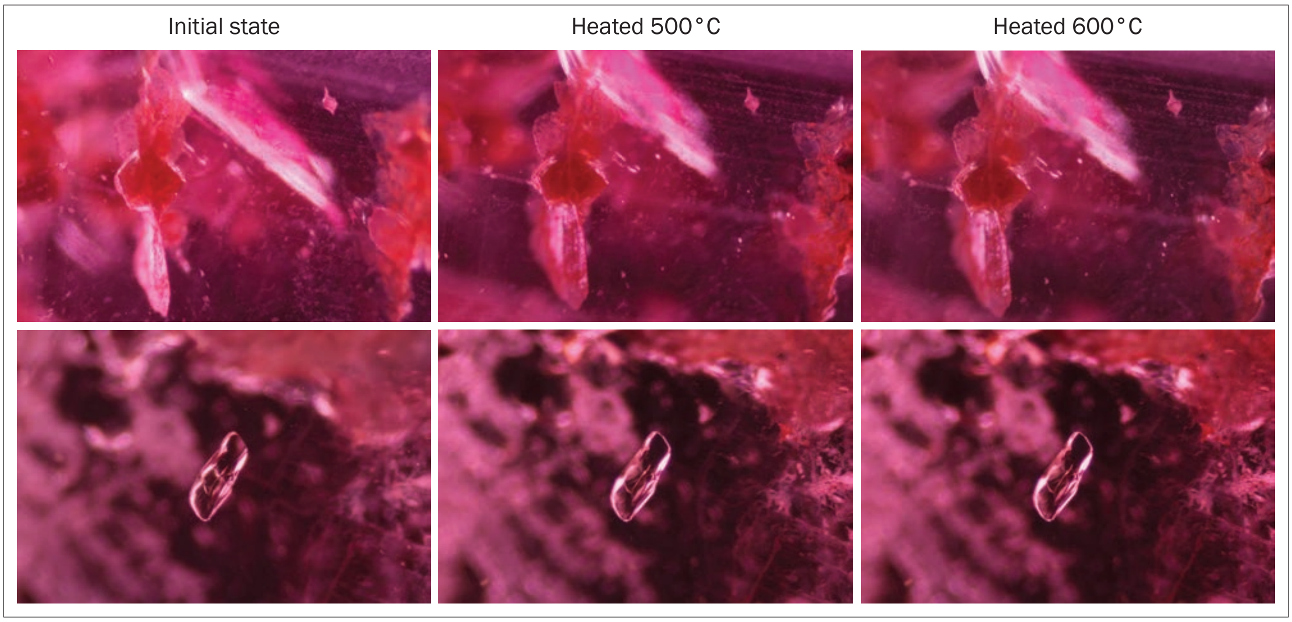


Figure 5: Heating of this Mozambique ruby produced a distinct change in the appearance of epigenetic iron staining within a fracture. Photomicrographs by Y. Lhongsomboon; image width 4.65 mm.

spectra of the iron-stained residues after heating identified them as hematite, Fe_2O_3 (Figure 3, centre and top). The characteristic Raman peaks of hematite at approximately 227, 245, 295 and 410 cm^{-1} were clearly evident after treatment at 500°C. Further heating to 600°C caused the Raman peaks to become slightly narrower, which may be due to increased crystal size and crystallinity of the hematite (Liu et al., 2013). Similar results were found in all samples, indicating that the transformation and dehydration of goethite to hematite in the iron-stained fractures easily occurs below 500°C, as suggested by Koivula (2013) and Liu et al. (2013). The appearance of other internal features (e.g. mineral inclusions) in the samples remained unchanged after heating to both 500°C and 600°C (Figure 6).

Infrared spectroscopy is useful for investigating absorption features related to structural OH groups in rubies, and can reveal trace impurities of diaspore, boehmite and/or kaolinite (Smith, 1995; Beran and Rossman, 2006). The spectra are commonly dominated by O-H stretching frequencies related to boehmite and/or kaolinite impurities, particularly in the 4000–3000 cm^{-1} region (e.g. Figure 7) that is useful for determining if a ruby or sapphire has been heated (Smith, 1995). However, low-temperature heat treatment may not cause boehmite and kaolinite to completely decompose (cf. Glass, 1954; Wanthanachaisaeng,

Figure 6: These inclusion scenes in Mozambique ruby (top: diaspore; bottom: amphibole) show no significant changes in appearance after heating to 500 °C and 600 °C. Photomicrographs by Y. Lhongsomboon; image width 1.8 mm.



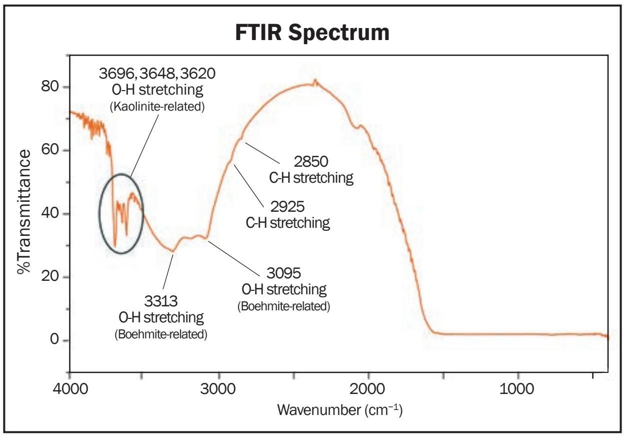


Figure 7: FTIR spectroscopy of OH-related features in ruby and sapphire can help gemmologists determine whether stones have undergone heat treatment. Frequently, the identification of low-temperature heating (i.e. below 600 °C) cannot be precisely achieved because the OH-related features may not have completely decomposed. (The peaks at ~2925 and 2850 cm^{-1} are probably due to contamination from finger oils or cutting residues; Cartier, 2009.)

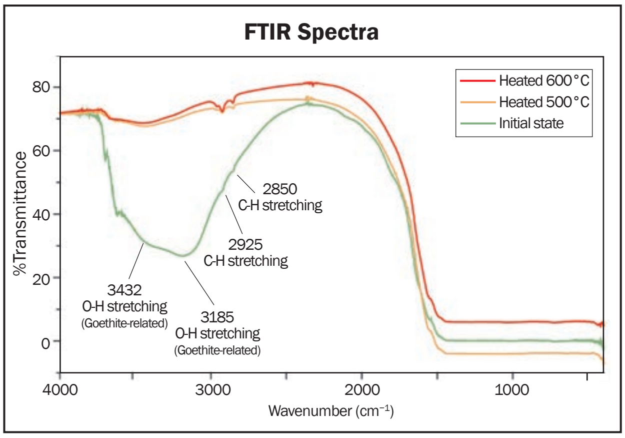


Figure 8: FTIR spectra are shown for a representative sample of Mozambique ruby before treatment and after heating to 500 °C and 600 °C. Goethite-related absorptions in the 3600–3000 cm^{-1} region are evident before heat treatment, but they nearly disappear after treatment.

2007). Unheated samples of Mozambique ruby in this study occasionally showed FTIR absorption bands associated with iron hydroxides (i.e. goethite, as identified by Raman spectroscopy), although only when the ruby samples were analysed in particular directions and positions (cf. Cambier, 1986). In the spectral range of 3600–3000 cm^{-1}, which is important for the detection of hydroxyl bonds (including goethite), the absorption bands in the unheated samples were slightly broadened rather than appearing as sharp peaks. After treatment at 500°C or 600°C, these absorption bands became barely visible due to dehydroxylation and recrystallization of goethite into hematite (Liu et al., 2013; Figure 8). Heating of goethite causes a gradual dehydration that begins at 260°C (Kammerling and Koivula, 1989; de Faria and Lopes, 2007; Koivula, 2013; Liu et al., 2013). It continues with the transformation of the yellow-to-orange goethite (orthorhombic) to dark orange-red hematite (trigonal), through the chemical reaction:

$$\underset{\text{Goethite}}{2\alpha\text{-FeO(OH)}} + \text{Heat} \rightarrow \underset{\text{Hematite}}{\alpha\text{-Fe}_2\text{O}_3} + \underset{\text{Water}}{\text{H}_2\text{O}}$$

Conclusions

Although the low-temperature heating of ruby and sapphire has been conducted for centuries, the detection of such treatment remains difficult. For ruby in particular, low-temperature treatment of material from Myanmar and Vietnam is well known (e.g. Smith, 2010; Wathanakul et al., 2011; Pardieu et al., 2015), but conclusive identification criteria remain elusive in many cases.

In recent years, Mozambique ruby has become important in the gem and jewellery market. Low-temperature heat treatment is successful for improving the colour of this material, but unfortunately many unethical traders have sold these heated stones as untreated. Microscopic observation of inclusions in such rubies is not reliable for identifying this treatment. However, heating intensifies the coloration of epigenetic iron-stained fractures, providing visual evidence of treatment. This change in appearance is due to the transformation of goethite to hematite by a dehydration mechanism that takes place during the heating process. Raman and FTIR spectroscopy are useful for detecting the presence of hematite residues in the iron-stained fractures, which is a key criterion to indicate heat treatment at relatively low temperatures in Mozambique ruby.

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