



Article Chemical and Spectral Variations between Untreated and Heat-Treated Rubies from Mozambique and Madagascar

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Abstract: The chemical composition and spectra of untreated and heat-treated rubies from Mozambique and Madagascar were analyzed by an electron probe microscopy analysis, laser ablation inductively coupled plasma quadrupole mass spectrometry, Fourier transform infrared spectroscopy, Raman spectroscopy and UV-visible spectroscopy. Due to the different content of Fe and different inclusions, rubies from Madagascar belong to alkaline basalt deposit, while rubies from Mozambique belong to amphibole metamorphic rock. The ruby samples were heated to 900 °C to change their color. As Fe and Ti ions can be transferred into different valences and diffused into the interior of rubies, Cr ions in cracks or cleavages entered the crystal lattice during heat treatment and the content of Fe and Ti decreased, while the content of Cr increased in heat-treated rubies. After heating, blue-purple decreased and the red hue increased, while the blue color band disappeared and yellow appeared in the cracks of the samples because of the chemical changes. Compared with untreated rubies, the infrared absorption peaks of 2123 cm⁻¹ and 1990 cm⁻¹ related to inclusions disappeared, and the existence of 3236 cm⁻¹ and 3186 cm⁻¹ absorption peaks was a typical characteristic of heat-treated ruby, which was produced by changes in its inclusion. In addition, due to the weakened charge transfer of Fe^{2+} and Ti^{4+} and the increasing reaction of $Fe^{2+} \rightarrow Fe^{3+}$ along with the heat treatment, the UV-visible absorption peak at 400 nm shifted to purple.

Keywords: ruby; Mozambique; Madagascar; heat treatment; gemological properties

1. Introduction

Ruby is one of the most precious gemstones on the market; it is a variety of corundum, and its structural formula is Al_2O_3 , in which a small amount of Al^{3+} is replaced by Cr^{3+} ions [1]. Most natural rubies show uneven color saturation, sometimes with bands of blue color. To overcome these issues, various processing methods have been developed, such as heat treatment [2], glass-filled [3], ion implantation [4], etc. Heat treatment is one of the earliest methods used to improve the color, clarity and value of rubies. Previous studies have shown that the dark core and blue color band of rubies can be removed by heat treatment under an oxidizing atmosphere [5,6]. This method simulates the growth environment of natural ruby, makes oxygen atoms diffuse into a ruby lattice at high temperature and pressure, changes the valence state of chromogenic ions, or changes the internal structural defects, thus eliminating the blue or purple colors that are superimposed on red and obtaining the ideal color [7,8]. Therefore, it is important to discriminate between untreated and heat-treated rubies on the base of their gemological characteristics and chemical composition, as the two types of gems have different values on the market.

Modern research is beginning to employ surface-sensitive techniques to analyze untreated and heat-treated rubies in many different areas, e.g., X-ray electron probe microscopy analysis (EPMA) [9]; secondary-ion mass spectrometry (SIMS) [10]; protoninduced X-ray emission spectrometry (PIXE) [11]; and X-ray photoelectron spectroscopy



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(XPS) [5]. Among these techniques, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a sensitive method that is used to analyze the trace element composition in the untreated and heat-treated rubies. In addition to the analytical techniques that are used to determine the chemical composition, there are also other techniques that allow the discrimination of untreated rubies from heat-treated ones, such as Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Photoluminescence, and UV–vis–NIR spectrometry to characterize gemstones [8].

In general, the formation of corundum requires a geological environment that is rich in Al and poor in Si; in addition, the formation of ruby also requires an abundance of Cr and little Fe [11]. Rubies from Mozambique are mainly found in amphibolite metamorphic deposits [7]. However, rubies from Madagascar have a complex geological background and several types of ruby deposits, such as basalt kimberlite, alkaline basalt and mafic ultramafic rock type, in which metamorphic rock deposits are widely distributed [12].

Rubies from Africa are mostly pink or purplish red and have large sizes and poor transparency. Madagascar and Mozambique are famous for producing rubies in Africa. The geological conditions for ruby formation are diverse [12]. Three major deposit types of gem-quality ruby exist: marble-hosted (Myanmar, Afghanistan, Vietnam); basalt-hosted (Thailand, Cambodia); and metasomatic type (Kenya, Sri Lanka, India) [13,14]. The gemological properties and geological settings of rubies from Madagascar and Mozambique are similar, and their distinction is therefore difficult [12]. The origin of natural rubies cannot be identified solely on the basis of microscopic observations of the inclusions. The accurate determination of trace elements such as Mg, Ti, V, Cr, Fe and Ga in rubies is essential to determine their origin. The trace element contents in rubies vary owing to their different natural origins. The various types of rubies can be recognized based on their chemical composition and the characteristics of the inclusions. However, heat treatment produces different appearances in the different types of rubies. It is difficult to distinguish untreated and heat-treated rubies because of their similar appearance, especially when they are heated at a low temperature (below 1000 °C) [5,7]. As the commercial value of heat-treated rubies is lower than that of natural rubies, it is important to distinguish heat-treated rubies from natural ones. In this paper, rubies from Madagascar and Mozambique are heated to 900 °C at an oxidizing atmosphere to change their color. EPMA and LA-ICP-MS are employed to compare the chemical composition and trace elements between untreated and heat-treated rubies from Madagascar and Mozambique. Moreover, the changes in color and spectral characteristics are also fully studied by microscope, FTIR, Raman spectroscopy and UVvis–NIR spectrometry. This provides a reference for the heat treatment and identification of rubies from Madagascar and Mozambique.

2. Materials and Methods

2.1. Materials

Six ruby samples from Madagascar (MD) and eight ruby samples from Mozambique (MS) are selected to study their gemological characteristics. The ruby samples from Mozambique are purple red, with a small amount of gray tint, and have the shape of a triangular plate. The color distribution is uneven and there is a blue color band in the center, surrounded by associated minerals. The Madagascar ruby samples are mostly columnar or barrel shaped, and a few are plate-shaped. Hexagonal columns and rhombohedrons can be observed in all of the samples. The ruby samples from Mozambique have a bright color, light pink and purplish red, and the color distribution of the samples is uniform. There are cleavages or cracks in all of the samples, which affects the transparency of the gemstone. Cleavage is the smooth surface that is produced along the crystallization direction under the external force, while crack is an irregular section under the external force, while track is an irregular section under the samples from 8.14 to 18.54 ct, the specific gravity (SG) of the samples ranges from 3.96 to 3.98 (obtained by hydrostatic weighing method), and the transparency of the samples ranges from slightly

Label	Color	Transparency	Weight (ct)	Specific Gravity (SG)	Appearance
MD-1	pink	slightly transparent	15.27	3.98	crack
MD-2	pink	slightly transparent	11.26	3.97	cleavage, crack
MD-3	pink	slightly transparent	11.26	3.98	cleavage, crack
MD-4	pink	slightly transparent	11.26	3.97	cleavage, crack
MD-5	pink	slightly transparent	11.26	3.98	cleavage, crack
MD-6	pink	slightly transparent	11.26	3.97	cleavage, crack
MS-1	purple red	opaque	18.54	3.97	cleavage
MS-2	purple red	opaque	14.35	3.98	cleavage
MS-3	purple red	opaque	10.02	3.96	cleavage
MS-4	purple red	opaque	8.14	3.97	yellow
MS-5	purple red	opaque	12.38	3.98	cleavage
MS-6	purple red	opaque	11.21	3.96	cleavage
MS-7	purple red	opaque	16.54	3.98	crack
MS-8	purple red	opaque	13.75	3.98	crack

Table 1. Gemological characteristics of ruby samples from Madagascar and Mozambique.

transparent to opaque. The basic gemological characteristics of all the samples are shown

2.2. Heat Treatment Experiments

in Table 1.

Ruby samples from Madagascar (MD-1, MD-2, MD-3) and Mozambique (MS-1, MS-2, MS-3) were selected and cut into two parts, one part for heat treatment, and the other untreated part for comparing their gemological properties. Before heat treatment, the raw samples were cleaned with isopropanol to remove any dirt and grease. The heat treatment was then carried out in a muffle furnace (SX2-4-10, Tianjin Central Experimental Electric Furnace Co., Tianjin, China). The furnace was heated to 900 °C at a rate of 10 °C/min with an open crucible (oxidizing atmosphere), and the peak temperature was maintained for 12 h. Then, the ruby samples were cooled in the air for further testing. The heat experiment was performed in the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Beijing).

2.3. Analytical Methods

Color distribution and inclusions were observed using a GI-MP22 binocular microscope. The chemical composition of the heat-treated and untreated samples was determined by a JXA-8100 electron microprobe (JEOL Ltd., Akishima, Japan). The accelerated voltage was 15 kV, the beam current was 20 nA, and the diameter of the beam spot was 10 μ m. The following standards were used for calibration: diopside for Si and Mg, rutile for Ti, hematite for Fe, rhodonite for Mn, wollastonite for Ca, synthetic NiO for Ni, and chromite for Cr. The intensity data were corrected using the ZAF3 method. The detection limits of the samples for EPMA were 100 ppm and the total error of the result was 1.5% (W/W). Trace elements were collected using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) systems, which was equipped with Angilent7900 laser ablation system (Agilent Technologies, Santa Clara, CA, USA). The laser repetition rate was 10 Hz and the laser wavelength was 193 nm. Ablation was carried out with 44 μ m spot sizes, and the energy density was 6.02 J/cm^2 . The detection limits varied slightly through the course of the analyses but were generally <10%. The detection limits of the analyzed samples by LA-ICP-MS were 0.1–0.3 ppm, 0.03–0.2 ppm, 1–3 ppm, 3–5 ppm and 5–20 ppm for Mg, V, Ti, Ga and Fe, respectively.

The IR spectra of the ruby samples were recorded by a Tensor 27Fourier transform infrared spectroscopy (CUGB, Beijing, China) in the 4000–400 cm⁻¹ region. Inclusions were identified, when possible, using an HR-Evolution Raman spectroscopy with a Renishaw in Via Raman microscope system (Horiba, Ltd., Kyoto, Japan). The Raman spectra of the inclusions were excited by a Mode-Laser. A Stellar-REN Arion laser produced highly polarized light at 532 nm and collected at a nominal resolution of 3 cm⁻¹ in the 2000–100 cm⁻¹ range. In many cases, the confocal capabilities of the Raman system allowed inclusions beneath the surface to be analyzed. The UV-visible spectra were recorded with a UV-3600 Spectrometer (Shimadzu Corporation, Kyoto, Japan) in the range of 300–900 nm, using a high-speed scanning and reflection method. The sampling interval was 1 s.

3. Results

3.1. Microscopic Examination

The color and appearance of the heat-treated (MD-H-1, MS-H-1) and untreated samples (MD-1, MS-1) were observed under a biomicroscope (Figure 1). After heat treatment, the red hue of the Madagascar sample (MD-H-1) increased, while the purple tone decreased significantly. Moreover, the color of the sample (MD-H-1) became bright, and the cracks more evident. The purple tone of the Mozambique sample (MS-H-1) was significantly weakened, showing a different degree of red tone. At the same time, sample (MS-H-1) showed a different degree of yellow on the surface and crack. In addition, the blue color band in the center of sample (MS-H-1) disappeared and the surrounding color became pure. It is speculated that the oxidization and diffusion of Fe ions are the main reason for the disappearance of the blue color band and the appearance of yellow [8], which needs further research in subsequent experiments. The white material on the sides of sample MS-H-1 is alumina, which is added before heat treatment.



Figure 1. Color and appearance of treated and untreated samples.

3.2. Electron Microprobe Analysis

In natural gemstones, it is normal to find chemical zoning in accordance with the crystallographic axes. For example, the MD-1 and MS-1 samples (Figure 1) both have a color band and inhomogeneous chemical composition along the c axis. The crystal plane for EPMA was selected parallel to the c axis, and the points were selected perpendicular to the blue color band. A total of 12 points were selected to compare their chemical composition, including three points of the untreated samples (MD-1, MD-2, MD-3); 3 points of the heat-treated samples (MD-H-1, MD-H-2, MD-H-3); 3 points of the untreated samples (MS-1, MS-2, MS-3); and 3 points of the heat-treated samples (MS-H-1, MS-H-2, MS-H-3) from Madagascar and Mozambique, respectively. The position of the ruby samples is shown in Figure 2.



MD-H-1 MD-H-2 MD-H-3 MS-H-1 MS-H-2 MS-H-3

Figure 2. Position of treated and untreated samples for EPMA.

The chemical composition of the untreated (MD-1, MD-2, MD-3, MS-1, MS-2, MS-3) and heat-treated samples (MD-H-1, MD-H-2, MD-H-3, MS-H-1, MS-H-2, MS-H-3) and average contents is reported in Table 2. Other than the main component of Al_2O_3 , all the samples have similar impurities, such as Na_2O , Cr_2O_3 , SiO_2 , MgO, FeO, TiO_2 , MnO and NiO. In the ruby samples from Madagascar, after heat treatment, the average Cr_2O_3 content increases from 0.190% to 0.275%; the average FeO content decreases from 0.594% to 0.506%; and the average TiO_2 content decreases from 1.104% to 0.732%. The result is consistent with the color changes, where the purple tone of the samples is reduced and the red hue is stronger after the heat treatment.

Table 2. Chemical composition of untreated and treated samples from different area (% W/W).

Label	Al ₂ O ₃	Na ₂ O	Cr ₂ O ₃	SiO ₂	TiO ₂	MgO	FeO	MnO	NiO
MD-1	99.489	0.010	0.156	0.021	1.078	0.007	0.664	0.012	0.041
MD-2	99.424	0.033	0.174	0.032	0.559	0.011	0.567	0.019	0.010
MD-3	98.809	0.079	0.241	0.015	1.675	0.009	0.551	0.021	0.029
Average	99.241	0.041	0.190	0.023	1.104	0.009	0.594	0.017	0.027
MD-H-1	98.308	0.019	0.271	0.005	0.559	0.012	0.616	0.016	0.062
MD-H-2	99.275	0.020	0.179	0.002	0.24	0.013	0.420	0.010	0.024
MD-H-3	98.632	0.016	0.376	0.010	1.397	0.014	0.481	0.019	0.029
Average	98.738	0.018	0.275	0.006	0.732	0.013	0.506	0.015	0.038
MS-1	98.925	0.026	0.080	0.012	1.665	0.006	0.364	0.009	0.017
MS-2	98.782	0.012	0.102	0.031	1.678	0.012	0.392	0.022	0.019
MS-3	98.216	0.024	0.093	0.021	2.477	0.016	0.301	0.021	0.018
Average	98.641	0.021	0.092	0.021	1.940	0.011	0.352	0.017	0.018
MS-H-1	99.201	0.031	0.117	0.017	1.397	0.021	0.349	0.019	0.021
MS-H-2	98.956	0.021	0.132	0.029	1.518	0.009	0.382	0.015	0.025
MS-H-3	99.251	0.012	0.121	0.004	1.199	0.017	0.247	0.019	0.140
Average	99.136	0.021	0.123	0.017	1.371	0.016	0.326	0.018	0.062

Similarly, after heat treatment, the average Cr_2O_3 content of the rubies from Mozambique increases from 0.092% to 0.123%, the FeO content decreases from 0.352% to 0.326%, while the TiO₂ content decreases from 1.940% to 1.371%. The results therefore show that after the heat treatment, the contents of Fe and Ti both decrease, which is why the purple-blue band disappears.

The red color and Cr ions of the untreated samples are unevenly distributed. After the heat treatment, the Cr ions on the surface or crack of the ruby samples enter the lattice, so that their distribution becomes uniform and the average Cr_2O_3 content increases, compared with the untreated samples. However, the Fe and Ti ions diffuse into the interior of the ruby samples after heating in oxidizing conditions, so their contents on the surface of the heat-treated samples are relatively low. At the same time, brown substances appear in the cracks of the heat-treated samples, and the FeO content in the cracks is relatively high. It

can be concluded that Fe²⁺ is oxidized to Fe³⁺ during heat treatment [15–17], and yellow appears on the surface and cracks (Figure 1), which is consistent with the results that are observed under the microscope.

3.3. LA-ICP-MS Analysis

The LA-ICP-MS trace element results of 12 points in six untreated and six heat-treated samples are reported in Table 3, and the points were selected perpendicular to the blue color band. Limited amounts of trace elements such as Cr, Fe, Ti, V, Mg and Ga were found in all the analyzed ruby samples. The geographic determination is based on the Fe content and not on the Cr content of ruby, which is not considered to be useful for the certification of origin [12]. Rubies can be divided into three types according to their Fe content, which are related to marble type, metasomatic rock type and basalt type deposits, respectively [18]. As pointed out in previous studies [18,19], the range of Fe content with marble type is 0–200 ppm, that with metasomatic rock is 200–2000 ppm, while that with basalt type deposits is >2000 ppm. Based on the data of Table 3, the average content of Fe (3219 ppm) in the rubies from Madagascar is higher than that of the rubies from Mozambique (1717 ppm). Thus, the rubies from Mozambique belong to amphibole metamorphic rock, and the rubies from Madagascar belong to alkaline basalt.

Table 3. Chemical composition of untreated and treated samples from different area.

Label	Cr (ppm)	Fe (ppm)	Ti (ppm)	Mg (ppm)	Ga (ppm)	V (ppm)
MD-1	842	3230	71.8	46.1	89.7	15.4
MD-2	880	3250	66.1	44.9	91.1	16.9
MD-3	838	3178	65.0	43.5	80.3	16.0
Average	853	3219	67.6	44.8	87.0	16.1
MD-H-1	1083	3080	38.0	24.5	87.8	14.7
MD-H-2	1142	2894	36.0	23.5	80.3	14.0
MD-H-3	1047	2992	36.5	24.2	81.5	13.8
Average	1090	2989	38.8	24.1	83.2	14.2
MS-1	650	1768	42.1	25.4	38.4	2.4
MS-2	640	1702	35.9	26.0	36.3	2.4
MS-3	703	1680	40.9	37.6	37.2	2.6
Average	664	1717	39.6	29.7	37.3	2.5
MS-H-1	684	1455	34.2	34.4	35.9	2.5
MS-H-2	703	1500	30.5	38.8	33.5	2.4
MS-H-3	767	1740	38.0	24.5	36.0	2.3
Average	718	1565	34.2	32.6	35.1	2.4

We can also observe that the average content of Cr in the rubies from Madagascar (853 ppm) is higher than that of the rubies from Mozambique (664 ppm). Thus, the rubies from Madagascar show red with a high saturation, while those from Mozambique show dark red with a blue band in the center. The Cr content of the samples from Madagascar is high, up to 1091 ppm, and it is close to that in basalt ruby deposit. Meanwhile, the Cr content of Mozambique ruby is relatively low, and it is consistent with the type of metasomatic rock [12].

In the rubies from Madagascar, after heat treatment, the average content of Ti decreases from 67.6 to 38.8 ppm; that of Fe decreases from 3219 to 2989 ppm; that of Ga decreases from 87.0 to 83.2 ppm; and Cr increases from 853 to 1091 ppm. In the Mozambique rubies, after heat treatment, the average content of Ti decreases from 39.6 to 34.2 ppm; that of Fe decreases from 1717 to 1565 ppm; that of Ga decreases from 37.3 to 35.1 ppm; and Cr increases from 664 to 718 ppm.

The ruby samples have an uneven color distribution, especially on the surface. During heating under oxidizing conditions, the Fe and Ti ions can be transferred into different valences and diffused into the interior of the ruby samples [6]. Therefore, the purple hue on the surface of the samples decreases and the red hue increases. During heat treatment, the

Cr ions in the cracks or cleavages of the samples enter the crystal lattice, causing the content of the Cr ions to increase and making the color of the surface more evenly distributed.

Comparing the data in Tables 2 and 3, discrepancies are observed on the chemical composition that is obtained with the EPMA and LA-ICP-MS analyses. Natural rubies have chemical heterogeneity in the ruby samples (Figure 1), and the points that are selected for EPMA are not the exactly same as the position for LA-ICP-MS. It is normal for there to be differences in the results of chemical composition between EPMA and LA-ICP-MS, such as Cr, Fe and Ti.

3.4. Infrared Spectra

Typical spectra in the spectral range of 3400 cm⁻¹ to 1500 cm⁻¹ before and after heat treatment at 900 °C are reported in Figure 3. The untreated samples of MD-1, MS-1 and the heat-treated samples of MD-H-1, MS-H-1 were selected to compare their changes in IR spectra. The absorption peak of 3310 cm^{-1} is the most characteristic peak in ruby, which is produced by the OH stretching band because of its inclusion, such as diaspore [20,21]. The intensity of the infrared peaks in the different samples is different, and this depends on the amount of diaspore that is present. The presence of diaspore shows that the ruby has not been heated or has been heated at a low temperature (below 1000 °C), and the absorption peak of 3310 cm^{-1} significantly weakens or even disappears completely after being heated [22]. The infrared spectra of the ruby samples from Madagascar show a weak absorption peak of 3310 cm^{-1} before heating (MD-1), and the absorption peak of 3310 cm^{-1} is significantly weakened after heating (MD-H-1). The absorption peak of 3310 cm^{-1} of (MS-1) is stronger than that of (MD-1), and the absorption peak of 3310 cm^{-1} decreases significantly after heating (MS-H-1). When the absorption peak of 3310 cm^{-1} is strong enough before heating, new peaks of 3236 cm⁻¹ and 3186 cm⁻¹ are generated after heating, which are produced by changes in its inclusion. The peaks of 3310 cm⁻¹, 3236 cm⁻¹ and 3186 cm⁻¹ are usually called 3309 cm⁻¹ series [23]. Therefore, the existence of 3236 cm⁻¹ and 3186 cm⁻¹ absorption is evidence that the ruby has been heated and still has inclusions after heat treatment [8].



Figure 3. FTIR spectra of untreated and treated samples in the range of (**a**) $3400-3000 \text{ cm}^{-1}$ and (**b**) $3000-1500 \text{ cm}^{-1}$.

Similarly, the spectra of samples MD-H-1, MS-H-1 in the spectral range of 3000 cm⁻¹ to 1500 cm⁻¹ in Figure 2 show that the absorption peaks of 2123 cm⁻¹ and 1990 cm⁻¹ disappeared after heat treatment in both samples (MS-1, MD-1), caused by diaspore or

The change in the IR spectra of heat-treated rubies can be seen in those with inclusions. It is worth noting that not all natural rubies have characteristic inclusions. Rubies without inclusions such as samples of MD-5, MD-6, MS-4 and MS-8 do not have these absorption peaks and the IR spectra of heat-treated rubies without inclusions are similar to natural rubies—other methods need to be used to determine whether they have been heat treated.

3.5. Raman Spectra

Rubies containing inclusions were then selected to identify the characteristics of the inclusions themselves. For example, focusing the incident light on the inclusions in the ruby samples of MD-2 and MS-1, Raman peaks at 138 cm⁻¹, 244 cm⁻¹, 432 cm⁻¹ and 609 cm⁻¹ can be observed in Figure 4a, indicating that the black inclusion in the samples of MD-2 and MS-1 is rutile [26,27]. In addition, diaspore inclusion is found in the ruby samples of MD-3 and MS-3 [28] (Figure 4b). The characteristic Raman peaks of feldspar at 199 cm⁻¹, 285 cm⁻¹, 505 cm⁻¹, 557 cm⁻¹ and 976 cm⁻¹ [29] (Figure 4c), and amphibole at 209 cm⁻¹, 673 cm⁻¹ and 1018 cm⁻¹ [30] (Figure 4d) are detected in MS-2, which is consistent with the previous conclusion that ruby from Mozambique belongs to amphibole metamorphic rock.



Figure 4. Raman spectra of inclusions in untreated samples: (**a**) rutile, (**b**) diaspore, (**c**) feldspar and (**d**) amphibole.

The Raman spectra of untreated and treated ruby samples that were measured at room temperature are shown in Figure 5. Since ruby has strong fluorescence, all Raman spectra are subjected to baseline correction to make the results more accurate. The typical peaks of 378 cm⁻¹, 416 cm⁻¹, 575 cm⁻¹ and 747 cm⁻¹ are observed due to Al-O vibrations of corundum [30,31]. Compared with the Raman spectra of the untreated (MD-1, MS-1) and

416 378 575 747 MS-1 Intensity(a.u.) MS-H-MD-1 MD-H-1 200 400 600 800 1000 1200 Ranman Shift (cm⁻¹)

heat-treated samples (MD-H-1, MS-H-1), the Raman band positions and peak intensities remain unchanged after heat treatment.

Figure 5. Raman spectra of untreated and treated samples.

3.6. UV-Visible Spectra

Optical absorption in the UV–visible region for the untreated and heat-treated ruby, recorded at room temperature, is reported in Figure 6. Since the transparency of the samples is poor (slightly transparent or opaque), the UV-VIS spectra are measured by the reflection method. The untreated MD-2 and MS-2 samples both have a strong absorption band at 560 nm, while the absorption band gradually moves to 555 nm for the heat-treated samples (MD-H-2, MS-H-2), which is formed by Cr^{3+} , due to its spin-allowed transition from the ground state ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$ [25,32], and the absorption intensity decreases evidently after heat treatment. Combined with the color change of the samples, the red hue increases in the heat-treated samples from both areas.



Figure 6. Optical absorption spectra of the untreated and treated samples (a) MD, (b) MS.

The absorption peak at 400 nm shifts to the purple area and the peak intensity also decreases significantly, which is caused by Fe^{3+} [33–36]. Combined with the chemical

composition of the samples, the reaction of $Fe^{2+} \rightarrow Fe^{3+}$ increases along with the heat treatment, while the charge transfer between Fe^{2+} and Ti^{4+} decreases. Moreover, Fe^{2+} is oxidized to Fe^{3+} after heat treatment, and the charge transfer between Fe^{2+} and Ti^{4+} is reduced [33], so the blue tone of the samples is reduced and the red hue is increased. Therefore, the absorption peak shifts to the purple area, the blue-purple tone of the ruby decreases, and the red hue increases, which is the main reason for the formation of the absorption band and the absorption peak moving to 385 nm and 388 nm, respectively. Such similar absorption bands due to both Cr and Fe have been reported for different rubies by previous research [20,25,37]. It has been observed that there is a decrease in the intensity of the band after heat treatment. This may be due to richer Fe^{3+} on the surface after the heat treatment than untreated rubies. The obvious emission of Cr^{3+} luminescent centers at 693 nm (MD) and 694 nm (MS) is shown in Figure 6, which also reveals a tremendous increase in the intensity of the 694 nm emission peak for the heat-treated samples.

4. Discussion

According to the results of the EPMA and LA-ICP-MS analyses, after heating, the FeO and TiO₂ contents of the rubies both decrease, and the Cr₂O₃ content increases, so the red hue of the treated rubies is stronger than the untreated ones, and the blue color band is reduced, which is due to the heat treatment in an oxidizing atmosphere. The increasing red hue enhances the value of rubies. This is consistent with previous research [38,39]. It is proved that low-temperature heating is documented as effective for improving the color and removing the blue color band of rubies. Therefore, the optimum temperature of heat treatment depends on the different quality and origin of the ruby samples.

Moreover, the color of the ruby samples changes from purplish red to bright red, with the blue band disappearing and the yellow appearing in the cracks of some samples. This coincides with the change in chemical composition. Such a change is also reflected in the spectra between the unheated and heat-treated samples. Natural rubies usually have inclusions such as boehmite and diaspore [24], which have the characteristic absorption peak of 3310 cm^{-1} , related to the inclusions [7,8,22]. After heating, the absorption peak of 3310 cm^{-1} decreases significantly, and the existence of 3236 cm^{-1} and 3186 cm^{-1} absorption is a characteristic of heat-treated ruby. Furthermore, the twin peak of 2123 cm^{-1} and 1990 cm^{-1} is a typical characteristic of untreated ruby.

Heat-treated and untreated rubies have similar Raman spectra. As the rubies are heat-treated at a low temperature (900 °C), the chemical composition changes a little, but it shows no obvious difference in the UV-VIS spectra concerning the bands. However, the absorption peak of 400 nm shifts to the blue area in the heat-treated rubies for the decrease in Fe²⁺ and Ti⁴⁺.

In addition, rubies have an obvious emission of Cr^{3+} luminescent centers in both areas. Since they have a certain amount of iron ions, the fluorescence of all ruby samples is weak. The change in heat-treated rubies with a high temperature will be (above 1000 °C) studied in further work.

5. Conclusions

Due to the different trace elements and inclusions, rubies from Madagascar belong to alkaline basalt deposit and have the characteristic inclusions of rutile and diaspore, while rubies from Mozambican belong to amphibole metamorphic rock and have the inclusions of diaspore, amphibole and feldspar. The ruby samples are heated at 900 °C under oxidizing conditions to change their color. After heating, the red color of the heat-treated rubies is brighter than the untreated ones, with the blue band disappearing and yellow appearing in the cracks of some samples. This change is also reflected in the chemical composition; the content of Cr increases, while the content of Fe and Ti decreases in heat-treated rubies. The IR spectra can be used to distinguish the heated rubies from the unheated ones, especially the rubies with inclusions. After heating, the absorption peak of 3210 cm⁻¹ related inclusions decreases significantly and the new absorption peaks of 3236 cm⁻¹ and

3186 cm⁻¹ appear. Therefore, the presence of 3236 cm⁻¹ and 3186 cm⁻¹ absorption is a characteristic of heat-treated ruby. After heating, the UV-visible absorption peak of the untreated samples at 400 nm shifts to purple due to increasing the reaction of $Fe^{2+} \rightarrow Fe^{3+}$ and the weakened charge transfer of Fe^{2+} and Ti^{4+} .

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