

**HEAT TREATMENT FOR SOME GREEN
SAPPHIRE FROM ATTAPEU OF LAOS**

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Abstract

A new source of sapphire was reportedly found in Attapeu area from southern Lao P.D.R. It is therefore interesting to investigate the gemological characteristics of this sapphire including the possibility of thermal enhancement. In this research, 70 rough sapphire samples were classified into 4 groups based on the color shade as blue (15), green (15), bluish green (20) and greenish blue (20) varieties.

Some rough samples show well-formed pyramid habits with occasionally having magmatic corroded surface. The basic gemological properties of all sapphires fall into a normal range of corundum. Typical internal characteristics are growth pattern, color zone, fingerprints which are often filled with reddish brown iron stains. The mineral inclusions are feldspar (as identified by Raman microscope) and other unidentified minerals. All of the samples contain rather high Fe_2O_3 (0.2-1.1%), moderate TiO_2 (0.01-0.6%) and extremely low Cr_2O_3 and V_2O_5 contents. The UV – VIS – NIR spectrograms show typical basaltic-type pattern of high iron sapphires. Corundum from Attapeu area is therefore likely related to alkali basalt nearby as suggested by well preserved crystal habits with

some magmatic corroded surface. The FTIR spectrograms show absorption peak of O - H stretching (3309 cm) before heating.

The heating experiment was carried out at 1,650°C for 5 hours in N₂ atmosphere. After the treatment blue hue was intensified in most types of samples. Therefore the green, greenish blue and bluish green varieties can be easily enhanced into blue sapphire with slight greenish tint. Other changes that could be detected after heat treatment are; color zone become apparently clear, healed fractures expanded and altered, tension cracks clearly developed. The UV – VIS – NIR spectrograms measured after heating show the increase in absorption peak due to Fe²⁺/Ti⁴⁺ pair peaked at 565 nm and Fe²⁺/Fe³⁺ pairs peaked between 840 and 900 nm. These bands are responsible for the intense blue after heating.

หัวข้อเรื่อง : การพัฒนาคุณภาพพลอยแซปไฟร์สีเขียวด้วยความร้อน จากแหล่งอัครตะปือ

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บทคัดย่อ

แหล่งพลอยจากบริเวณพื้นที่อัครตะปือเป็นแหล่งพลอยแซปไฟร์แหล่งใหม่ทางตอนใต้ของประเทศสาธารณรัฐประชาธิปไตยประชาชนลาว จึงเป็นเรื่องที่น่าสนใจที่จะทำการศึกษาคูณสมบัติทางอัญมณี และทำการทดลองการเผาเพื่อเพิ่มคุณภาพพลอยดังกล่าว ในการศึกษานี้ได้ใช้พลอยแซปไฟร์ดิบที่ยังไม่ได้เจียรไนจำนวน 70 ตัวอย่าง สามารถแบ่งกลุ่มพลอยออกได้เป็น 4 กลุ่ม โดยพิจารณาจากสีเป็นหลัก ได้แก่ กลุ่มตัวอย่างพลอยสีน้ำเงินจำนวน 15 ตัวอย่าง กลุ่มตัวอย่างพลอยสีเขียวจำนวน 15 ตัวอย่าง กลุ่มตัวอย่างพลอยสีเขียวม่น้ำเงินจำนวน 20 ตัวอย่าง และ กลุ่มตัวอย่างพลอยสีน้ำเงินอมเขียวจำนวน 20 ตัวอย่าง

พบว่าพลอยดิบบางเม็ดยังคงรูปร่างผลึก รูปปิรามิด บางครั้งรูปปิรามิดแสดงผิวที่ถูกต้องกว่าจากแมกมาใต้ผิวโลก ผลการศึกษาคูณสมบัติพื้นฐานทางอัญมณีพบว่าทุกกลุ่มตัวอย่างของพลอยแซปไฟร์มีค่าอยู่ในช่วงปกติของพลอยคอร์ันดัมทั่วไป ลักษณะภายในที่เด่นชัดของพลอยแซปไฟร์จากแหล่งนี้คือ แถบสีแนวการเจริญเติบโตของผลึก และรอยแตกสมานซึ่งพบเหล็กออกไซด์แทรกอยู่ตามระนาบของรอยแตก ชนิดมลทินผลึกที่พบคือ Feldspar และ มลทินผลึกแร่ที่ไม่สามารถตรวจสอบได้ว่าเป็นแร่ใด ทุกกลุ่มตัวอย่างพลอยสีน้ำเงิน สีน้ำเงินแกมเขียว สีเขียว และ สีเขียวแกมน้ำเงิน พบว่ามีปริมาณธาตุร่องรอย Fe_2O_3 สูงมาก

(0.2-1.1%) ปริมาณธาตุร่องรอย TiO_4 ปานกลาง (0.01-0.6%) ในขณะที่ปริมาณธาตุร่องรอยของ V_2O_5 และ Cr_2O_3 มีปริมาณน้อยอย่างเห็นได้ชัด ผลการศึกษาแถบการดูดกลืนรังสีช่วงยูวีถึงอินฟราเรดระยะใกล้ พบว่าแสดงลักษณะการดูดกลืนที่มักพบในแหล่งพลอยคอร์ันดัมที่มีกำเนิดสัมพันธ์กับหินบะซอลต์ ดังนั้นพลอยแซปไฟร์จากอิตาลีน่าจะมีกำเนิดมาจากหินบะซอลต์ที่อยู่ไม่ไกลนัก เนื่องจากพลอยยังคงสภาพรูปร่างผลึกที่ดีอยู่และผิวที่แสดงการกัดกร่อนจากแมกมาใต้ผิวโลก ผลการศึกษาแถบการดูดกลืนรังสีอินฟราเรดช่วงระยะกลางและระยะไกล พบว่าทุกกลุ่มตัวอย่างพลอยแสดงการดูดกลืนอันเนื่องมาจาก O-H Stretching ที่ตำแหน่ง 3309 เวฟนัมเบอร์

เมื่อทำการทดลองเผาที่อุณหภูมิ 1,650 °C เป็นเวลา 5 ชั่วโมงในบรรยากาศไนโตรเจน พบว่าพลอยทุกกลุ่มมีสีน้ำเงินเข้มขึ้น ดังนั้นพลอยกลุ่มที่ติดสีเขียว เช่น เขียว เขียวอมน้ำเงิน และน้ำเงินอมเขียว น่าจะเผาให้เป็นพลอยน้ำเงินที่อมเขียวบ้างเล็กน้อยได้โดยง่าย ลักษณะอื่นๆที่พบหลังเผาได้แก่ แถบสีน้ำเงินที่ปรากฏชัดขึ้น พบลักษณะรอยแตกล้อมรอบมลทินผลึกของแข็ง และการพัฒนายอยแตกแผ่ขยายออกไป พบว่ารอยแตกสมานมีการแผ่ขยายออกไปมากขึ้น แถบการดูดกลืนรังสีช่วงยูวีถึงอินฟราเรดระยะใกล้แสดงการยกตัวที่มีสาเหตุมาจาก Fe^{2+}/Ti^{4+} ที่ตำแหน่ง 565 nm and Fe^{2+}/Fe^{3+} pairs ที่ตำแหน่ง 840 and 900 nm อย่างชัดเจนซึ่งสัมพันธ์กับสีน้ำเงินที่เพิ่มขึ้น

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CHAPTER I

Introduction

Laos P.D.R. (People's Democratic Republic) is a landlocked socialist republic communist state in Southeast Asia, bordered by Myanmar (Burma) and the People's Republic of China to the northwest, Vietnam to the east, Cambodia to the south, and Thailand to the west.

In 2005, a group of Thai people, who has a timber concession in Lao PDR., found a new corundum resource from the Attapeu area in southern Lao PDR. The type of stones is green sapphires of moderate quality. The heat treatment could enhance quality for this corundum and may increase the value.





Figure 1: Map showing the area of Lao P.D.R. and the location of Attpeu area in the south (marked red star).

(After Lao Flying Service Co., Ltd., www.thaiflyingclub.com)

Objectives

Owing to the fact that sapphires from Attapeu area of Laos PDR are a new occurrence, hence the objectives of this study are; 1) to investigate their physical, optical, spectroscopic and chemical characteristics, and 2) to test the possibility of color enhancement of these sapphires by heat treatment.

Theoretical concept

Green to blue sapphires may turn into a deeper blue when heating in reduced condition at high temperature.

Method of Study

This study included literature review of the previous works. Then the samples were cut and polished parallel and perpendicular to the c-axis. After cutting, the samples were classified into four groups based on the color appearance. Each individual sample was weighted and examined for the basic physical and optical properties, such as specific gravity, color, refractive indices using basic

gem instruments, a hydrostatic balance and a refractometer. Internal features in those samples were then investigated using a gem microscope. Some inclusions were analyzed by Laser Raman microscope. Then the samples were recorded for absorption spectra by UV – VIS – NIR and FTIR spectrometers and analyzed for the trace elements by EDXRF. The samples were then subjected to thermal treatment at high temperature in reduction condition. After the treatment, the absorption spectra of the samples were measured once again by with UV – VIS – NIR and FTIR Spectrometers. Then all data were interpreted and put together as a report.

Literature Review

1. Bootsri and Bussai (2001) studied the gemological properties and their internal characteristics of the sapphires from Diego Suarez area. Northern Madagascar by comparing both before and after thermal enhancement at 1, 350°C and 1,650°C. The result was that all the sapphires from Diego Suarez area showed the intense color after heating. After heating at 1, 350°C, the color zones have intense color, dust inclusions were disappeared and the sample showed the clarity. After heating at 1, 650°C, the tension cracks and healed fracture were more developing than heating at 1, 350°C.

2. Hansawak (2005) studied the condition and thermal enhancement of some sapphires from Ilakaka – Sakaraha area by comparing both before and after thermal enhancement at reduction state and oxidation state. Heating in reduction atmosphere, blue sapphires turn intense blue. While heating in oxidation atmosphere was suitable for rubies and yellow sapphires. The result was that most samples were more intense color after heating, and some samples were light-colored after heating at high temperature.
3. Pisutha – Amond et al. (2005) studied the coloration of the heat treatment sapphire. The details of this study was heating at high temperature in reduction atmosphere, if the Mg/Ti ratio were less than or approximate 1, the sapphires turn blue. Because after heating there were the formation of FeTiO_3 and Fe^{3+} might also have been reduced to Fe^{2+} . If the Mg/Ti ratio were more than 1, the sapphires turn colorless. Because the yellow color centers were destroyed.
4. Somboon (2000) studied the gemological and internal characteristics of the same set of sapphires from Ilakaka area by comparing both before and after thermal enhancement at 1,000 and 1,650 °C. The result was that all sapphires from Ilakaka area turn more intense color after heating. The internal inclusions are altered such as the rutile silks became to dot pattern, tension crack developing around the inclusion after heating and healed fractures had a little change.

5. Suthirat et al. (2005) studied the trace elements and inclusions such as rutile silks, turbidity and tension crack of mineral inclusions and the causes of color by the thermal treatment sapphire from different area.

CHAPTER II

Geology in Brief

Quaternary Basaltic Lavas in Lao PDR.

The Bolovens plateau east of Pakse and some other smaller upland areas in the east and southeast are made up of basaltic lavas resting upon Mesozoic sandstones. These lavas, like similar occurrences nearby in Vietnam, Cambodia and Thailand, are Pleistocene, and perhaps partly Neogene's, in age. Similar basalts are found in the extreme northwest near Ban Houei Sai, but these cover only a small area.

Corundum Occurrence

Corundum deposits related to alkali basalts are common in many regions such as Southeast Asia. The alkali basalts are thought to carry the corundum crystals to the surface from the earth's interior, where they formed. The latter gems are thought to be derived from metamorphic or metasomatism source rocks in the earth's interior. Sapphire – bearing alluvial derived from the erode alkali basalts was deposited in weathered alkali basalt soil.

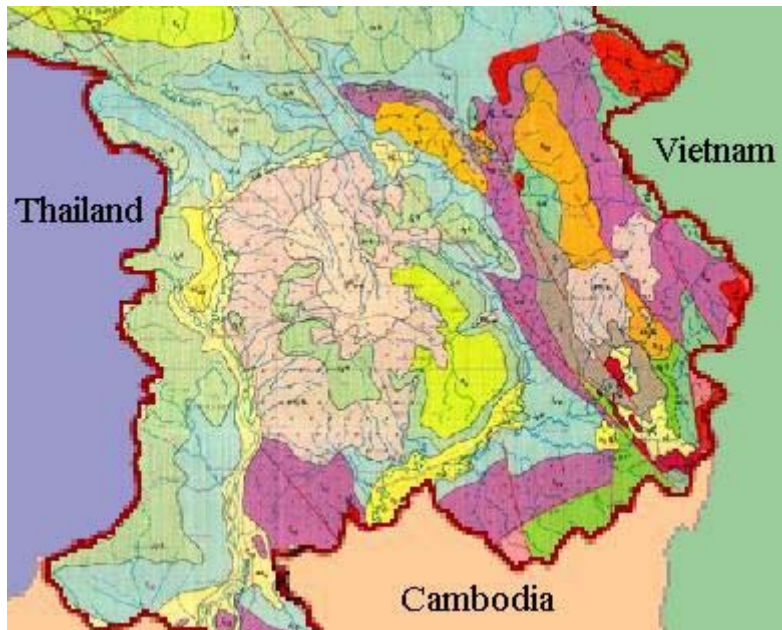


Figure 2: Showing the geologic map of southern area of Lao PDR.

(After Geol Survey Vietnam, 1991 2nd edition (1:1,000,000) Geologic Map)

CHAPTER III

Study before Thermal Enhancement

3.1 Sample and classification

Seventy samples of rough green sapphires from the Attapeu area, southern Lao P.D.R. were used for this study. These samples were mixture of many hue and tone such as, blue, green, greenish blue and bluish green. Almost all of the samples are translucent and vitreous luster. The weights are from 0.34 to 2.71 carats. The samples mostly show rough crystal forms suggesting that they did not transport too far from their sources. Their crystal habits are mostly pyramid.



Figure 3: Showing some rough crystals of pyramid habits (upper photos) and rounded pyramid habit with magmatic corroded surface (lower photo) from Attapeu area.

The rough sapphires were classified into 4 types based on the color shade.

1. Type I: blue sapphires (APLB), 15 samples.



Figure 4: Close-up of a blue sapphire (APLB8)

2. Type II: green sapphires (APLG), 15 samples.



Figure 5: Close-up of a greenish blue sapphire (APLGB 13)

3. Type III: bluish green sapphires (APLGB), 20 samples.



Figure 6: Close-up of a green sapphire (APLG1)

4. Type IV: greenish blue sapphires (APLGB), 20 samples.



Figure 7: Close-up of a bluish green sapphire (APLGB19)

All of the samples were cut and polished into 2 parallel sets, one set was perpendicular and the other set was parallel to c-axis for determination of the gemological properties. The basic gemological properties of all types of sapphires and color code based on GIA color set were systematically determined by using the basic gemological equipment (Table 1).

Table 1: Showing the physical and optical properties of all 70 sapphire samples.

Sample No.	Weight (Ct.)	S.G.	Color	R.F.
APLB 1	1.0630	4.032	vstgB 8/3	1.763 – 1.773
APLB 2	0.3400	3.967	vslgB 6/3	1.765 – 1.772
APLB 3	0.6175	3.960	vstgB 6/4	1.762 – 1.771
APLB 4	0.9990	3.956	gB 6/3	1.767 – 1.775
APLB 5	0.7250	4.024	vstgB 6/4	1.767 – 1.773
APLB 6	0.6700	3.990	gB 6/3	1.769 – 1.775
APLB 7	0.8850	4.016	vslgB 6/5	1.766 – 1.775
APLB 8	0.9140	3.994	vslgB 6/5	1.764 – 1.774
APLB 9	0.8020	3.950	vslgB 7/5	1.762 – 1.771
APLB 10	1.5380	3.998	vslgB 7/5	1.768 – 1.775
APLB 11	0.4780	4.097	vslgB 5/5	1.764 – 1.772
APLB 12	1.0680	3.968	vslgB 7/5	1.765 – 1.771
APLB 13	0.7765	3.963	vslgB 7/5	1.766 – 1.771
APLB 14	1.0140	3.933	vslgB 7/5	1.762 – 1.771
APLB 15	0.5000	3.963	vslgB 7/5	1.765 – 1.771
APLG 1	0.9550	3.930	slyG 3/3	1.763 – 1.773
APLG 2	1.5625	4.009	slyG 2/4	1.767 – 1.772
Sample No.	Weight (Ct.)	S.G.	Color	R.F.
APLG 3	1.2765	3.981	yG 4/3	1.765 – 1.771
APLG 4	0.9465	3.987	yG 3/3	1.767 – 1.775
APLG 5	0.7940	3.992	vslbG 3/4	1.765 – 1.772
APLG 6	0.8780	3.915	vslbG 3/4	1.765 – 1.773
APLG 7	1.1575	3.980	slyG 3/3	1.765 – 1.771
APLG 8	2.6930	3.983	styG 5/3	1.765 – 1.774
APLG 9	1.6585	3.935	StyG 5/4	1.765 – 1.772
APLG 10	0.8350	3.927	yG 6/4	1.766 – 1.762
APLG 11	1.0540	3.945	slyG 2/4	1.767 – 1.772
APLG 12	0.5510	3.995	vslbG 4/4	1.762 – 1.770
APLG 13	0.8990	3.984	yG 4/3	1.763 – 1.770
APLG 14	0.7840	3.897	vslbG 3/4	1.765 – 1.771
APLG 15	2.7260	3.899	StyG 7/3	1.764 – 1.772
APLBG 1	1.0440	4.001	vstbG 6/4	1.765 – 1.775
APLBG 2	0.7010	4.042	GB/ BG 5/3	1.765 – 1.772
APLBG 3	1.2790	3.985	vstgB 6/4	1.763 – 1.772
APLBG 4	2.5440	4.006	vslbG 5/3	1.763 – 1.772

APL BG 5	1.3360	3.982	vstgB 6/4	1.768 – 1.772
APL BG 6	0.8655	3.949	GB/ BG 6/1	1.766 – 1.775
APL BG 7	1.0110	4.003	gB 7/4	1.763 – 1.771
APL BG 8	2.0300	4.000	vstgB 4/3	1.766 – 1.773
APL BG 9	1.0735	3.936	vstgB 4/3	1.767 – 1.775
APL BG 10	1.3885	4.008	vstbG 4/5	1.765 – 1.772
APL BG 11	1.4030	3.996	vstgB 5/2	1.767 – 1.774
APL BG 12	1.8995	3.983	GB/ BG 6/4	1.765 – 1.772
APL BG 13	2.9005	3.970	vstgB 6/4	1.765 – 1.772
APL BG 14	1.4025	3.975	vstgB 5/2	1.764 – 1.771
APL BG 15	2.5065	3.873	vstgB 7/2	1.765 – 1.772
APL BG 16	1.4685	4.009	vstgB 7/5	1.765 – 1.772
APL BG 17	1.7585	3.991	vstbG 5/5	1.764 – 1.771
APL BG 18	2.3730	4.017	G 4/3	1.769 – 1.775
APL BG 19	2.6800	4.005	vstgB 6/4	1.763 – 1.773
APL BG 20	1.7820	3.915	G 5/1	1.766 – 1.771
APL GB 1	1.1720	3.986	G 4/2	1.767 – 1.775
APL GB 2	1.3075	3.957	vstbG 4/3	1.768 – 1.773
Sample No.	Weight (Ct.)	S.G.	Color	R.F.
APL GB 3	2.1465	3.966	vstbG 6/4	1.768 – 1.771
APL GB 4	0.5470	3.971	G 4/2	1.763 – 1.771
APL GB 5	1.3920	3.830	G 6/2	1.764 – 1.770
APL GB 6	1.1860	3.999	G 6/2	1.764 – 1.772
APL GB 7	2.2025	3.988	G 4/2	1.765 – 1.773
APL GB 8	2.5160	3.920	GB/ BG 6/1	1.763 – 1.771
APL GB 9	2.7155	3.985	vstbG 5/3	1.765 – 1.773
APL GB 10	0.5850	4.031	vstbG 5/3	1.762 – 1.770
APL BG 11	2.4685	3.987	G 5/1	1.768 – 1.774
APL GB 12	0.9925	3.928	G 4/2	1.765 – 1.775
APL GB 13	0.8150	3.958	GB/ BG 5/3	1.764 – 1.772
APL GB 14	0.7400	4.004	vstbG 5/3	1.765 – 1.772
APL GB 15	0.9955	3.959	vstbG 8/3	1.768 – 1.775
APL GB 16	0.6330	4.015	bG 3/3	1.764 – 1.771
APL GB 17	0.9065	3.925	vstbG 5/3	1.762 – 1.770
APL GB 18	0.9285	3.977	vstbG 7/4	1.766 – 1.771
APL GB 19	0.5865	3.993	vstbG 5/3	1.763 – 1.772
APL GB 20	0.6375	3.975	bG 4/3	1.766 – 1.774

As shown in Table 1, the refractive indices (RI) and specific gravity (S.G.) of all types of samples fall into a typical range of corundum.

3.2 Chemical Analysis

The chemical composition of corundum consists of two atoms of aluminums and three atoms of oxygen combined in alpha format plus impurities. Corundum is colorless in purest form. When corundum contains color – bearing elements, know as chromophores, they appear in corundum as impurities. The chromophores such as Fe, Ti, Cr and V content will be used as basis for understanding the color variation in those samples.

In this study, the trace element concentrations of the sapphires from the Attapeu area, southern Lao PDR were analyzed semi-quantitatively by using the Oxford Energy Dispersive X-ray Fluorescence spectrometer (EDXRF) at the Gem and Jewelry Institute of Thailand (GIT). The analytical method was employed by means of “standard less fundamentals parameter analysis”. That is the signals were counted for Al, Fe, Ti, Cr, V and Ga which are the most typical elements formed in normal corundum beside oxygen. Then the result was normalized to 100% and conventionally expressed as Al_2O_3 , Fe_2O_3 , TiO_2 , Cr_2O_3 , V_2O_5 and Ga_2O_3 in weight %.

The result of the chemical composition of four different types of sapphires from the Attapeu area is shown in Table 2. As shown in The Table 2, there seems to be no differences among those four types of sapphires. It should however be noted that the Fe_2O_3 contents in those samples are relatively high

(0.2-1.1%) which is typical for basaltic-type origin. TiO_2 contents are moderate (0.01-0.6%) and Cr_2O_3 and V_2O_5 contents are negligible.

Table 2: Showing the trace element of all type of sapphires from Attapeu area.

Sample	TiO_2 (Wt %)	V_2O_5 (Wt %)	Cr_2O_3 (Wt %)	Fe_2O_3 (Wt %)	Ga_2O_3 (Wt %)
APLB 2	0.02	0.06	0.02	1.11	0.02
APLB 3	0.08	0.01	0.00	1.39	0.03
APLB 5	0.02	0.01	0.11	0.94	0.02
APLB 6	0.02	0.00	0.00	1.38	0.03
APLB 12	0.19	0.00	0.00	1.44	0.07
APLB 14	0.32	0.00	0.00	1.51	0.04
APLB 14 (Colorless)	0.01	0.00	0.00	1.27	0.03
APLBG 4	0.05	0.01	0.00	1.25	0.03
APLBG 6	0.31	0.00	0.00	1.13	0.03
APLBG 7	0.04	0.00	0.00	1.61	0.03
APLBG 10	0.11	0.01	0.00	1.53	0.04
APLBG 17	0.06	0.01	0.00	1.53	0.03
APLBG 20	0.03	0.00	0.00	1.02	0.03

Sample	TiO ₂ (Wt %)	V ₂ O ₅ (Wt %)	Cr ₂ O ₃ (Wt %)	Fe ₂ O ₃ (Wt %)	Ga ₂ O ₃ (Wt %)
APLG 1	0.02	0.00	0.00	1.10	0.04
APLG 2	0.02	0.00	0.00	1.17	0.03
APLG 5	0.02	0.00	0.00	1.34	0.02
APLG 6	0.02	0.01	0.00	1.12	0.02
APLG 7	0.03	0.00	0.00	1.24	0.03
APLG 13	0.04	0.00	0.00	1.01	0.03
APLGB 2	0.04	0.01	0.00	1.43	0.02
APLGB 5	0.03	0.00	0.00	1.09	0.07
APLGB 7	0.01	0.00	0.00	1.14	0.03
APLGB 11	0.02	0.00	0.00	1.20	0.02
APLGB 17	0.02	0.02	0.00	1.22	0.03
APLGB 20	0.03	0.01	0.00	1.52	0.03

3.3 Internal Characteristics

The studies of inclusions in gemstone are of considerable importance, as the inclusions yield information about the genesis of gemstone and therefore it may be with some restrictions –

essential for determining authenticity (i.e., natural versus synthetic) or even the origin of a gemstone. In this study, all of the internal features were observed under a stereo – zoom gemological microscope and were photographed by a digital camera. The species of the mineral inclusions were determined by a Laser Raman microscope. Not all the mineral inclusions could be identified due to the depth of inclusion from surface. Those that were too deep would give too weak signal for identification.

Type I: Blue sapphire (APLB)

Internal features found in the blue variety of sapphire samples are healed fractures, unidentified colorless, long prismatic and trigonal prismatic?, mineral inclusions. Reddish brown iron stains were commonly found on the surface of the samples.

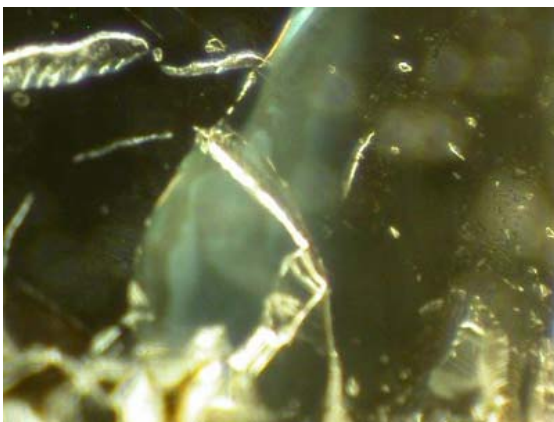
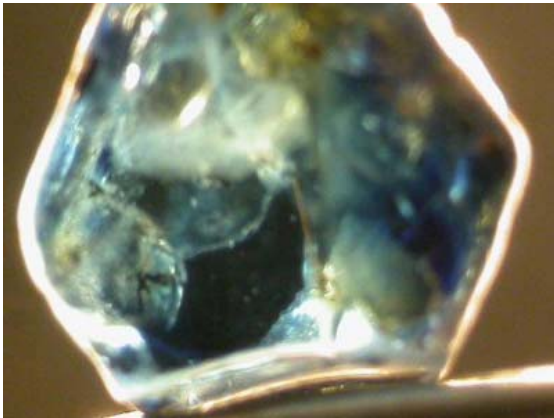


Figure 8: Showing fractures filled with brown iron stains without color zones in APLB12 (left) and healed fractures in APLB14 (right).

Type II: Greenish blue sapphire (APLBG)

Similar internal features and inclusions are also found in this greenish blue variety of sapphires.

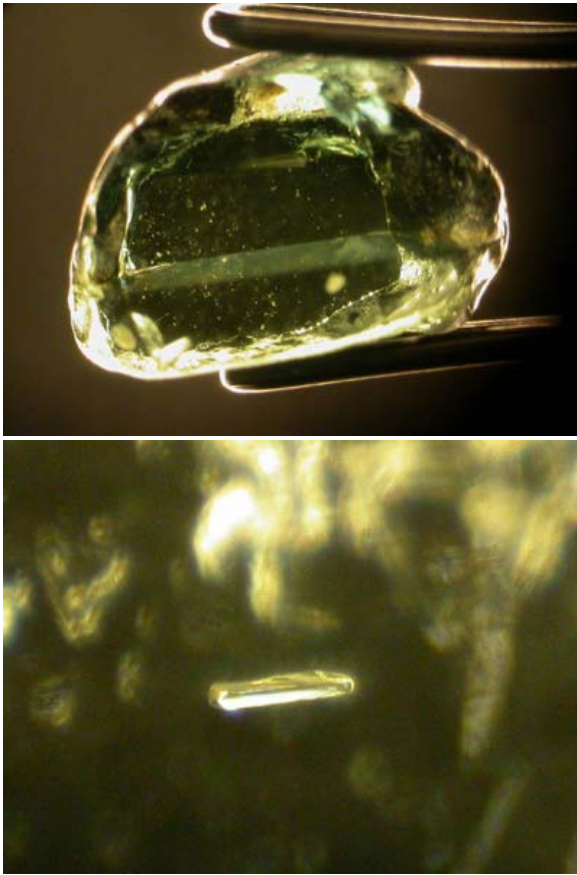


Figure 9: Showing the healed fractures in APLBG4 (left) and a long prismatic crystal in APLBG6 (right).

Type III: Green sapphire (APLG)

The most common internal features are healed fracture which was filled by iron oxide, growth zone intersecting at 120° angles. The mineral inclusion is feldspar which typically shows facet shape. Unidentified mineral inclusions are colorless and long prismatic?

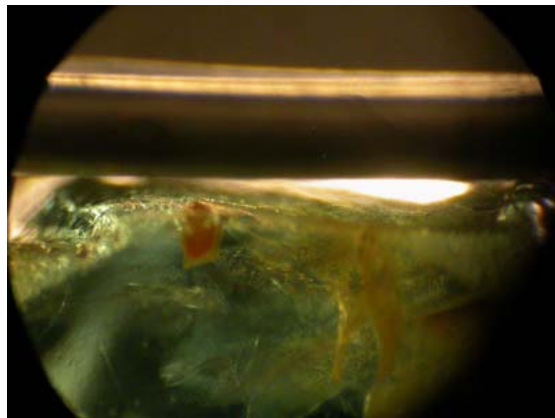
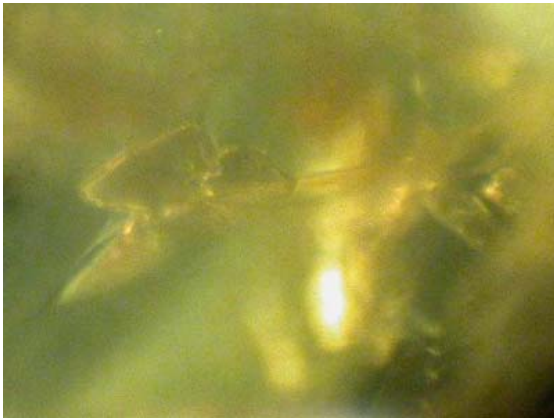


Figure 10: Showing the mineral inclusion in APLG1 (upper left), a feldspar inclusion in APLG5 (upper right) and fractures filled with brown iron stain in APLG6 (lower).

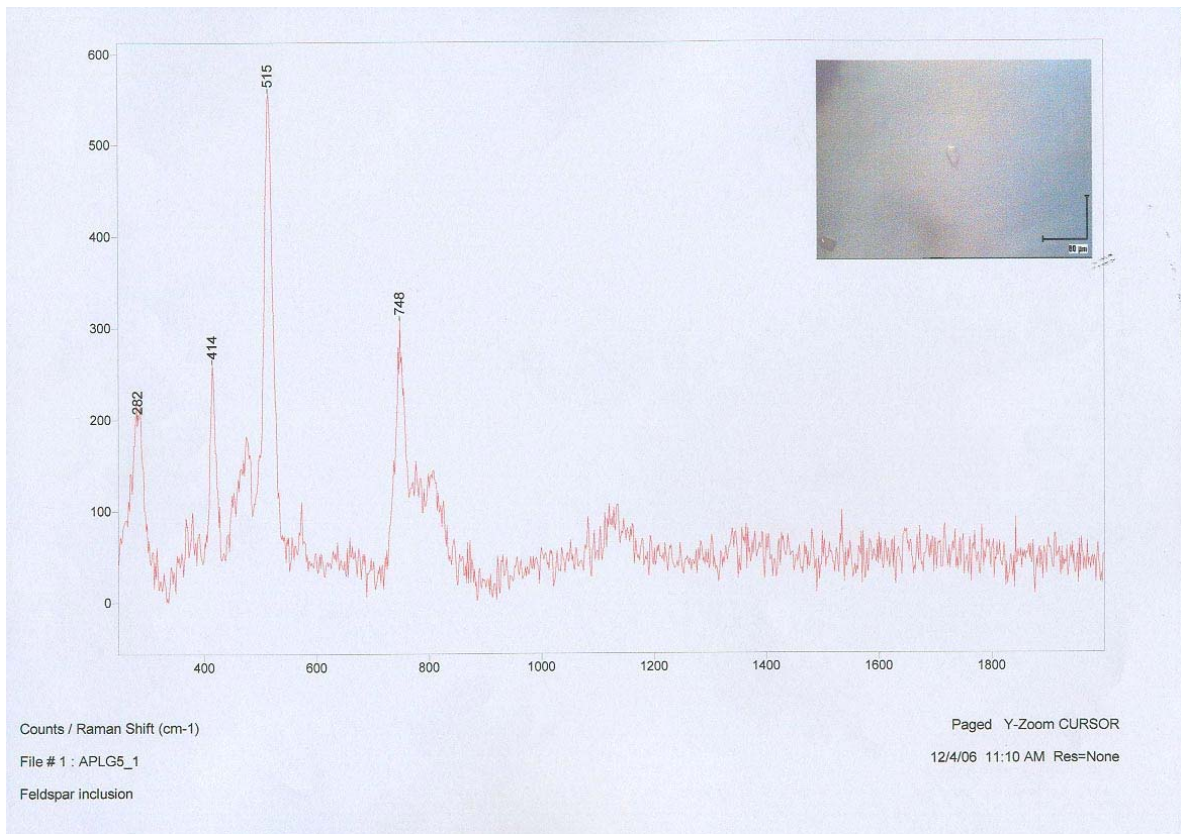


Figure 11: Showing the Raman spectrum of a feldspar inclusion in green sapphires.(APLG5)

Type IV: Bluish green sapphire (APLGB)

The most common inclusions are healed fracture which was filled by iron oxide. Unidentified mineral inclusions are colorless and short prismatic, reddish brown and trigonal prismatic? Iron stains were commonly found on the surface of the samples.

3.4 Characteristic Spectra

All 4 types of sapphires from Attapeu area were measured the absorption spectra in the UV

–VIS–NIR range by using UV –VIS –NIR Spectrometer at GIT.

1. Type I: Blue sapphire (APLB)

The UV –VIS –NIR spectrograms of unheated blue sapphire from Attapeu area show absorption bands due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfers with the maximum at 565 and 850 nm, respectively, and absorption peaks due to Fe^{3+} at 377, 388 and 450 nm (Figure 12). The absorption band in the near infrared (NIR) with a maximum at around 850 nm is typically found in basaltic sapphire. Based on this spectral pattern as well as the high iron content, blue sapphire from Attapeu area is also likely to be of a basaltic source.

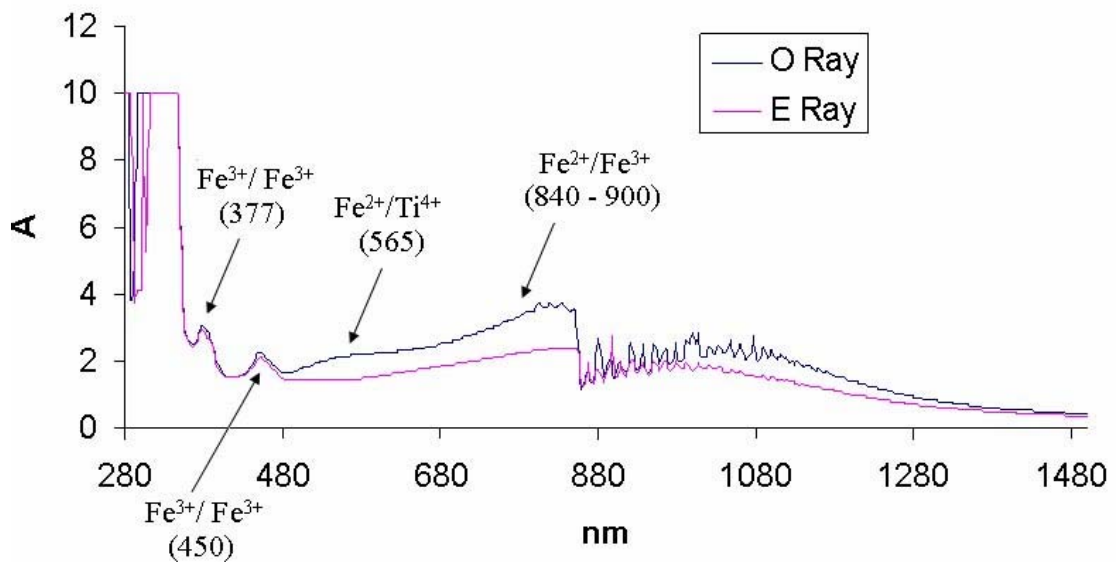


Figure 12: Showing a typical UV –VIS –NIR spectrogram of a blue sapphire (APLB12) from Attapeu area.

Type II: Greenish blue sapphire (APL BG)

The UV – VIS – NIR spectrograms of unheated blue sapphire from Attapeu area show similar absorption bands due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfers with the maximum at 565 and 850 nm, respectively, and absorption peaks due to Fe^{3+} at 377, 388 and 450 nm (Figure 13).

Hence the greenish blue sapphire from Attapeu area is also likely to be of a basaltic source as well

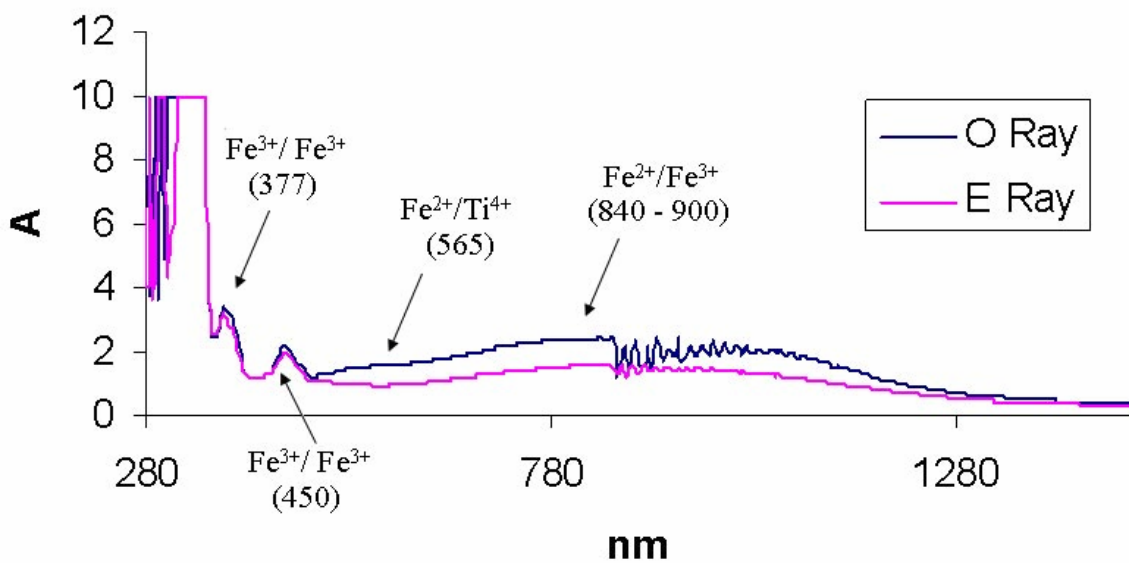


Figure 13: Showing the UV – VIS – NIR spectrogram of a greenish blue sapphire (APL BG17)

from Attapeu area.

Type III: Green sapphire (APLG)

The UV – VIS – NIR spectrograms of unheated blue sapphire from Attapeu area show similar absorption bands due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfers with the maximum at

565 and 850 nm, respectively, and absorption peaks due to Fe^{3+} at 377, 388 and 450 nm (Figure 14).

Hence the greenish blue sapphire from Attapeu area is also likely to be of a basaltic source as well.

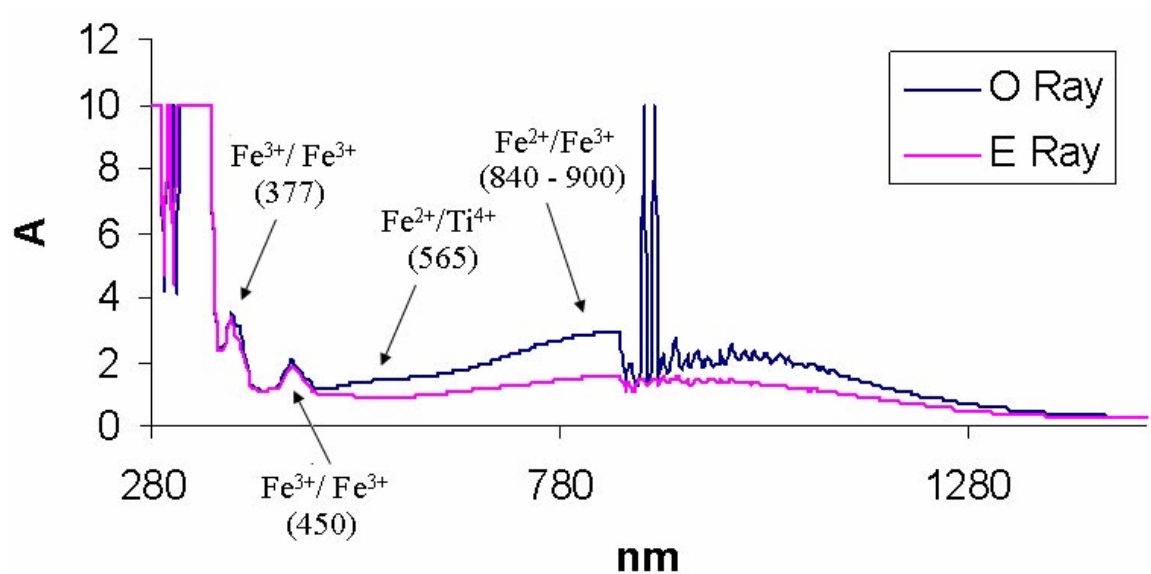


Figure 14: Showing the UV – VIS – NIR spectrogram of a green sapphire (APLG2) from

Attapeu area.

Type IV: Bluish Green sapphire (APLGB)

The UV – VIS – NIR spectrograms of unheated blue sapphire from Attapeu area show similar absorption bands due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ intervalence charge transfers with the maximum at 565 and 850 nm, respectively, and absorption peaks due to Fe^{3+} at 377, 388 and 450 nm (Figure 15).

Hence the greenish blue sapphire from Attapeu area is also likely to be of a basaltic source as well.

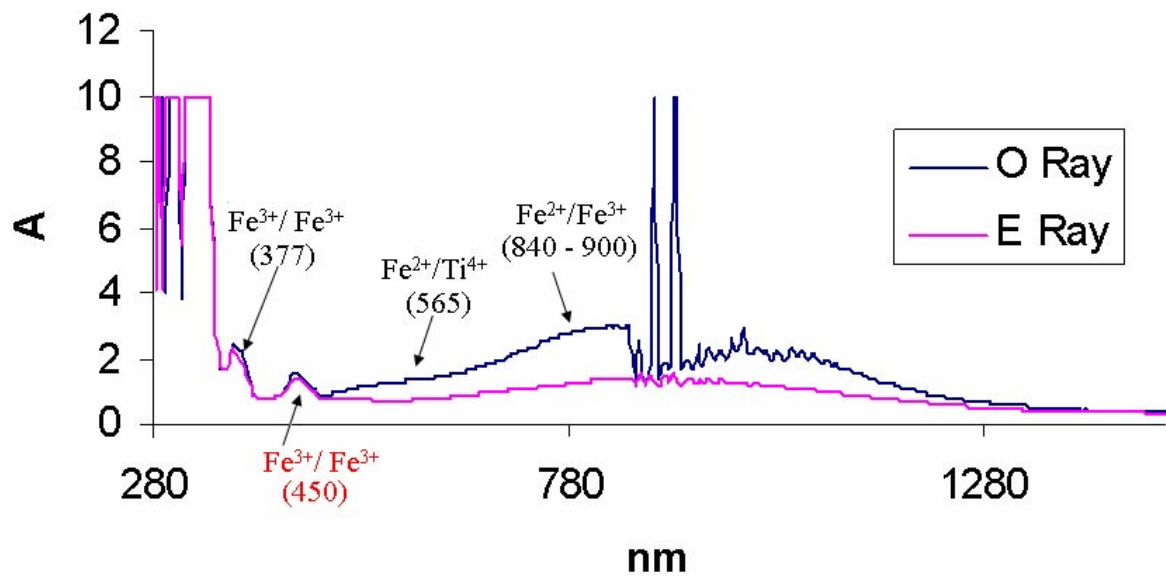


Figure 15: Showing the UV – VIS – NIR spectrogram of bluish green sapphires (APLGB17)

from Attapeu area.

3.6 FTIR spectra

The absorption spectra in the mid and far infrared of all four types of unheated sapphire from Attapeu area were also measured by using FTIR spectrophotometer at the GIT. The characteristic spectrograms of all four types appear essentially the same (Figures 16-19). They generally show almost complete absorption at above 2100 cm^{-1} , which is typical for most corundum. The FTIR spectra also show absorption peaks of moisture (H_2O), C – H stretching and CO_2 probably due to contamination from the air and on surface. They also show strong absorption due to O – H stretching at 3309 , 3232 , and 3183 cm^{-1} .

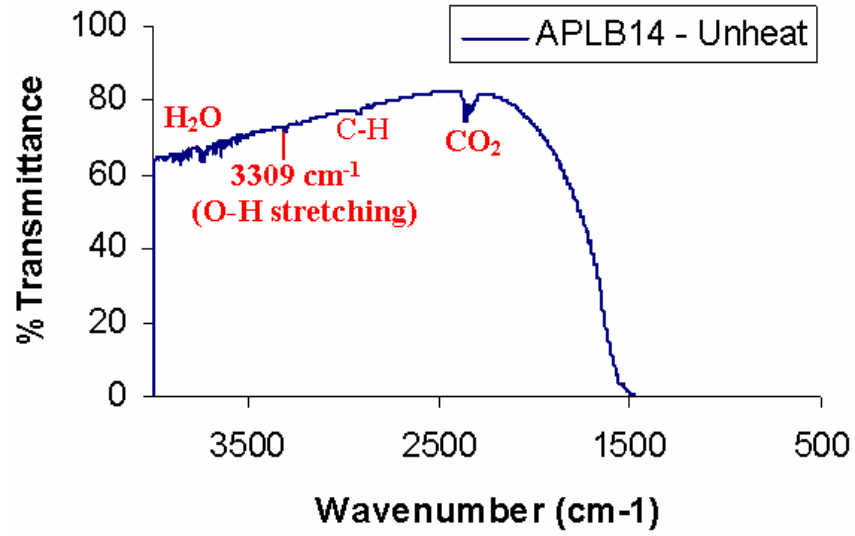


Figure 16: Showing the FTIR spectrogram of a blue sapphire (APLB14) from Attapeu area.

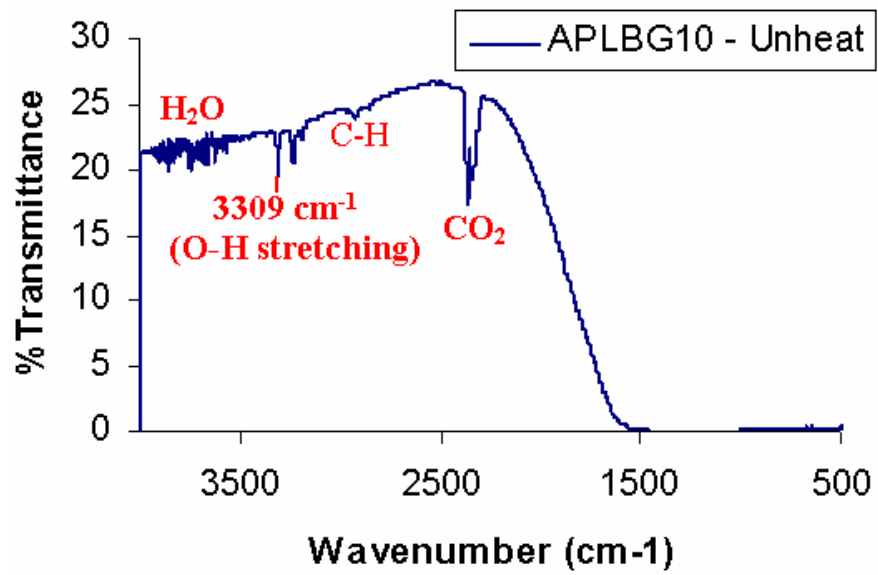


Figure 17: Showing the FTIR spectrogram of a greenish blue sapphire (APLBG10) from Attapeu

area.

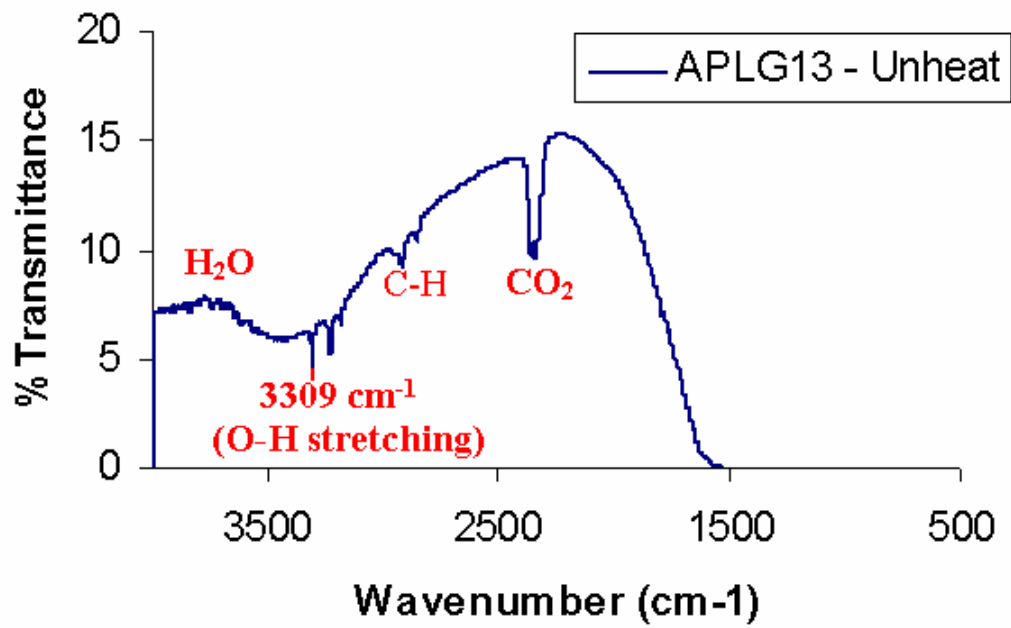


Figure 18: Showing the FTIR spectrogram of a green sapphire (APLG13) from Attapeu area.

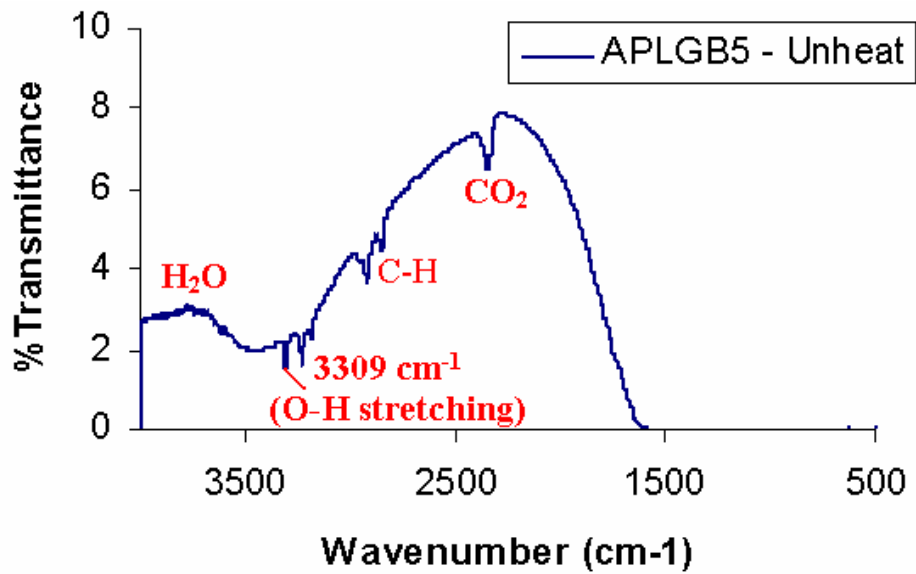


Figure 19: Showing the FTIR spectrogram of a bluish green sapphire (APLGB5) from Attapeu area.

CHAPTER IV

Study after Heat Treatment

Heat Treatment condition

All four types of sapphire were heat-treated at 1,650°C for 5 hours. This condition was selected because the 1,650°C heating is a normal temperature used in the industry and 5 hour soaking time was chosen because from the previous study this was enough to see the color change. The samples were heated in an electric furnace under N₂ atmosphere.

Heating Cycle

Every heating process is characterized by successive segments, heat up, processing (soaking) and cool – down. Temperature and times are the two parameters involved in any of these segments (Themelis, 1992). In electric furnace that was used in this work the temperature was controlled in all segments of the heating process, using the temperature programmer.

1. **Heat up:** The rate of temperature increase were controlled at about 3.8°C/ minute for heating to 1,650°C
2. **Processing (soaking):** In this condition, the duration of soaking temperatures was 1,650°C and the soaking time was 5 hours.
3. **Cool – down:** The cool – down segment is initiated from the time the temperature starting to decrease from the processing segment, until it eventually reaches a determined temperature, normally at about 50°C before opening up the furnace.

The effect of thermal enhancement on the internal characteristics

When samples were heated at 1,650°C for 5 hours, some internal features are changed or developed. For example, the color zones of some samples which were unclear before treatment became obvious after the heat treatment (Figure 20). The fingerprints show somewhat altered (Figure 21). Tension cracks are well developed surrounding solid crystals after the treatment (Figures 22 and 24). Some turbid appearance became clear (Figure 23). Reddish brown Iron oxides in fractures were disappeared after treatment (Figure 25).

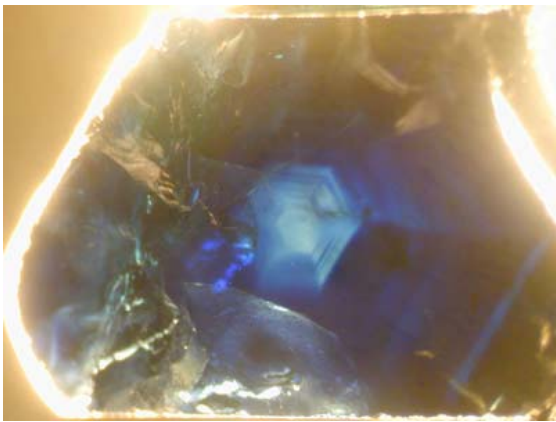
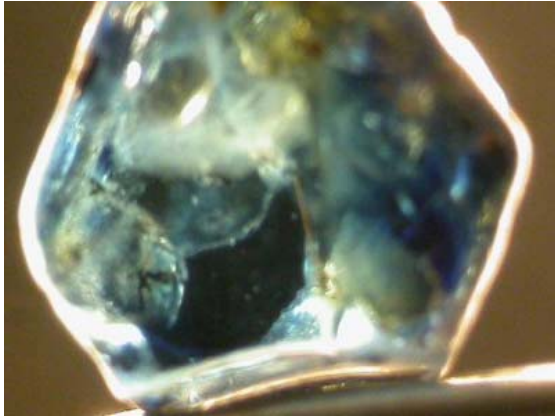


Figure 20: Showing clear development of hexagonal color zones after heating (APLB12).

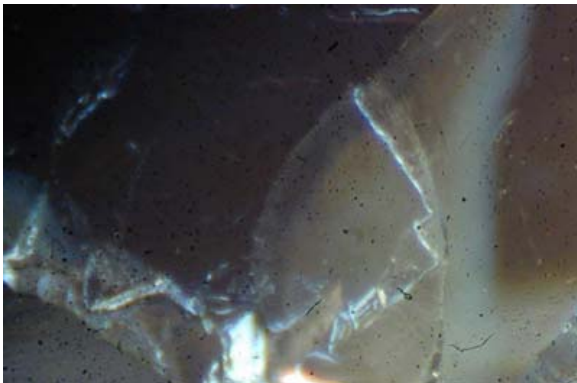
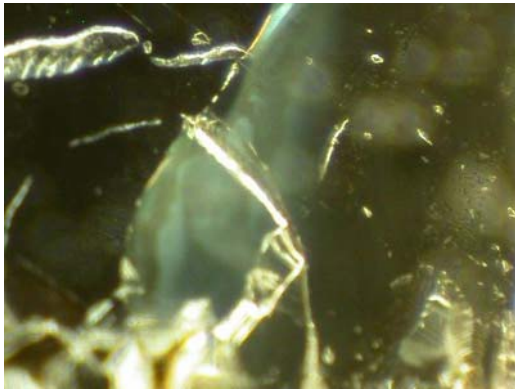


Figure 21: Showing the healing fracture before in APLB14 (left) and was altered after heating (right).

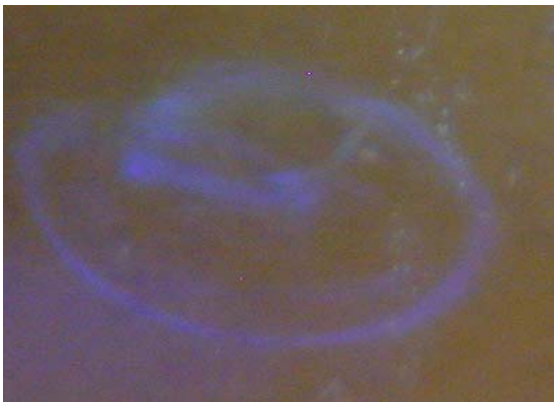
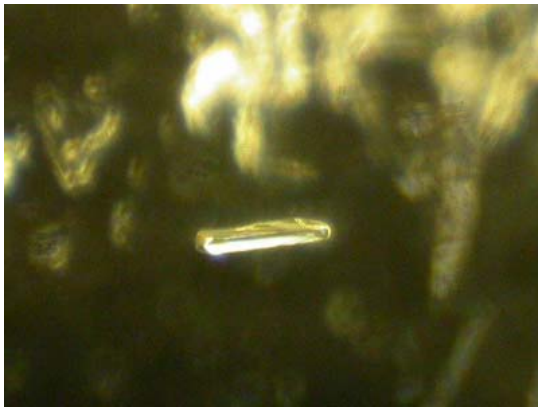


Figure 22: Showing the long prismatic crystal inclusion before treatment (left) in APLBG6 and tension crack developing around the inclusion after heating (right).

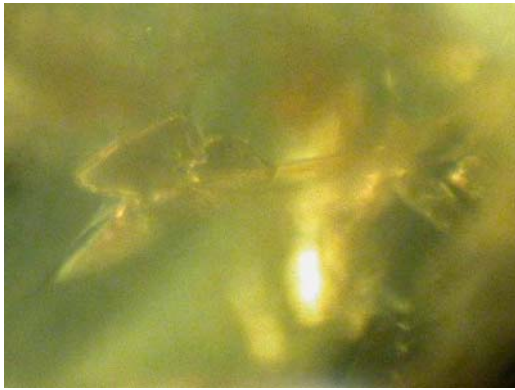


Figure 23: Showing turbid appearance before treatment (left) in APLG1 and clearer view after heat treatment (right).



Figure 24: Showing the feldspar crystal inclusion before treatment (left) in APLG5 and tension crack developing around the inclusion after heating (right).



Figure 25: Showing green color with healing fracture filled with reddish brown iron stain before treatment in APLG6 (left) and turns blue without reddish brown stain after heating (right).

Color Appearance and UV – VIS – NIR spectra

The color appearance before and after heat treatment is directly related to UV – VIS – NIR absorption spectra. Therefore, the sample can show a difference in wavelength absorption and differently in color both before and after thermal enhancement by UV – VIS – NIR spectrophotometer.

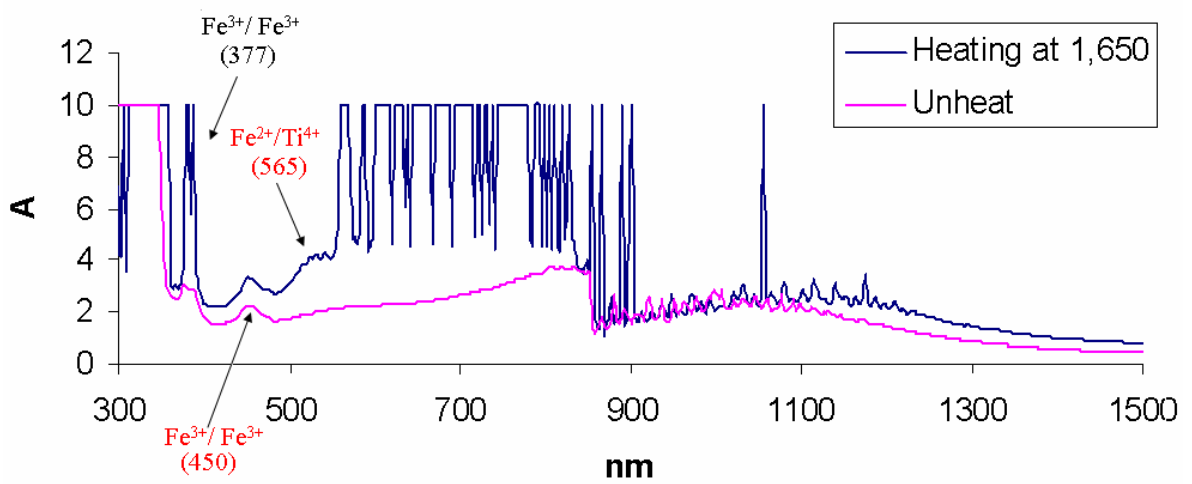
1. Type I: Blue sapphire (APLB)

Most blue sapphires turn deeper blue after the heat treatment (Figure 26). The UV – VIS – NIR spectrograms show the increase in absorption band due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ pair at 565 nm and $\text{Fe}^{2+}/\text{Fe}^{3+}$

pairs between 840 and 900 nm (Figure 27). These bands are responsible for the intense blue after heating. The Fe^{3+} peaks at 377, 388 and 450 nm are still remaining.



Figure 26: Showing the color appearance in a blue sapphire (APLB8) before (left) and after heating (right).



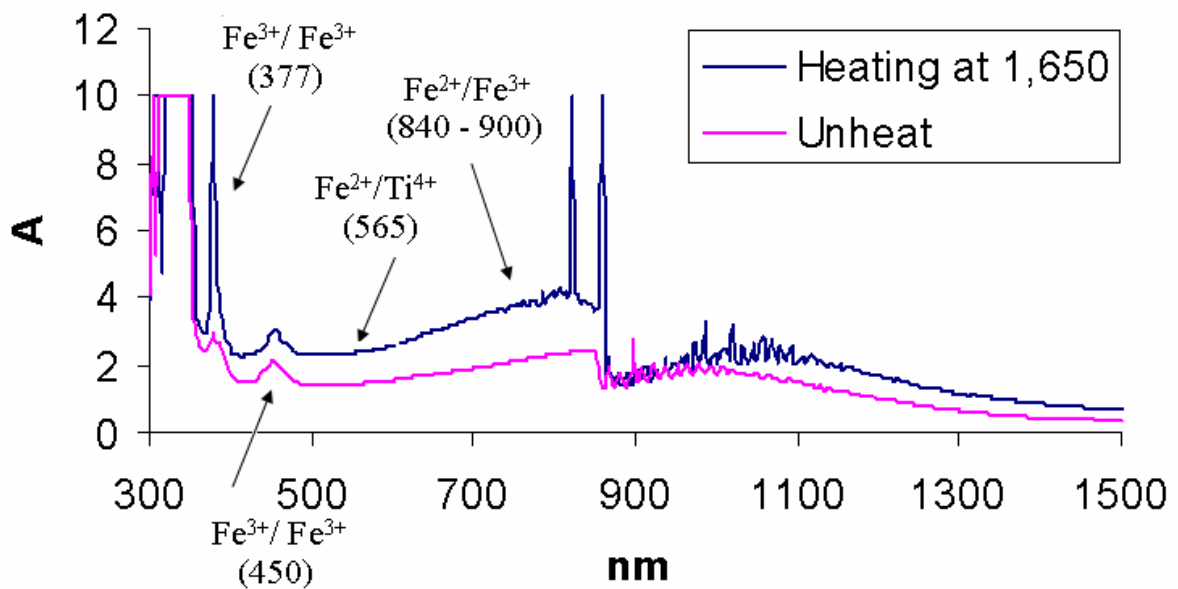


Figure 27: Showing the UV – VIS – NIR spectrogram of O – Ray (above) and E – Ray (below) of blue sapphires (APLB12) before and after heating.

2. Type II: Greenish blue sapphire (APLBG)

Most greenish blue sapphires turn into nice blues after the heat treatment (Figures 28 and 29).

The UV – VIS – NIR spectrograms show the increase in absorption band due to $\text{Fe}^{2+}/\text{Ti}^{4+}$ pair at 565 nm and $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs between 840 and 900 nm (Figure 30). These bands are responsible for the intense blue after heating. The Fe^{3+} peaks at 377, 388 and 450 nm are still remaining.



Figure 28: Showing the color appearance in a greenish blue sapphire (APLBG13)

before (left) and after heating (right).

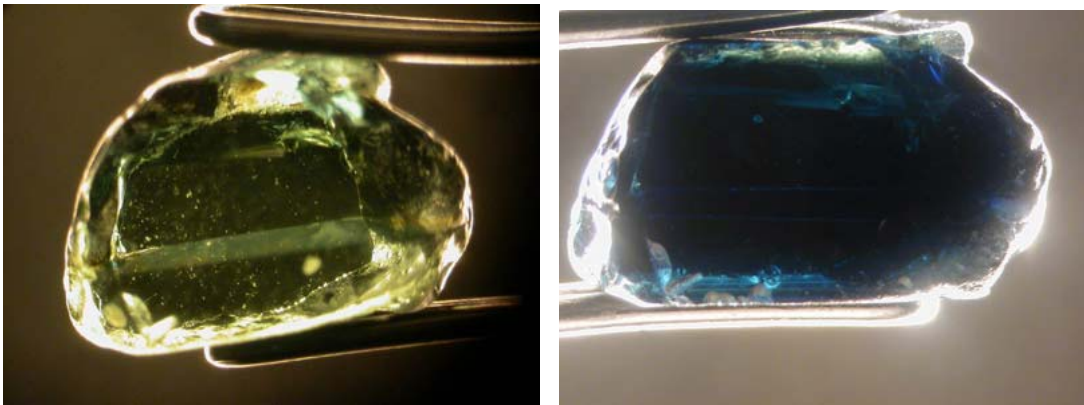


Figure 29: Showing a greenish blue before treatment in APLBG4 (left) but turn deep

blue after heating (right).

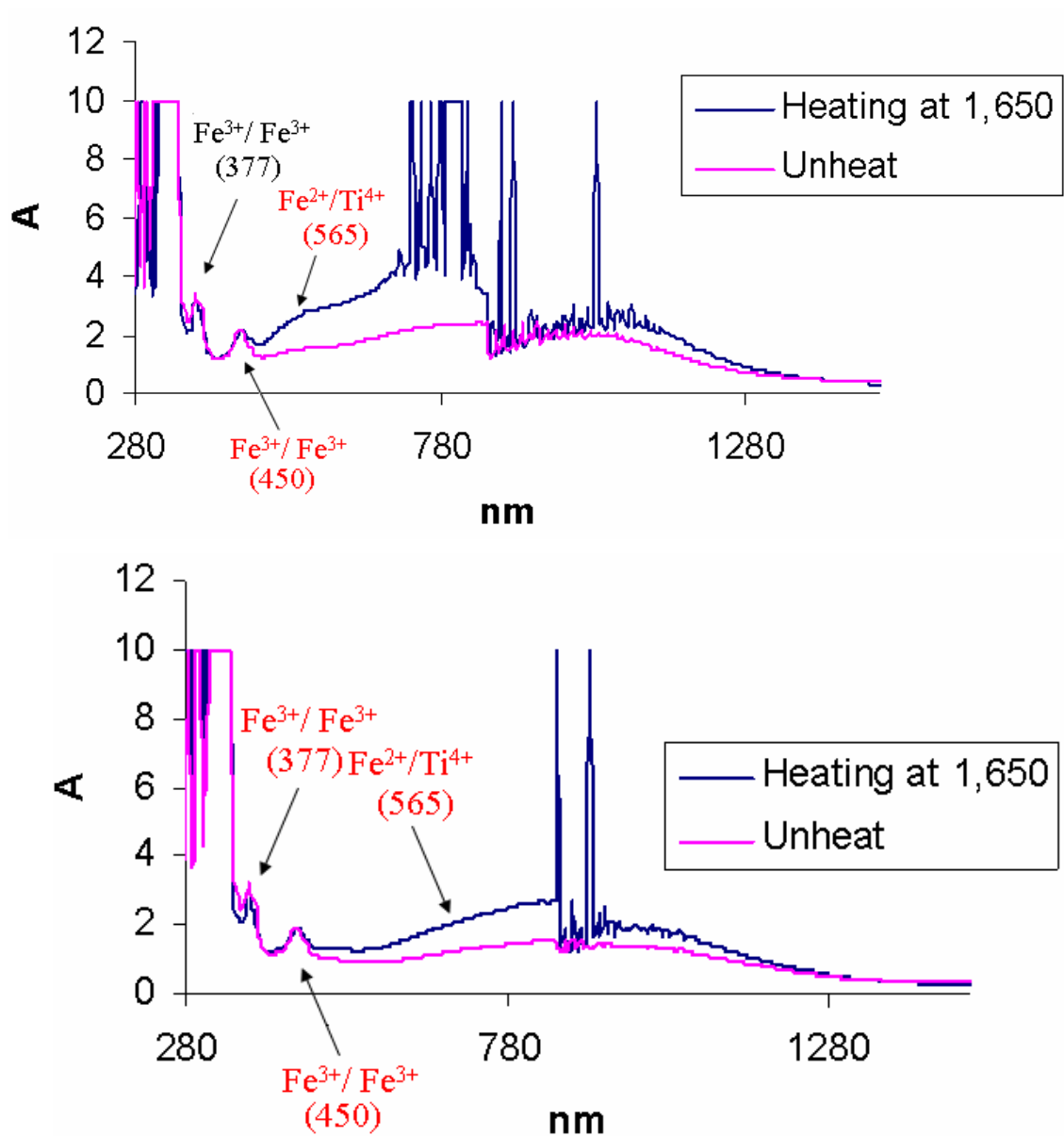


Figure 30: Showing the UV – VIS – NIR spectrogram of O – Ray (above) and E – Ray (below) of greenish blue sapphires (APL BG17) before and after heating.

3. Type III: Green sapphire (APLG)

Most green sapphires turn into nice blues after the heat treatment (Figures 25 and 31). The UV – VIS – NIR spectrograms show the increase in absorption band due to Fe²⁺/Ti⁴⁺ pair at 565

nm and $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs between 840 and 900 nm (Figure 32). These bands are responsible for the intense blue after heating. The Fe^{3+} peaks at 377, 388 and 450 nm are still remaining.



Figure 31: Showing the color appearance in a green sapphire (APLG1) before (left) and after heating (right).

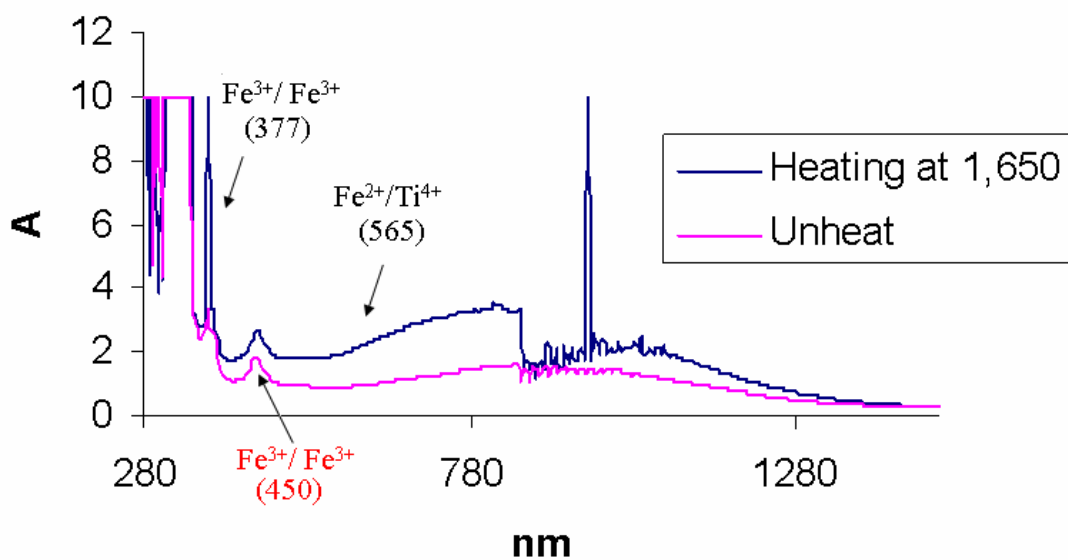
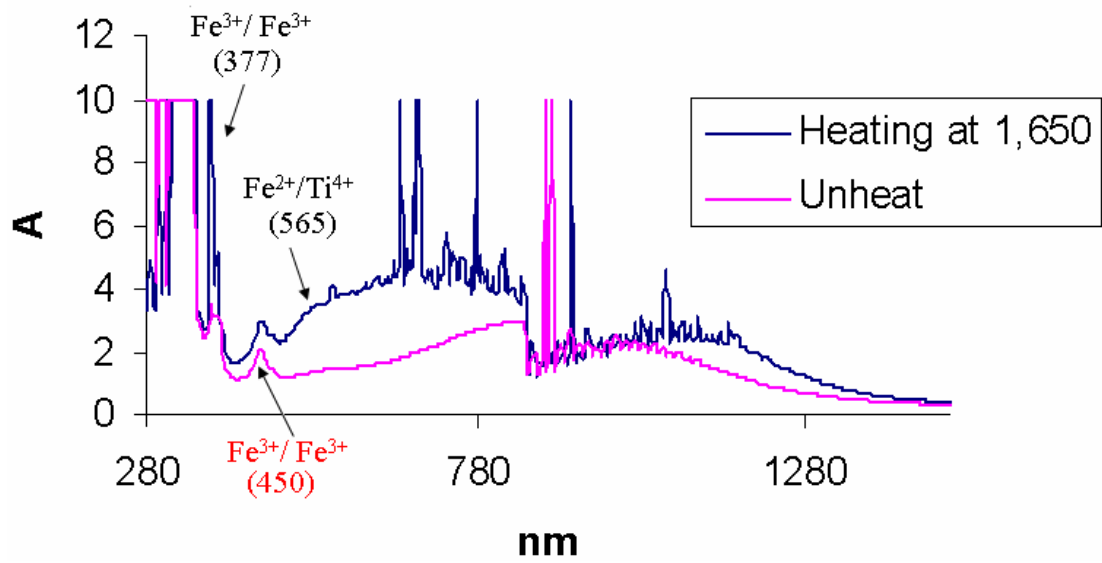


Figure 32: Showing the UV – VIS – NIR spectrogram of O – Ray (above) and E – Ray (under) of green sapphires (APLG2) before and after heating.

4. Type IV: Bluish Green sapphire (APLGB)

Most bluish green sapphires turn into nice blues after the heat treatment (Figure 33). The UV – VIS – NIR spectrograms show the increase in absorption band due to Fe^{2+}/Ti^{4+} pair at 565 nm and

$\text{Fe}^{2+} / \text{Fe}^{3+}$ pairs between 840 and 900 nm (Figure 34). These bands are responsible for the intense blue after heating. The Fe^{3+} peaks at 377, 388 and 450 nm are still remaining.



Figure 33: Showing the color appearance in a bluish green sapphire (APLGB13) before (left) and after heating (right).

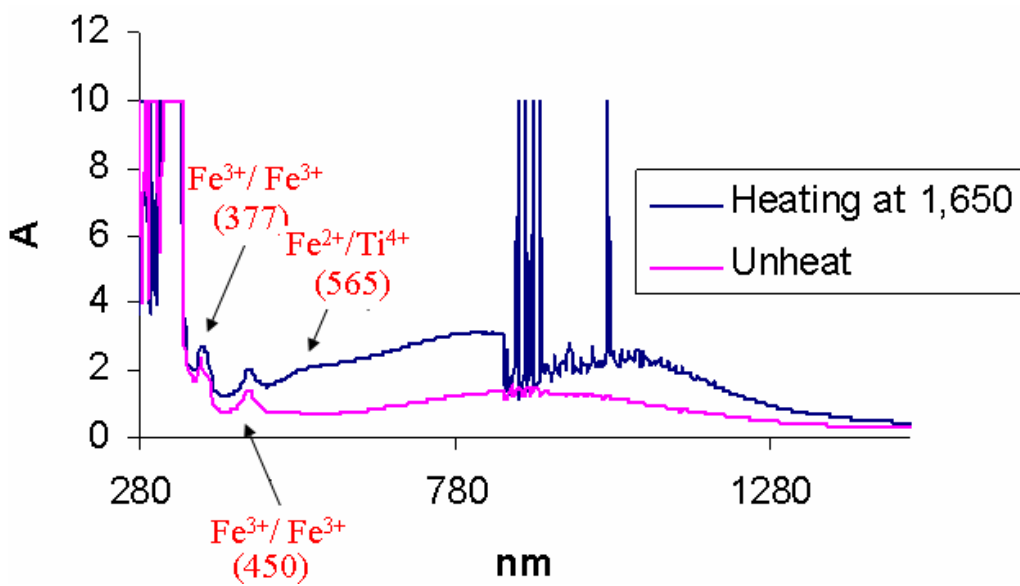
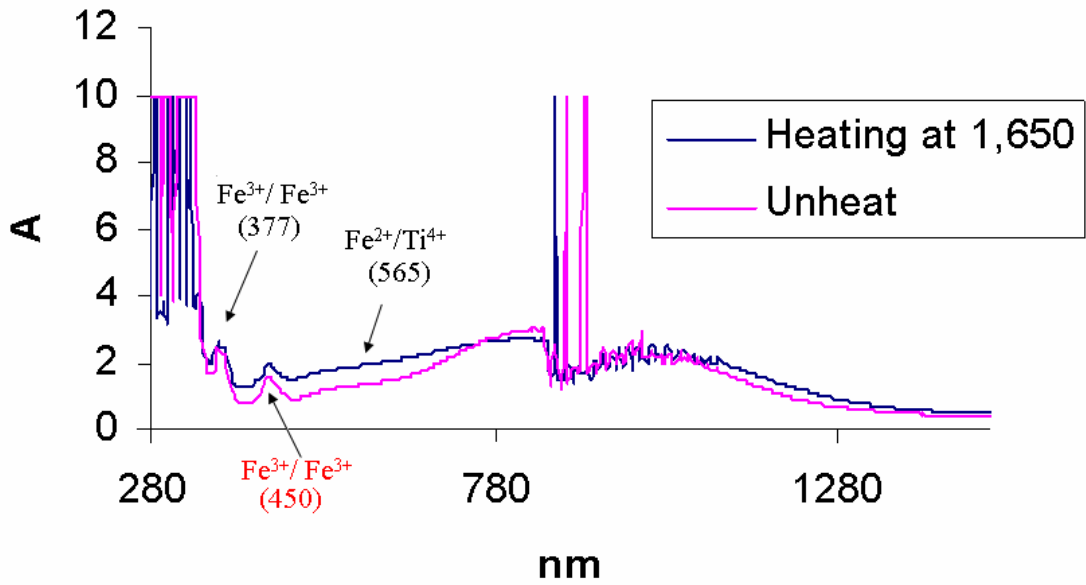


Figure 34: Showing the UV – VIS – NIR spectrogram of O – Ray (above) and E – Ray (under) of bluish green sapphires (APLGB17) before and after heating.

FTIR Spectrogram

After the treatment the O – H absorption peak at 3309 cm^{-1} are disappeared in all samples.

The absorption peaks of H₂O also decrease.

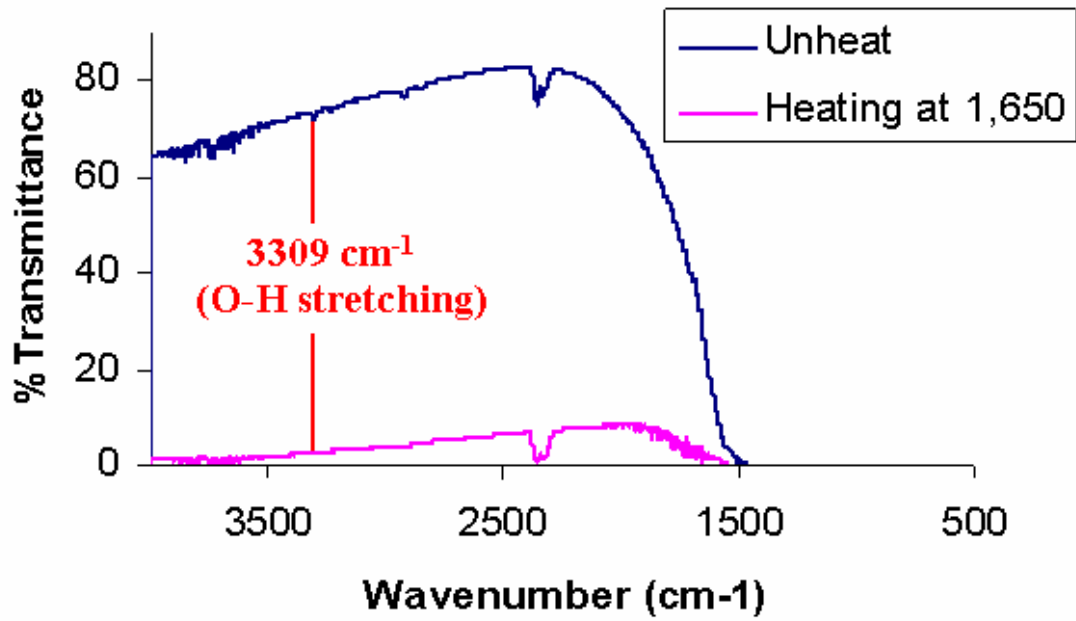


Figure 35: Showing the FTIR spectrogram of blue sapphires (APLB14) before and after heating.

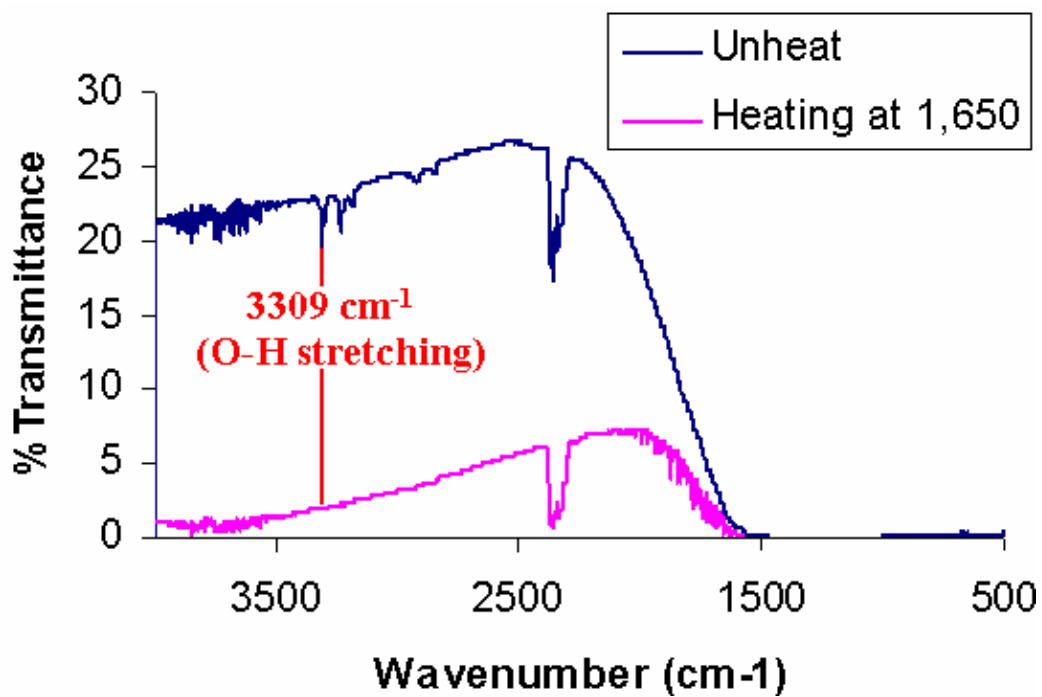


Figure 36: Showing the FTIR spectrogram of greenish blue sapphires (APLBG10) before and after heating.

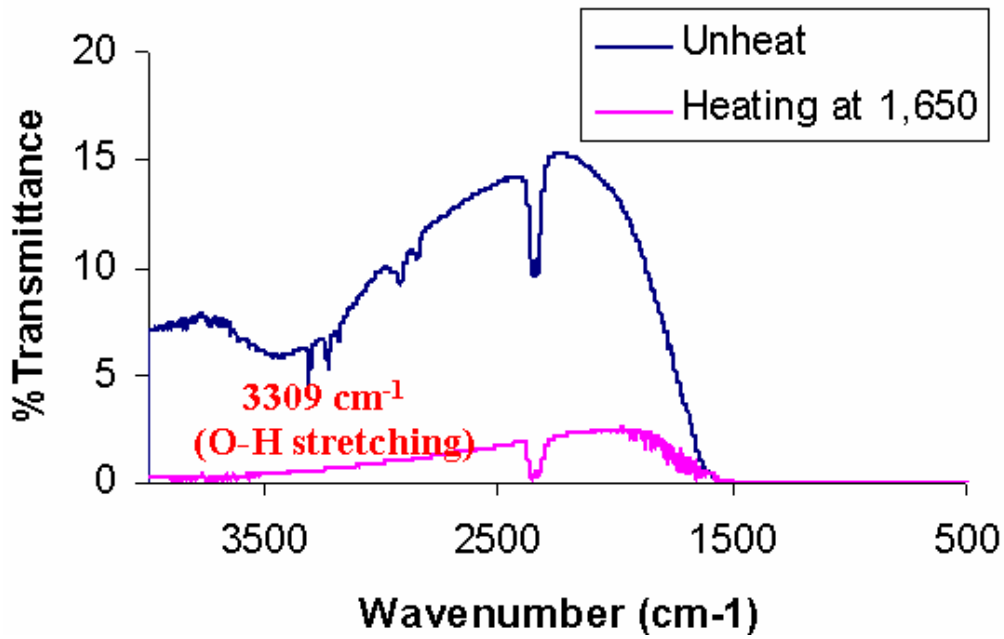


Figure 37: Showing the FTIR spectrogram of green sapphires (APLG13) before and after heating.

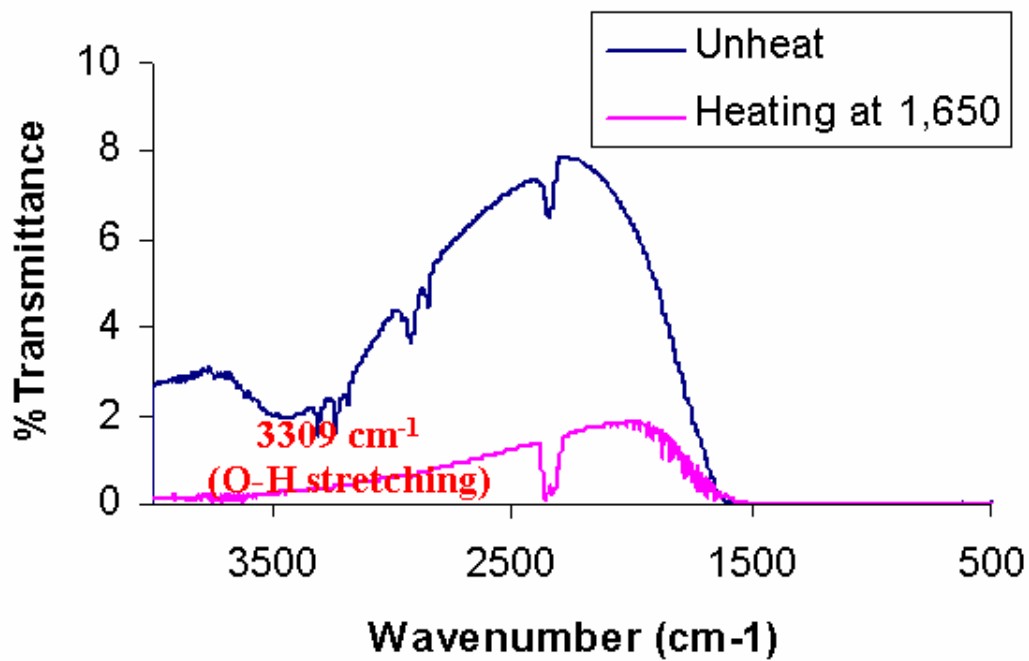


Figure 38: Showing the FTIR spectrogram of bluish green sapphires (APLGB5) before and after heating.

CHAPTER V

Conclusions

Before heat treatment

1. The basic physical and optical properties of all types of sapphires from Attapeu area fall into a normal range of corundum.
2. The external characteristics of all samples are magmatic corroded surface.
3. The some of samples show well-formed pyramid habits.
4. The internal characteristics of all un-treated samples are healed fractures filled with reddish brown iron stains and mineral inclusions such as feldspar, unidentified and colorless prism mineral inclusions.
5. The chemical analysis show high Fe_2O_3 but low V_2O_5 , TiO_4 and Cr_2O_3 contents which are typical for basaltic origin.
6. The result of study on UV – VIS – NIR spectrum show absorption peaks typical of basaltic origin.
7. Sapphires from Attapeu area, southern Lao P.D.R. show characteristic of basaltic origin. The sapphires were probably derived not far from eroded alkali basaltic source rocks.

After heat treatment

1. All types of samples show more intense blue development than before the treatment which are also clearly observed in UV-VIS- NIR spectra
2. Color zones appear, healed fractures are altered and tension cracks are developed and expanded after the treatment.

3. The O-H stretching peaks at 3309 cm^{-1} were disappeared after the treatment.

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