THERMAL ENHANCEMENT OF SAPPHIRES FROM DENIYAYA, SRI LANKA

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THERMAL ENHANCEMENT OF SAPPHIRES FROM DENIYAYA, SRI LANKA

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Abstract: New sapphire deposits have been discovered in Deniyaya, Southwestern Sri Lanka. However, these sapphires are usually low quality in color. Therefore, they were collected for experiments of heat treatment. Twenty nine samples were categorized into 3 varieties including blue, yellow and colorless sapphires. Their internal features are mainly composed of fingerprint, rutile needle, cloud and fracture. Chemical analyses from EDXRF and EPMA, yielded traces of Fe, Ti, Mg, V and Ga.

Each sample variety was divided into 2 batches for heat treatments at 1650ºC with 5 hours soaking time under reduction and oxidation conditions, respectively. After heating under reduction condition, most samples turned into blue or deep blue. On the other hand,, heating under oxidation condition introduced yellow and deep yellow in some samples. However, some samples of blue variety may also be intensified to deep blue under oxidizing heat. UV-VIS-NIR absorption spectra and trace element analyses show that interaction between Fe:Ti:Mg is significant cause of color changing. Blue shade appears to have been caused by absorptions of Fe^{+2}/Ti^{+4} and Fe^{+3} that are increased after reducing heat. Besides, yellow shade seems to be caused by absorption of Fe^{+3}/ Fe^{+3} that is increased after oxidizing heat.

FTIR spectra of several samples show similarly that AlOOH absorption is disappeared after heating in both conditions. This is because AlOOH may be changed to Al_2O_3 after heating. Thus, it is a crucial evidence of heated sapphires.

In conclusion, Deniyaya sapphires have potential for thermal enhancement at 1650ºC under both reduction and oxidation conditions.

Keywords: Heat-treatment, Sapphires, Sri Lanka

การปรับปรุงคุณภาพด้วยความร้อนของพลอยแซปไฟร์จากแหล่งเดนิยายา ประเทศศรีลังกา

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แหล่งพลอยแซปไฟร์เดนิยายา ประเทศศรีลังกา เป็นแหล่งพลอยใหม่ โดยพลอยแซปไฟร์ที่พบมักมีคุณภาพต่ำจึงได้นำตัวอย่างพลอยมาทดลองปรับปรุงคุณภาพด้วยความร้อน ตัวอย่างพลอยแซปไฟร์ดิบที่ใช้ในการศึกษาครั้งนี้มีทั้งสิ้น 29 ตัวอย่าง โดยแบ่งเป็น 3 กลุ่มสี คือ สีน้ำเงิน สีเหลือง และไม่มีสี โดยนำตัวอย่างทั้งหมดไปศึกษาข้อมูลพื้นฐาน และลักษณะมลทินภายใน พบมลทินลายนิ้วมือ มลทินเส้นเข็ม มลทินขนาดเล็กคล้ายฝุ่น และรอยแตก การวิเคราะห์ผลเคมี โดยใช้เครื่อง EDXRF และ EPMA พบธาตุร่องรอย เหล็ก(Fe) ไททาเนียม (Ti) แมกนีเซียม (Mg) วาเนเดียม (V) และแกลเลียม (Ga)

ตัวอย่างในแต่ละกลุ่มถูกแบ่งเป็นสองส่วน เพื่อนำไปปรับปรุงคุณภาพด้วยความร้อนภายใต้สภาวะรีดักชั่น และออกซิเดชั่นตามลำดับ โดยให้ความร้อนที่อุณหภูมิ 1,650 องศาเซลเซียส ใช้เวลาในการคงอุณหภูมิสูงสุด 5 ชั่วโมง พบว่าตัวอย่างที่ได้รับความร้อนภายใต้สภาวะรีดักชั่นจะมีสีน้ำเงินเข้มขึ้นหรือเปลี่ยนเป็นสีน้ำเงิน ในส่วนของสภาวะออกซิเดชั่นจะมีสีเหลืองเพิ่มขึ้น หรือเปลี่ยนเป็นสีเหลือง แต่ในบางตัวอย่างในกลุ่มสีน้ำเงินก็มีสีน้ำเงินเพิ่มขึ้น จากผลวิเคราะห์ด้วยเครื่องมือขั้นสูง พบว่าสเปคตรัมการดูดกลืนรังสีอัลตราไวโอเลตถึงอินฟราเรดระยะใกล้ และองค์ประกอบธาตุร่องรอยในอัตราส่วนระหว่าง Fe : Ti : Mg มีความสัมพันธ์กับการเกิดสี โดยสีน้ำเงินจะเกิดจากการเปลี่ยนแปลงภายใต้สภาวะรีดักชั่น ทำให้ปริมาณการดูดกลืนแสงจาก Fe^{+2}/Ti^{+4} และ Fe^{+3} เพิ่มขึ้น ส่วนสีเหลืองเกิดจากการเปลี่ยนแปลงภายใต้สภาวะออกซิเดชั่น ทำให้ปริมาณการดูดกลืนแสงจาก Fe^{+3}/Fe^{+3} มีค่าเพิ่มขึ้น

ในการวิเคราะห์โดยเครื่องมือ FTIR ของทุกตัวอย่างแสดงผลคล้ายกัน โดยก่อนปรับปรุงคุณภาพจะพบการดูดกลืนจากกลุ่ม AlOOH แต่ภายหลังการปรับปรุงคุณภาพจะไม่พบ AlOOH เนื่องจาก AlOOH ได้เปลี่ยนเป็น Al_2O_3 ซึ่งเป็นข้อมูลบ่งชี้ว่าพลอยผ่านการปรับปรุงคุณภาพโดยสรุปพลอยแซปไฟร์จากแหล่งเดนิยายา ประเทศศรีลังกา มีศักยภาพในการเพิ่มคุณภาพด้วยความร้อนที่อุณหภูมิ 1,650 องศาเซลเซียส ทั้งภายใต้สภาวะรีดักชั่น และออกซิเดชั่น

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CHAPTER I

INTRODUCTION

1.1 General Statement

Gem and jewelry industries of Thailand have been a world's renowned center of colored stones for a long time. Rough gem materials from all over the world have been imported for enhancing, cutting and jewelry making before exporting to the world market. Ruby and sapphire are the most popular gemstones which have been used for jewelry and ornament worldwide. This is an important factor for discovery of the new gem deposits and development of gem and jewelry. Among these deposits, Sri Lanka has been a famous deposit for many centuries (Mumme, 1988). In fact, this island was known to the ancient geographers as *Ratnadvipa* (meaning the island of gems). Recently, Deniyaya has become a new sapphire mining area in the south-western part of Sri Lanka. (see Fig.1.1).

Heat treatment of corundum has been applied to enhance corundum's qualities such as color, clarity and phenomena. These enhanced gemstones appear to be stable and durable; besides, heated corundum without additional chemical agents are acceptable in the world market. Rarity and beauty make them more expensive; therefore, quality enhancements of sapphire are required for the lower quality gemstones. Thus, sapphires from Deniyaya, Sri Lanka need to be studied for further thermal enhancement.

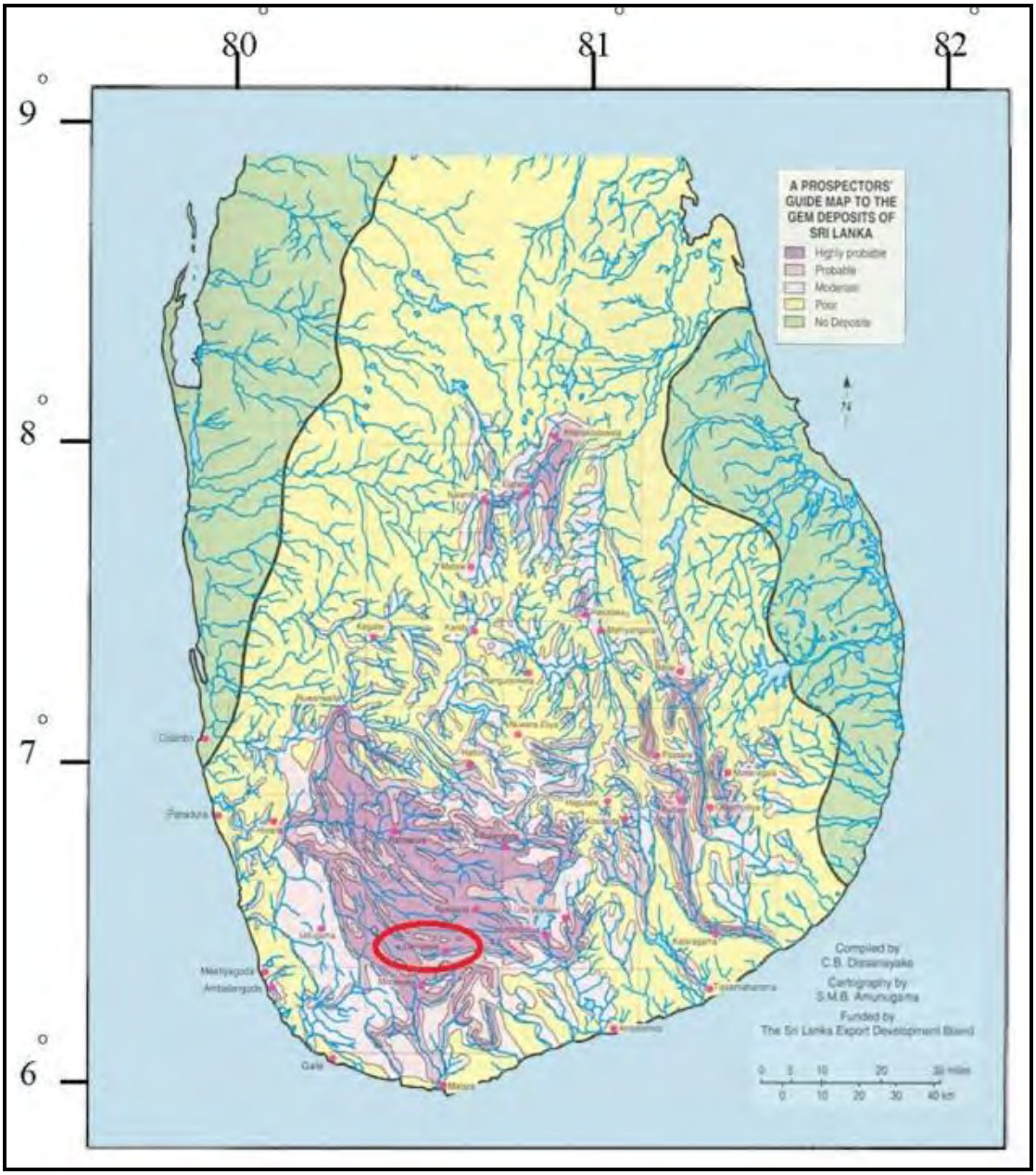


Fig.1.1 Prospectors' guide map of gem deposits in Sri Lanka, showing location of deniyaya deposit (Modified from Dissanayake and Rupasinghe, 1993).

1.2 Literature Reviews

Sri Lanka gem deposits have been very well known as a main source of high quality gems, particularly sapphires. It was a part of the southern Indian sub-continent which appears to have separated due to shallow tectonic movement. Therefore, Sri Lanka Island contains a main basement of highly metamorphosed Precambrian rocks. These basements are subdivided into three major lithological units, i.e., Highland Complex, Wanni Complex and Vijayan Complex (Buadee, 2008) (see Fig.1.2).

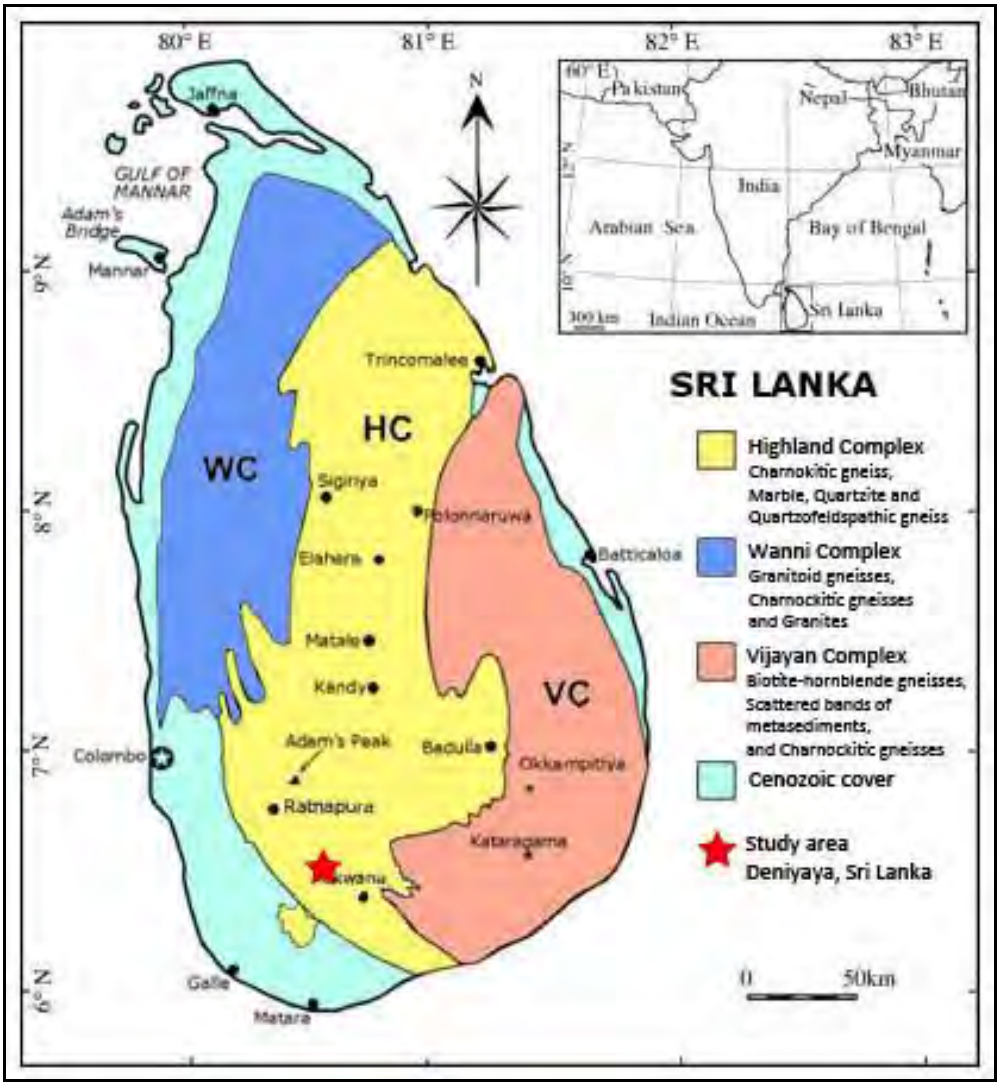


Fig.1.2 Geological map of Sri Lanka showing major lithological rock unit

(Modified after Bancroft, 1984 and Cooray, 1994)

Deniyaya area is located in the highly potential gem deposits of Sri Lanka (Dissanayake and Rupasinghe, 1993). Many mining activities have been operated around the area. Recently, Deniyaya becomes a new sapphire mining area. Geologically, it is situated in the terrain of highland complex which is extensively formed by Proterozoic metamorphic rocks, mainly belonging to granulite facies. Secondary deposits appear to be the most potential where alluvial have been derived from the primary sources. New gem deposits have been discovered and mined around the Gin Ganga River and Mederapitiya. Sapphire collection contains a variety of colors ranging from colorless to pale blue, violet, purple and pink (Sutthirat et al., 2011).

Somboon (2000) studied internal characteristics of corundum resulting from thermal enhancement of a group of some sapphires from Ilakaka and Madagascar. Electric furnace was used to heat at 1000˚C for 3hours and 1650˚C for 3 hours. At 1000˚C, most of the internal features were still unchanged, but a few characteristics were observed such as development of tension disc, slightly altered fingerprint. When the samples were re-heated up to 1650˚C many internal characteristics change; long rutile needles were partially dissolved and forming a broken dot pattern. Moreover, fingerprints become obviously altered and formed fussy boundary, cloudy zone became clearer and color zones were intensified.

Pattamalai (2002) studied heat treatment of some corundums from Madagascar by step-heating experiments that performed under oxidizing atmosphere at different maximum temperatures (i.e., 800˚C, 1000˚C, 1200˚C, 1400˚C and 1600˚C). Consequently, most of sapphire samples could be treated ultimately to reduce their blue color at 1000˚C-1200˚C. The causes of color could be explained by interaction between the ratios of Mg, Ti and Fe as proposed by Haeger (2001).

Tipprasert (2006) studied thermal enhancements and characteristics of sapphires from Wellawaya, Sri Lanka by heat treatment under reducing condition using an electric furnace; the coloration was generally intensified when heating at 1650˚C. Most sapphires appear to be dark blue after step heat treatment. Wellawaya sapphires have potential for thermal enhancement.

Kitbutrawat (2006) studies heat treatment of green sapphire from Attapeu area, Southern Lao P.D.R. The heat experiment was carried out at 1650˚C for 5 hours in N_2 atmosphere. After the treatment blue hue was intensified in most types of samples and the green, greenish blue and

bluish green varieties could be enhanced into blue sapphires with slight greenish tints. Other changes after heat were clarification of color zone, expansion and alteration of healed fractures, and development of tension cracks.

Buadee (2008) studied gemological characteristics of sapphires from Awissawella Deposit, Ratnapura Gem Field, Sri Lanka. Awissawella sapphire samples could be separated based on trace element proportions, from basaltic sapphire and some metamorphic sapphire. These sapphires had high potential to improve their colors. Yellow variety appeared to be intensified by heating at 1650°C in oxidizing atmosphere. On the other hand, blue variety can be increased blue shades by heating at 1650°C in reducing atmosphere.

1.3 General Characteristics of Corundum

Chemical composition	Al_2O_3
Crystal system	Hexagonal-Trigonal
Transparency	Transparent to Translucent
Color	yellow, blue, green, red, orange, pink, purple, violet, brown, black, gray and colorless
Optical properties	double refraction, uniaxial negative
Optical phenomena	star, cat's eye (rare)
Refractive Index	1.762-1.770
Birefringence	0.008-0.010
Density	3.986 g/cm^3
Specific gravity	3.98-4.06
Cause of color	blue: Fe, Ti red and pink: Cr
Luster	vitreous to adamantine
Fracture	conchoidal
Hardness	9

1.4 Problem Define

Sapphires from Deniyaya deposit, Sri Lanka will be a crucial source, if their qualities are improved by heat treatment. Therefore, thermal enhancement of sapphires from Deniyaya, Sri Lanka should be experimented.

1.5 Objectives

The main objective of this study is to enhance thermally the sapphire samples from Deniyaya, Sri Lanka.

CHAPTER II

METHODOLOGY

2.1 Methodology

Methods under this project can be summarized in Fig. 2.1 and described below.

1. Literature reviews include geology of Sri Lanka Gem Deposits, gemological characteristics and thermal enhancements of Sri Lanka. These reviews gave basic knowledge prior to design study plan and experiment.
2. Sample characterization is aimed to grade sapphire samples into color varieties. The sample was collected by the Gem and Jewelry Institute of Thailand (GIT).
3. Physical and optical properties comprise size, weight, specific gravity (SG), refractive indices (RI), fluorescence under short and long wave UV and color under daylight in comparison with the GIA color standard set.
4. Internal features were observed using gemological microscope initially prior to analyses of mineral inclusions using Electron Probe Micro-Analyzer (EPMA). EPMA and Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF) were also engaged for mineral chemistry of host sapphires.
5. Absorption spectroscopy was focused on Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) spectrophotometry for indication of the cause of color in samples both before and after heat treatment. Besides, Fourier Transform Infrared (FTIR) spectrophotometer was used to study Infrared absorption patterns that may be useful for identification of heat treatment.
6. Thermal enhancements using electric furnace at 1650°C under reducing and oxidizing environments were carried out. The experiment was set using optimum conditions that have been reported by previous researches. The blue color should be developed by heating

under reduction environment whereas the yellow color should be developed by oxidizing heat.

7. Physical properties, optical properties and absorption spectroscopy were also investigated again after heat treatment for comparison.
8. Discussion and Conclusions in crucial aspects were made using data obtained from the research and literatures.
9. Report and presentation were then carried out.

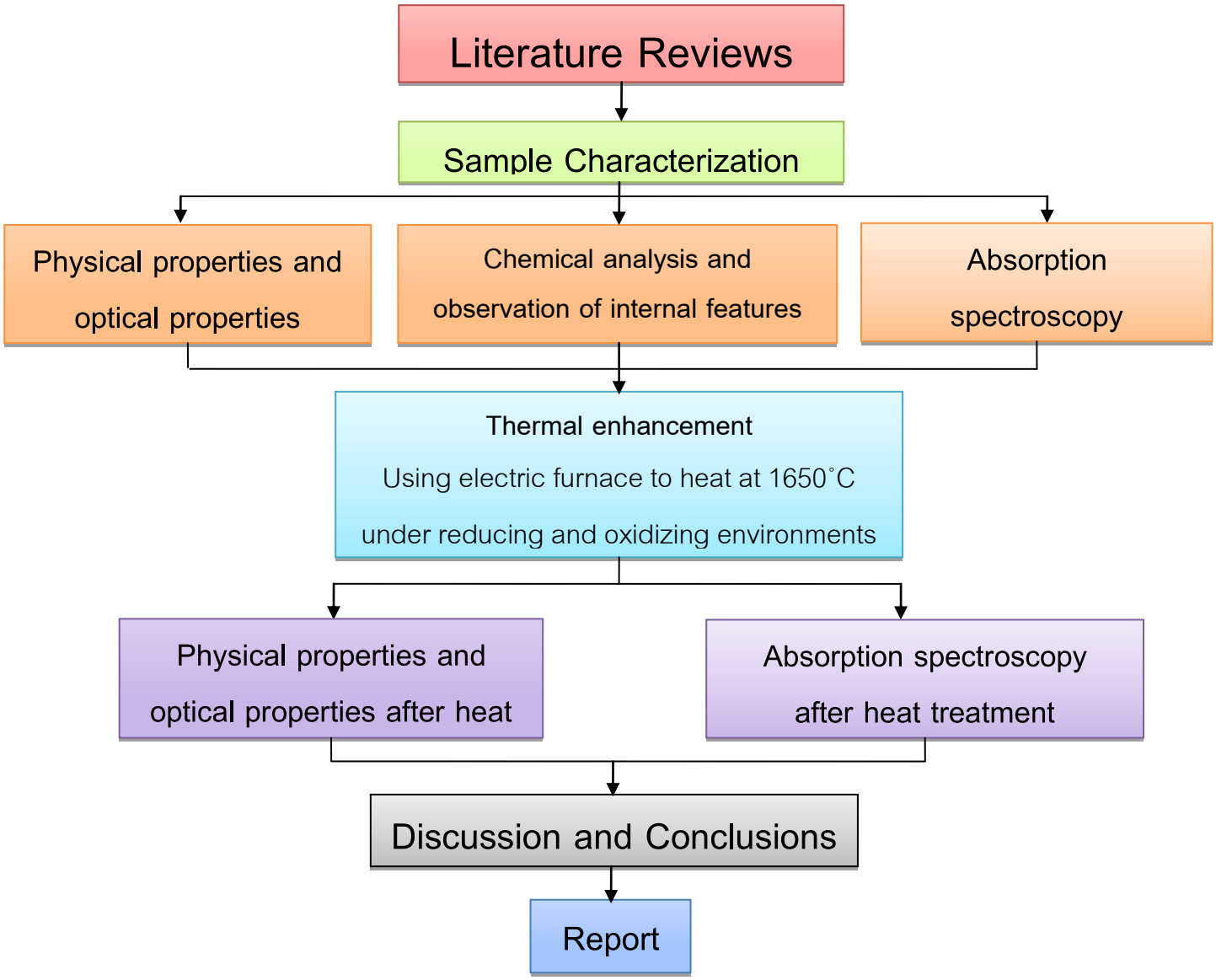


Fig. 2.1 The method of study is summarized as a flow chart

2.2 DataAcquisition and Analysis

Basic Physical and Optical Properties: All selected 29 rough samples were weighed and measured for their specific gravities by a hydrostatic balance (see Fig. 2.2) and were measured the refractive index by refractometer. (see Fig. 2.3). Fluorescence under short and long wave UV was also recorded under Ultraviolet lamp box (see Fig. 2.4). The samples' colors were graded under a daylight box compared with the GIA gem color set (see Fig. 2.5).

Fig. 2.2 Hydrostatic Balance

Fig. 2.3 Standard Refractometer

Fig. 2.4 Long and short wave Ultraviolet lamp box

Fig. 2.5 GIA gem color set

Internal Features: A gemological microscope was basically used to investigate the internal feature in the sapphire samples. This information can generally determine authenticity of gemstone. (see Fig. 2.6).

Fig. 2.6 Gemological microscope

Laser Raman Spectroscope (RAMAN) is a powerful light scattering technique used to diagnose the internal structure of molecules and crystals. The technique gives the information of internal vibration and lattice vibrations. However, the equipment cannot distinguish clearly some mineral inclusions that set deep into the samples. The best result is obtained from mineral inclusions that are exposed or very close to the sample surface (see Fig. 2.7).

Fig. 2.7 Laser Raman Spectroscope (Model 1000, Ranishaw) at GIT

Absorption Spectroscopic Measurement: Fourier Transform Infrared Spectrophotometer (FTIR) (see Fig. 2.8) can be used for recording the absorption or transmission spectra in the range of near to far infrared. The infrared spectra give information about the structures and specific bonding in mineral specimen.

Fig. 2.8 Fourier Transform Infrared Spectrophotometer (NICOLET 6700) at GIT

UV-VIS-NIR Spectrophotometer contains a light source generating wavelengths over the range of ultraviolet (UV), visible light (VIS) and near infrared (NIR). Absorption spectra are detected and then signal is transferred to display on monitor. UV-VIS-NIR Spectrophotometer (see Fig. 2.9) gives information about the absorption spectra that may be related to electron transitions of trace elements or other structural defects in sapphires.

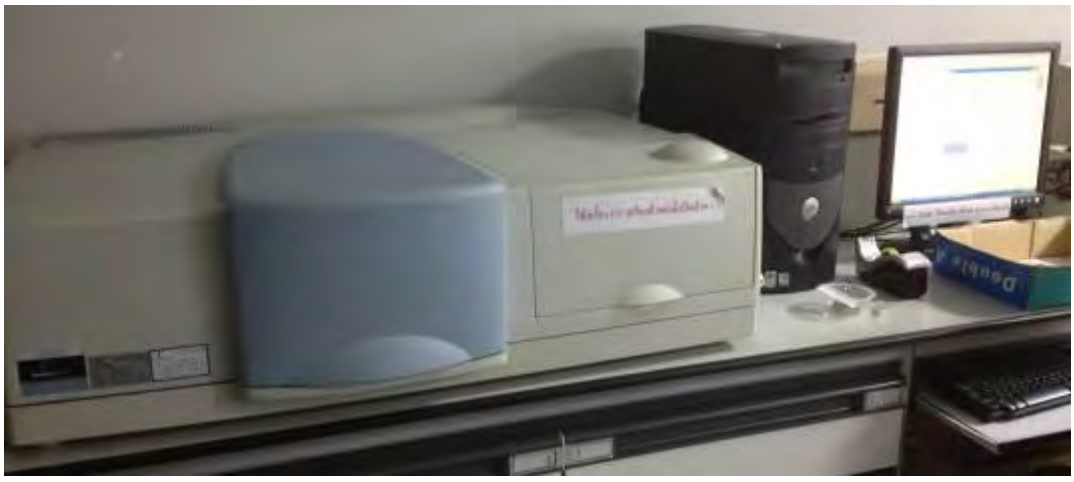


Fig. 2.9 Perkin-Elmer UV-VIS-NIR Spectrophotometer at GIT

Chemical Analysis: Electron Probe Micro-Analyzer (EPMA) (see Fig. 2.10) is a quantitatively analytical instrument which is able to analyze within a certain tiny area in micrometer scale. The electron beam is focused on the surface of a sample and activates electrons around the analytical area.. Several applicatiions including secondary electron imaging, back scatter electron imaging, X-ray mapping, qualitative and quantitative analyses, can be taken from this technique.

Fig. 2.10 Electron Probe Micro-Analyzer (JEOL JXA-8100) based at Geology Department, Faculty of Science, Chulalongkorn University

Energy Dispersive X-Ray Fluorescence Spectrometer: EDXRF (see Fig. 2.11) is a semi-quantitatively analytical instrument which can be used for monitoring major and minor components of samples.

Fig. 2.11 Energy Dispersive X-Ray Fluorescence Spectrometer (model EAGLE III) at GIT.

High Temperature Furnace: The electric furnace is applied for heat treating gem samples. Under this study, all of the samples were annealed at 1,650°C in reducing condition (nitrogen feeding) or oxidizing condition (oxygen feeding) for 5 hours soaking. Samples were prepared and place into an alumina crucible (see Fig. 2.12). . The furnace used in this project is Linn electric furnace, Model HT 1800 Plus VAC Bottom Loader at the Department of Geology, Faculty of Science, Chulalongkorn University (see Fig. 2.13).

Fig. 2.12 Alumina crucible

Fig. 2.13 Linn electric furnace, Model HT 1800 Plus VAC Bottom Loader at Department of Geology, Faculty of Science, Chulalongkorn University.

CHAPTER III

CHARACTERISTICS OF DENIYAYA SAPPHIRES BEFORE TREATMENT

3.1 Samples

The Deniyaya sapphires used in this study include 29 rough samples that were classified into 3 groups based on their color varieties; Group B consisting of 7 samples are light blue (Fig. 3.1); Group C consisting of 11 samples are colorless (Fig. 3.2); Group Y consisting of 11 samples are light yellow (Fig. 3.3).

Fig.3.1 Deniyaya blue sapphires (Group B)

Fig.3.2 Deniyaya colorless sapphires (Group C)

Fig.3.3 Deniyaya yellow sapphires (Group Y)

3.2 Basic Gemological Properties

The general physical and optical properties of each group Deniyaya sapphires are summarized in Tables 3.1-3.3

Table 3.1 Summary of general properties of rough sapphires Group B from Deniyaya, Sri Lanka.

Weight (ct.)	RI		Birefringence	SG	Fluorescence	
	n_o	n_e			SW	LW
0.700-2.980	1.770-1.771	1.761-1.763	0.007-0.009	3.855-3.980	Inert	Inert

Table 3.2 Summary of general properties of rough sapphires Group C from Deniyaya, Sri Lanka.

Weight (ct.)	RI		Birefringence	SG	Fluorescence	
	n_o	n_e			SW	LW
0.660-4.130	1.768-1.771	1.760-1.763	0.007-0.010	3.872-4.003	Inert	Moderate

Table 3.3 Summary of general properties of rough sapphires Group Y from Deniyaya, Sri Lanka.

Weight (ct.)	RI		Birefringence	SG	Fluorescence	
	n_o	n_e			SW	LW
0.995-3.170	1.768-1.773	1.760-1.765	0.007-0.010	3.921-4.002	Inert	Weak

3.3 Internal Characteristics

Internal features observed under a gem microscope are mainly composed of fingerprints, small needles, fracture, cloud, dust and rutile as summarized in Table 3.4 and representatively shown in Figs. 3.4-3.7. Moreover, Raman spectra in 0-2,000 cm^{-1} range were used to identify mineral inclusions of these sapphires before treatment. Raman spectra (Fig. 3.8 and 3.9) indicate the main inclusions of diaspore, apatite and rutile.

Table 3.4 Summary of internal features observed in Deniyaya sapphires.

Type of inclusions	Group B	Group C	Group Y
- Fingerprints	***	***	***
- Small needles	**	***	**
- Cloud and dust	***	**	***
- Fracture	*	***	***
- Mineral inclusions	*	-	***

* Rarely found ** Found *** Often found

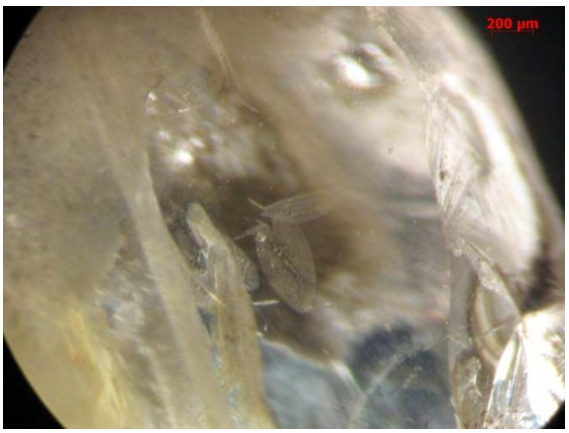


Fig.3.4 Fingerprints (sample Y4).

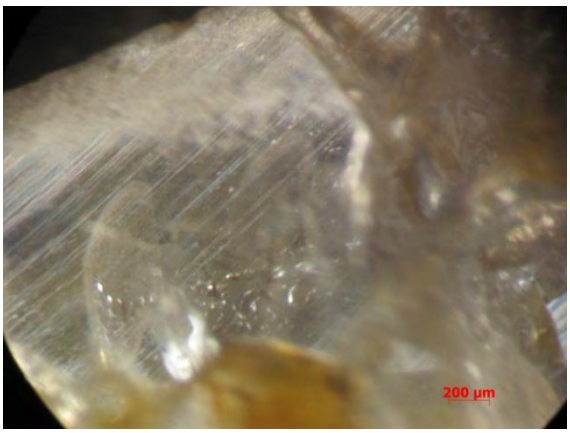


Fig.3.5 Needle inclusions and two phase inclusions (sample Y3).

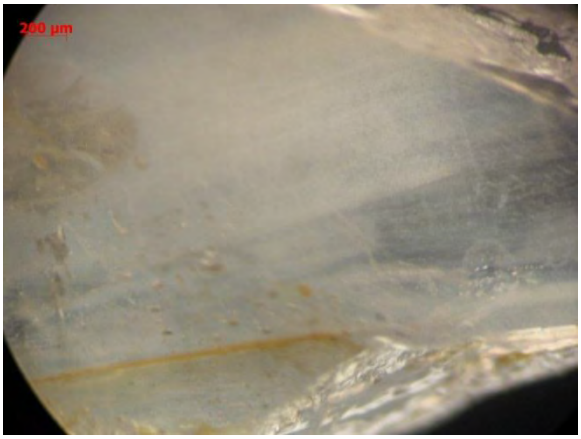


Fig.3.6 Cloud and small rutiles (sample C1).

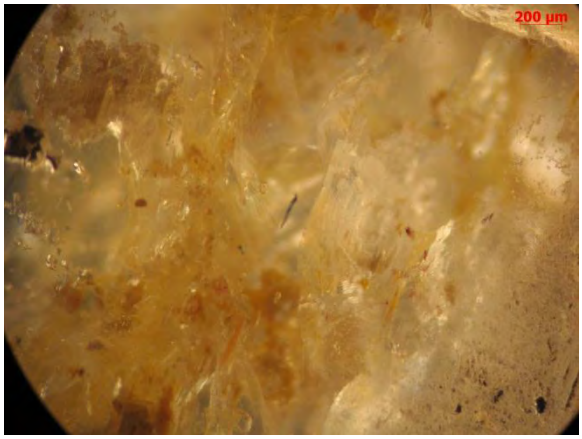


Fig.3.7 Fractures (sample Y9).

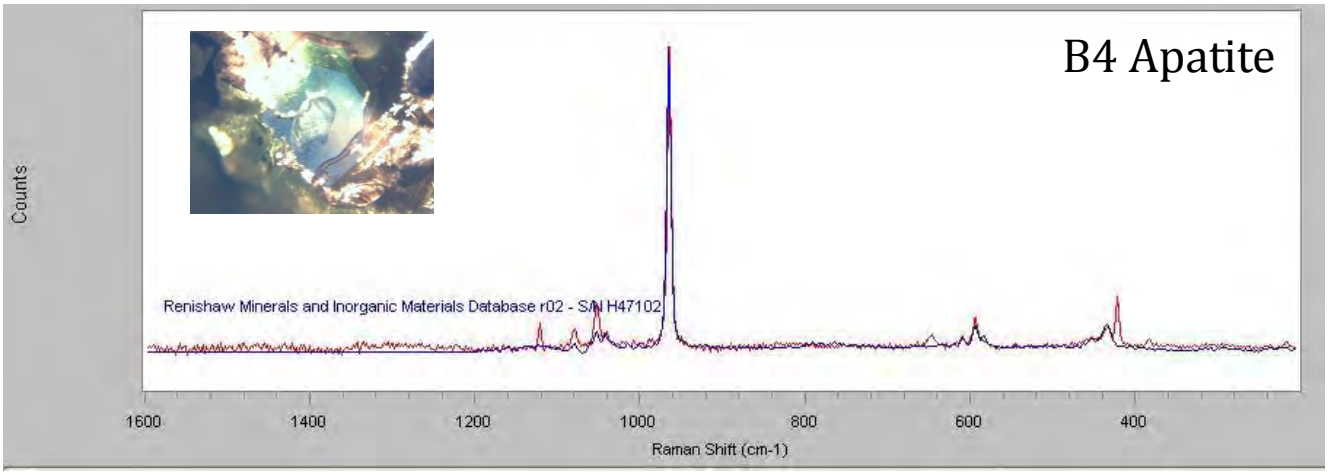


Fig.3.8 Raman spcetrum of Apatite, sample B4, Deniyaya sapphires Group B.

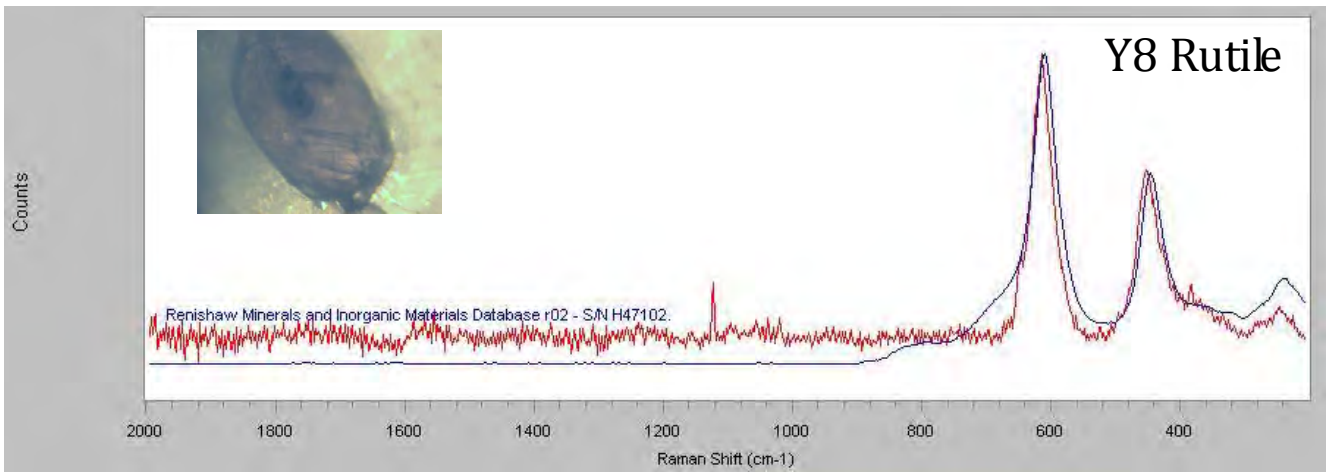


Fig.3.9 Raman spectrum of Rutile, sample Y8, Deniyaya sapphires Group Y.

3.4 UV-VIS-NIR Absorption Spectra

Color appearance of a stone is directly related to absorption spectrum. UV-VIS-NIR absorption spectra of each sample measured before and after heat treatment may help to understand the cause of color change due to the treatment. The UV-VIS-NIR absorption spectra between 250-1500 nm obtained from 29 rough sapphires before treatment were recorded. These spectra show similar patterns which representative spectra (O- and E-rays) of some samples before heat-treatment are displayed in Figs.3.10-3.12. These UV-VIS-NIR absorption spectra relate to electron transitions of trace elements or other structural defects in sapphires. Blue sapphires usually show Fe^{+3}/Fe^{+3} pairs with absorption peaks at 374,377 and 450 nm, Fe^{+3} with absorption peaks at 697 nm and Fe^{+2}/Ti^{+4} pairs with absorption band and peaks at 565 and 697 nm (Fig. 3.10). Yellow sapphires show Fe^{+3} absorption peaks at 328, 386, 388 and 470 nm (Fig. 3.12). On the other hand, colorless sapphires appear to have lower absorption (Fig. 3.11).

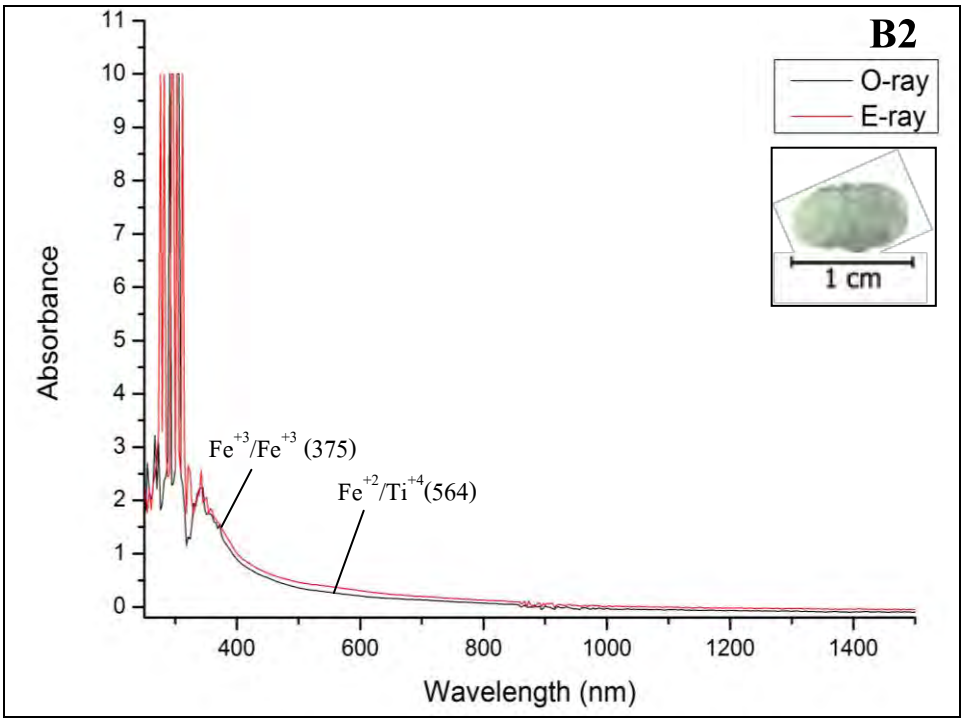


Fig.3.10 UV-VIS-NIR absorption spectra of sample B2, Deniyaya sapphires Group B, before heat-treatment.

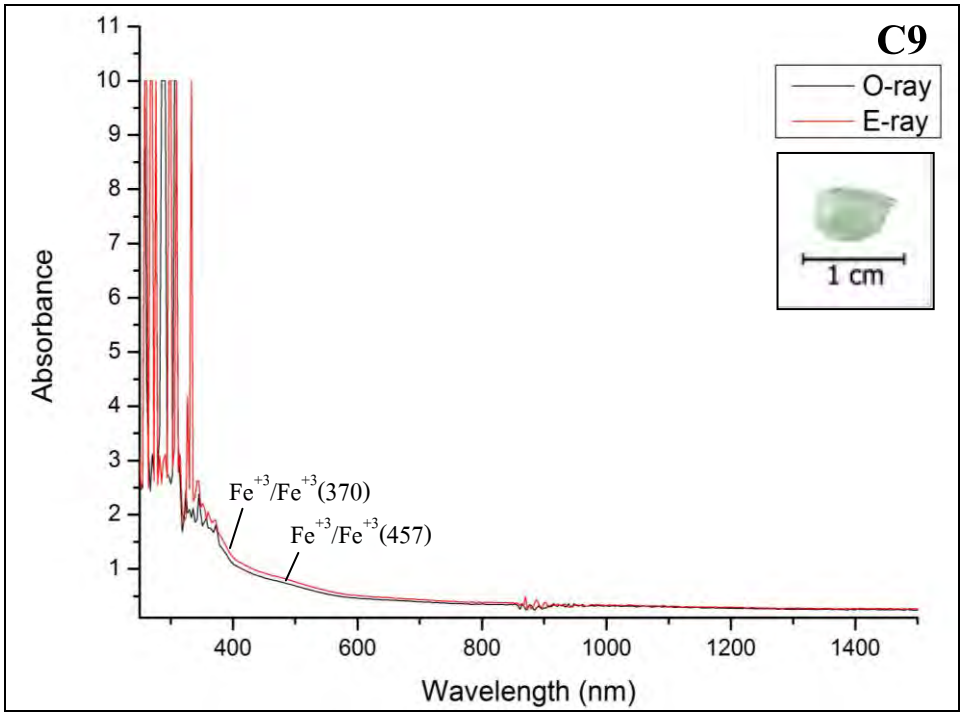


Fig.3.11 UV-VIS-NIR absorption spectra of sample C9, Deniyaya sapphires Group C, before heat-treatment.

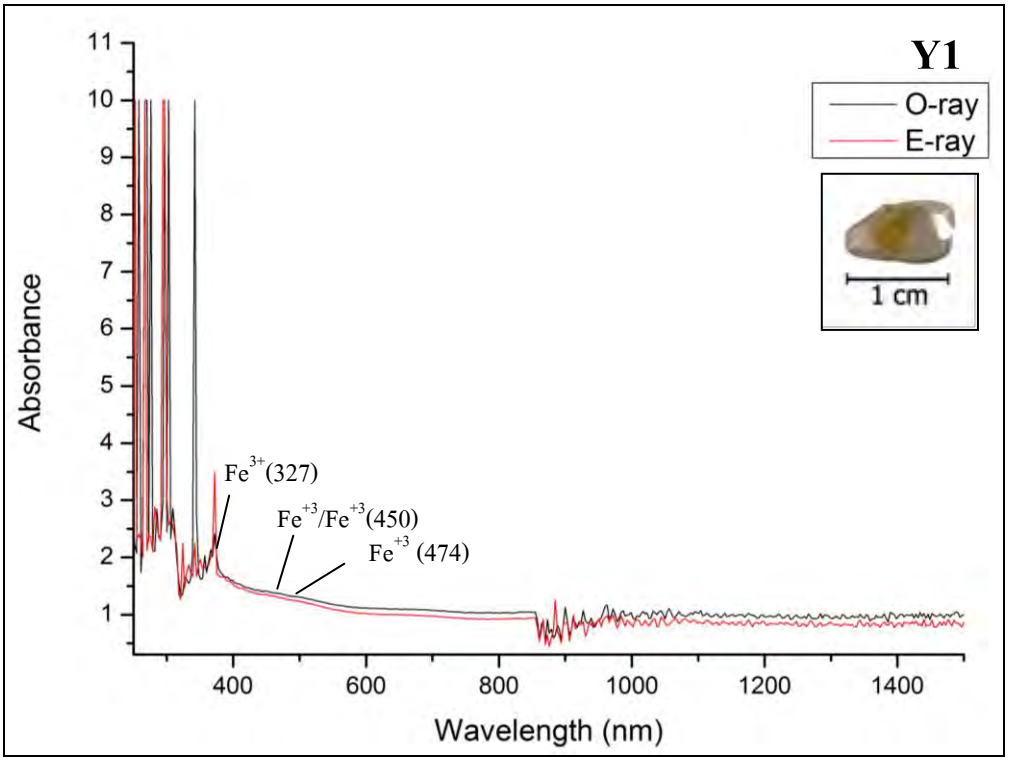


Fig.3.12 UV-VIS-NIR absorption spectra of sample Y1, Deniyaya sapphires Group Y, before heat-treatment.

3.5 Fourier Transform Infraed (FTIR) spectra

The FTIR absorption spectra within 400-4000 cm^{-1} range of 29 rough sapphires were observed before treatment. The spectra show a similar patterns which representative spectra of samples are displayed in Figs.3.13-3.16. In general, all sapphires show absorption patterns of H_2O, CO_2 and CH-Stretching; besides, some samples show absorption patterns of AlOOH.

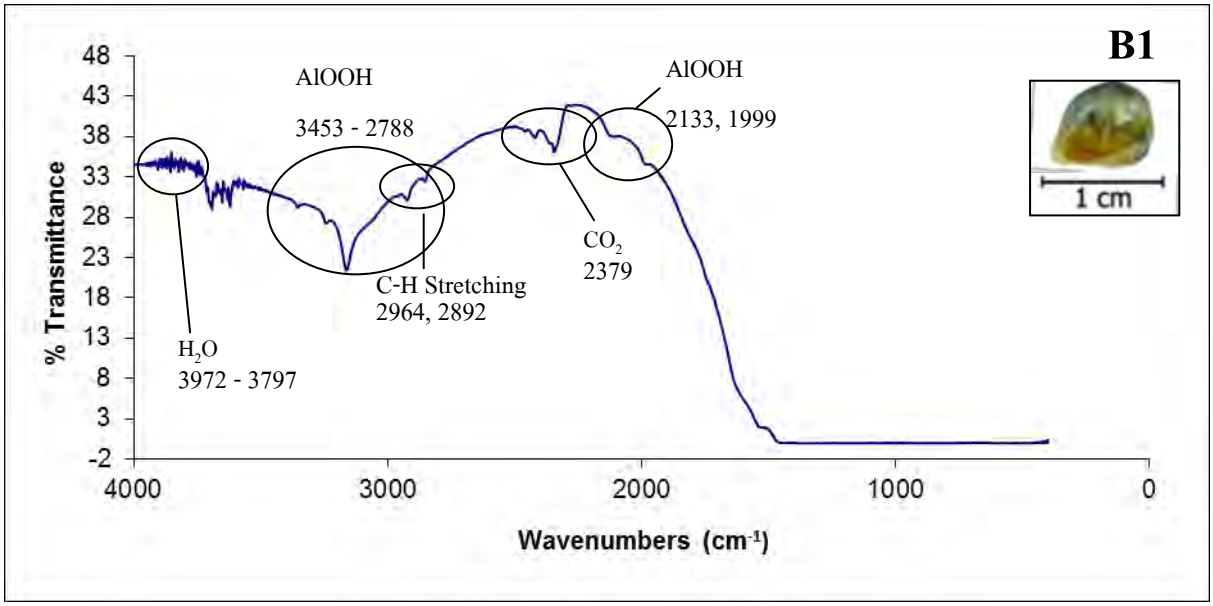


Fig.3.13 FTIR absorption spectrum of sample B1, Deniyaya sapphire Group B, before heat-treatment.

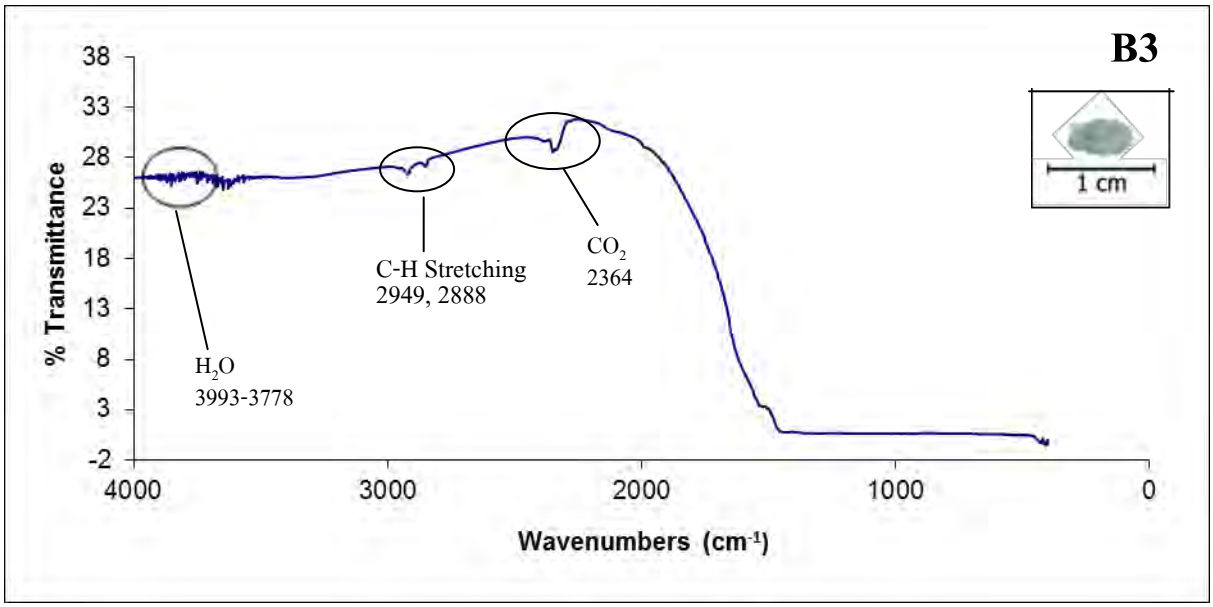


Fig.3.14 FTIR absorption spectrum of sample B3, Deniyaya sapphire Group B, before heat-treatment.

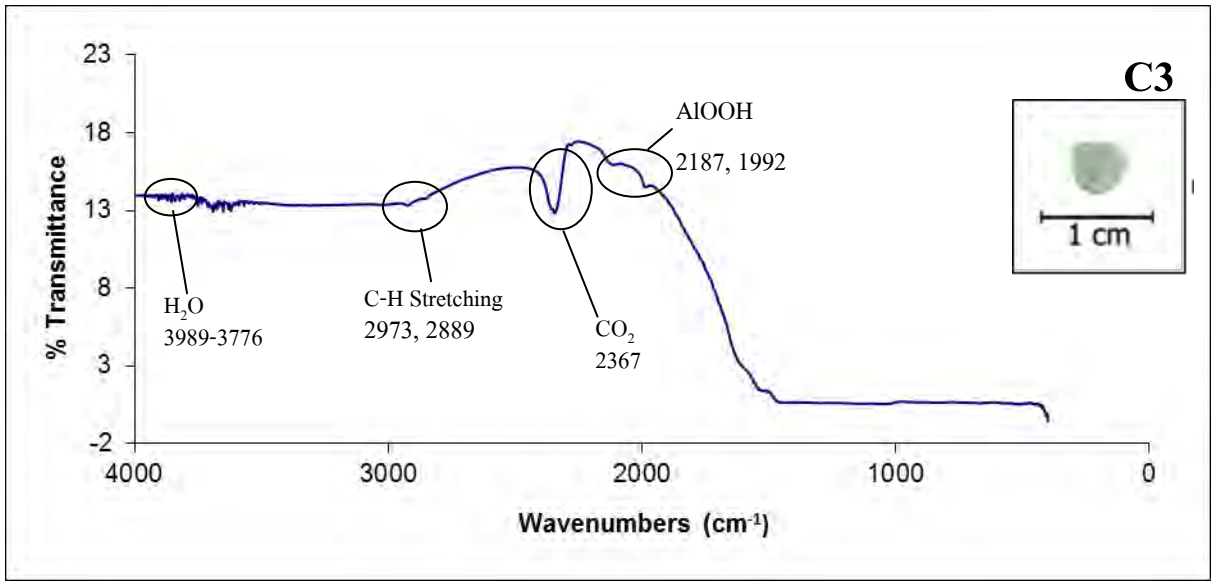


Fig.3.15 FTIR absorption spectrum of sample C3, Deniyaya sapphire Group C, before heat-treatment.

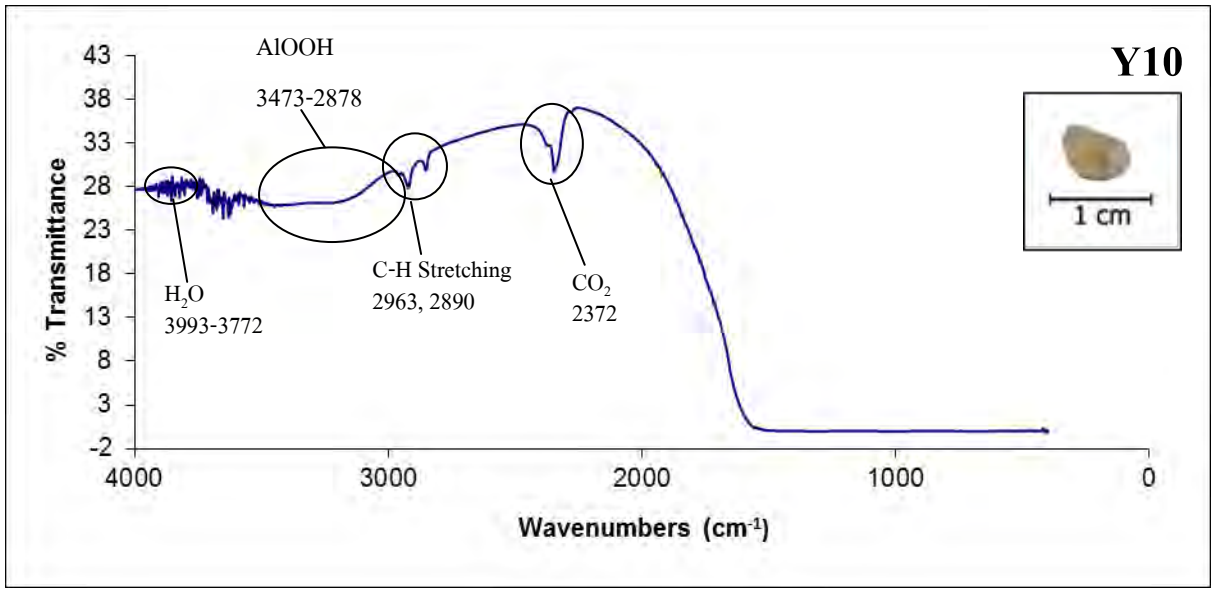


Fig.3.16 FTIR absorption spectrum of sample Y10, Deniyaya sapphire Group Y, before heat-treatment

3.6 Energy Dispersive X-Ray Fluorescence (EDXRF)

Summary of chemical contents of 29 rough samples of Deniyaya sapphires analyzed by EDXRF is displayed in Table 3.5.

Table 3.5 Summary of chemical contents of 29 rough samples of Deniyaya sapphires.

	Group B (B1-B7 Samples)		Group C (C1 and C3-C12 Samples)		Group Y (Y2-Y12 Samples)	
	MIN-MAX (wt %)	MEAN±SD (wt %)	MIN-MAX (wt %)	MEAN±SD (wt %)	MIN-MAX (wt %)	MEAN±SD (wt %)
Al_2O_3	99.615-99.847	99.711±0.078	99.603-99.900	99.752±0.087	99.283-99.912	99.718±0.173
TiO_2	0.044-0.220	0.106±0.067	0.016-0.146	0.050±0.037	0.012-0.141	0.054±0.039
V_2O_5	0.011-0.036	0.019±0.008	0.000-0.044	0.013±0.013	0.000-0.035	0.017±0.009
Cr_2O_3	0.000-0.012	0.006±0.004	0.000-0.023	0.009±0.008	0.000-0.022	0.011±0.007
Fe_2O_3	0.042-0.241	0.141±0.074	0.054-0.220	0.143±0.052	0.028-0.585	0.180±0.145
Ga_2O_3	0.008-0.023	0.017±0.005	0.007-0.080	0.033±0.021	0.006-0.056	0.020±0.014

3.7 Electron Probe Micro-Analyzer (EPMA)

Rough samples of Deniyaya sapphires were quantitatively analyzed by EPMA. The major and trace element analyses are summarized in Table 3.6-3.8 and all analyses are reported in Appendix C.

Table 3.6 Representative EPMA analyses of Deniyaya sapphires, Group B

Sample	B1	B2	B3	B4	B5	B6	B7
Al_2O_3	99.84	99.77	99.61	100.08	100.08	99.73	99.64
SiO_2	0.02	0.00	0.01	0.00	0.01	0.01	0.00
TiO_2	0.06	0.32	0.07	0.13	0.01	0.06	0.05
Cr_2O_3	0.02	0.01	0.02	0.01	0.00	0.01	0.00
V_2O_3	0.01	0.01	0.00	0.00	0.00	0.02	0.04
Ga_2O_3	0.00	0.02	0.07	0.05	0.00	0.00	0.00
FeO	0.11	0.04	0.19	0.03	0.04	0.06	0.19
MgO	0.00	0.03	0.02	0.00	0.00	0.02	0.02
MnO	0.00	0.00	0.00	0.00	0.01	0.03	0.00
K_2O	0.00	0.01	0.00	0.01	0.00	0.00	0.01
Na_2O	0.00	0.01	0.00	0.00	0.01	0.01	0.00
Total	100.07	100.22	100.03	100.31	100.17	99.95	99.94
Nos. of ions	B1	B2	B3	B4	B5	B6	B7
Al	1.9977	1.9944	1.9956	1.9968	1.9993	1.9978	1.9971
Si	0.0002	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000
Ti	0.0006	0.0032	0.0007	0.0013	0.0001	0.0006	0.0005
Cr	0.0003	0.0002	0.0005	0.0003	0.0000	0.0002	0.0000
V	0.0001	0.0001	0.0000	0.0000	0.0000	0.0004	0.0009
Ga	0.0000	0.0004	0.0014	0.0010	0.0000	0.0000	0.0000
Fe	0.0011	0.0004	0.0019	0.0003	0.0004	0.0006	0.0019
Mg	0.0000	0.0003	0.0002	0.0000	0.0000	0.0002	0.0002
Mn	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003	0.0000
K	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001
Na	0.0000	0.0001	0.0000	0.0000	0.0002	0.0001	0.0000
Total	2.0001	1.9993	2.0004	1.9997	2.0003	2.0002	2.0006

Table 3.7 Representative EPMA analyses of Deniyaya sapphires, Group C

Sample	C1	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Al_2O_3	99.80	98.73	99.96	99.45	97.64	99.76	99.76	98.54	99.96	99.81	99.64
SiO_2	0.00	0.02	0.02	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00
TiO_2	0.01	0.00	0.03	0.01	0.01	0.04	0.02	0.03	0.02	0.00	0.01
Cr_2O_3	0.02	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
V_2O_3	0.02	0.02	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.01
Ga_2O_3	0.09	0.03	0.00	0.00	0.07	0.02	0.06	0.02	0.04	0.00	0.07
FeO	0.06	0.03	0.08	0.09	0.06	0.13	0.08	0.03	0.04	0.08	0.03
MgO	0.01	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.02	0.00
MnO	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.01
K_2O	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Total	100.04	98.84	100.12	99.60	97.82	100.02	99.98	98.69	100.09	99.92	99.78
Nos. of ions	C1	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Al	1.9968	1.9986	1.9982	1.9991	1.9976	1.9973	1.9977	1.9988	1.9985	1.9993	1.9981
Si	0.0000	0.0002	0.0002	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Ti	0.0001	0.0000	0.0003	0.0001	0.0001	0.0004	0.0002	0.0003	0.0002	0.0000	0.0001
Cr	0.0005	0.0000	0.0003	0.0000	0.0001	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000
V	0.0003	0.0003	0.0003	0.0000	0.0000	0.0006	0.0000	0.0000	0.0000	0.0000	0.0001
Ga	0.0018	0.0006	0.0000	0.0000	0.0015	0.0004	0.0011	0.0004	0.0009	0.0000	0.0013
Fe	0.0006	0.0003	0.0008	0.0009	0.0006	0.0013	0.0008	0.0003	0.0004	0.0008	0.0003
Mg	0.0001	0.0000	0.0000	0.0000	0.0001	0.0003	0.0000	0.0000	0.0001	0.0002	0.0000
Mn	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001
K	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001
Na	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0002
Total	2.0004	2.0001	2.0001	2.0005	2.0002	2.0004	2.0004	2.0000	2.0001	2.0004	2.0003

Table 3.8 Representative EPMA analyses of Deniyaya sapphires, Group Y

Sample	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12
Al_2O_3	99.53	99.93	99.94	99.55	99.86	99.72	99.62	99.89	99.82	100.07	100.09
SiO_2	0.00	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.01	0.03
TiO_2	0.02	0.02	0.00	0.01	0.00	0.02	0.01	0.02	0.01	0.02	0.02
Cr_2O_3	0.02	0.01	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_3	0.01	0.00	0.02	0.02	0.02	0.00	0.06	0.00	0.01	0.00	0.00
Ga_2O_3	0.07	0.00	0.05	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
FeO	0.05	0.06	0.06	0.06	0.05	0.09	0.13	0.08	0.12	0.06	0.04
MgO	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.02	0.01	0.02
MnO	0.02	0.00	0.03	0.00	0.02	0.02	0.00	0.00	0.04	0.01	0.00
K_2O	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.01
Na_2O	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Total	99.74	100.02	100.12	99.69	100.01	99.92	99.83	100.03	100.03	100.20	100.24
Nos. of ions	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12
Al	1.9972	1.9991	1.9977	1.9987	1.9984	1.9981	1.9977	1.9991	1.9986	1.9990	1.9988
Si	0.0000	0.0000	0.0000	0.0000	0.0003	0.0003	0.0000	0.0000	0.0000	0.0001	0.0003
Ti	0.0002	0.0002	0.0000	0.0001	0.0000	0.0002	0.0001	0.0002	0.0001	0.0002	0.0002
Cr	0.0003	0.0002	0.0004	0.0004	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
V	0.0003	0.0000	0.0003	0.0003	0.0003	0.0000	0.0013	0.0000	0.0001	0.0000	0.0001
Ga	0.0015	0.0001	0.0009	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000
Fe	0.0005	0.0006	0.0006	0.0006	0.0005	0.0009	0.0013	0.0008	0.0012	0.0006	0.0004
Mg	0.0000	0.0000	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0002	0.0001	0.0002
Mn	0.0002	0.0000	0.0003	0.0000	0.0002	0.0002	0.0000	0.0000	0.0004	0.0001	0.0000
K	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003	0.0002	0.0000	0.0001
Na	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000
Total	2.0003	2.0002	2.0004	2.0002	2.0002	2.0003	2.0005	2.0004	2.0006	2.0004	2.0001

CHAPTER IV

CHARACTERISTICS OF DENIYAYA SAPPHIRES AFTER HEAT-TREATMENT

4.1 Heat-Treatment Condition

Each sample group was divided into two parts for heat-treatment at 1,650°C in reducing and oxidizing conditions. Thus, there were 15 samples heated at 1,650°C in reducing atmosphere and 14 samples heated at 1,650°C in oxidizing atmosphere. These conditions were selected because the 1,650°C heating is a normal temperature used in the industry. From the previous reports, this temperature with five hours soaking time was suggested to modify the color. Yellow variety appears to be intensified by heating at 1650˚C in oxidizing atmosphere. On the other hand, blue variety can be increased blue shades by heating at 1650˚C in reducing atmosphere.

4.2 Selected Samples for Treatment

Deniyaya sapphires used in this study were selected from 29 rough stones with three main color varieties as reported in the last chapter. They were randomly selected and mixed from those color varieties. Two sample groups contain: Group 1 (see Fig.4.1), 15 samples, consists of 4 samples of blue variety (B), 6 samples of colorless variety (C) and 5 samples of yellow variety (Y); Group 2 (see Fig.4.2), 14 samples, consists of 3 samples of blue variety (B), 5 samples of colorless variety (C) and 6 samples of yellow variety (Y)

Fig.4.1 Group 1 samples of Deniyaya sapphires for heating at 1,650°C in reducing atmosphere.

Fig.4.2 Group 2 samples of Deniyaya sapphires for heating at 1,650°C in oxidizing atmosphere.

Basic gemological properties of Deniyaya sapphires after treatment

The color and fluorescence of Deniyaya sapphires before and after treatment are summarized from each group in Tables 4.1-4.3.

Table 4.1: Summary of color and fluorescence of samples before and after treatment, rough sapphires Group B from Deniyaya, Sri Lanka

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
B1	B2/2	vB5/3	Inert	Inert	Strong	Moderate	Y2/2+cl	B2/2+B3/1
B2	B3/1	bV8/3	Weak	Weak	Moderate	Weak		
B3	bV2/3	B8/3	Inert	Inert	Weak	Weak		
B4	B2/2	B3/4	Inert	Inert	Strong	Weak		
B5	B2/2	B3/3	Inert	Inert	Moderate	Weak	Cloud	Cloud
B6	B2/2	B3/1	Inert	Inert	Moderate	Weak		
B7	VsigB2/2	B4/2	Inert	Inert	Strong	Moderate		

Table 4.2: Summary of color and fluorescence of samples before and after treatment, rough sapphires Group C from Deniyaya, Sri Lanka

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
C1	colorless	B3/3	Weak	Weak	Strong	Strong		
C3	colorless	colorless	Inert	Moderate	Weak	Weak		
C4	colorless	colorless	Weak	Weak	Moderate	Moderate		
C5	colorless	colorless	Inert	Moderate	Moderate	Weak		Cloud
C6	colorless	vB3/3	Inert	Moderate	Strong	Moderate		

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
C7	colorless	B3/3	Inert	Moderate	Strong	Moderate		cl
C8	colorless	Y4/5	Inert	Weak	Moderate	Moderate		Cloud
C9	colorless	B3/1	Weak	Weak	Strong	Weak	Cloud+Y2/2	Cloud
C10	colorless	B2/2	Inert	Inert	Strong	Moderate	Y2/2	Cloud
C11	colorless	colorless	Inert	Moderate	Moderate	Weak		
C12	colorless	colorless	Weak	Moderate	Moderate	Moderate		

Table 4.3: Summary of color and fluorescence of samples before and after treatment, rough sapphires Group Y from Deniyaya, Sri Lanka

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
Y2	Y3/3	Cl	Inert	Weak	Moderate	Moderate		Cloud
Y3	Y3/5	B3/3+cl	Inert	Weak	Strong	Moderate		
Y4	Y2/3	cl+B2/2	Inert	Inert	Weak	Weak		
Y5	Y2/2	vB4/4	Inert	Inert	Weak	Weak		
Y6	Y2/2	Cl	Weak	Weak	Strong	Strong	cl	
Y7	Y2/2	Cl	Weak	Weak	Weak	Weak	cl	
Y8	Y2/3	cl+Y4/5	Inert	Moderate	Moderate	Weak	B3/1	
Y9	Y2/2	Y4/5	Weak	Weak	Moderate	Weak	cl	
Y10	Y3/3	cl+B3/1	Inert	Weak	Strong	Weak	cl	
Y11	Y2/2	Y3/5	Weak	Weak	Moderate	Moderate	cl	Cl
Y12	Y2/2	Cl	Inert	Inert	Strong	Moderate		Cloud

4.3 Color Appearances after Heat Treatment

After heat-treatment at 1,650°C for five hours in reducing atmosphere, some samples of Group 1 changed color into light to dark blue whereas the others were still colorless (see Fig.4.3). On the other hand, some samples in Group 2 after reducing heat changed color into light to dark yellow and light to dark blue; the others were still colorless. (see Fig.4.4).

Fig.4.3 Color changing of Group1 Deniyaya sapphires after heat treatment in reducing atmosphere.

Fig.4.4 Color changing of Group2 Deniyaya sapphires after heat-treatment in oxidizing atmosphere.

Their colors and fluorescence before and after treatments are compared and summarized in Tables 4.4-4.6. The blue color was appeared to be increased in both reduction and oxidation conditions whereas yellow color seems to be intensified only in oxidizing condition.

Table 4.4 Summary of color and fluorescence of blue variety samples before and after treatment. * = oxidizing heat ** = reducing heat

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
B1**	B2/2	vB5/3	Inert	Inert	Strong	Moderate	Y2/2+cl	B2/2+B3/1
B2**	B3/1	bV8/3	Weak	Weak	Moderate	Weak		
B3**	bV2/3	B8/3	Inert	Inert	Weak	Weak		
B4**	B2/2	B3/4	Inert	Inert	Strong	Weak		
B5*	B2/2	B3/3	Inert	Inert	Moderate	Weak	Cloud	Cloud
B6*	B2/2	B3/1	Inert	Inert	Moderate	Weak		
B7*	VsigB2/2	B4/2	Inert	Inert	Strong	Moderate		

Table 4.5 Summary of color and fluorescence of colorless variety samples before and after treatment. * = oxidizing heat ** = reducing heat

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
C1**	Colorless	B3/3	Weak	Weak	Strong	Strong		
C3**	Colorless	colorless	Inert	Moderate	Weak	Weak		
C4**	Colorless	colorless	Weak	Weak	Moderate	Moderate		
C5**	Colorless	colorless	Inert	Moderate	Moderate	Weak		Cloud
C6**	Colorless	vB3/3	Inert	Moderate	Strong	Moderate		

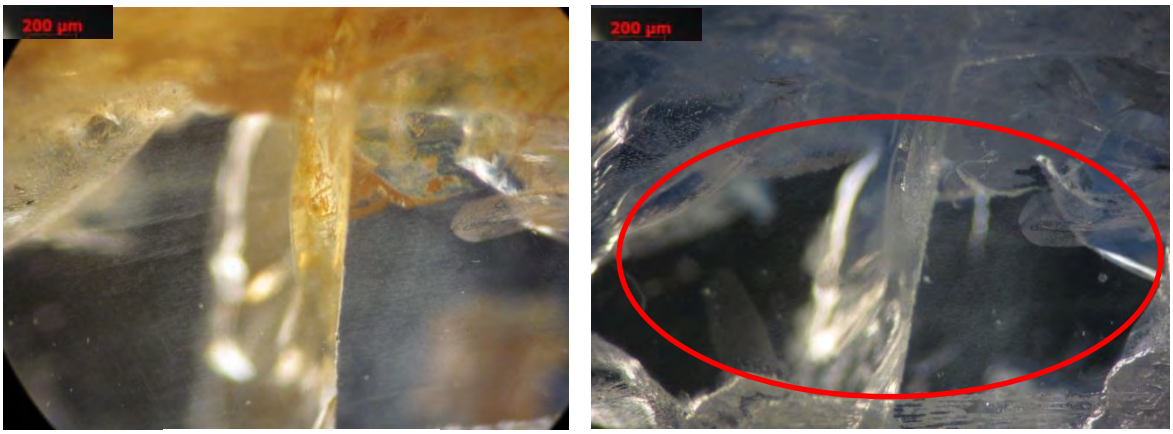
sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
C7**	Colorless	B3/3	Inert	Moderate	Strong	Moderate		cl
C8*	Colorless	Y4/5	Inert	Weak	Moderate	Moderate		Cloud
C9*	Colorless	B3/1	Weak	Weak	Strong	Weak	Cloud+Y2/2	Cloud
C10*	Colorless	B2/2	Inert	Inert	Strong	Moderate	Y2/2	Cloud
C11*	Colorless	colorless	Inert	Moderate	Moderate	Weak		
C12*	Colorless	colorless	Weak	Moderate	Moderate	Moderate		

Table 4.6 Summary of color and fluorescence of yellow variety samples before and after treatment. * = oxidizing heat ** = reducing heat

sample I.D.	Color		Fluorescence				REMARK	
	Before	After	Before		After		Before	After
			SW	LW	SW	LW		
Y2**	Y3/3	Cl	Inert	Weak	Moderate	Moderate		Cloud
Y3**	Y3/5	B3/3+cl	Inert	Weak	Strong	Moderate		
Y4**	Y2/3	cl+B2/2	Inert	Inert	Weak	Weak		
Y5**	Y2/2	vB4/4	Inert	Inert	Weak	Weak		
Y6**	Y2/2	Cl	Weak	Weak	Strong	Strong	cl	
Y7*	Y2/2	Cl	Weak	Weak	Weak	Weak	cl	
Y8*	Y2/3	cl+Y4/5	Inert	Moderate	Moderate	Weak	B3/1	
Y9*	Y2/2	Y4/5	Weak	Weak	Moderate	Weak	cl	
Y10*	Y3/3	cl+B3/1	Inert	Weak	Strong	Weak	cl	
Y11*	Y2/2	Y3/5	Weak	Weak	Moderate	Moderate	cl	Cl
Y12*	Y2/2	Cl	Inert	Inert	Strong	Moderate		Cloud

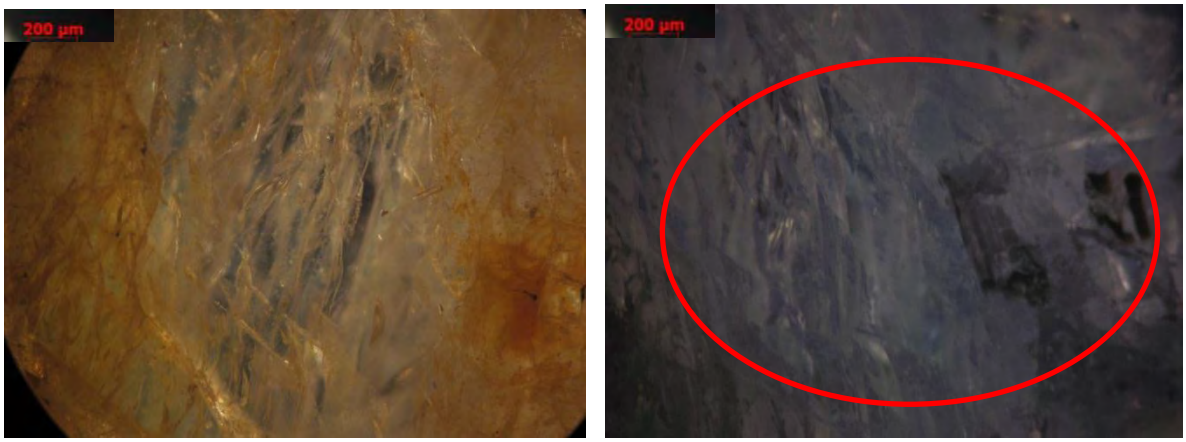
4.4 Modification of Internal Features

Internal features, such as fingerprints, dust, and some needles inclusions, were still remaining and some samples were turned to turbid because two phase inclusions were dispersed after heated under reduction and oxidation conditions. (see Figs.4.6, 4.9 and 4.11). However, some of rutile inclusions were disappeared in sample B1 and C1 after heat treatment. The samples were clearer and changes into blue color. (see Figs.4.5 and 4.7).



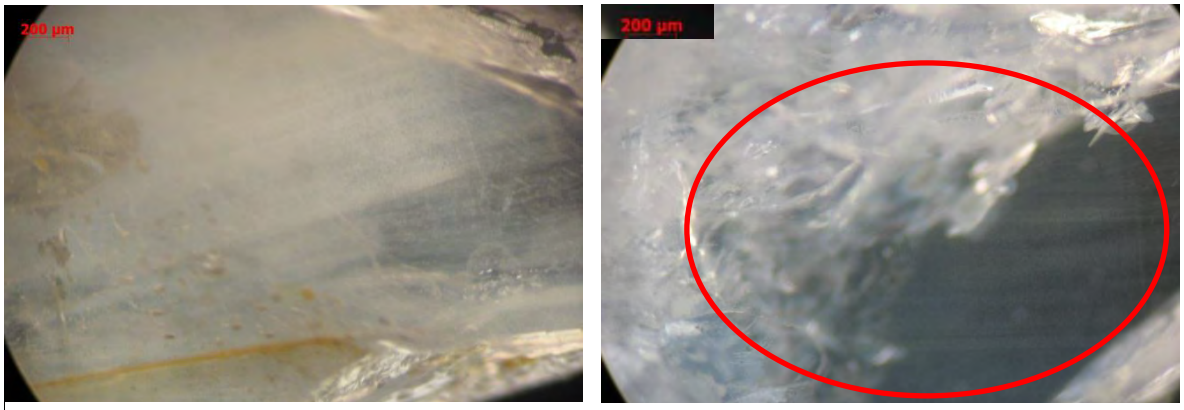
Before treatment After treatment under reducing condition

Fig.4.5 Deniyaya sapphire (B1) before and after heat-treatment in reducing atmosphere



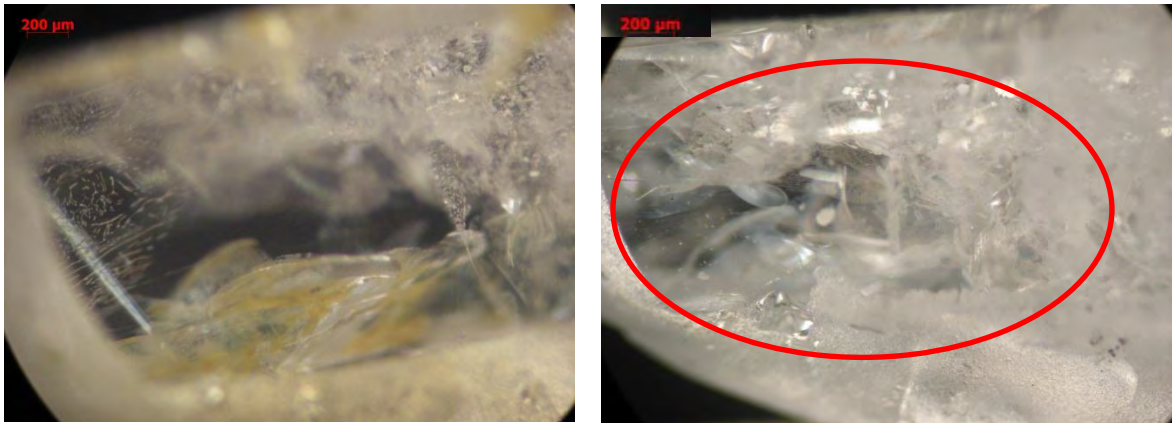
Before treatment After treatment under oxidizing condition

Fig.4.6 Deniyaya sapphires (B7) before and after heat-treatment in oxidizing atmosphere



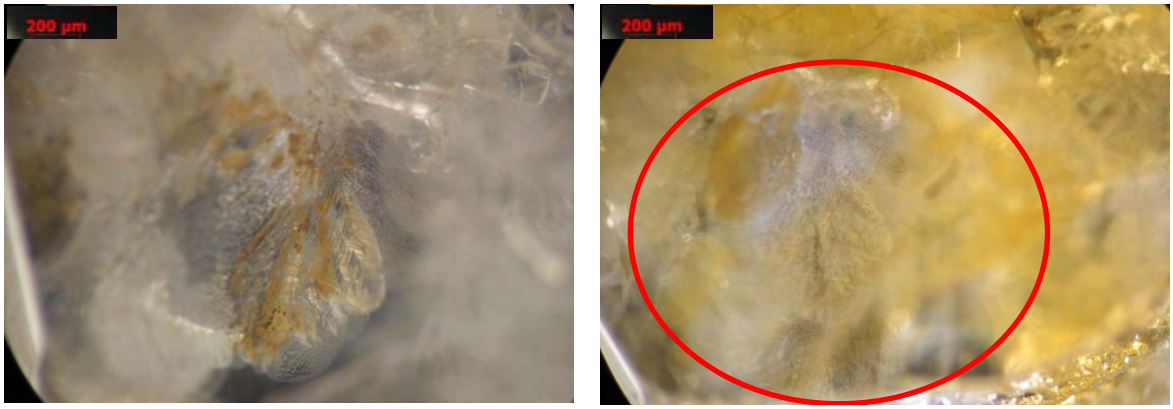
Before treatment After treatment under reducing condition

Fig.4.7 Deniyaya sapphires (C1) before and after heat-treatment in reducing atmosphere



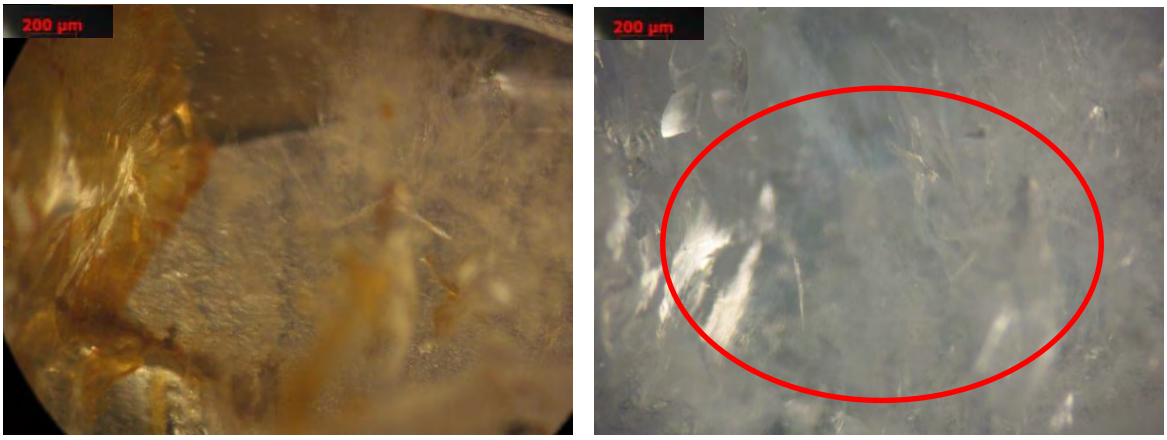
Before treatment After treatment under reducing condition

Fig.4.8 Deniyaya sapphires (C5) before and after heat-treatment in reducing atmosphere



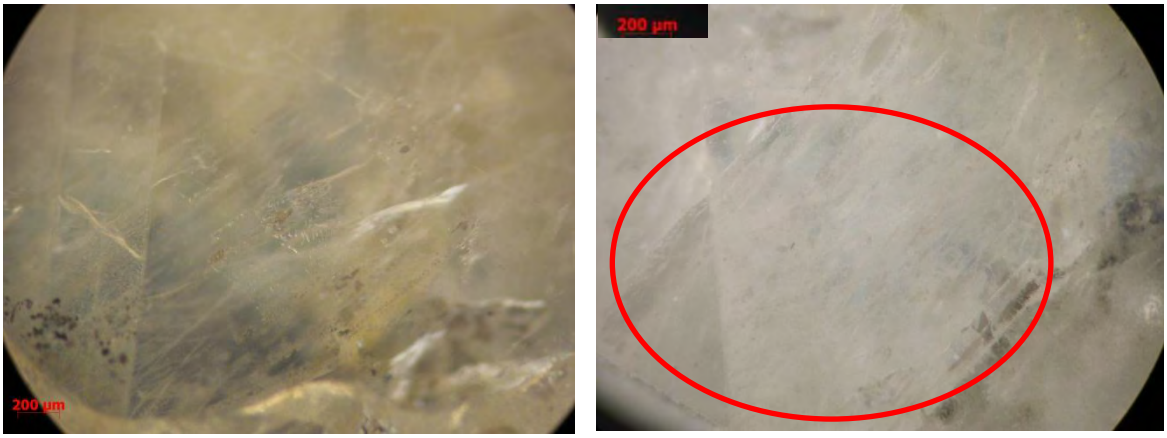
Before treatment After treatment under oxidizing condition

Fig.4.9 Deniyaya sapphires (C8) before and after heat-treatment in oxidizing atmosphere



Before treatment After treatment under reducing condition

Fig.4.10 Deniyaya sapphires (Y2) before and after heat-treatment in reducing atmosphere



Before treatment After treatment under oxidizing condition

Fig.4.11 Deniyaya sapphires (Y12) before and after heat-treatment in oxidizing atmosphere

4.5 UV-VIS-NIR Absorption Spectra

The UV-VIS-NIR absorption spectra were recorded between 250-1500 nm. The spectrum recorded after heat-treatment is compared with that before treatment and shown in Figs.4.12-4.16. Figures.4.12 and 4.13, these samples were changed to dark blue after heating at 1650˚C in reducing atmosphere. The absorption peaks were increased at Fe^{+3}/Fe^{+3} and Fe^{+2}/Ti^{+4} positions. On the other hand, some samples were changed to dark yellow after heating at 1650˚C in reducing atmosphere; their absorption peaks were increased at positions of Fe^{+3} and Fe^{+3}/Fe^{+3} (Fig.4.14). Figures.4.15-4.16 belong to colorless sapphires after heating at 1650˚C in reducing and oxidizing atmospheres. Their absorption peaks usually lower absorptions of Fe^{+3}, Fe^{+3}/Fe^{+3} and Fe^{+2}/Ti^{+4}.

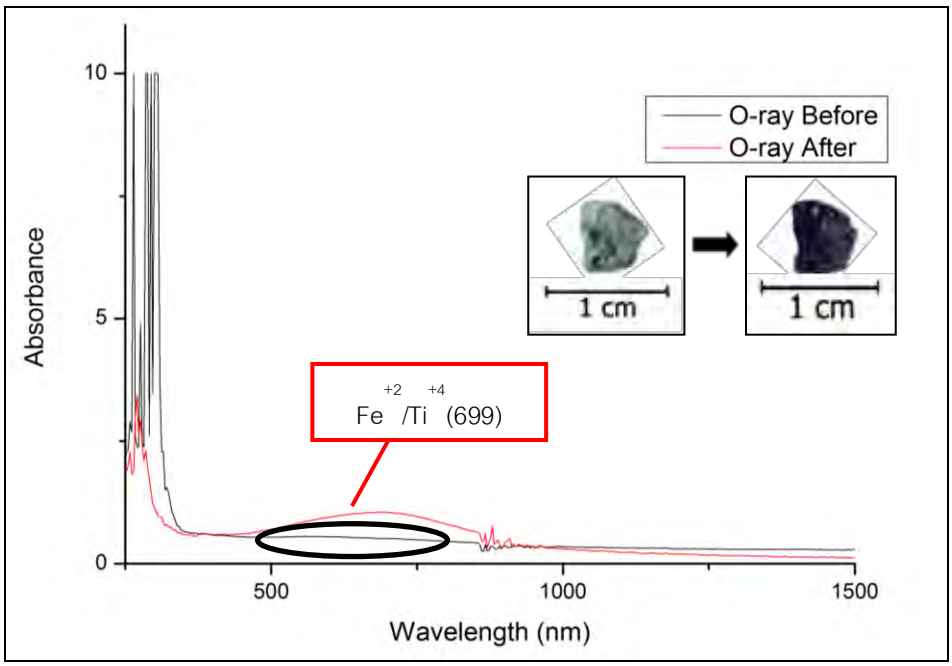


Fig.4.12 UV-VIS-NIR absorption spectra of sample B4, before and after heat-treatment in reducing atmosphere.

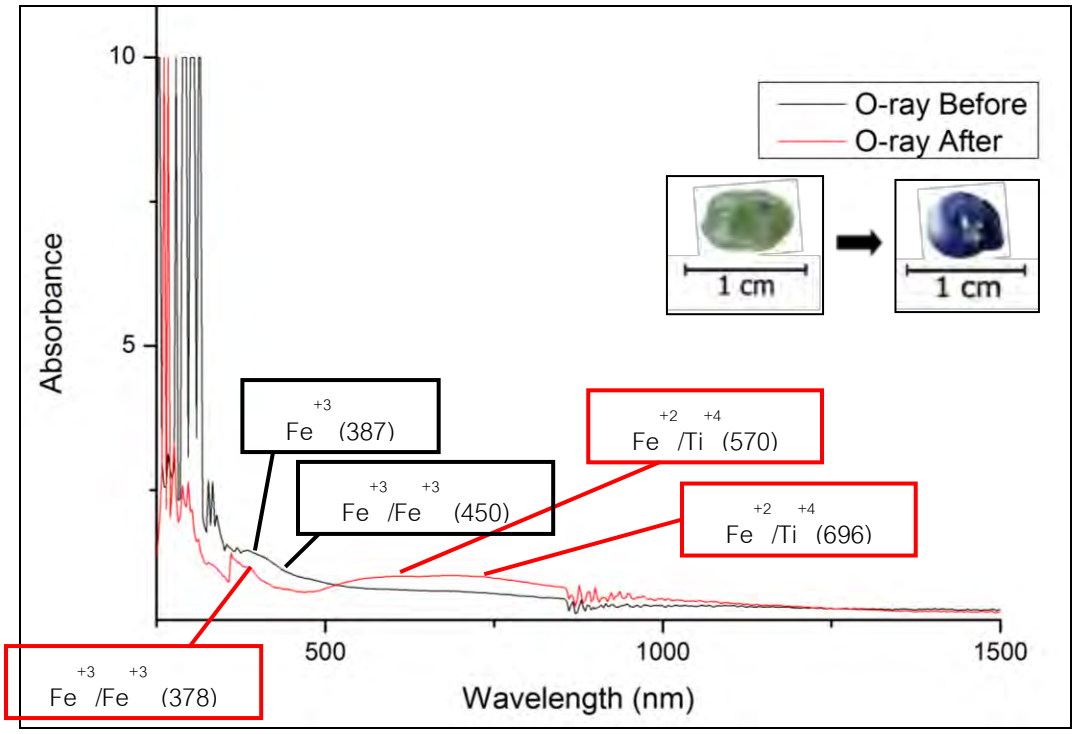


Fig.4.13 UV-VIS-NIR absorption spectra of sample B7, before and after heat-treatment in oxidizing atmosphere.

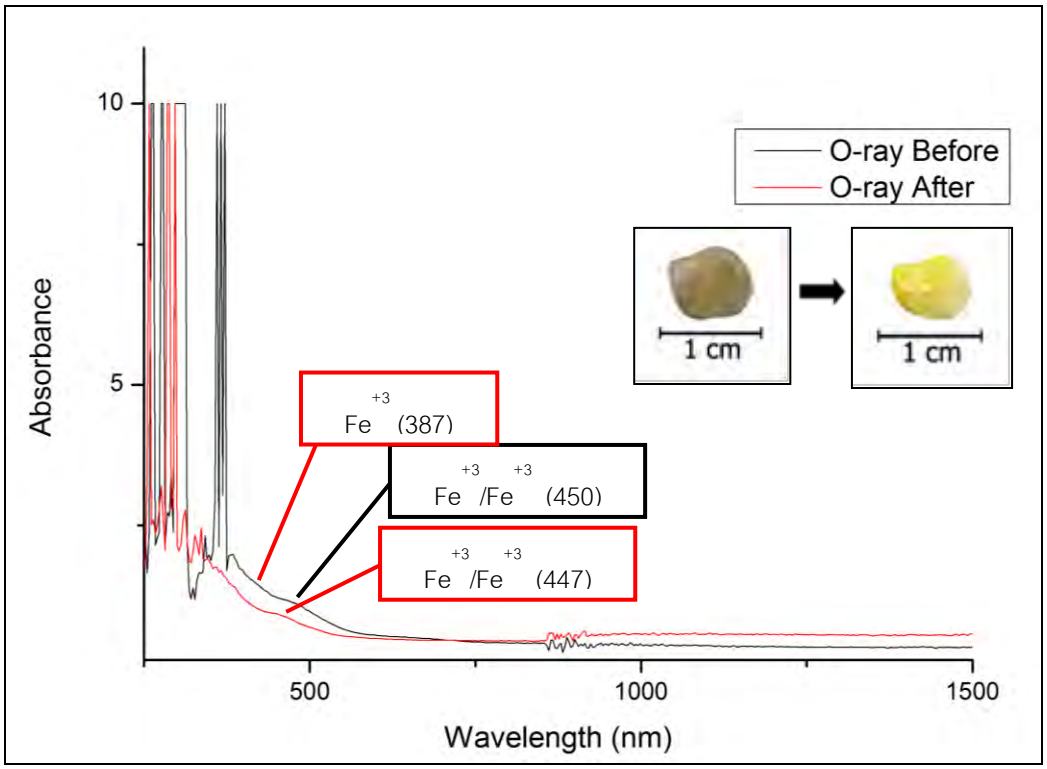


Fig.4.14 UV-VIS-NIR absorption spectra of sample Y8, before and after heat-treatment in oxidizing atmosphere.

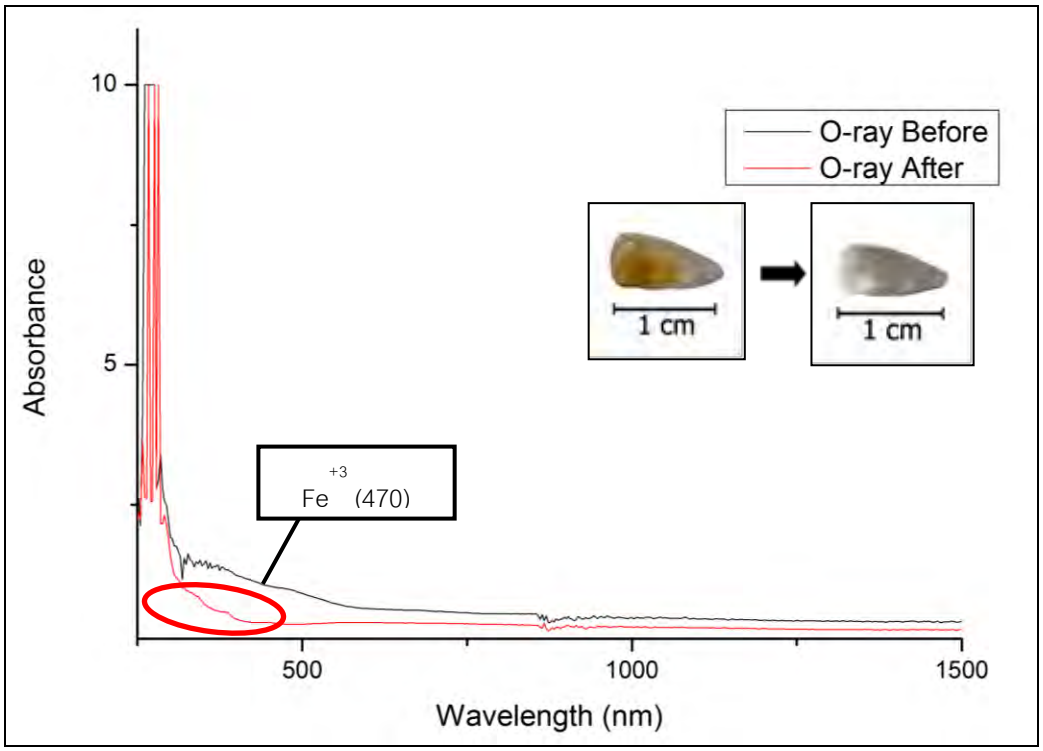


Fig.4.15 UV-VIS-NIR absorption spectra of sample Y2, before and after heat-treatment in reducing atmosphere

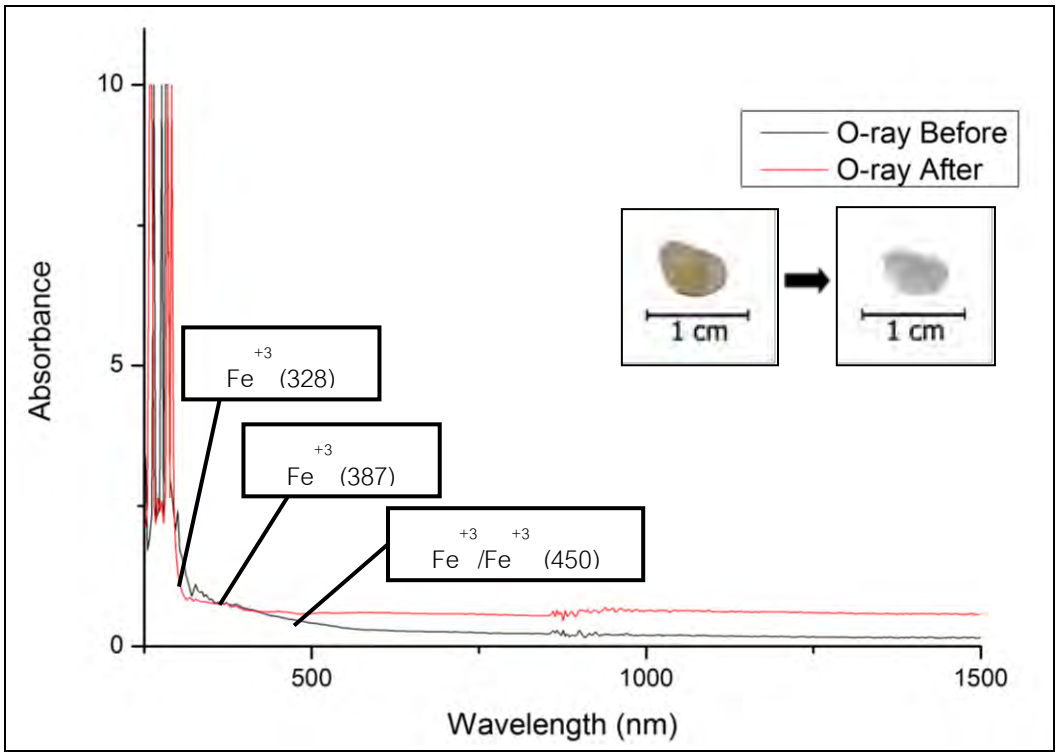


Fig.4.16 UV-VIS-NIR absorption spectra of sample Y10, before and after heat-treatment in oxidizing atmosphere

4.6 Fourier Transform Infraed (FTIR) Absorption Spectra

The spectra show similar pattern which representative spectra before and after heat treatment of some samples are displayed in Figs.4.17-4.20. After heat treatment, absorption patterns of AlOOH of all sapphires were disappeared. However, all samples still show absorption patterns of H_2O, CO_2, and CH-Stretching; besides, some samples show absorption peak of OH^- Stretching at 3309 cm^{-1}.

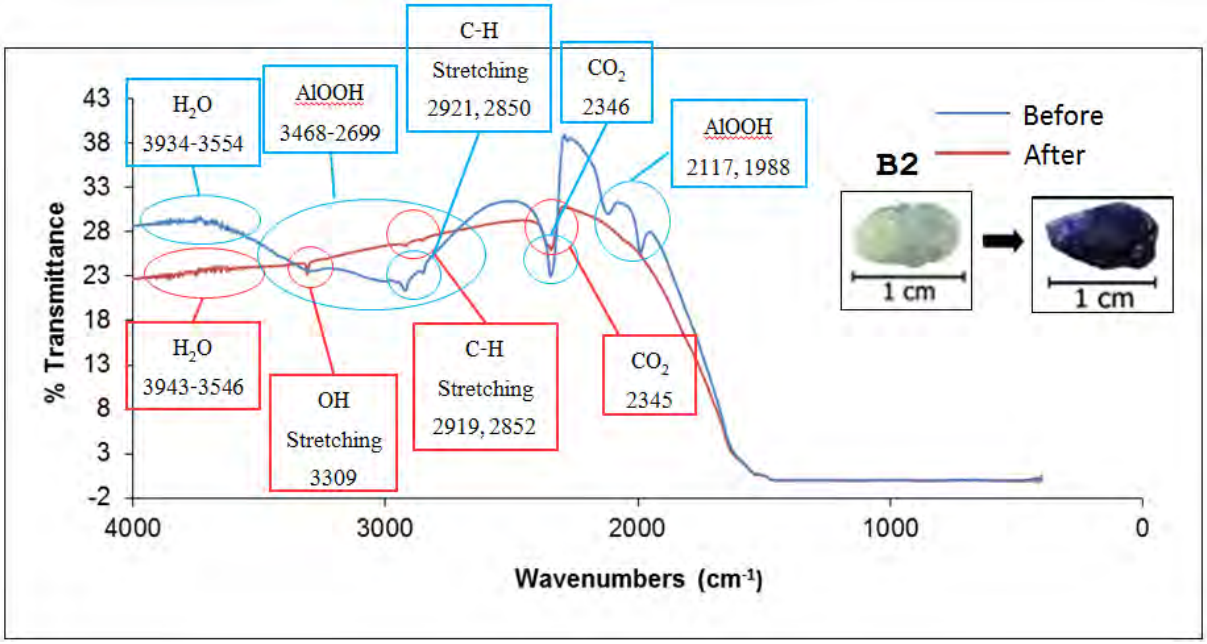


Fig.4.17 FTIR absorption spectra before and after treatment under reducing condition of sample B2.

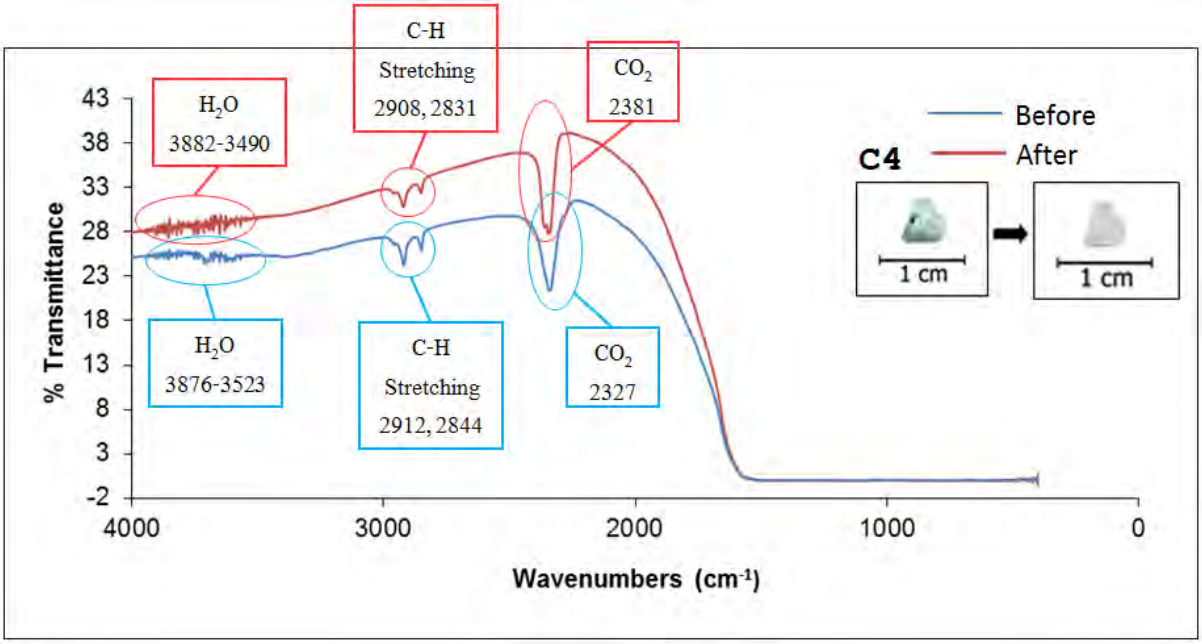


Fig.4.18 FTIR absorption spectram before and after treatment under reducing condition of sample C4.

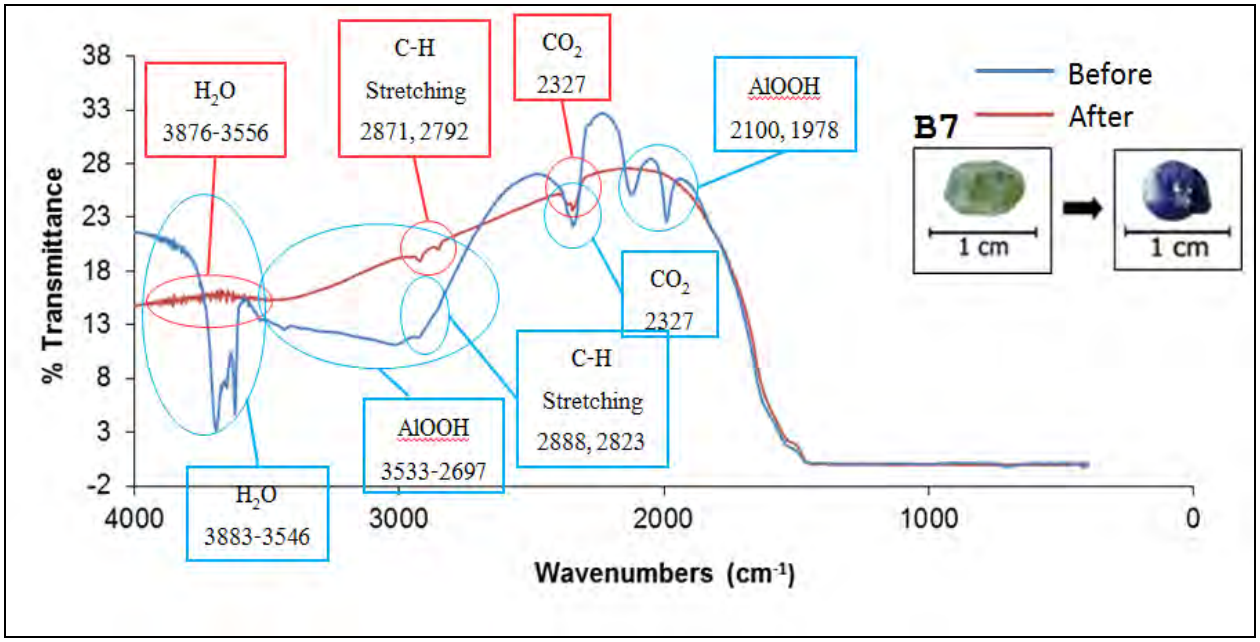


Fig.4.19 FTIR absorption spectra before and after treatment under oxidizing condition of sample B7.

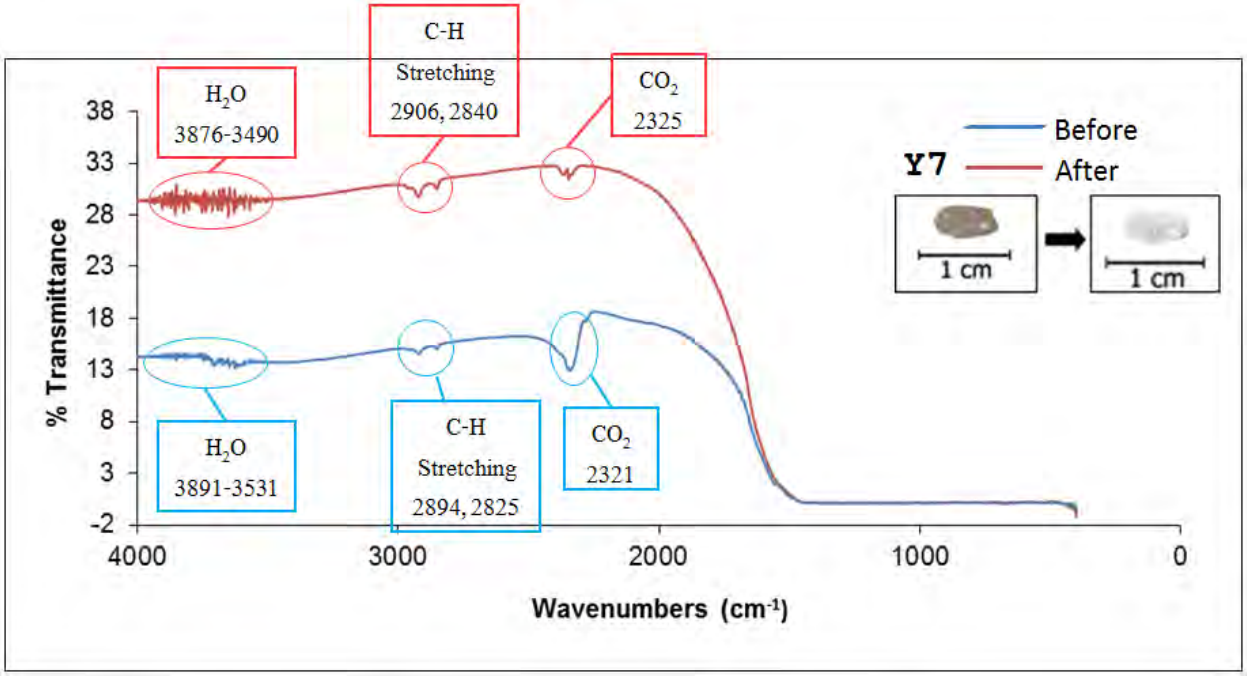


Fig.4.20 FTIR absorption spectra before and after treatment under oxidizing condition of sample Y7.

CHAPTER V
DISCUSSION AND CONCLUSIONS

5.1 Cause of Color Change after Heat Treatment

The heat treatment at 1650ºC under reducing condition of colorless, light blue and light yellow appear to produce blue color. Blue color in sapphires samples are caused by intervalence transition between Fe^{2+} and Ti^{4+} replacing Al^{3+} in adjacent octahedral sites and the Fe^{2+}/Fe^{3+} charge transfer.

$$Fe_2O_3 + N_2 \longrightarrow 2FeO + N_2O \quad \text{; Reduction atmosphere (Nitrogen gas)}$$

$$Fe^{2+} + Ti^{4+} \rightleftharpoons Fe^{3+} + Ti^{3+} \quad \text{; Charge transfer process}$$

Moreover, natural inclusions of rutile (TiO_2) in sapphires can be dissolved at high temperature around 1600 ºC. Thus, there are more titanium contents to react with iron in charge transfer process.

$$TiO_2 + (Al^{3+},Fe^{3+})_2O_3 \longrightarrow (Al^{3+}, Ti^{4+},Fe^{2+})_2O_3$$

rutile colorless sapphires blue sapphires

On the other hand, heat treatment at 1650ºC under oxidizing condition of colorless, light blue and light yellow trend to produce yellow and blue color.

$$2FeO + O_2 \longrightarrow Fe_2O_3 \quad \text{; Oxidation atmosphere (Oxygen gas)}$$

Yellow color in sapphires samples are caused by color centers which is the interaction of Mg, Ti and Fe in sapphires. Mg and Ti are usually from colorless $MgTiO_3$ clusters. The excess of Mg after the calculation of $MgTiO_3$ clusters will lead in combination with Fe form $MgFeO_3$ clusters to produce stable yellow color center. On the other hand, the excess of Ti in combination with Fe could form color active $FeTiO_3$ clusters to produce the blue color (Häger, 2001).

Atomic proportions of Mg, Ti and Fe were normalized into 100% and plotted in triangular diagram of heat treating model in reducing and oxidizing atmospheres proposed by Häger (2001). All analyses of individual blue and yellow sapphires are plotted in Figs.5.1 and 5.3.

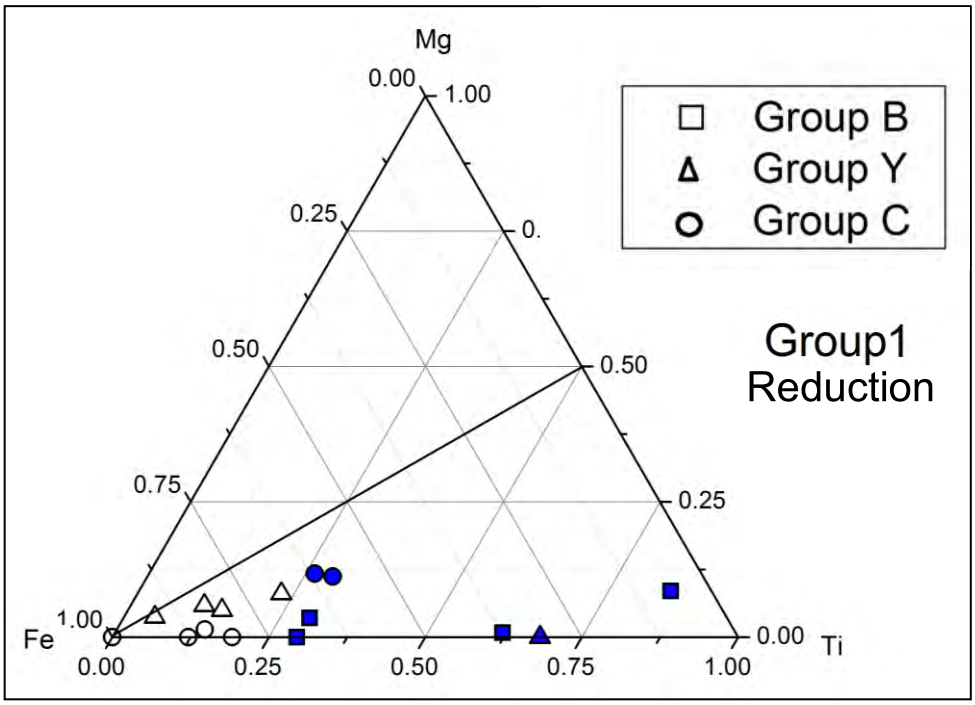


Fig.5.1 Triangular diagram showing atomic proportion between Mg, Fe, and Ti of Deniyaya sapphires Group 1. The analyses were performed using EPMA after heating at 1650˚C under reducing condition

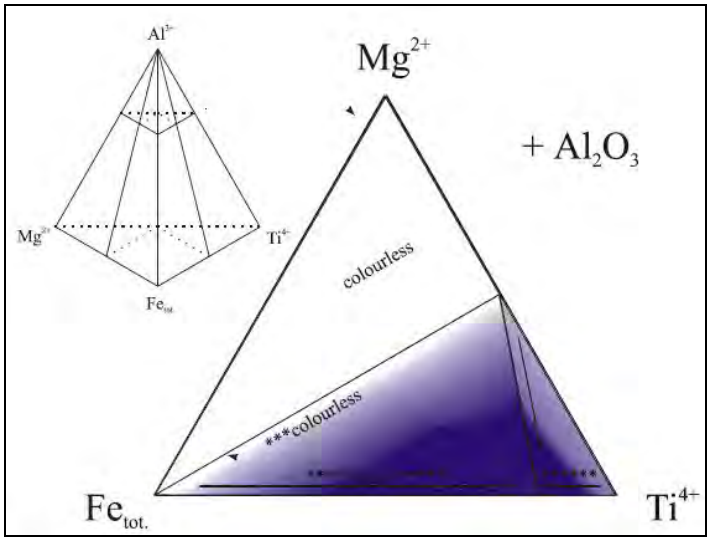


Fig.5.2 Model of sapphires heated at 1750ºC inreducing atmospheres (Häger, 2001)

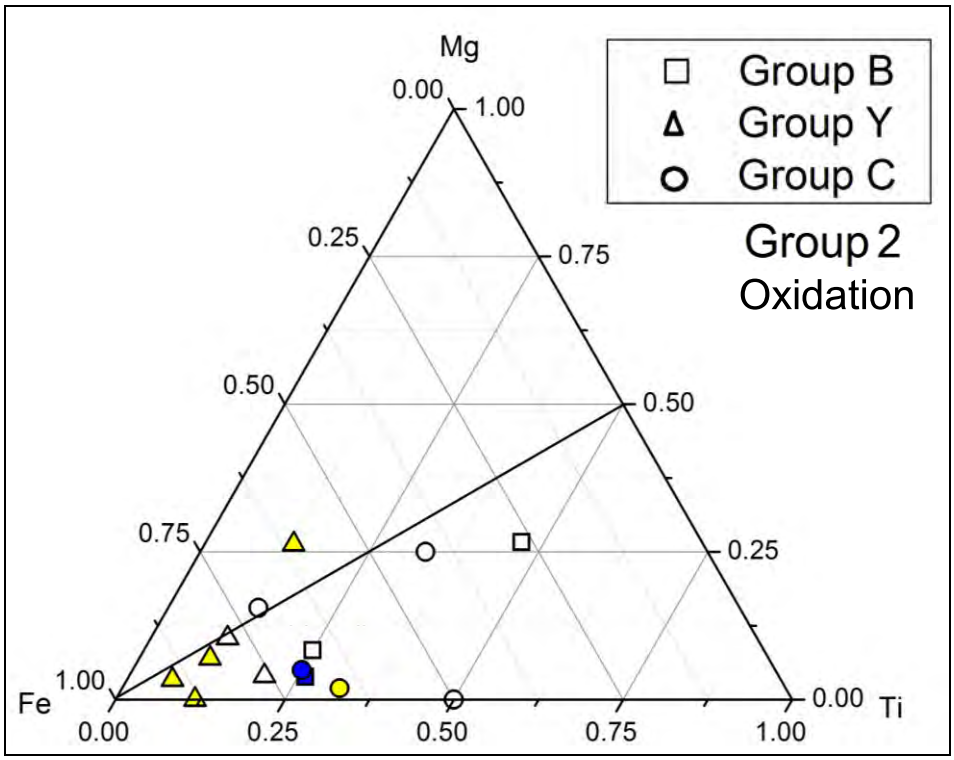


Fig.5.3 Triangular diagram showing atomic proportion of Mg, Fe, and Ti of Deniyaya sapphires Group 2. The analyses were performed using EPMA after heating at 1650˚C under oxidizing condition.

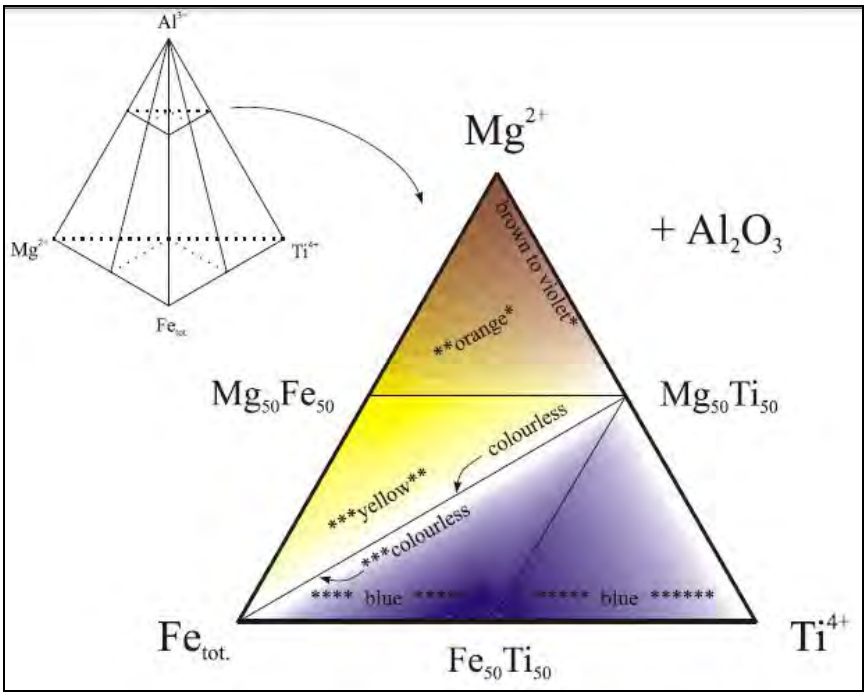


Fig.5.4 Model of sapphires heated at 1850ºC in oxidizing atmospheres (Häger, 2001).

5.2 Conclusions

1. Deniyaya sapphires samples were classified into 3 groups, based on the color shade, such as blue, yellow, and colorless. Luminescences of the samples under ultraviolet lamp are inert to moderate under long wave and mostly inert under short wave.
2. The most common inclusions are fingerprints, small rutile needles, cloud and dust. Mineral inclusions are apatite and rutile.
3. The samples were divided for heating into two conditions, i.e., reduction and oxidation atmospheres, at 1650ºC for five hours soaking times. The blue color was appeared to be increased in both reduction and oxidation conditions whereas yellow color seems to be intensified only in oxidizing condition. Rutile inclusions in some samples were dissolvedand disappeared after heated under reduction condition. The samples were clearer and changes into blue color. But some samples were turned to turbid because two phase inclusions were dispersed after heated under reduction and oxidation conditions.
4. FTIR spectra of several samples show the similar tendency. After heat-treatment, AlOOH absorption is mostly disappeared, because AlOOH may be changed to Al_2O_3 in both conditions. Some spectra show OH-Stratching peak at 3309 cm^{-1}. Therefore, it may be a crucial evidence of heated sapphires.
5. The UV-VIS-NIR Spectra show the absorption peaks at 387 nm are related Fe^{3+} and at 565 and 697 nm are related Fe^{2+}/Ti^{4+} for blue color. Yellow color shows the absorption peaks at 374, 377, and 450 nm mostly related to Fe^{3+}/Fe^{3+}.
6. The chemical analysis based on EDXRF, blue color group has the highest average titanium concentration and the iron content of yellow group is the highest. The EPMA analysis reveals that the interaction of Mg, Ti and Fe in sapphires is the cause of color.
7. In conclusion, Deniyaya sapphires have potential for thermal enhancement at 1650ºC under both reduction and oxidation condition. Most sapphires may be turned into dark blue and yellow.

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APPENDIX A

A.1 Basic gemological properties of Deniyaya sapphires before heat-treatment

Table A1: Basic properties of rough sapphires from Deniyaya, Sri lanka Group B before heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	B1	2.395	1.770	1.761	0.009	3.977	B2/2	Inert	Inert	Y2/2+cl
2	B2	2.980	1.770	1.762	0.008	3.944	B3/1	Weak	Weak	
3	B3	0.700	1.771	1.762	0.009	3.938	bV2/3	Inert	Inert	
4	B4	0.850	1.770	1.763	0.007	3.855	B2/2	Inert	Inert	
5	B5	2.705	1.771	1.762	0.009	3.976	B2/2	Inert	Inert	Cloud
6	B6	1.620	1.770	1.762	0.008	3.980	B2/2	Inert	Inert	
7	B7	1.480	1.770	1.761	0.009	3.863	VsigB2/2	Inert	Inert	

Table A2: Basic properties of rough sapphires from Deniyaya, Sri lanka Group C before heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	C1	1.125	1.778	1.760	0.008	4.003	colorless	Weak	Weak	
2	C3	1.075	1.770	1.762	0.008	3.958	colorless	Inert	Moderate	
3	C4	0.660	1.770	1.762	0.008	3.963	colorless	Weak	Weak	
4	C5	1.260	1.768	1.760	0.008	3.985	colorless	Inert	Moderate	
5	C6	1.430	1.770	1.762	0.008	3.970	colorless	Inert	Moderate	
6	C7	0.690	1.770	1.763	0.007	3.874	colorless	Inert	Moderate	
7	C8	3.140	1.770	1.762	0.008	3.872	colorless	Inert	Weak	
8	C9	2.360	1.768	1.760	0.008	3.944	colorless	Weak	Weak	Cloud+Y2/2
9	C10	2.540	1.770	1.762	0.008	3.974	colorless	Inert	Inert	Y2/2
10	C11	4.130	1.770	1.762	0.008	3.969	colorless	Inert	Moderate	
11	C12	1.930	1.770	1.762	0.008	3.960	colorless	Weak	Moderate	

Table A3: Basic properties of rough sapphires from Deniyaya, Sri lanka Group Y before heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	Y2	2.76	1.770	1.762	0.008	3.970	Y3/3	Inert	Weak	
2	Y3	2.910	1.770	1.763	0.007	3.972	Y3/5	Inert	Weak	
3	Y4	2.645	1.773	1.765	0.008	3.966	Y2/3	Inert	Inert	
4	Y5	2.835	1.768	1.760	0.008	3.970	Y2/2	Inert	Inert	
5	Y6	1.560	1.770	1.762	0.008	3.942	Y2/2	Weak	Weak	cl
6	Y7	0.955	1.770	1.763	0.007	4.002	Y2/2	Weak	Weak	cl
7	Y8	2.295	1.768	1.760	0.008	3.934	Y2/3	Inert	Moderate	B3/1
8	Y9	1.915	1.770	1.760	0.010	3.970	Y2/2	Weak	Weak	cl
9	Y10	1.340	1.770	1.762	0.008	3.990	Y3/3	Inert	Weak	cl
10	Y11	3.170	1.769	1.760	0.009	3.921	Y2/2	Weak	Weak	cl
11	Y12	2.285	1.768	1.760	0.008	3.981	Y2/2	Inert	Inert	

A.2 Basic gemological properties of Deniyaya sapphires after heat-treatment

Table A4: Basic properties of rough sapphires from Deniyaya, Sri lanka Group B after heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	B1	2.303	1.768	1.759	0.009	3.947	vB5/3	Strong	Moderate	B2/2+B3/1
2	B2	2.880	1.770	1.758	0.012	3.958	bV8/3	Moderate	Weak	
3	B3	0.650	1.771	1.758	0.013	3.896	B8/3	Weak	Weak	
4	B4	0.791	1.772	1.762	0.010	3.848	B3/4	Strong	Weak	
5	B5	2.642	1.773	1.762	0.011	3.942	B3/3	Moderate	Weak	Cloud
6	B6	1.602	1.770	1.763	0.007	3.910	B3/1	Moderate	Weak	
7	B7	1.428	1.768	1.757	0.011	3.947	B4/2	Strong	Moderate	

Table A5: Basic properties of rough sapphires from Deniyaya, Sri lanka Group C after heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	C1	1.100	1.769	1.759	0.010	3.962	B3/3	Strong	Strong	
2	C3	1.024	1.769	1.760	0.009	3.943	colorless	Weak	Weak	
3	C4	0.644	1.766	1.759	0.007	3.930	colorless	Moderate	Moderate	
4	C5	1.239	1.769	1.760	0.009	3.909	colorless	Moderate	Weak	Cloud
5	C6	1.462	1.768	1.760	0.008	3.933	vB3/3	Strong	Moderate	
6	C7	0.667	1.772	1.765	0.007	3.959	B3/3	Strong	Moderate	cl
7	C8	3.040	1.770	1.761	0.009	3.911	Y4/5	Moderate	Moderate	Cloud
8	C9	2.288	1.769	1.762	0.007	3.971	B3/1	Strong	Weak	Cloud
9	C10	2.441	1.770	1.760	0.010	3.940	B2/2	Strong	Moderate	Cloud
10	C11	4.006	1.767	1.759	0.008	3.954	colorless	Moderate	Weak	
11	C12	1.864	1.768	1.761	0.007	3.956	colorless	Moderate	Moderate	

Table A6: Basic properties of rough sapphires from Deniyaya, Sri lanka Group Y after heat-treatment

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
1	Y2	2.525	1.768	1.760	0.008	3.944	Cl	Moderate	Moderate	Cloud
2	Y3	2.449	1.768	1.759	0.009	3.968	B3/3+cl	Strong	Moderate	
3	Y4	1.364	1.769	1.761	0.008	3.950	cl+B2/2	Weak	Weak	
4	Y5	2.696	1.771	1.759	0.012	3.932	vB4/4	Weak	Weak	
5	Y6	1.377	1.768	1.759	0.009	3.910	Cl	Strong	Strong	
6	Y7	0.556	1.769	1.760	0.009	4.030	cl	Weak	Weak	
7	Y8	2.401	1.768	1.759	0.009	3.957	cl+Y4/5	Moderate	Weak	
8	Y9	1.416	1.768	1.760	0.008	3.917	Y4/5	Moderate	Weak	

No.	sample I.D.	Weight (ct)	RI		Birefringence	SG	Color	Fluorescence		REMARK
			n_o	n_e				SW	LW	
9	Y10	1.179	1.769	1.760	0.009	3.938	cl+B3/1	Strong	Weak	
10	Y11	2.999	1.769	1.761	0.008	3.886	Y3/5	Moderate	Moderate	Cl
11	Y12	1.857	1.768	1.760	0.008	3.949	Cl	Strong	Moderate	Cloud

A.3 29 Samples of Deniyaya Sapphires, Sri Lanka

Table A7: Rough sapphires sample from Deniyaya, Sri lanka Group B, before and after treatment

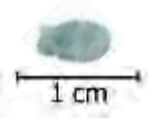
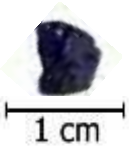
Sample	Before heat-treatment	After heat-treatment
B1		
B2		
B3		
B4		
B5		
B6		
B7		

Table A8: Rough sapphires sample from Deniyaya, Sri lanka Group C, before and after treatment

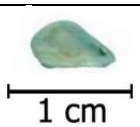
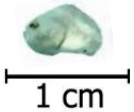
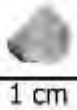
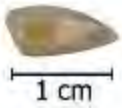
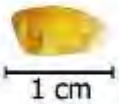
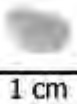
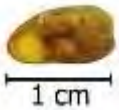
Sample	Before enhance	After enhance
C1		
C3		
C4		
C5		
C6		
C7		
C8		
C9		
C10		
C11		
C12		

Table A8: Rough sapphires sample from Deniyaya, Sri lanka Group C, before and after treatment

Sample	Before enhance	After enhance
Y2		
Y3		
Y4		
Y5		
Y6		
Y7		
Y8		
Y9		
Y10		
Y11		
Y12		

A.4 Internal characteristics before heat-treatment

Fig.A1 Fingerprints and cloud (sample B1)

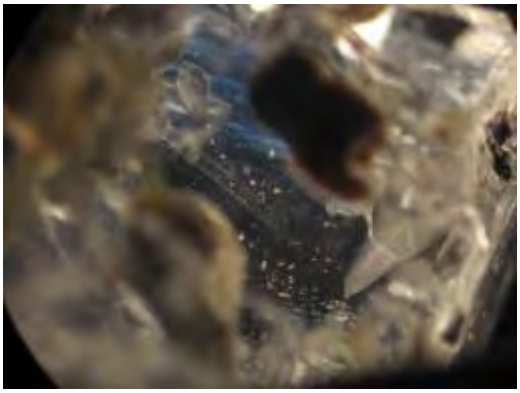


Fig.A2 small needles (sample B4)

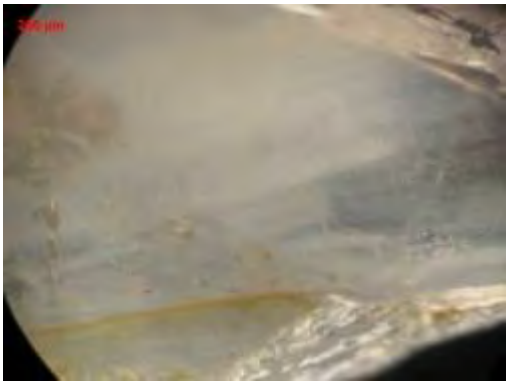


Fig.A3 Cloud and small rutiles (sample C1)

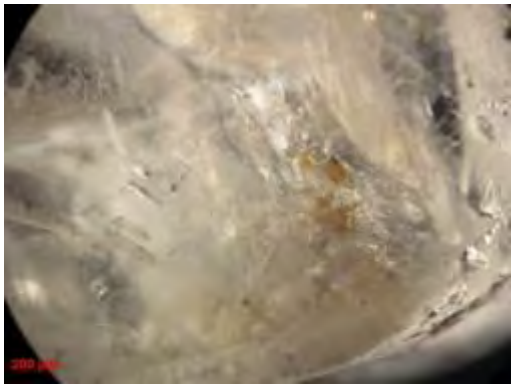


Fig.A4 Negative crystals (sample C3)

Fig.A5 Fingerprints (sample C4)

Fig.A6 small needles (sample C7)

Fig.A7 Fingerprints (sample C8)

Fig.A8 Needle inclusions and fingerprints (sample C8)

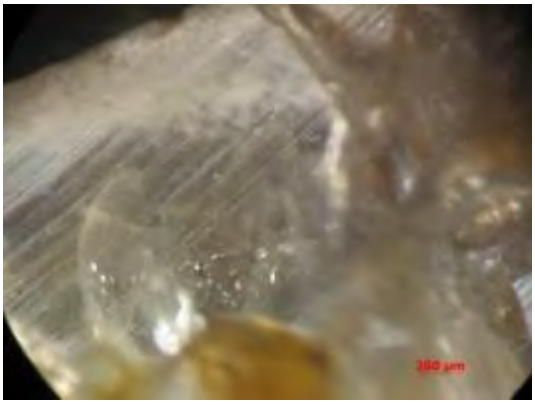


Fig.A9 Needle inclusions

(sample Y3)

Fig.A10 Negative crystals and cloud

(sample Y4)

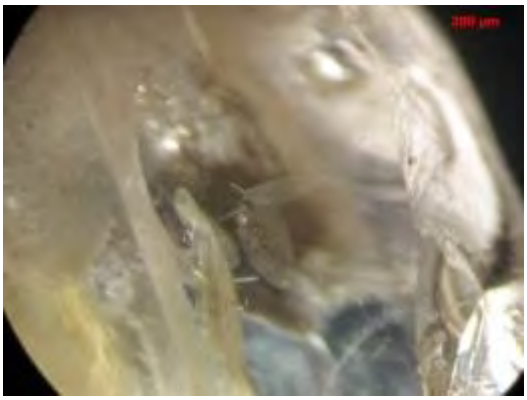


Fig.A11 Fingerprints (sample Y4)

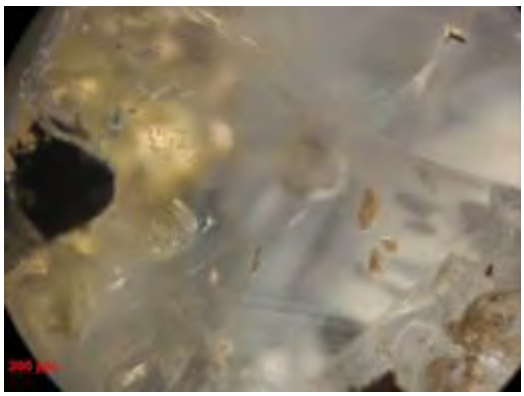
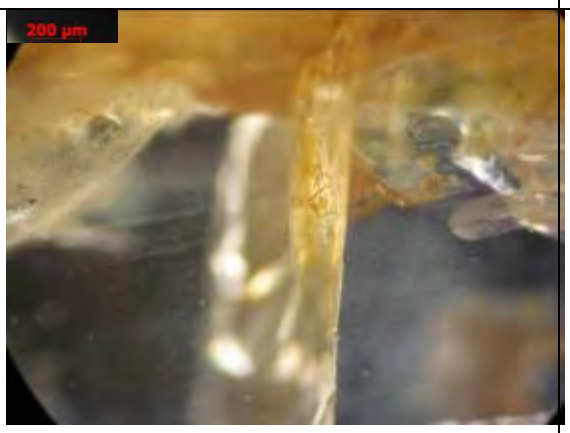
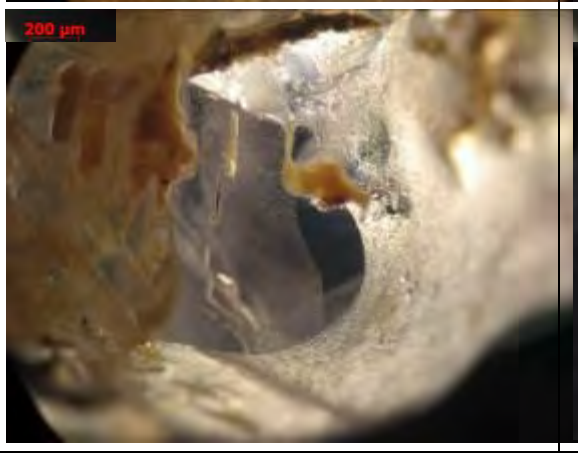
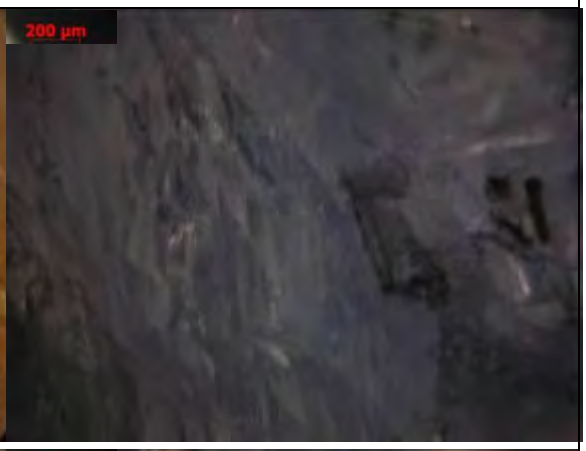
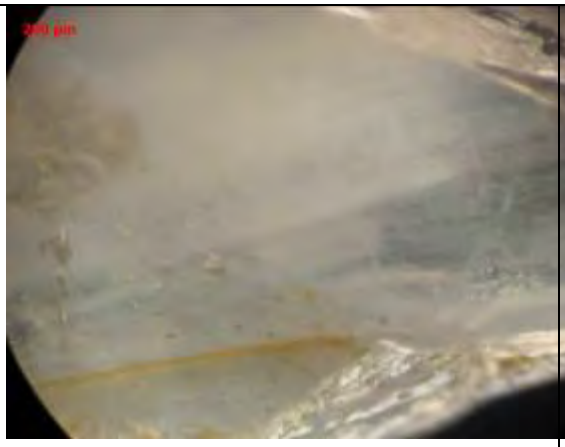
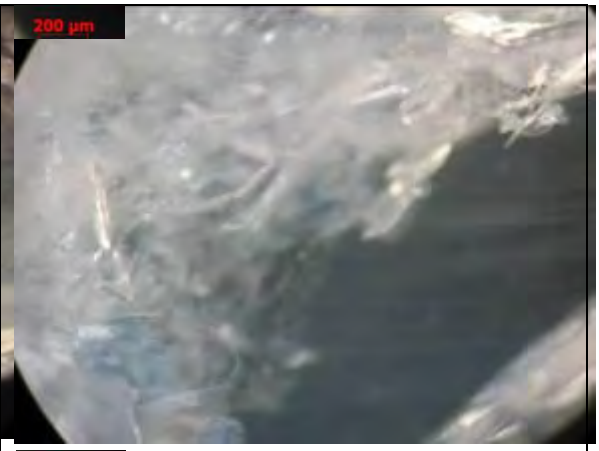
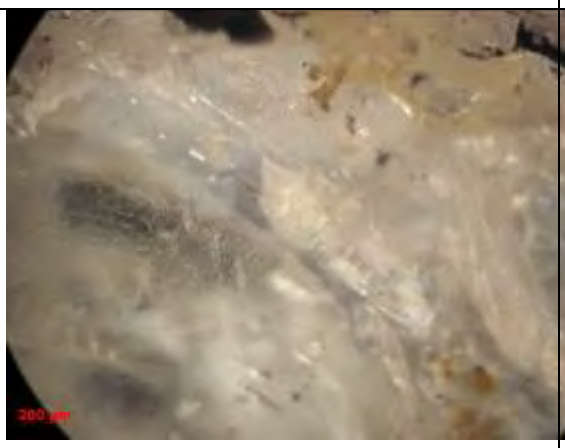
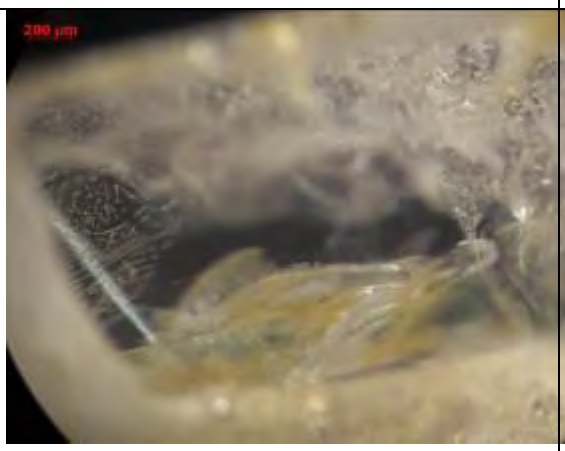


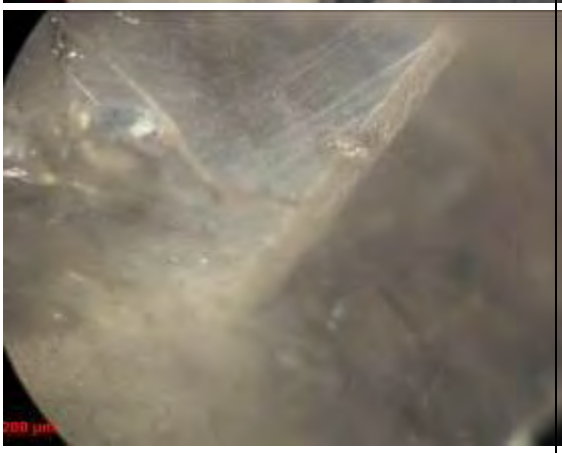
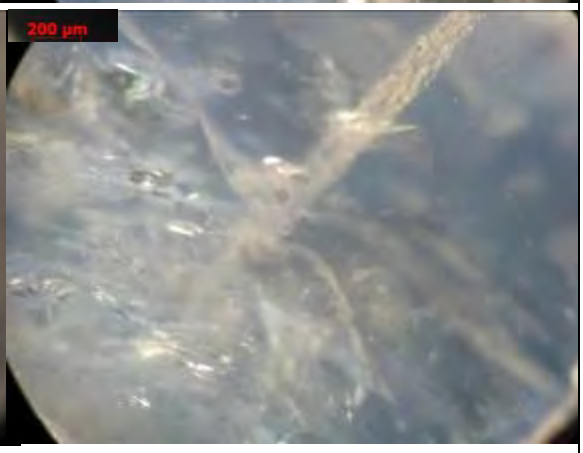
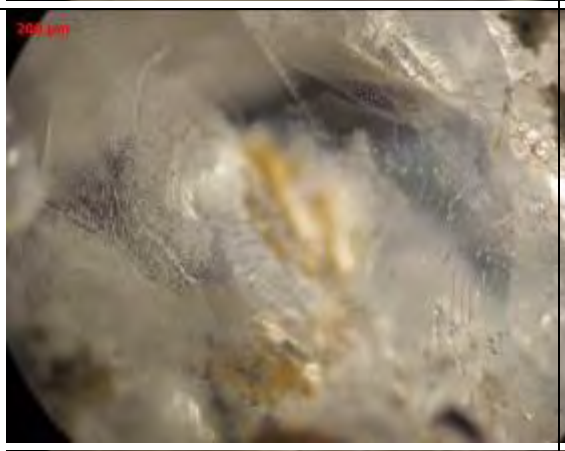
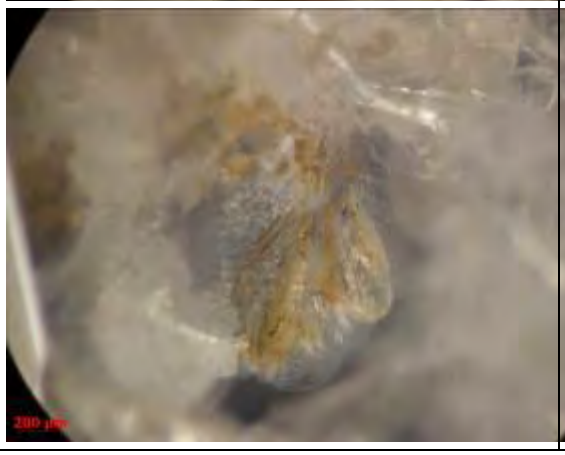
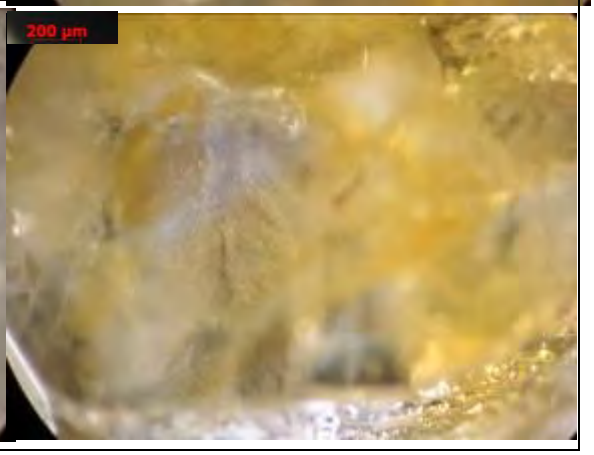
Fig.A12 Fingerprints, rutiles

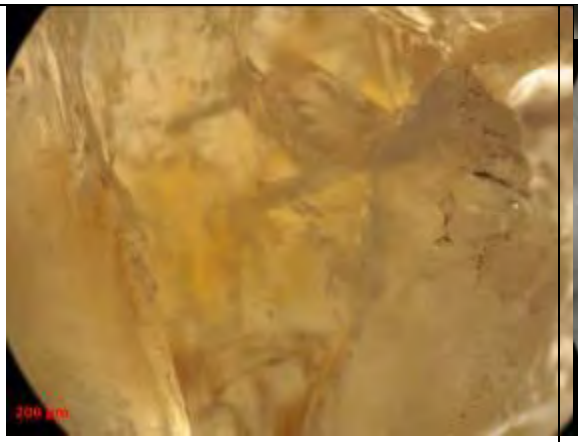
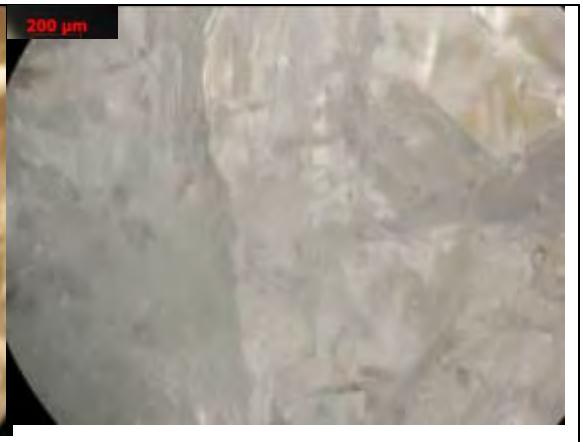
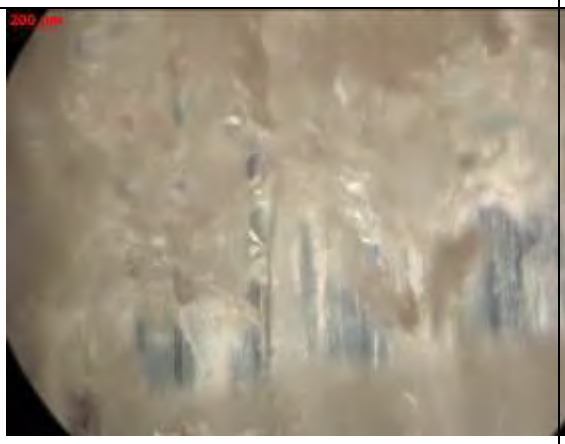
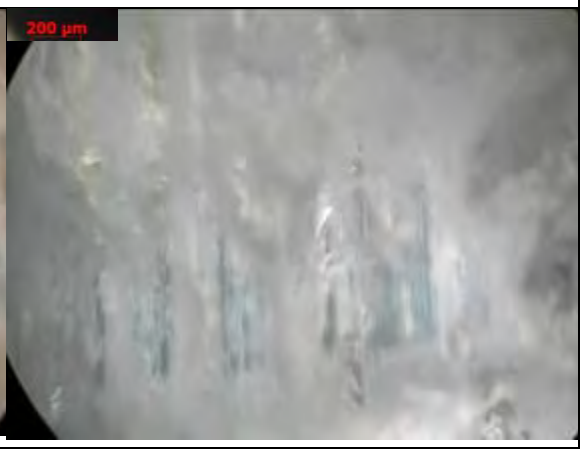
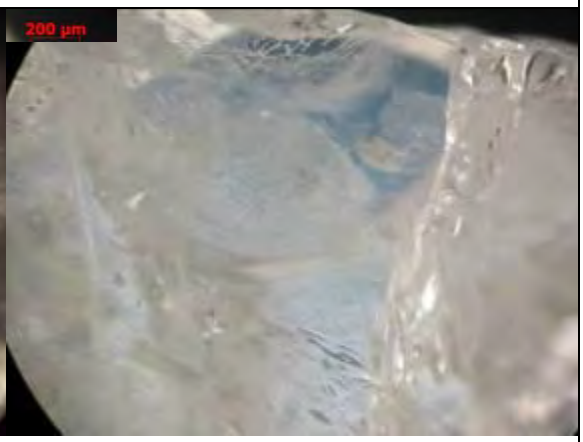
and fractures (sample Y8)

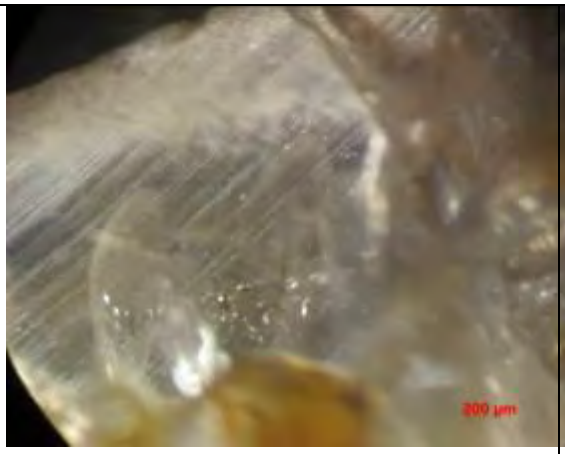
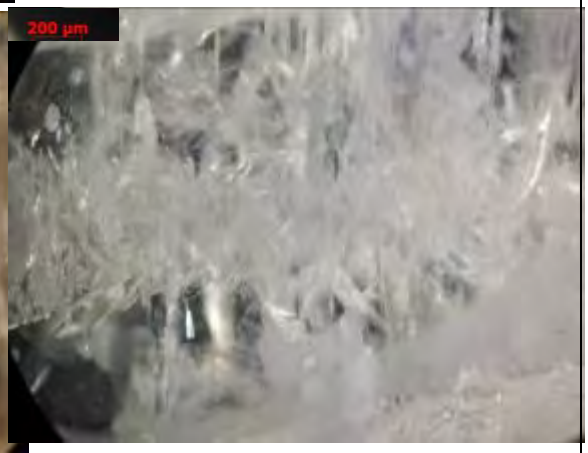
A.5 Internal characteristics before and after heat-treatment

Sample	Before heat-treatment	After heat-treatment
B1		
B7	 	 

C1		
C3		
C5		
C6		

C7		
		
C8		
		

C9		
C11		
C12		
Y2		

Y3		
Y6		
		
Y12		

APPENDIX B

B.1 Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry

Summary of chemical contents of 29 rough samples of Deniyaya sapphires that were analyzed by EDXRF (EAGLE III) displayed in Table B1.

Table B1: Chemical contents of 29 rough samples of Deniyaya sapphires

Sample Number	Al_2O_3 (wt%)	TiO_2 (wt%)	V_2O_5 (wt%)	Cr_2O_3 (wt%)	Fe_2O_3 (wt%)	Ga_2O_3 (wt%)
B1	99.754	0.094	0.036	0.011	0.098	0.008
B2	99.698	0.220	0.020	0.002	0.042	0.018
B3	99.691	0.074	0.016	0.008	0.190	0.022
B4	99.615	0.179	0.014	0.004	0.164	0.023
B5	99.847	0.057	0.011	0.000	0.064	0.020
B6	99.738	0.044	0.012	0.004	0.188	0.014
B7	99.636	0.078	0.021	0.012	0.241	0.014
C1	99.603	0.146	0.006	0.007	0.220	0.019
C2	99.771	0.023	0.014	0.011	0.149	0.032
C3	99.836	0.039	0.015	0.021	0.082	0.007
C4	99.768	0.037	0.000	0.000	0.155	0.040
C5	99.727	0.026	0.019	0.012	0.150	0.066
C6	99.727	0.036	0.014	0.006	0.201	0.016
C7	99.606	0.095	0.044	0.023	0.213	0.019
C8	99.720	0.058	0.028	0.013	0.149	0.032
C9	99.810	0.058	0.008	0.007	0.095	0.024
C10	99.819	0.034	0.005	0.004	0.104	0.035
C11	99.741	0.036	0.000	0.000	0.142	0.080
C12	99.900	0.016	0.004	0.000	0.054	0.027
Y1	99.808	0.066	0.006	0.005	0.109	0.006
Y2	99.714	0.029	0.016	0.008	0.216	0.017
Y3	99.283	0.080	0.013	0.009	0.585	0.030
Y4	99.742	0.107	0.020	0.013	0.102	0.016
Y5	99.836	0.023	0.014	0.000	0.117	0.009

Sample Number	Al_2O_3 (wt%)	TiO_2 (wt%)	V_2O_5 (wt%)	Cr_2O_3 (wt%)	Fe_2O_3 (wt%)	Ga_2O_3 (wt%)
Y6	99.764	0.062	0.020	0.022	0.127	0.007
Y7	99.837	0.018	0.022	0.020	0.081	0.022
Y8	99.912	0.032	0.000	0.016	0.028	0.012
Y9	99.824	0.012	0.015	0.007	0.133	0.010
Y10	99.728	0.049	0.035	0.004	0.159	0.025
Y11	99.496	0.141	0.013	0.014	0.279	0.056
Y12	99.675	0.027	0.030	0.017	0.227	0.026
Mean	99.730	0.064	0.016	0.009	0.157	0.024
Min	99.283	0.012	0.000	0.000	0.028	0.006
Max	99.912	0.220	0.044	0.023	0.585	0.080
SD	0.124	0.050	0.011	0.007	0.101	0.017

APPENDIX C

C.1 Electron Probe Micro-Analysis (EPMA)

The rough samples of Deniyaya sapphires were analyzed for quantitative analysis by EPMA and content oxides by weight of the major and trace element are summarized in Tables C1-C3.

Table C1: Quantitative analysis by EPMA of Deniyaya sapphires, Group B

Sample	B1	B2	B3	B4	B5	B6	B7
Comment	B5-2	B6-5	B1-3	B2-3	B3-1	D3-3	B4-1
Al_2O_3	99.84	99.77	99.61	100.08	100.08	99.73	99.64
SiO_2	0.02	0.00	0.01	0.00	0.01	0.01	0.00
TiO_2	0.06	0.32	0.07	0.13	0.01	0.06	0.05
Cr_2O_3	0.02	0.01	0.02	0.01	0.00	0.01	0.00
V_2O_3	0.01	0.01	0.00	0.00	0.00	0.02	0.04
Ga_2O_3	0.00	0.02	0.07	0.05	0.00	0.00	0.00
FeO	0.11	0.04	0.19	0.03	0.04	0.06	0.19
MgO	0.00	0.03	0.02	0.00	0.00	0.02	0.02
MnO	0.00	0.00	0.00	0.00	0.01	0.03	0.00
K_2O	0.00	0.01	0.00	0.01	0.00	0.00	0.01
Na_2O	0.00	0.01	0.00	0.00	0.01	0.01	0.00
Total	100.07	100.22	100.03	100.31	100.17	99.95	99.94
Nos.of ions	B1	B2	B3	B4	B5	B6	B7
Al	1.9977	1.9944	1.9956	1.9968	1.9993	1.9978	1.9971
Si	0.0002	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000
Ti	0.0006	0.0032	0.0007	0.0013	0.0001	0.0006	0.0005
Cr	0.0003	0.0002	0.0005	0.0003	0.0000	0.0002	0.0000
V	0.0001	0.0001	0.0000	0.0000	0.0000	0.0004	0.0009
Ga	0.0000	0.0004	0.0014	0.0010	0.0000	0.0000	0.0000
Fe	0.0011	0.0004	0.0019	0.0003	0.0004	0.0006	0.0019
Mg	0.0000	0.0003	0.0002	0.0000	0.0000	0.0002	0.0002
Mn	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003	0.0000
K	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001
Na	0.0000	0.0001	0.0000	0.0000	0.0002	0.0001	0.0000
Total	2.0001	1.9993	2.0004	1.9997	2.0003	2.0002	2.0006

Table C2: Quantitative analysis by EPMA of Deniyaya sapphires, Group C

Sample	C1	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Comment	C7-1	D6-4	C1-4	C2-5	D5-1	C3-1	C4-2	D7-3	C5-5	D1-4	C6-4
Al_2O_3	99.80	98.73	99.96	99.45	97.64	99.76	99.76	98.54	99.96	99.81	99.64
SiO_2	0.00	0.02	0.02	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.00
TiO_2	0.01	0.00	0.03	0.01	0.01	0.04	0.02	0.03	0.02	0.00	0.01
Cr_2O_3	0.02	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
V_2O_3	0.02	0.02	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.01
Ga_2O_3	0.09	0.03	0.00	0.00	0.07	0.02	0.06	0.02	0.04	0.00	0.07
FeO	0.06	0.03	0.08	0.09	0.06	0.13	0.08	0.03	0.04	0.08	0.03
MgO	0.01	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.02	0.00
MnO	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.01	0.01
K_2O	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Total	100.04	98.84	100.12	99.60	97.82	100.02	99.98	98.69	100.09	99.92	99.78
Nos.of ions	C1	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
Al	1.9968	1.9986	1.9982	1.9991	1.9976	1.9973	1.9977	1.9988	1.9985	1.9993	1.9981
Si	0.0000	0.0002	0.0002	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000
Ti	0.0001	0.0000	0.0003	0.0001	0.0001	0.0004	0.0002	0.0003	0.0002	0.0000	0.0001
Cr	0.0005	0.0000	0.0003	0.0000	0.0001	0.0000	0.0003	0.0000	0.0000	0.0000	0.0000
V	0.0003	0.0003	0.0003	0.0000	0.0000	0.0006	0.0000	0.0000	0.0000	0.0000	0.0001
Ga	0.0018	0.0006	0.0000	0.0000	0.0015	0.0004	0.0011	0.0004	0.0009	0.0000	0.0013
Fe	0.0006	0.0003	0.0008	0.0009	0.0006	0.0013	0.0008	0.0003	0.0004	0.0008	0.0003
Mg	0.0001	0.0000	0.0000	0.0000	0.0001	0.0003	0.0000	0.0000	0.0001	0.0002	0.0000
Mn	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001
K	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001
Na	0.0000	0.0000	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0002
Total	2.0004	2.0001	2.0001	2.0005	2.0002	2.0004	2.0004	2.0000	2.0001	2.0004	2.0003

Table C3: Quantitative analysis by EPMA of Deniyaya sapphires, Group Y

Sample	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12
Comment	A3-3	A4-4	A5-4	A9-3	A6-2	A8-1	D2-5	A7-5	A2-2	D4-1	A1-4
Al_2O_3	99.53	99.93	99.94	99.55	99.86	99.72	99.62	99.89	99.82	100.07	100.09
SiO_2	0.00	0.00	0.00	0.00	0.03	0.03	0.00	0.00	0.00	0.01	0.03
TiO_2	0.02	0.02	0.00	0.01	0.00	0.02	0.01	0.02	0.01	0.02	0.02
Cr_2O_3	0.02	0.01	0.02	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00
V_2O_3	0.01	0.00	0.02	0.02	0.02	0.00	0.06	0.00	0.01	0.00	0.00
Ga_2O_3	0.07	0.00	0.05	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
FeO	0.05	0.06	0.06	0.06	0.05	0.09	0.13	0.08	0.12	0.06	0.04
MgO	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.02	0.01	0.02
MnO	0.02	0.00	0.03	0.00	0.02	0.02	0.00	0.00	0.04	0.01	0.00
K_2O	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.01
Na_2O	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00
Total	99.74	100.02	100.12	99.69	100.01	99.92	99.83	100.03	100.03	100.20	100.24
Nos.of ions	Y2	Y3	Y4	Y5	Y6	Y7	Y8	Y9	Y10	Y11	Y12
Al	1.9972	1.9991	1.9977	1.9987	1.9984	1.9981	1.9977	1.9991	1.9986	1.9990	1.9988
Si	0.0000	0.0000	0.0000	0.0000	0.0003	0.0003	0.0000	0.0000	0.0000	0.0001	0.0003
Ti	0.0002	0.0002	0.0000	0.0001	0.0000	0.0002	0.0001	0.0002	0.0001	0.0002	0.0002
Cr	0.0003	0.0002	0.0004	0.0004	0.0003	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
V	0.0003	0.0000	0.0003	0.0003	0.0003	0.0000	0.0013	0.0000	0.0001	0.0000	0.0001
Ga	0.0015	0.0001	0.0009	0.0000	0.0000	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000
Fe	0.0005	0.0006	0.0006	0.0006	0.0005	0.0009	0.0013	0.0008	0.0012	0.0006	0.0004
Mg	0.0000	0.0000	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0002	0.0001	0.0002
Mn	0.0002	0.0000	0.0003	0.0000	0.0002	0.0002	0.0000	0.0000	0.0004	0.0001	0.0000
K	0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003	0.0002	0.0000	0.0001
Na	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000
Total	2.0003	2.0002	2.0004	2.0002	2.0002	2.0003	2.0005	2.0004	2.0006	2.0004	2.0001

APPENDIX D

D.1 UV-VIS-NIR Absorption Spectra before heat-treatment

The UV-VIS-NIR absorption spectra between 250-1500 nm from 29 rough sapphires before treatment were recorded. The spectra of all samples show similar patterns in which representative spectra (O- and E-rays) of some sample before heat-treatment are displayed in Figs.D1-D29.

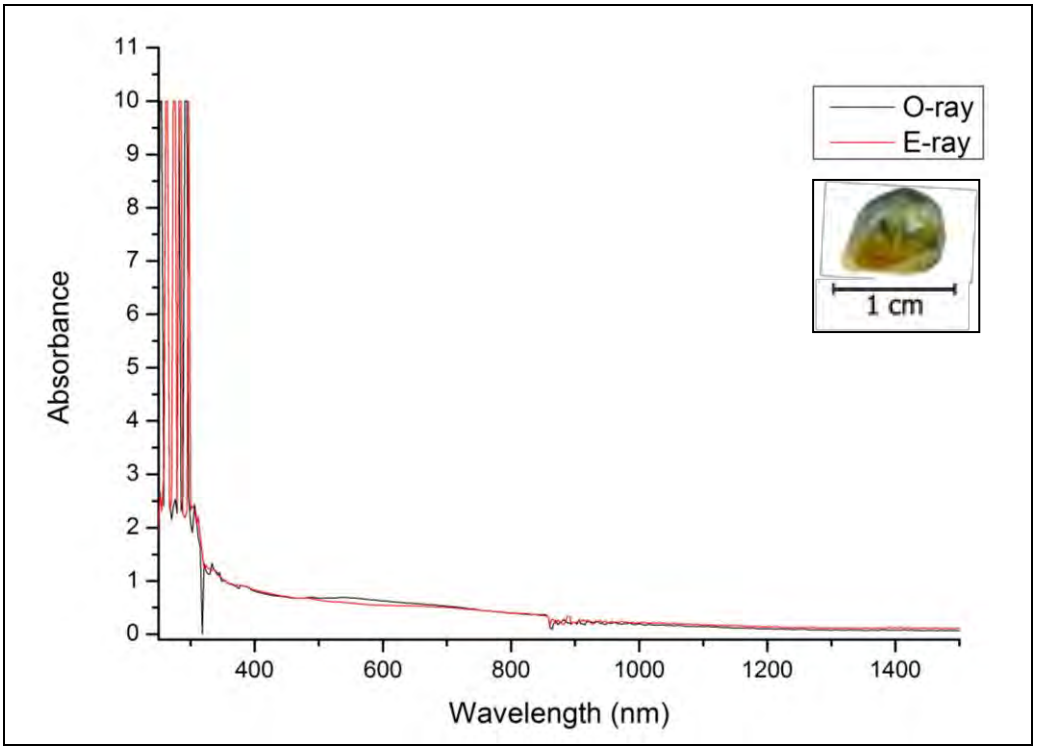


Fig.D1 UV-VIS-NIR absorption spectra of sample B1, before heat-treatment

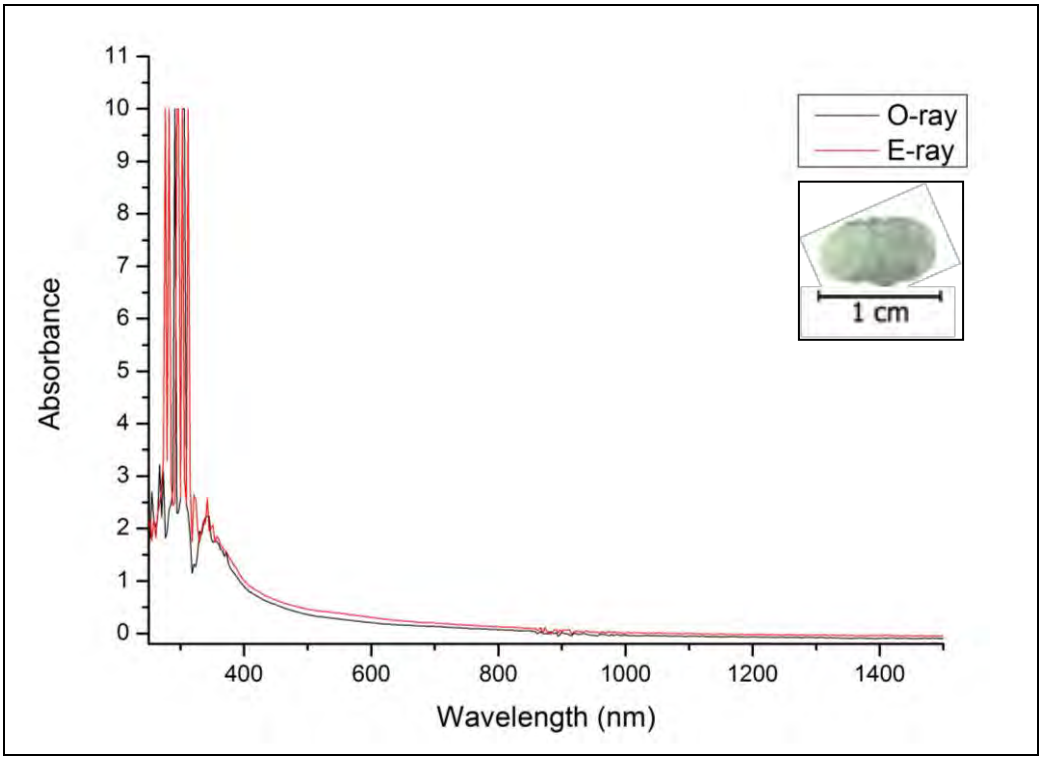


Fig.D2 UV-VIS-NIR absorption spectra of sample B2, before heat-treatment

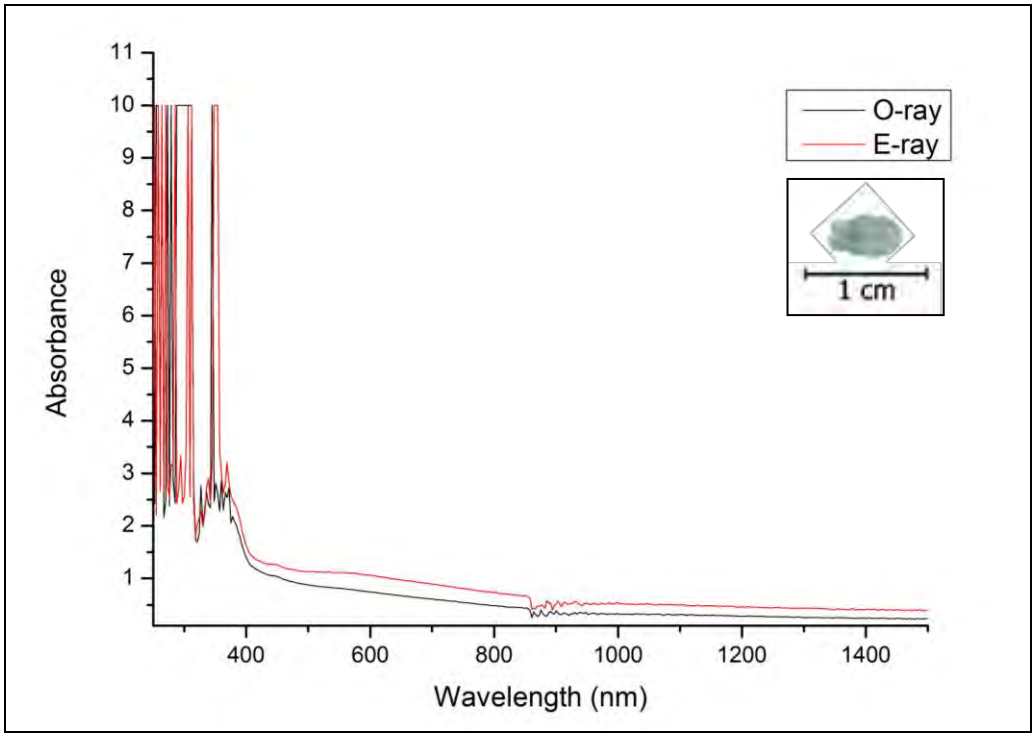


Fig.D3 UV-VIS-NIR absorption spectra of sample B3, before heat-treatment

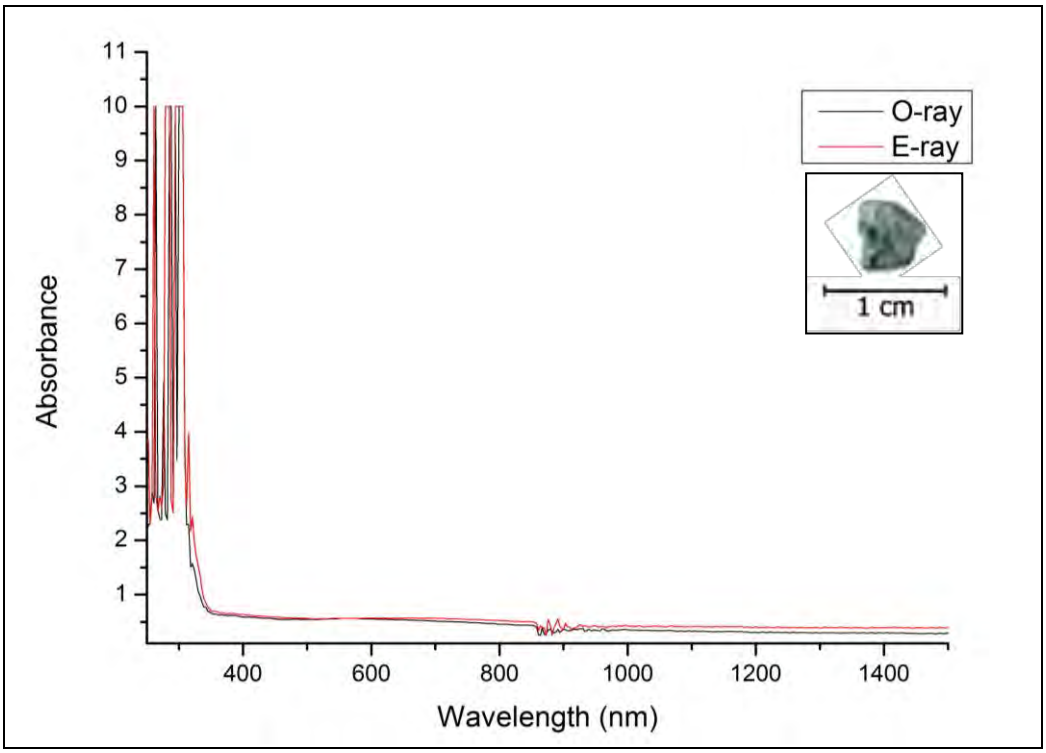


Fig.D4 UV-VIS-NIR absorption spectra of sample B4, before heat-treatment

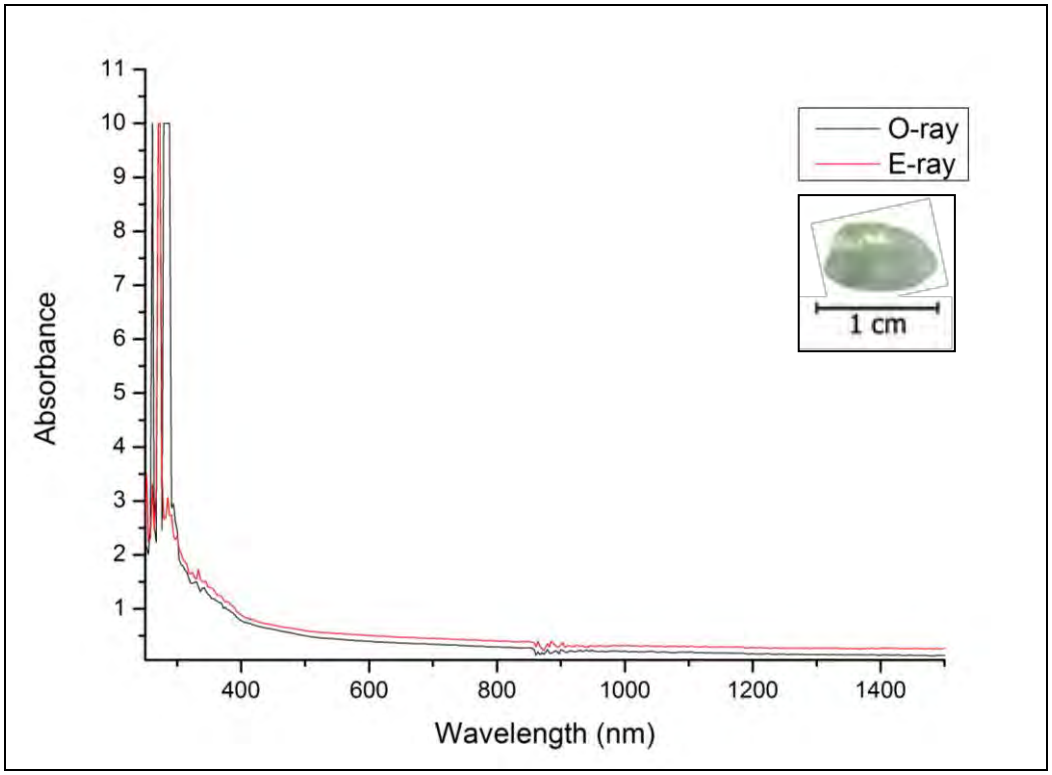


Fig.D5 UV-VIS-NIR absorption spectra of sample B5, before heat-treatment

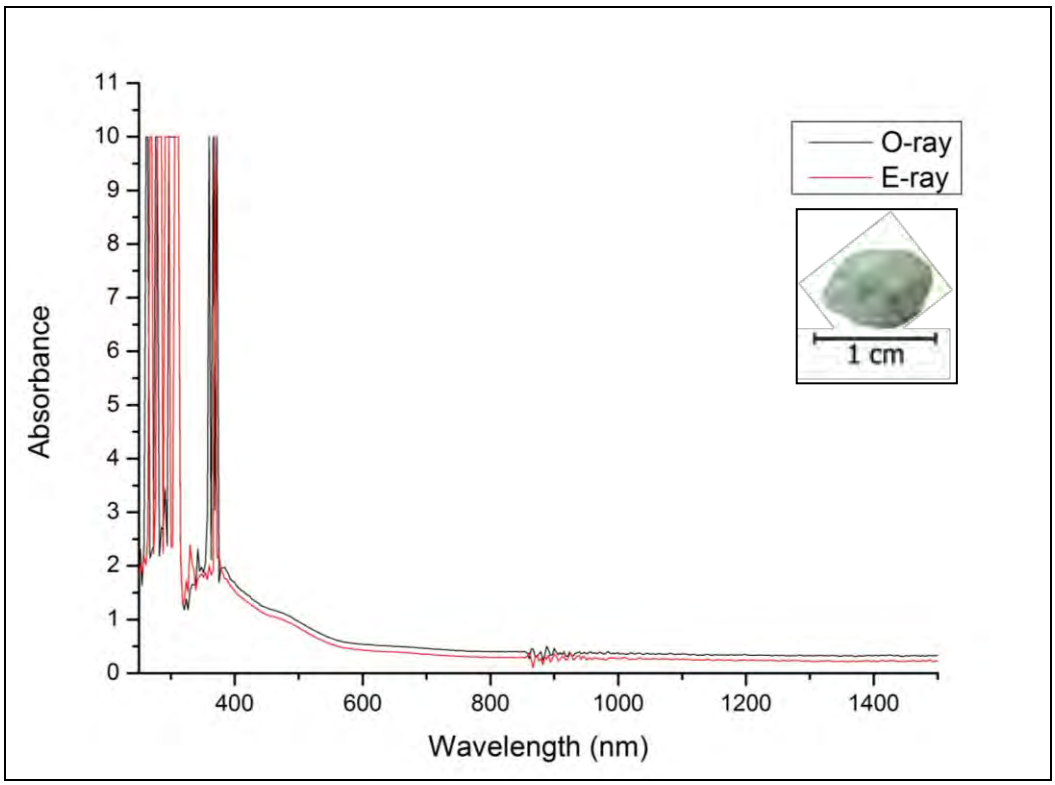


Fig.D6 UV-VIS-NIR absorption spectra of sample B6, before heat-treatment

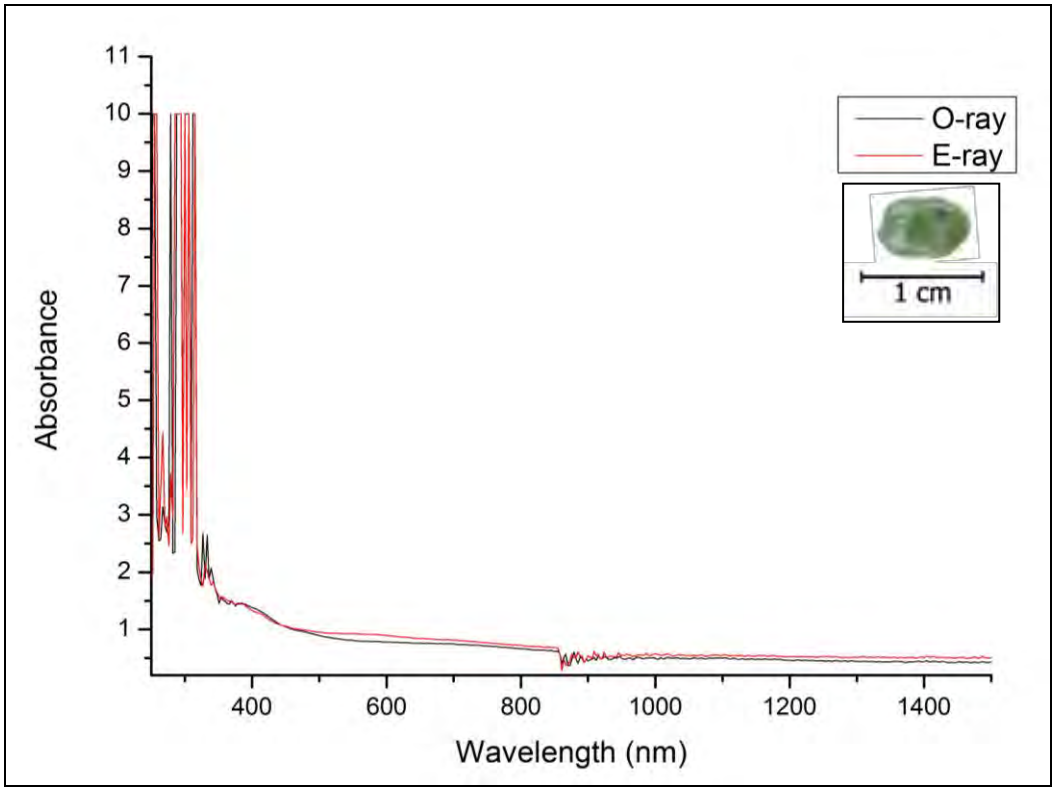


Fig.D7 UV-VIS-NIR absorption spectra of sample B7, before heat-treatment

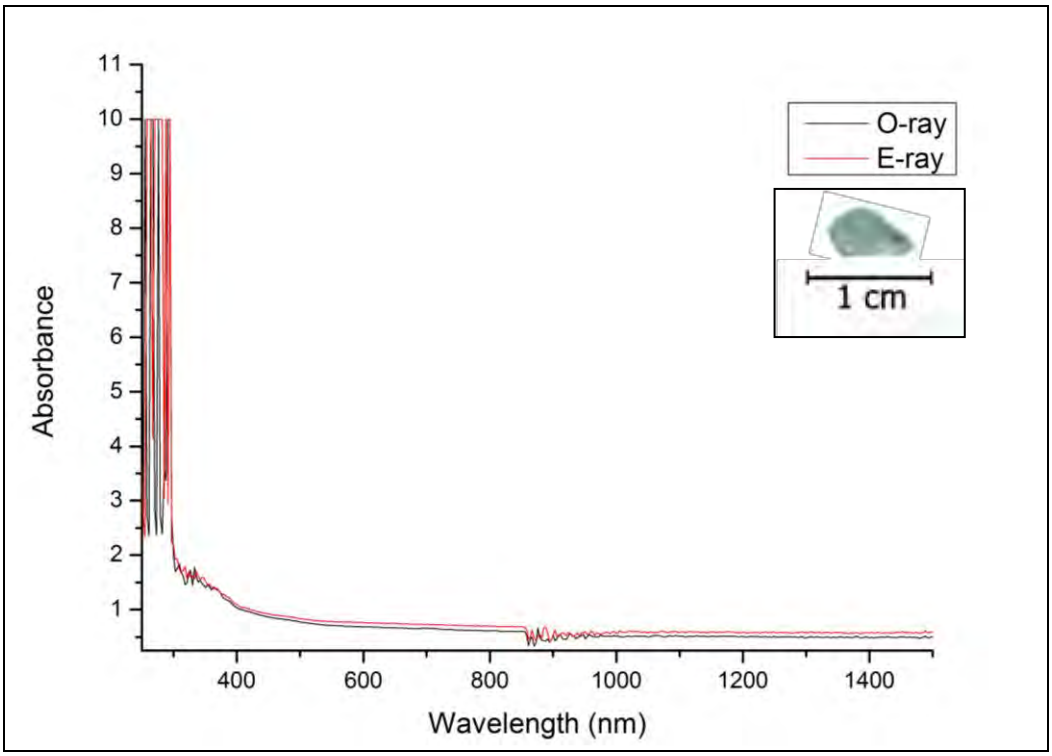


Fig.D8 UV-VIS-NIR absorption spectra of sample C1, before heat-treatment

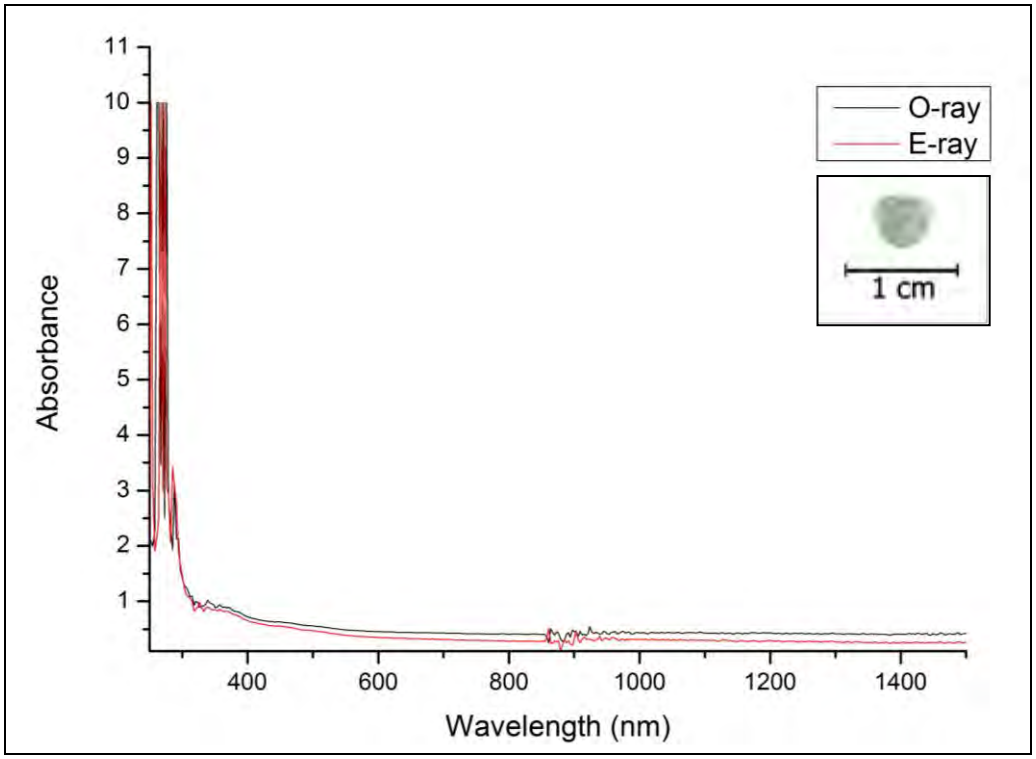


Fig.D9 UV-VIS-NIR absorption spectra of sample C3, before heat-treatment

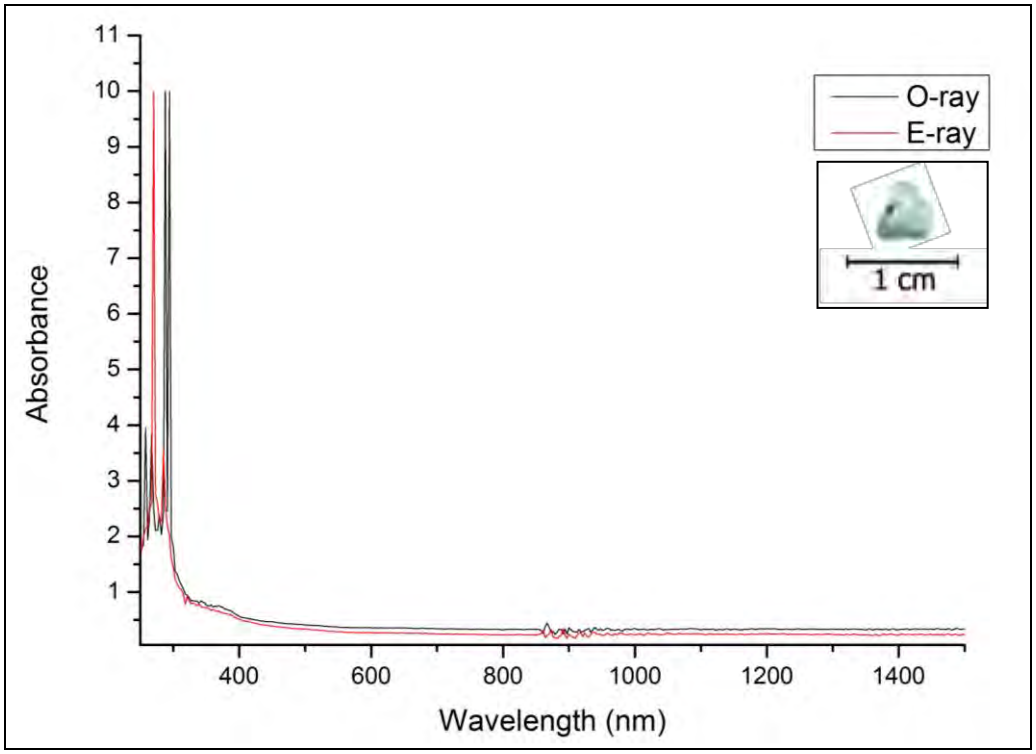


Fig.D10 UV-VIS-NIR absorption spectra of sample C4, before heat-treatment

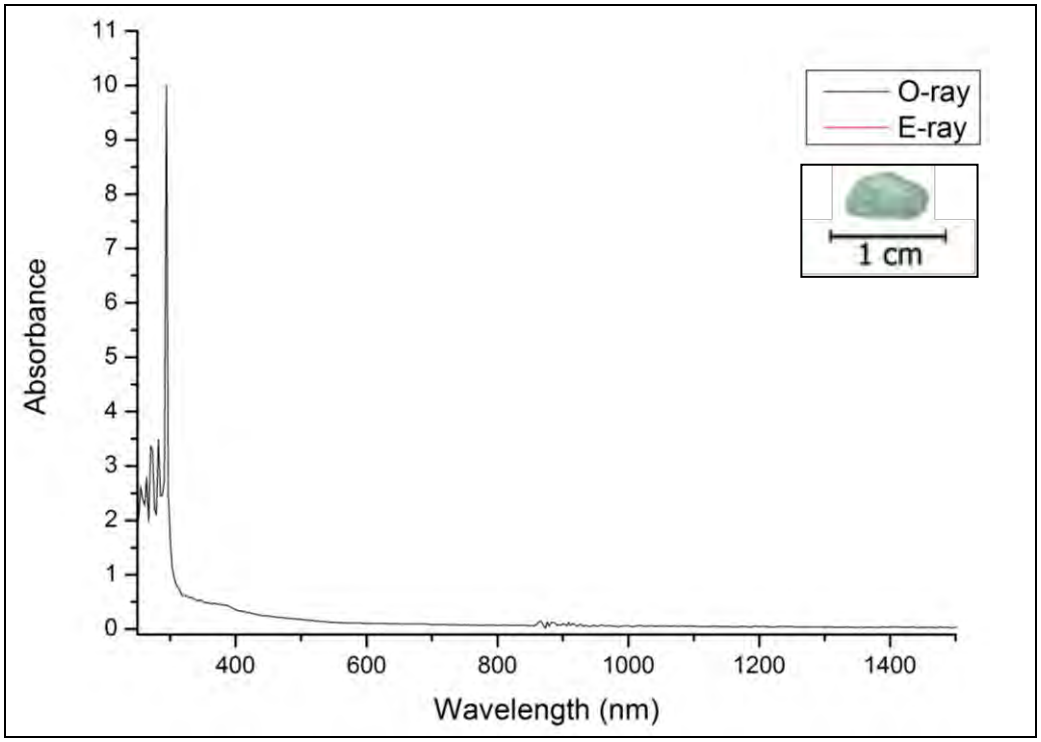


Fig.D11 UV-VIS-NIR absorption spectra of sample C5, before heat-treatment

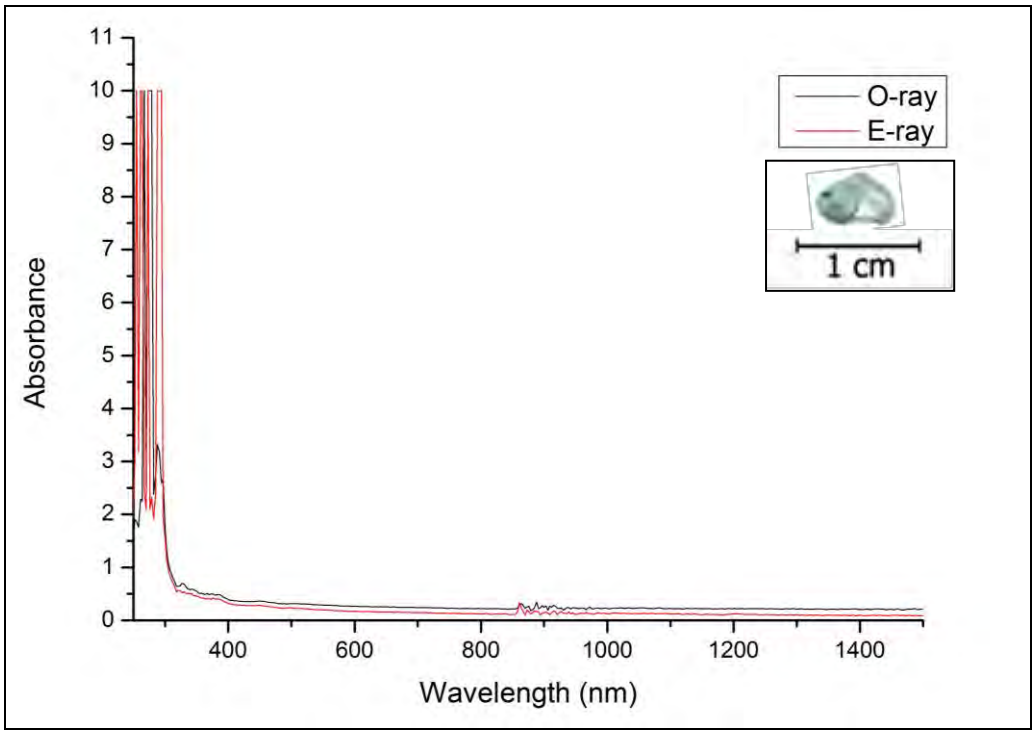


Fig.D12 UV-VIS-NIR absorption spectra of sample C6, before heat-treatment

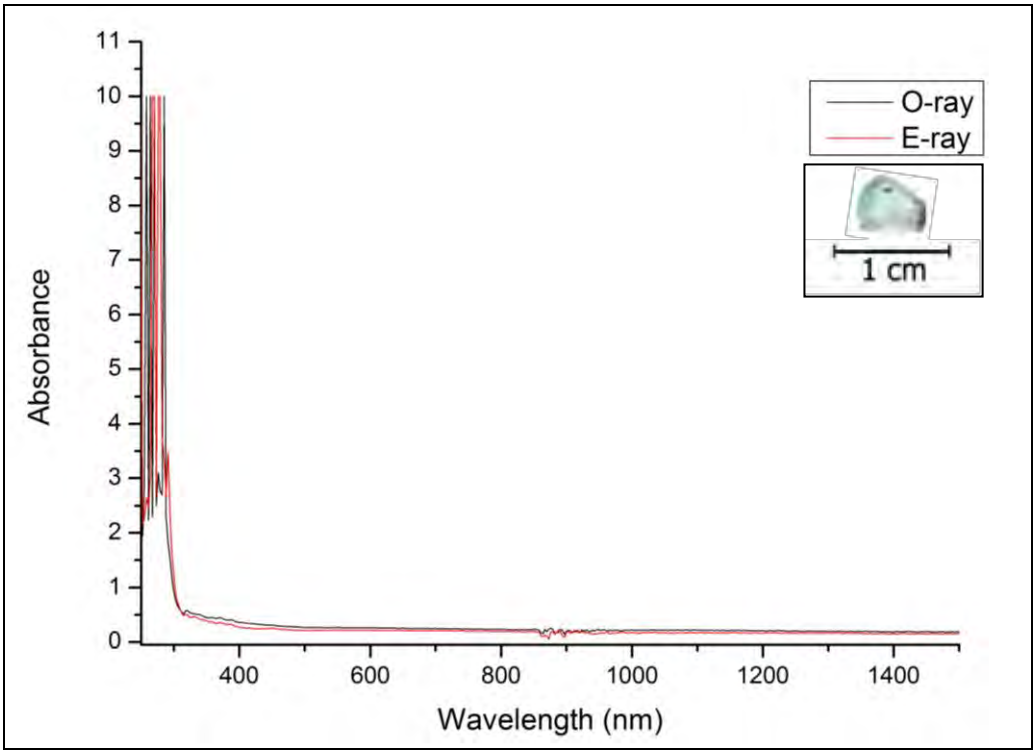


Fig.D13 UV-VIS-NIR absorption spectra of sample C7, before heat-treatment

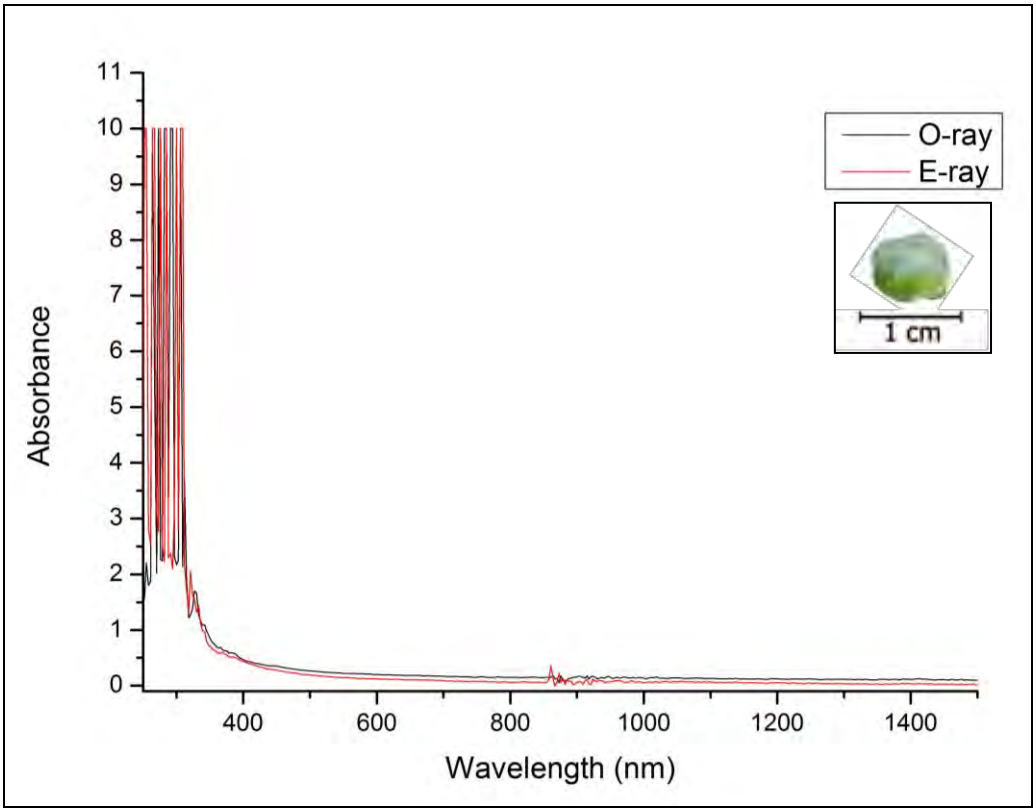


Fig.D14 UV-VIS-NIR absorption spectra of sample C8, before heat-treatment

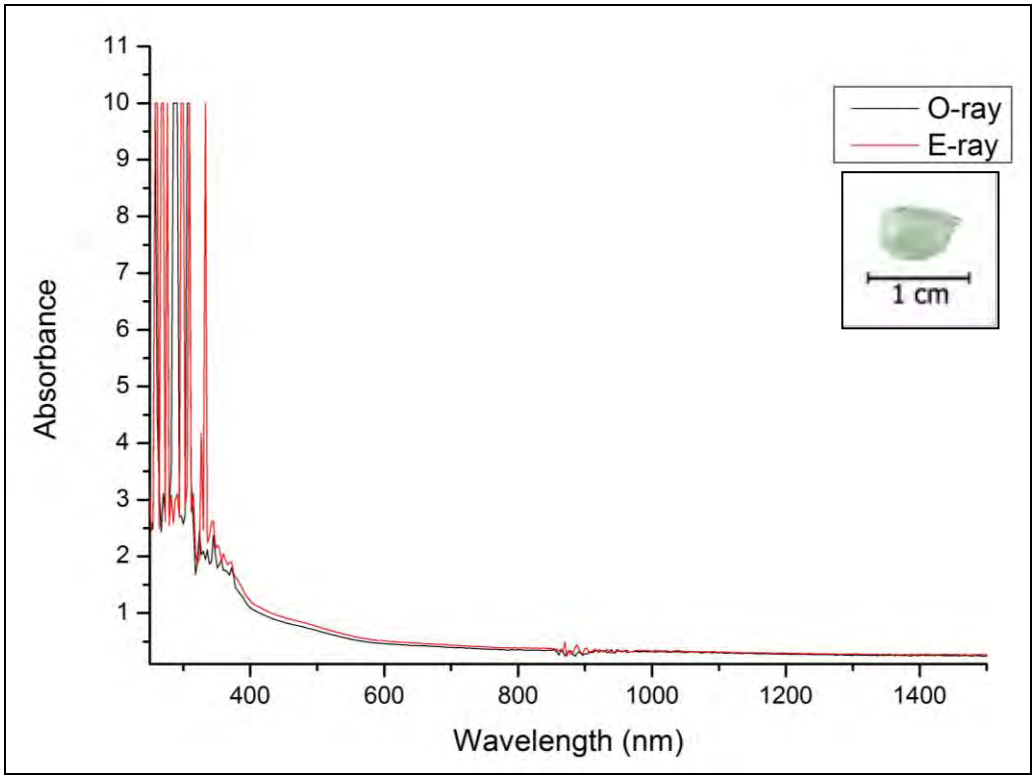


Fig.D15 UV-VIS-NIR absorption spectra of sample C9, before heat-treatment

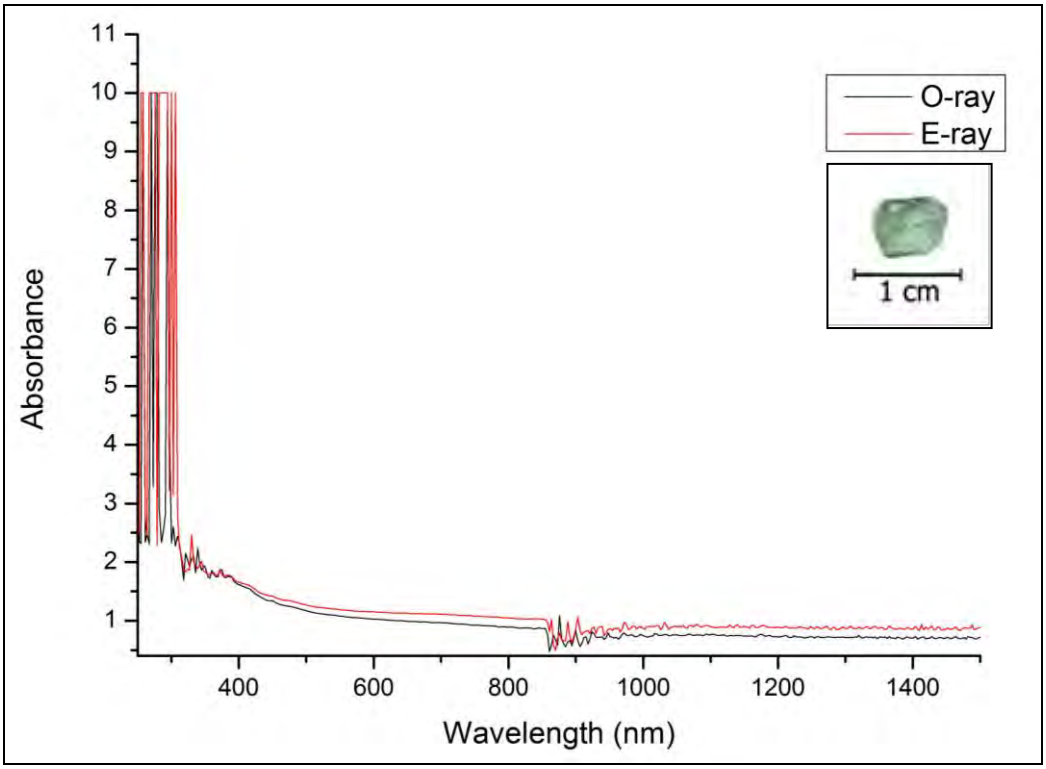


Fig.D16 UV-VIS-NIR absorption spectra of sample C10, before heat-treatment

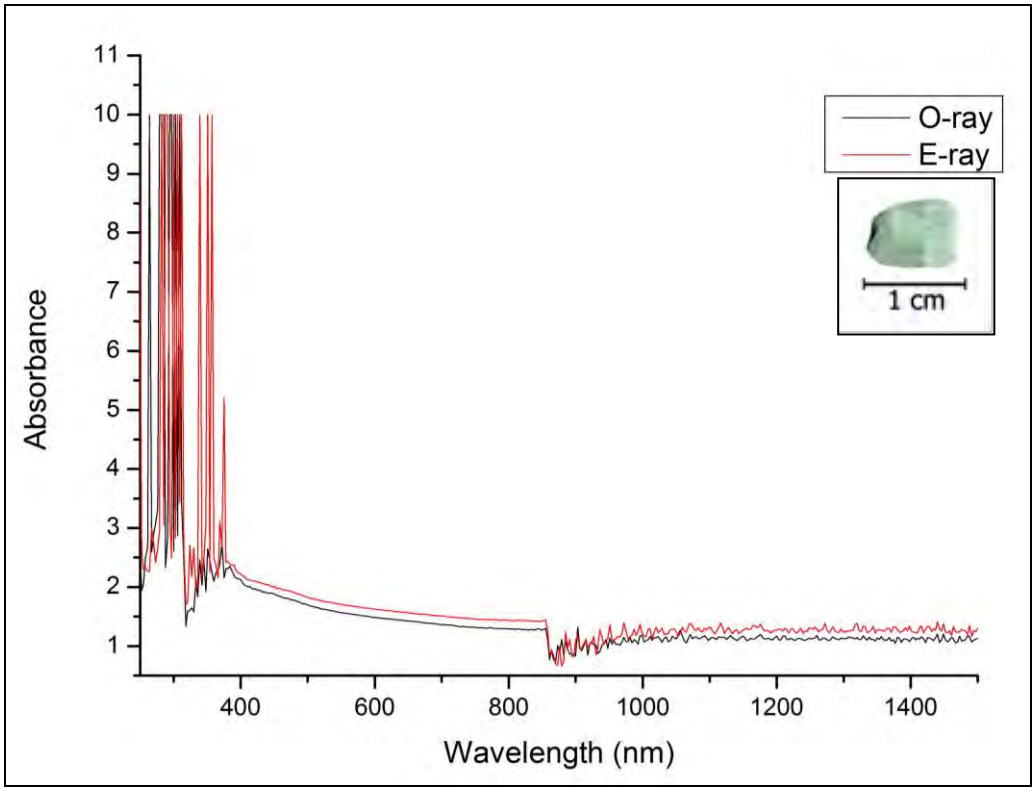


Fig.D17 UV-VIS-NIR absorption spectra of sample C11, before heat-treatment

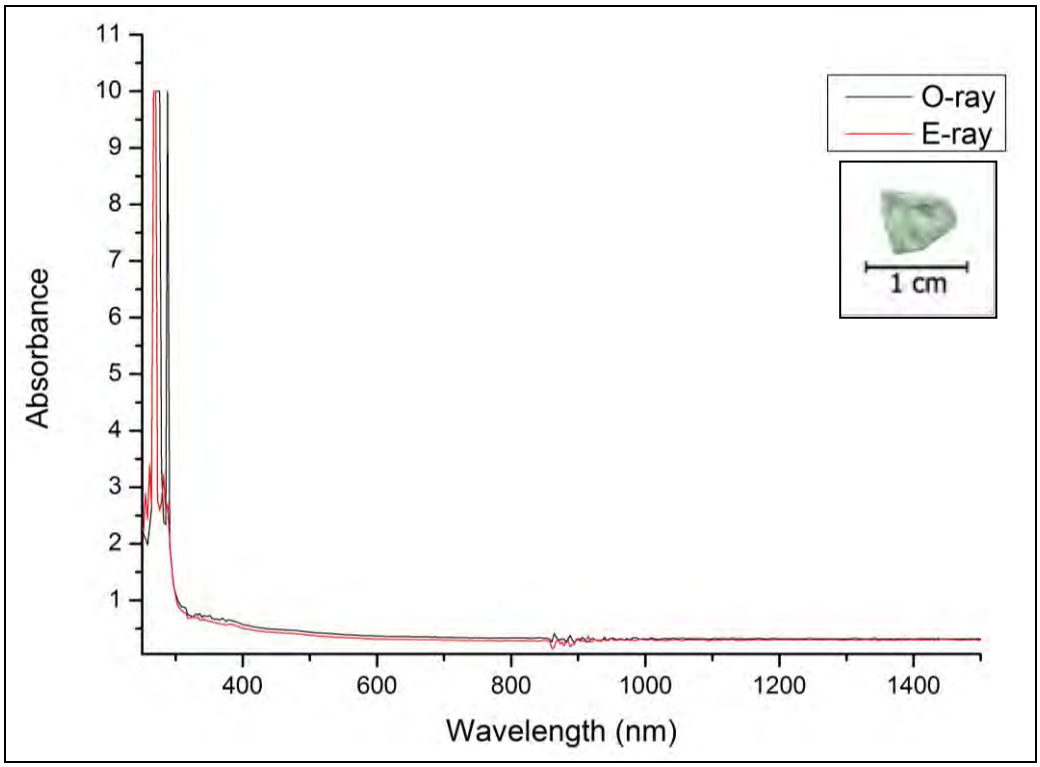


Fig.D18 UV-VIS-NIR absorption spectra of sample C12, before heat-treatment

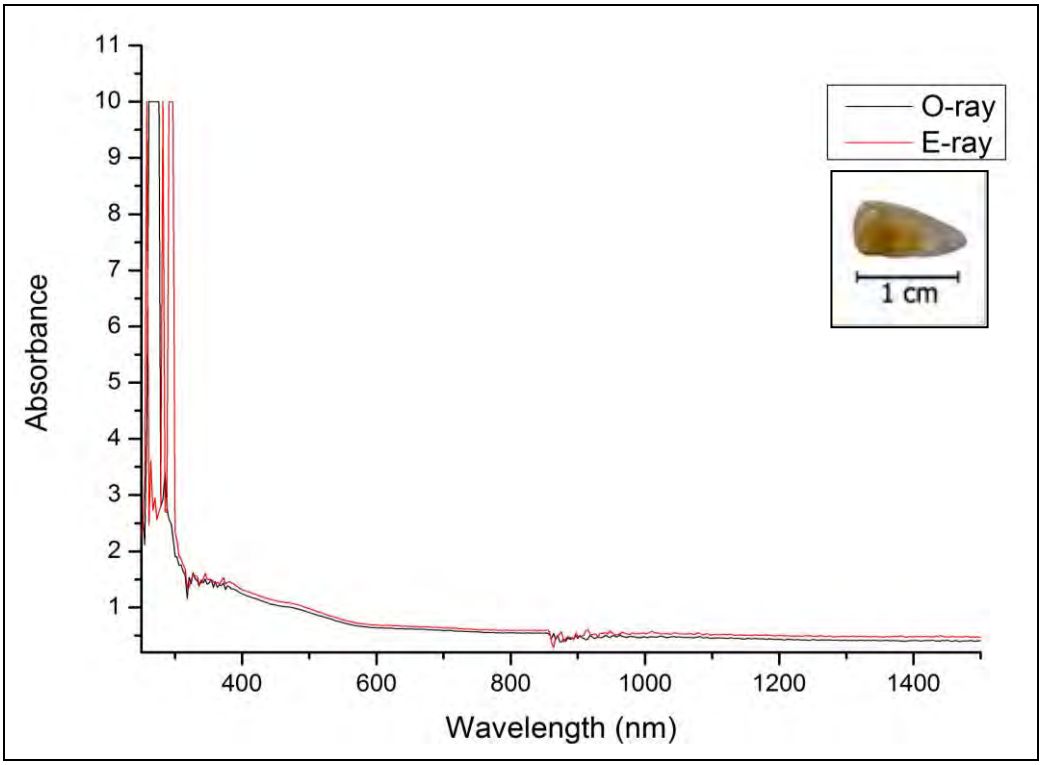


Fig.D19 UV-VIS-NIR absorption spectra of sample Y2, before heat-treatment

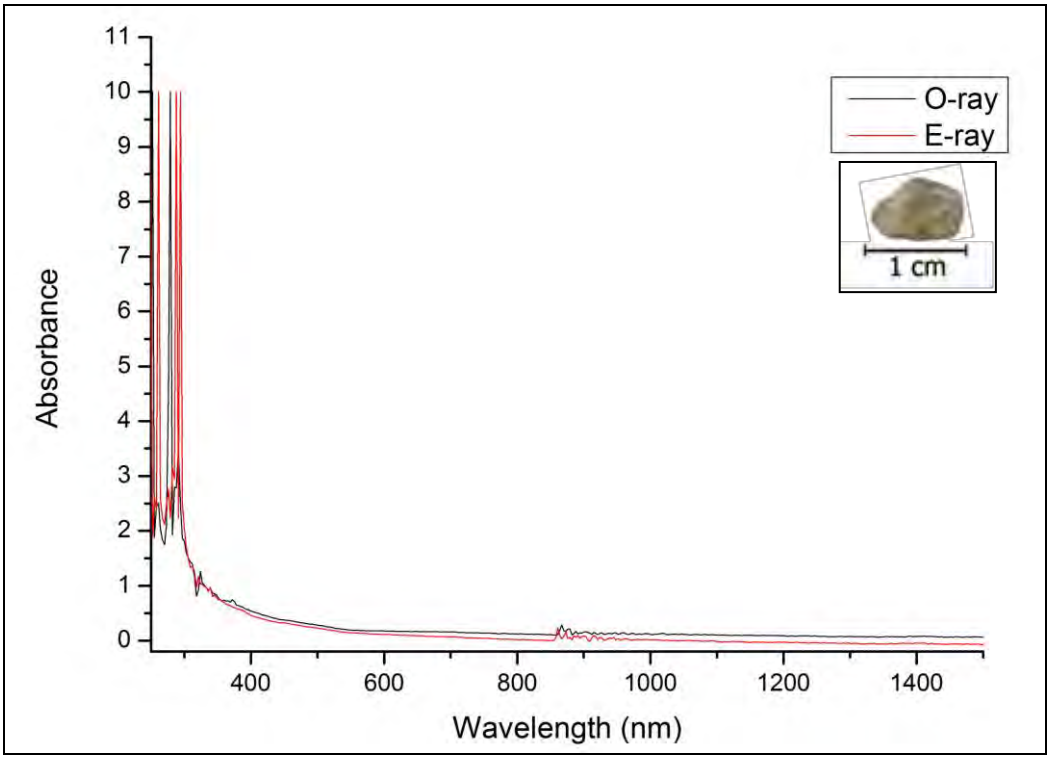


Fig.D20 UV-VIS-NIR absorption spectra of sample Y3, before heat-treatment

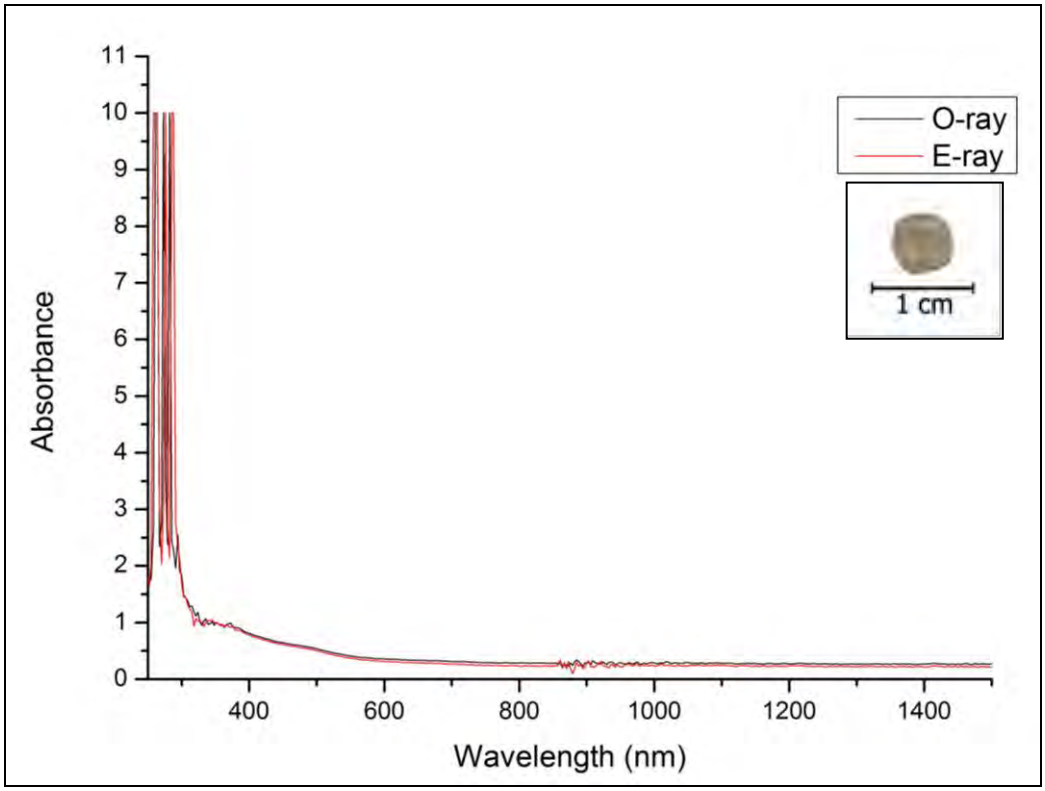


Fig.D21 UV-VIS-NIR absorption spectra of sample Y4, before heat-treatment

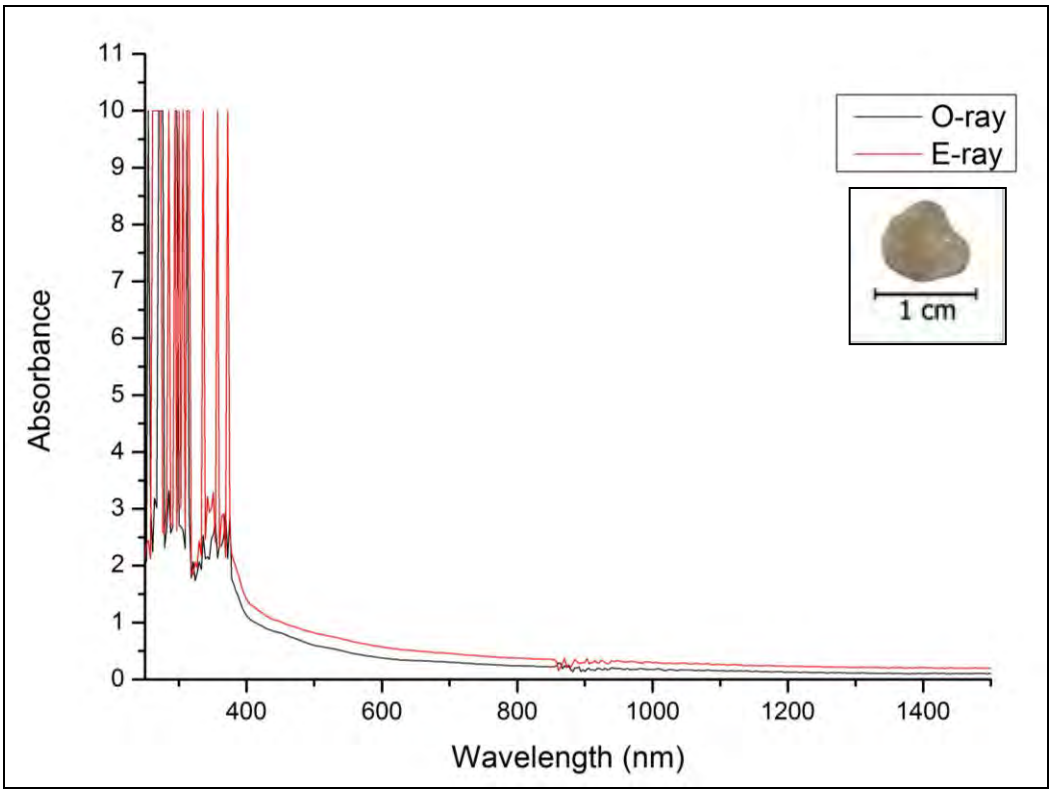


Fig.D22 UV-VIS-NIR absorption spectra of sample Y5, before heat-treatment

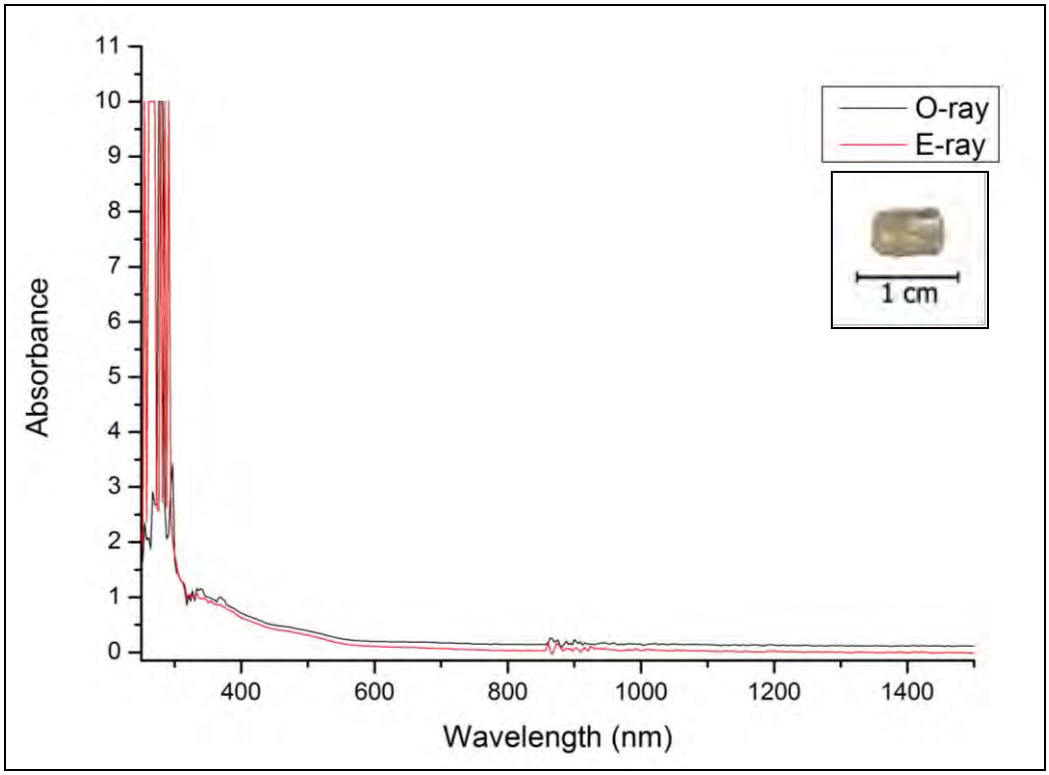


Fig.D23 UV-VIS-NIR absorption spectra of sample Y6, before heat-treatment

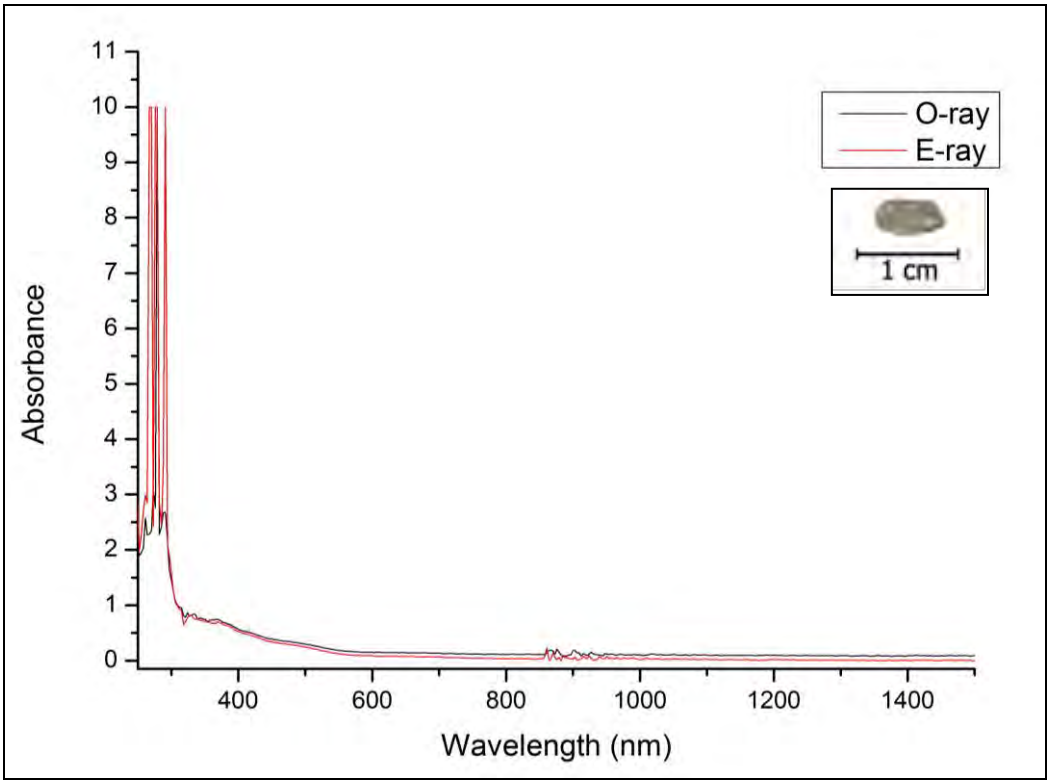


Fig.D24 UV-VIS-NIR absorption spectra of sample Y7, before heat-treatment

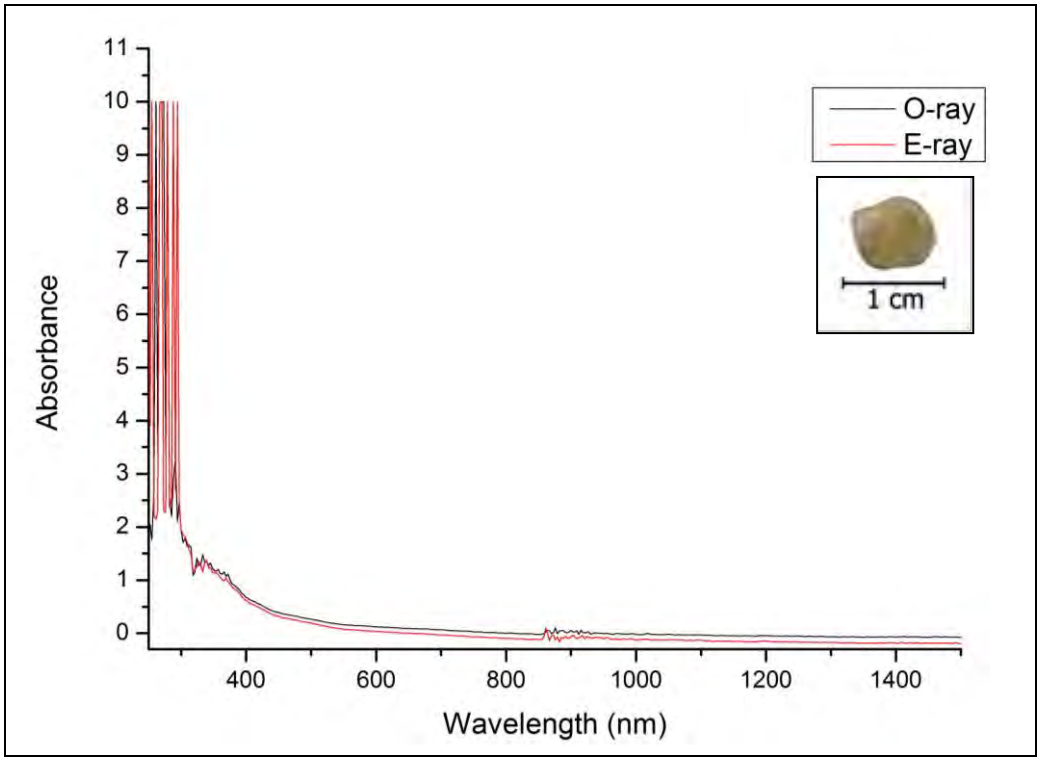


Fig.D25 UV-VIS-NIR absorption spectra of sample Y8, before heat-treatment

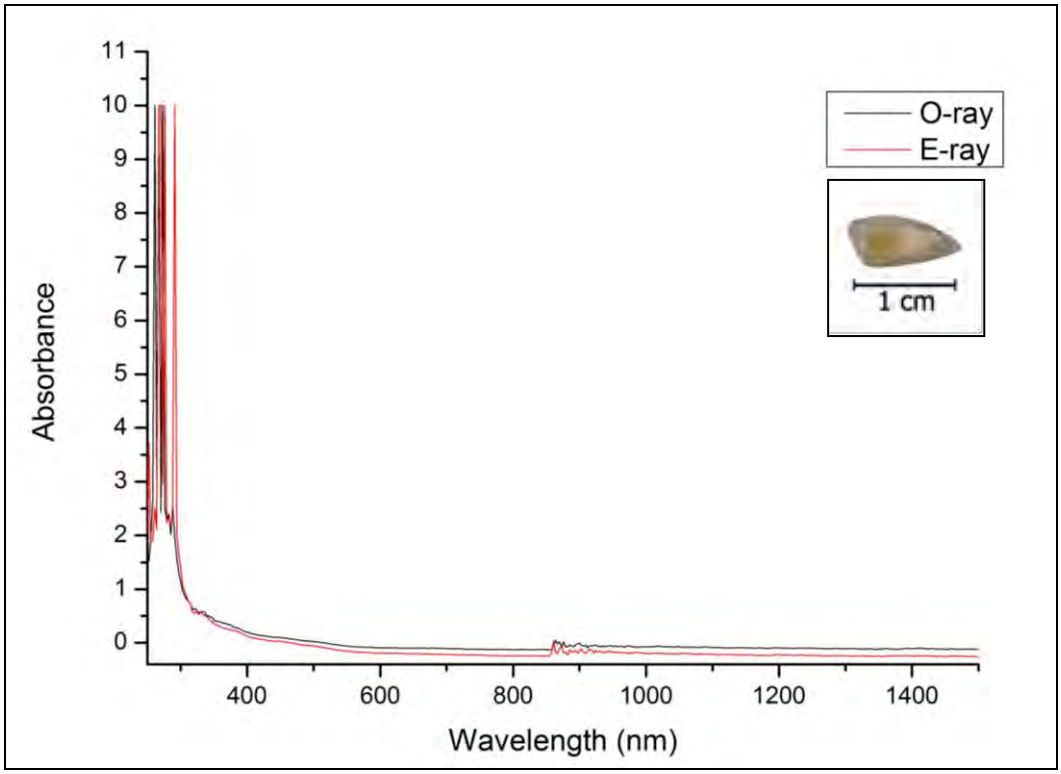


Fig.D26 UV-VIS-NIR absorption spectra of sample Y9, before heat-treatment

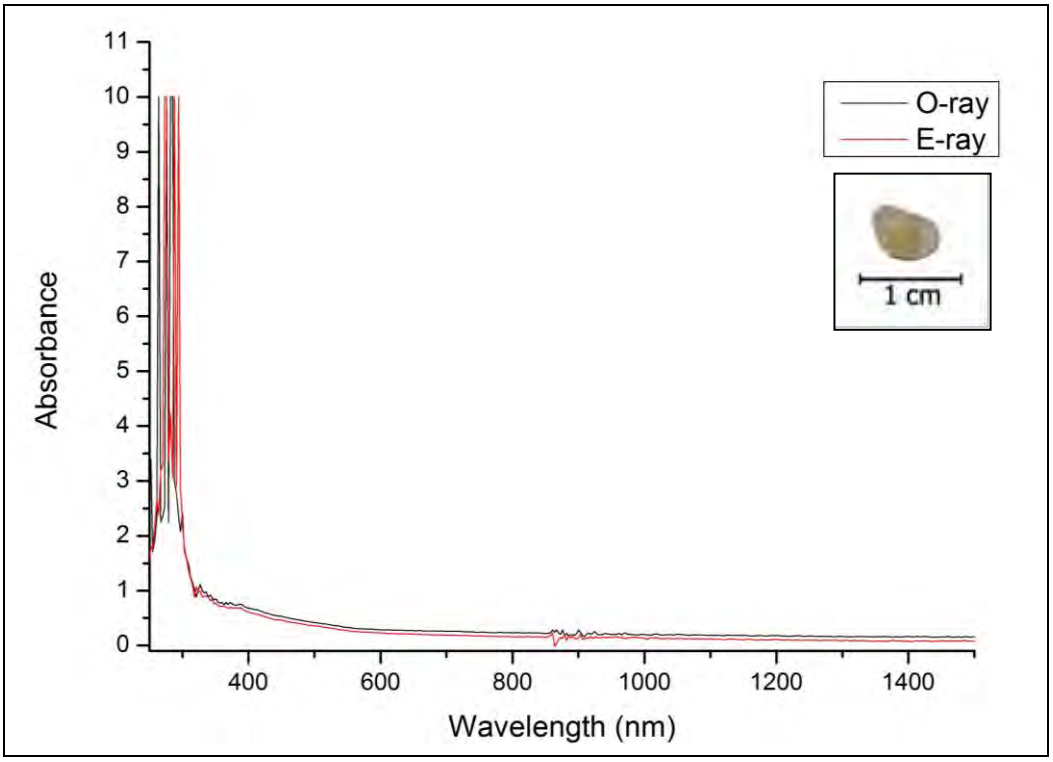


Fig.D27 UV-VIS-NIR absorption spectra of sample Y10, before heat-treatment

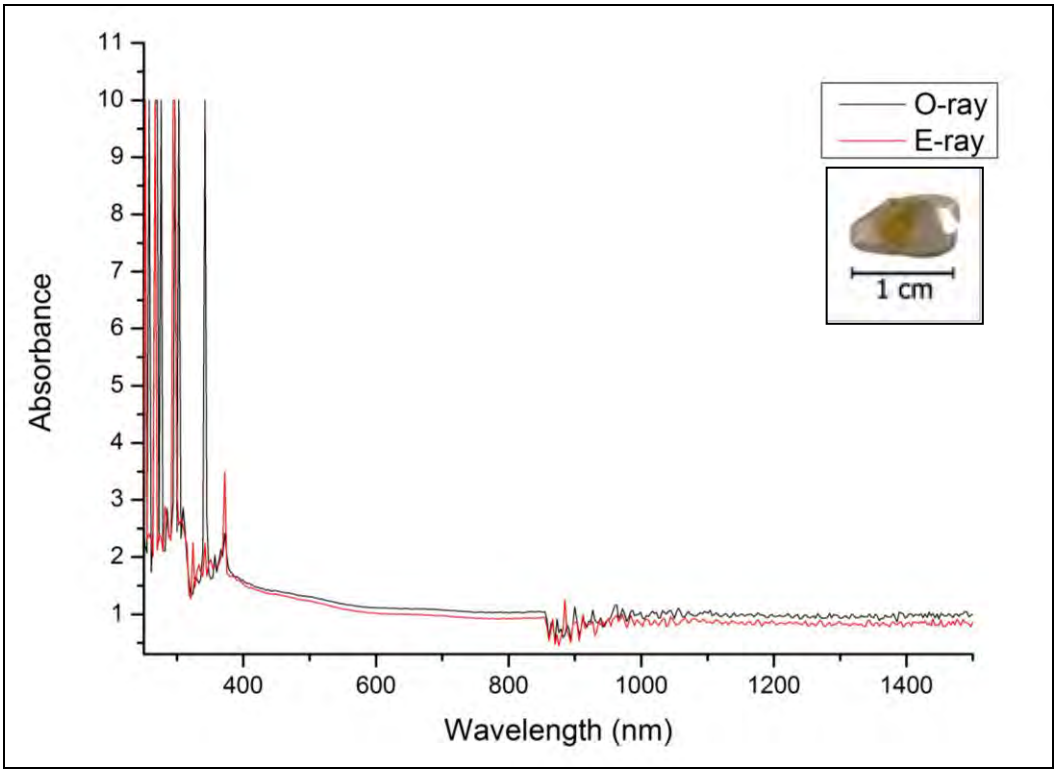


Fig.D28 UV-VIS-NIR absorption spectra of sample Y11, before heat-treatment

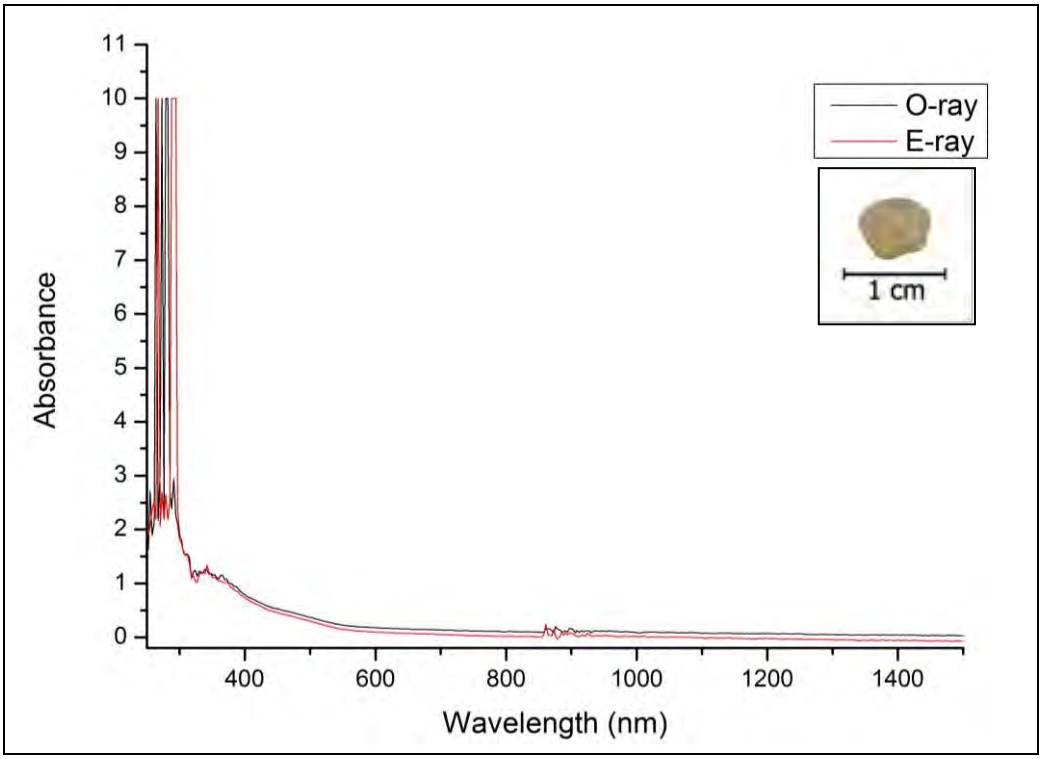


Fig.D29 UV-VIS-NIR absorption spectra of sample Y12, before heat-treatment

D.2 UV-VIS-NIR Absorption Spectra after heat-treatment

The UV-VIS-NIR absorption spectra between 250-1500 nm from 29 rough sapphires before and after treatment were recorded. The spectra of all samples show similar patterns in which representative spectra (before and after heated O-rays) of sample are displayed in Figs.D30-D58.

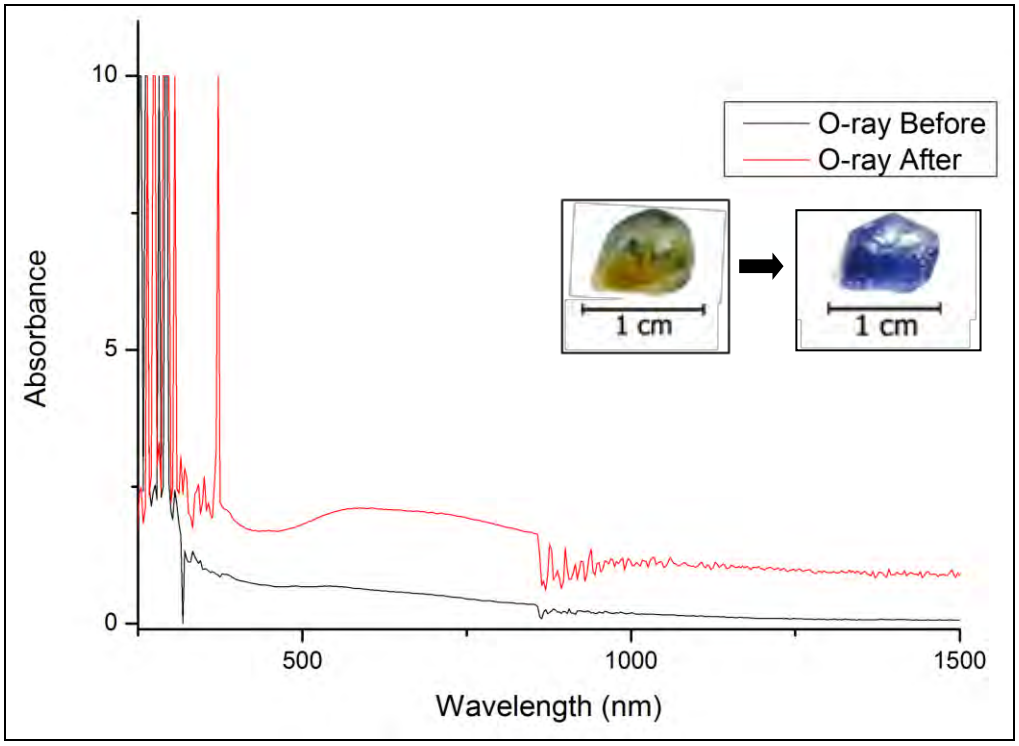


Fig.D30 UV-VIS-NIR absorption spectra of sample B1, before and after heat-treatment

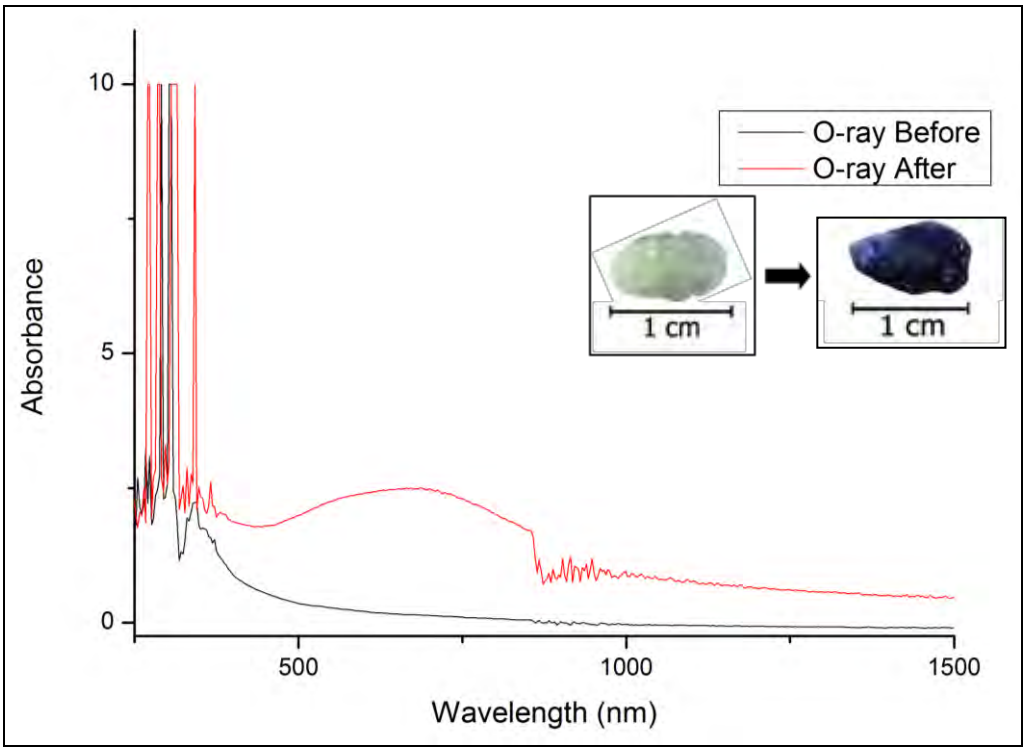


Fig.D31 UV-VIS-NIR absorption spectra of sample B2, before and after heat-treatment

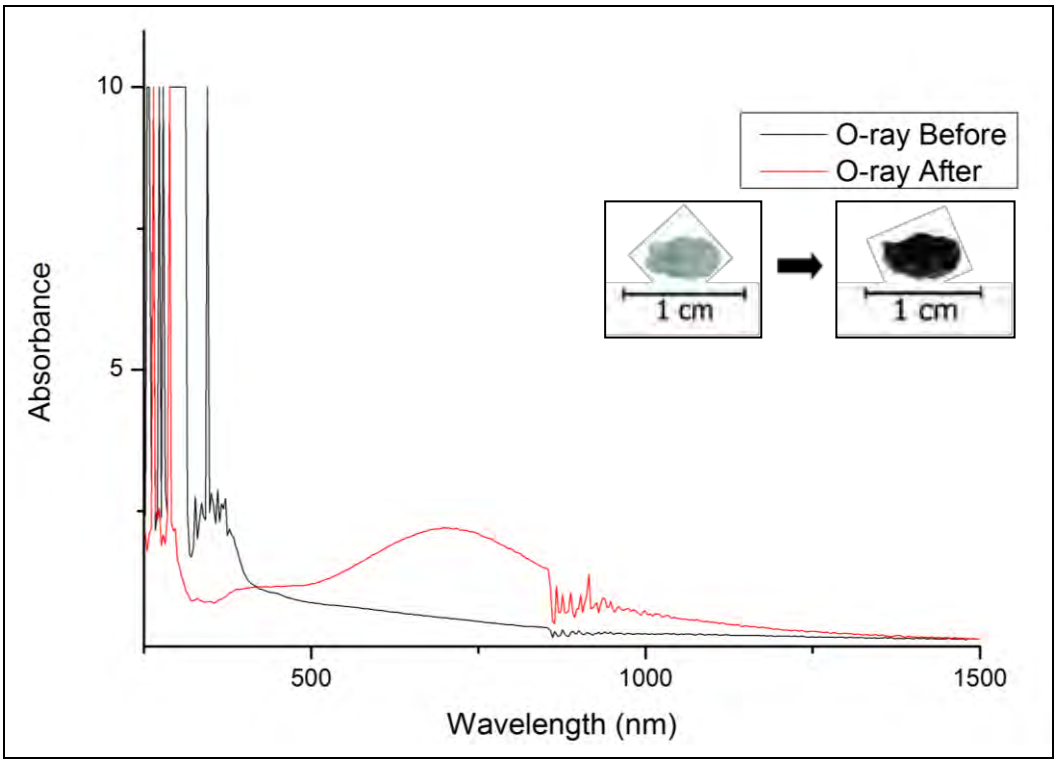


Fig.D32 UV-VIS-NIR absorption spectra of sample B3, before and after heat-treatment

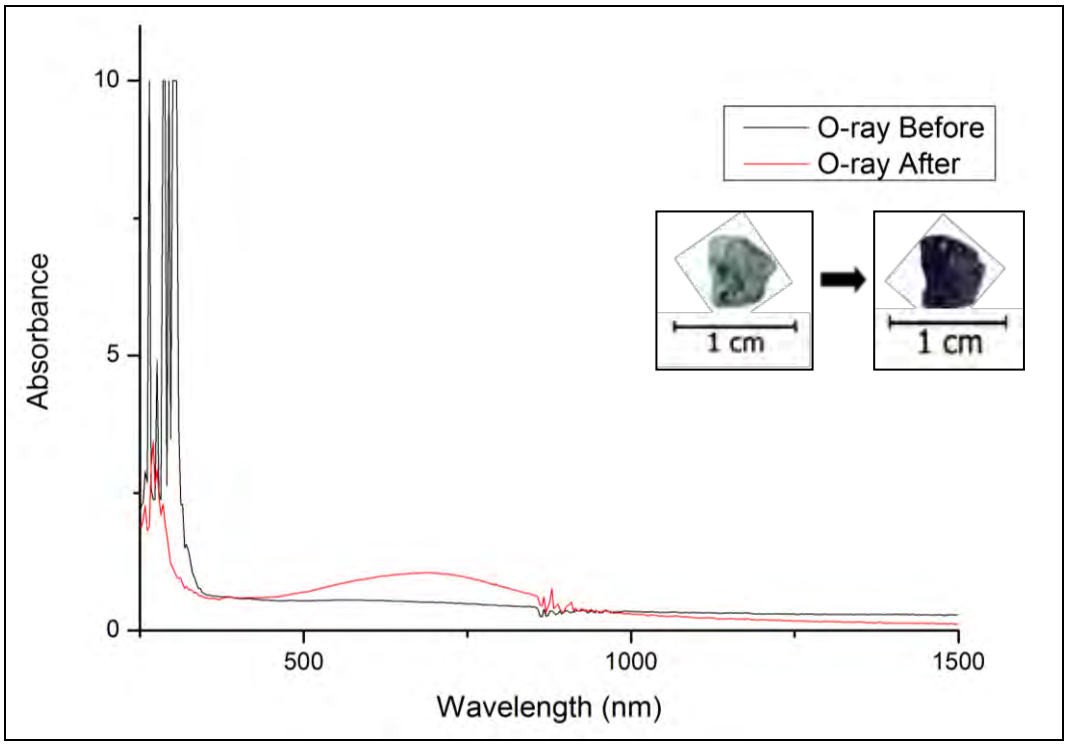


Fig.D33 UV-VIS-NIR absorption spectra of sample B4, before and after heat-treatment

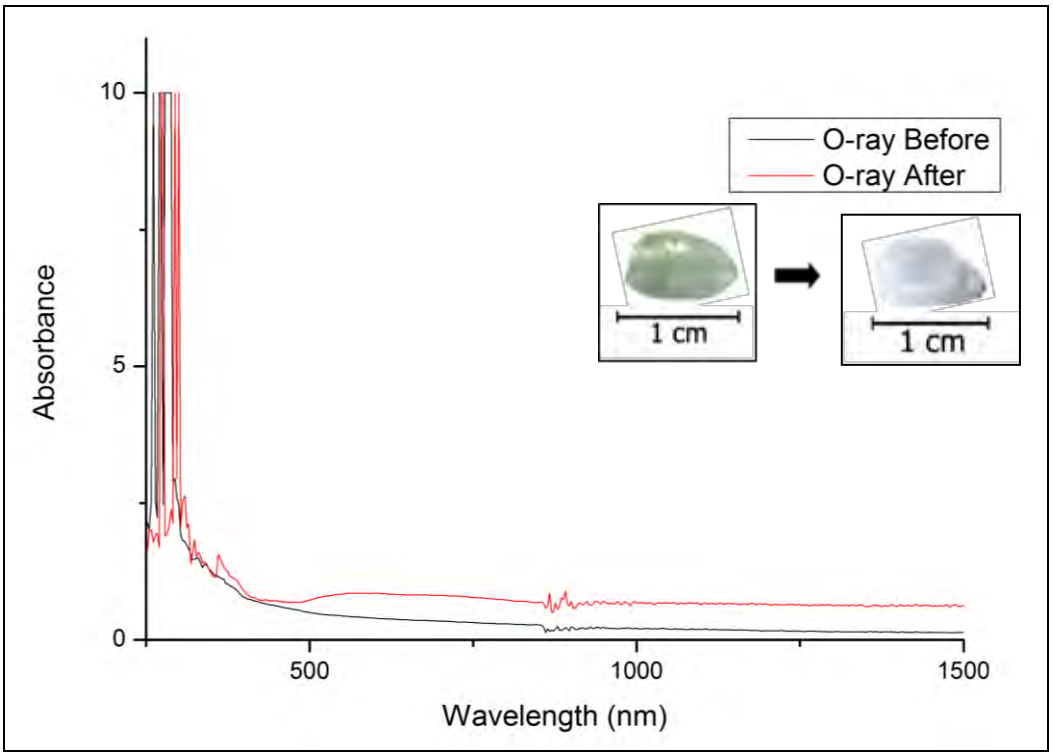


Fig.D34 UV-VIS-NIR absorption spectra of sample B5, before and after heat-treatment

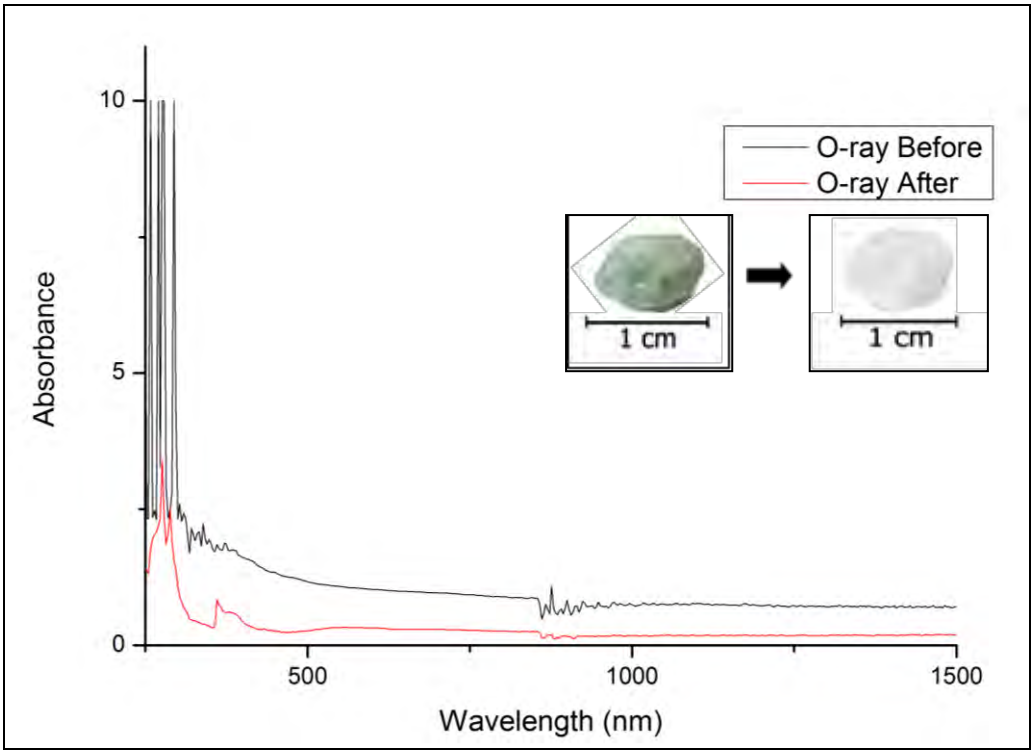


Fig.D35 UV-VIS-NIR absorption spectra of sample B6, before and after heat-treatment

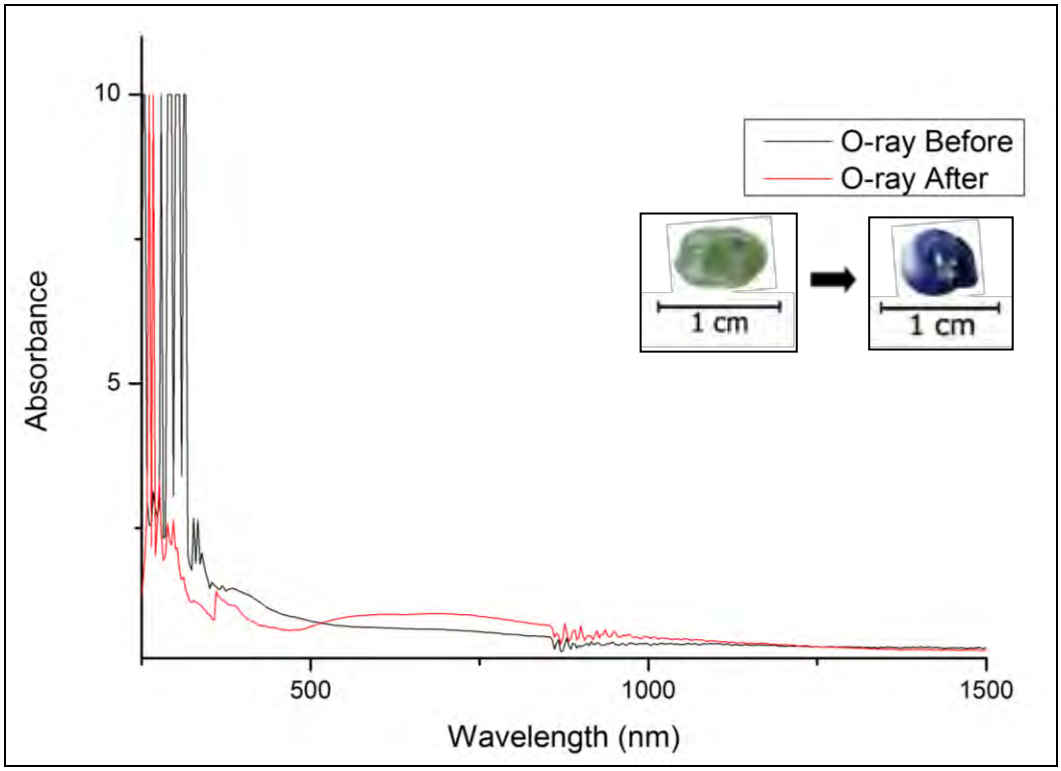


Fig.D36 UV-VIS-NIR absorption spectra of sample B7, before and after heat-treatment

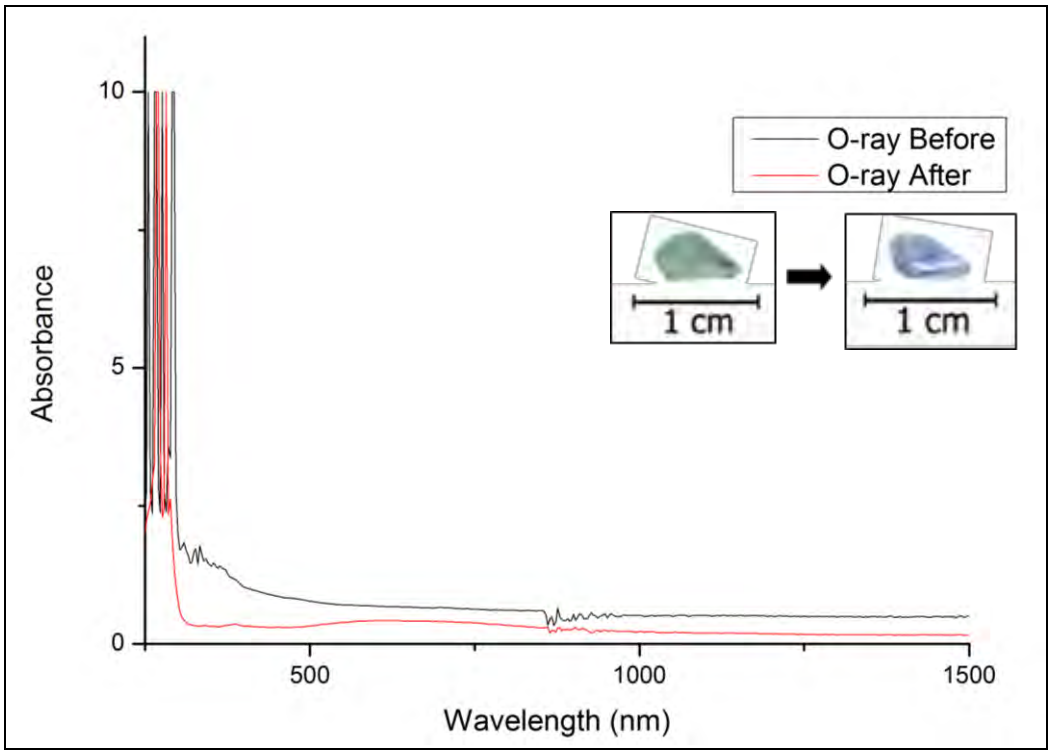


Fig.D37 UV-VIS-NIR absorption spectra of sample C1, before and after heat-treatment

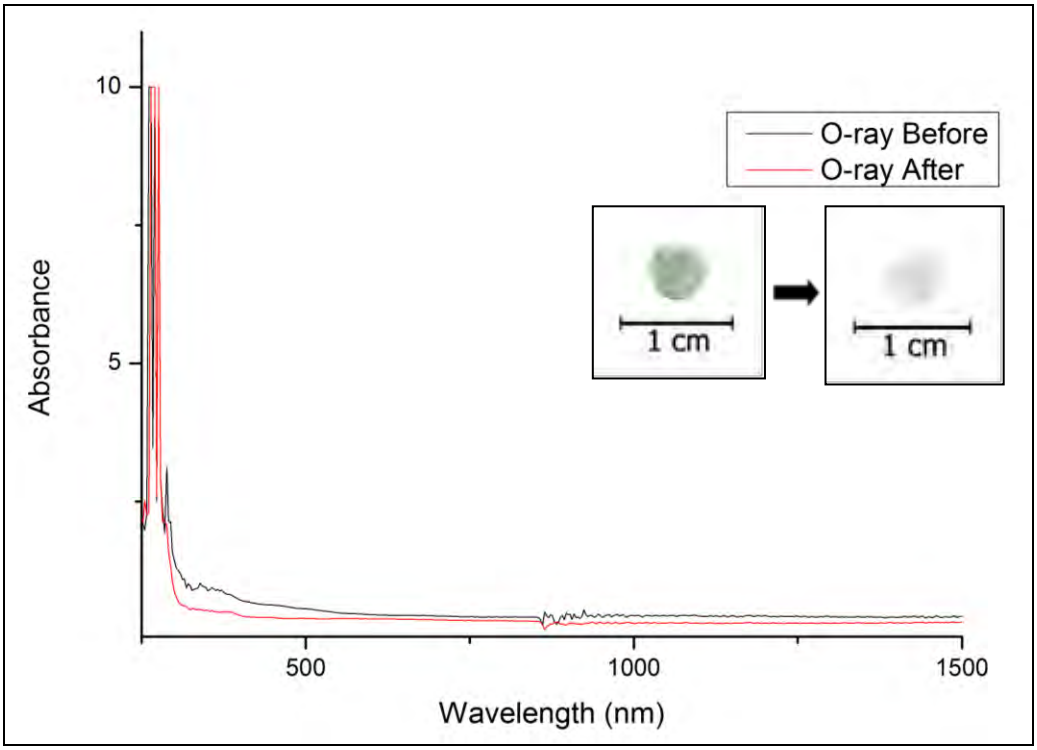


Fig.D38 UV-VIS-NIR absorption spectra of sample C3, before and after heat-treatment

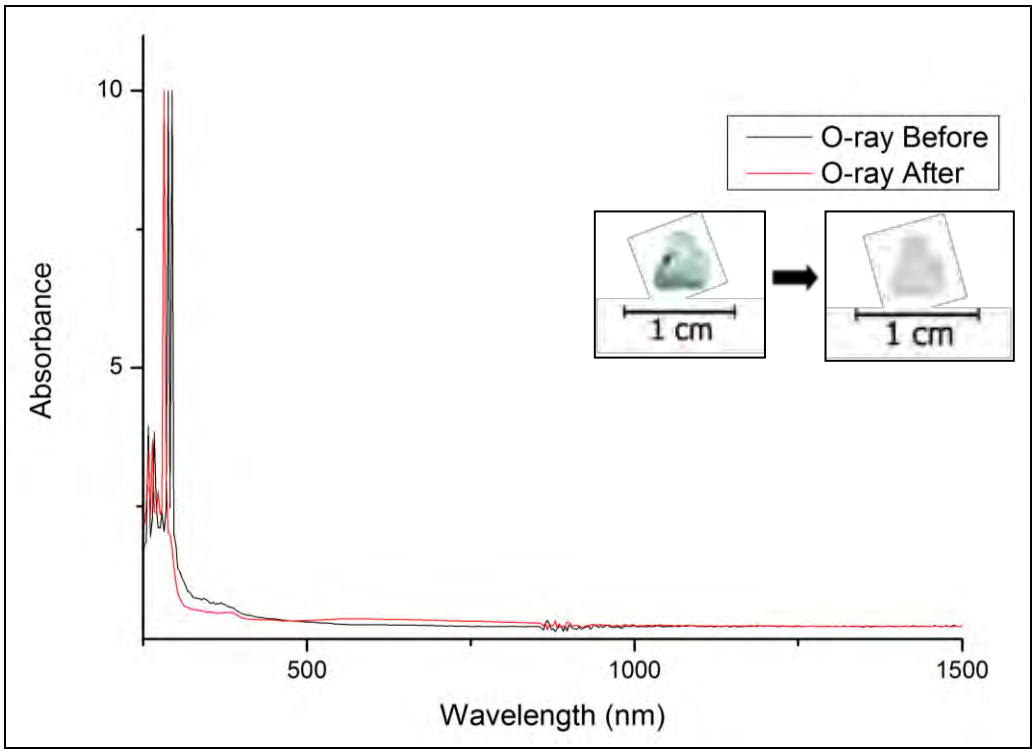


Fig.D39 UV-VIS-NIR absorption spectra of sample C4, before and after heat-treatment

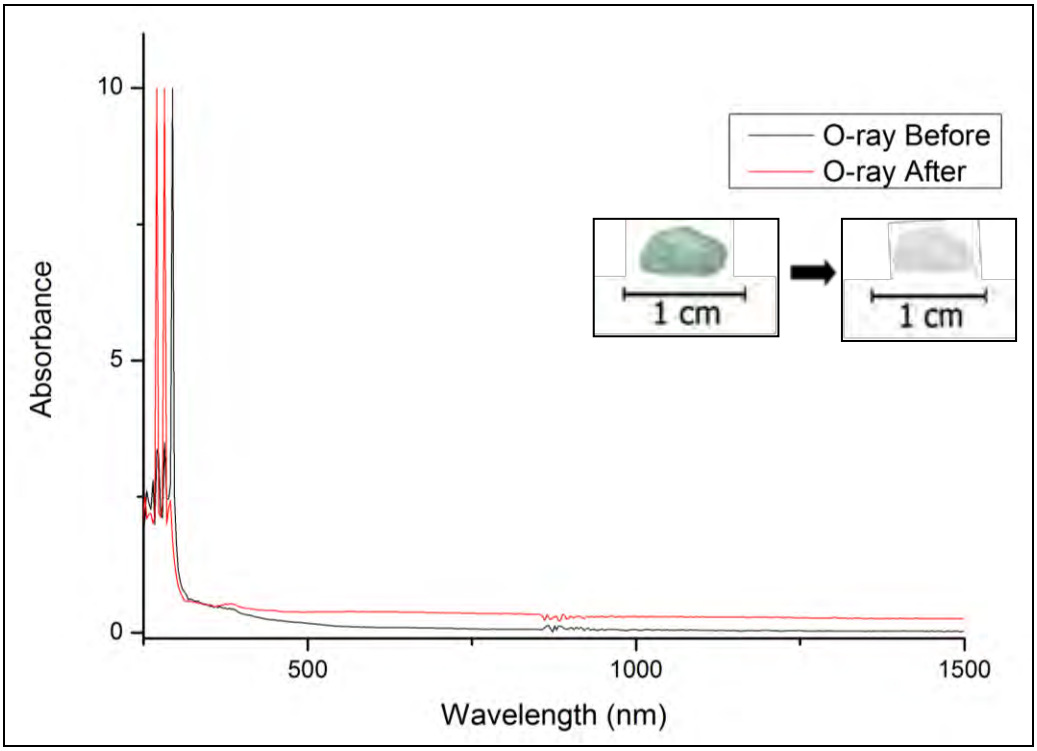


Fig.D40 UV-VIS-NIR absorption spectra of sample C5, before and after heat-treatment

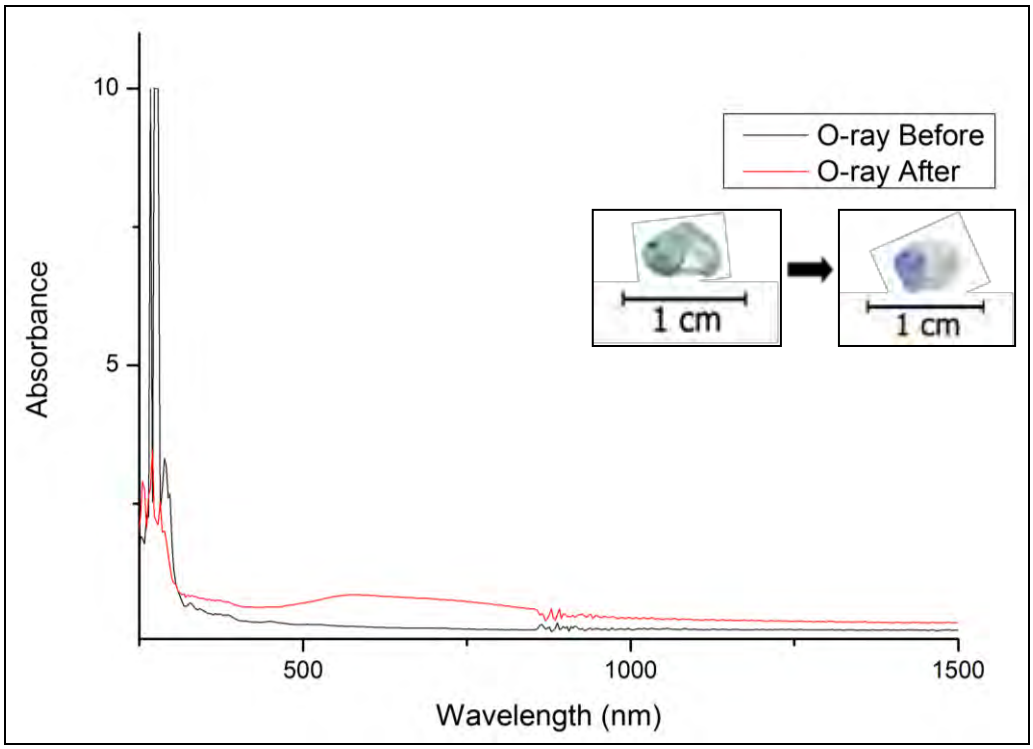


Fig.D41 UV-VIS-NIR absorption spectra of sample C6, before and after heat-treatment

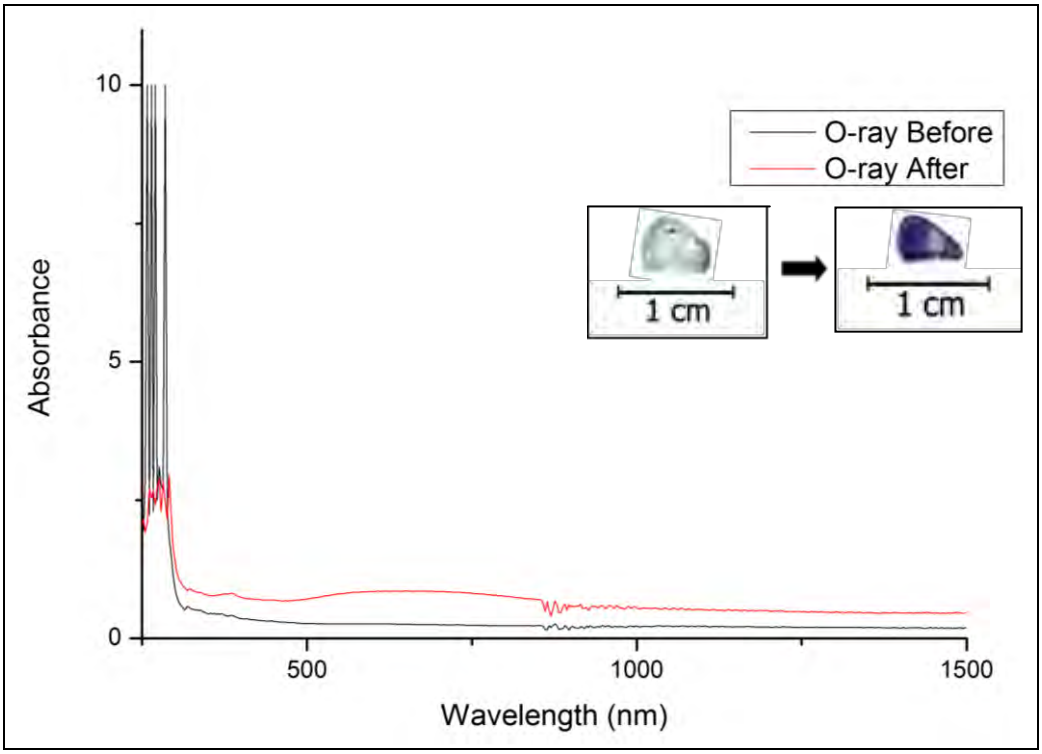


Fig.D42 UV-VIS-NIR absorption spectra of sample C7, before and after heat-treatment

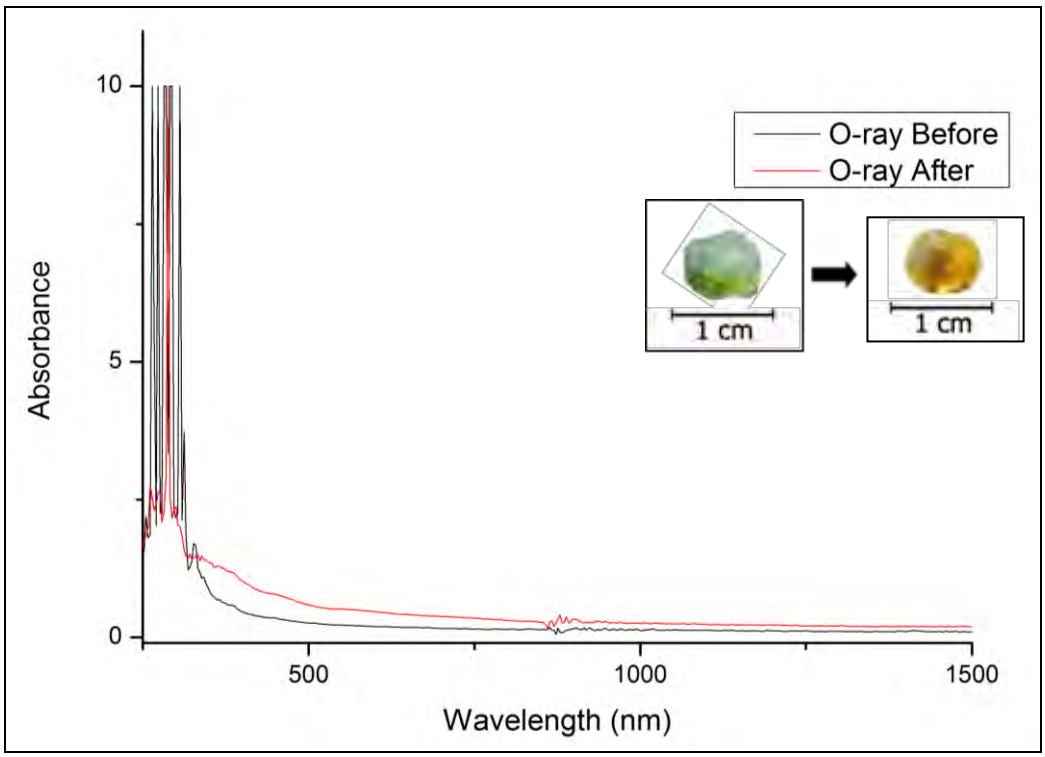


Fig.D43 UV-VIS-NIR absorption spectra of sample C8, before and after heat-treatment

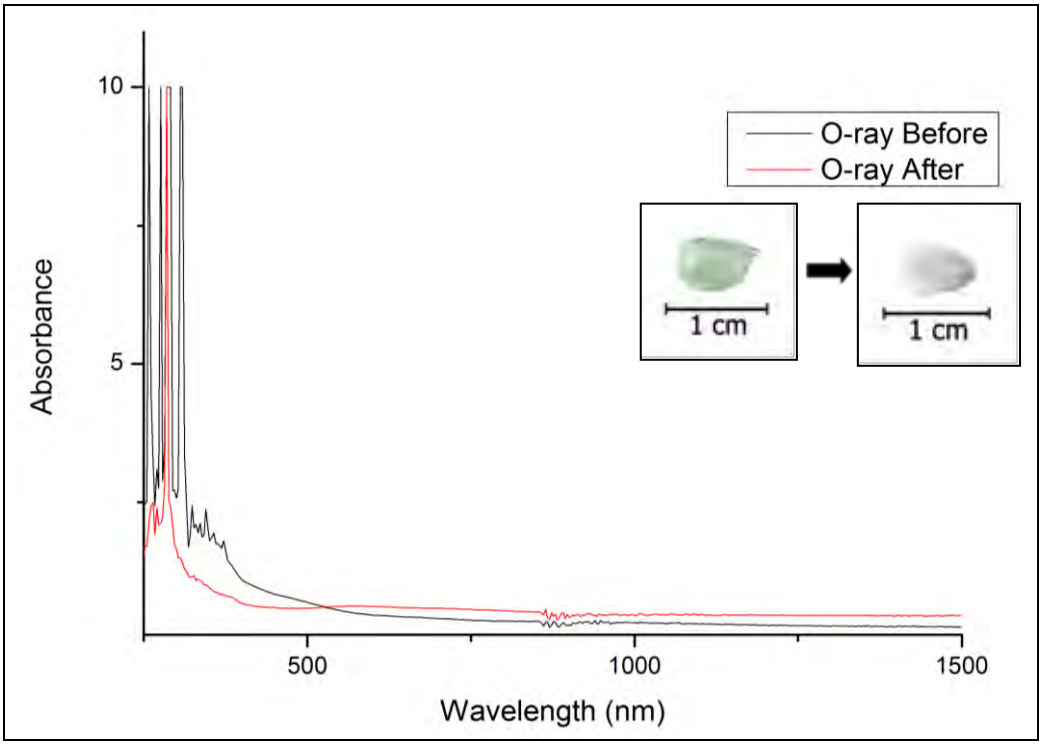


Fig.D44 UV-VIS-NIR absorption spectra of sample C9, before and after heat-treatment

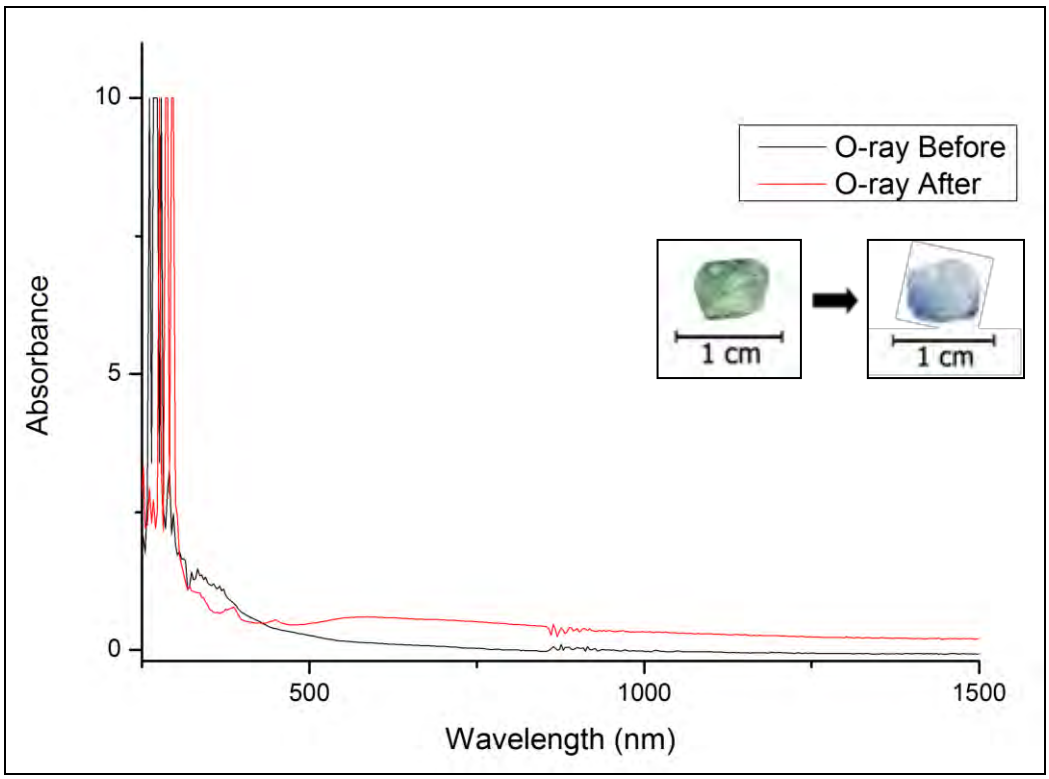


Fig.D45 UV-VIS-NIR absorption spectra of sample C10, before and after heat-treatment

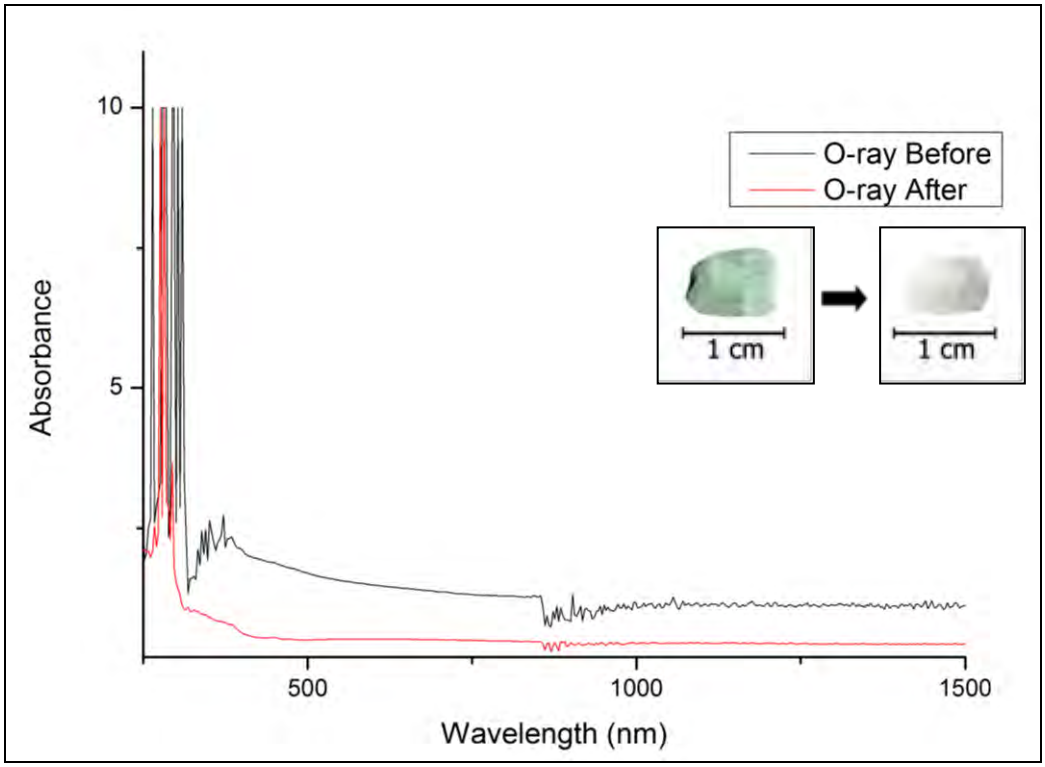


Fig.D46 UV-VIS-NIR absorption spectra of sample C11, before and after heat-treatment

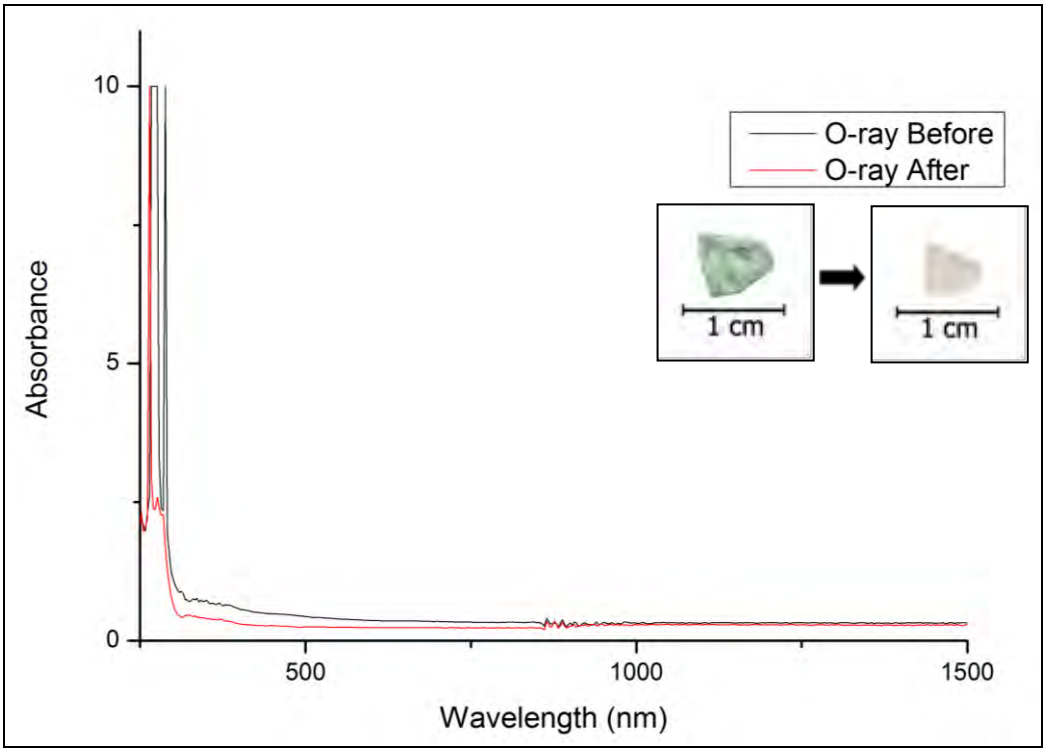


Fig.D47 UV-VIS-NIR absorption spectra of sample C12, before and after heat-treatment

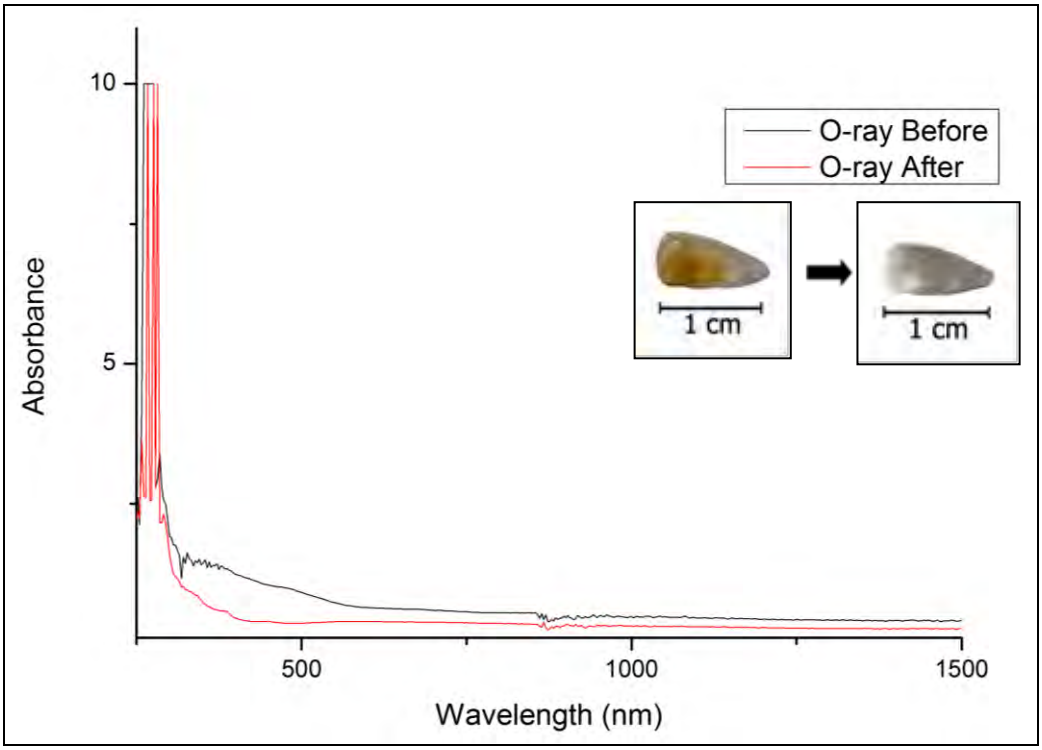


Fig.D48 UV-VIS-NIR absorption spectra of sample Y2, before and after heat-treatment

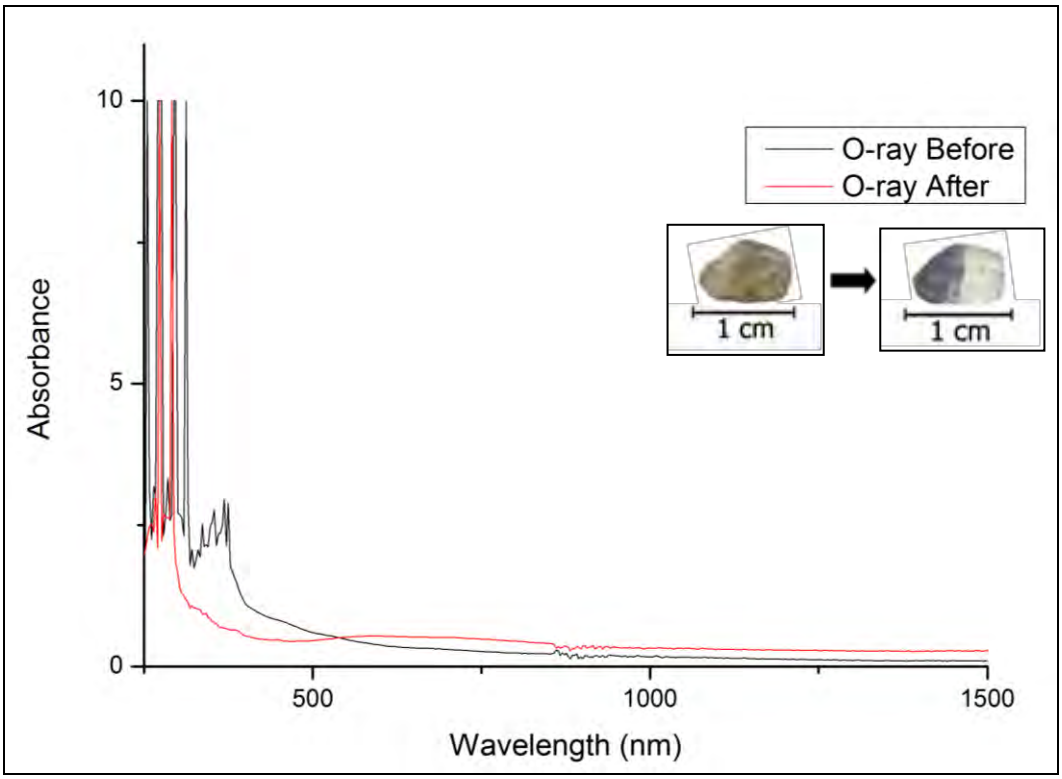


Fig.D49 UV-VIS-NIR absorption spectra of sample Y3, before and after heat-treatment

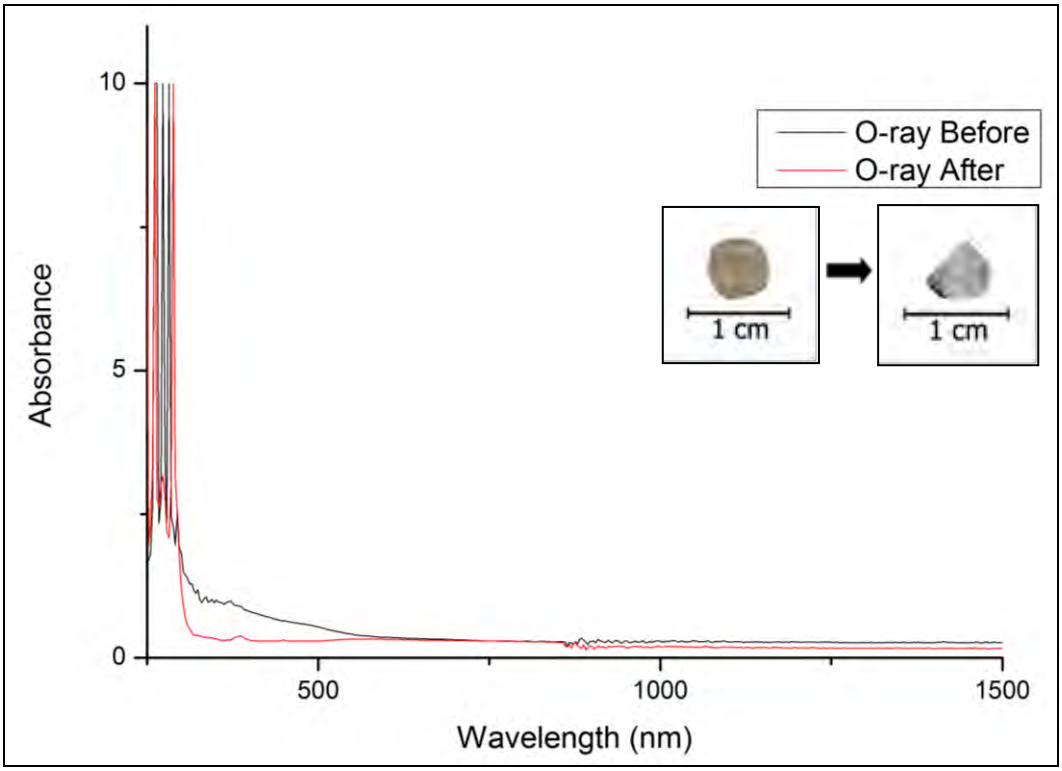


Fig.D50 UV-VIS-NIR absorption spectra of sample Y4, before and after heat-treatment

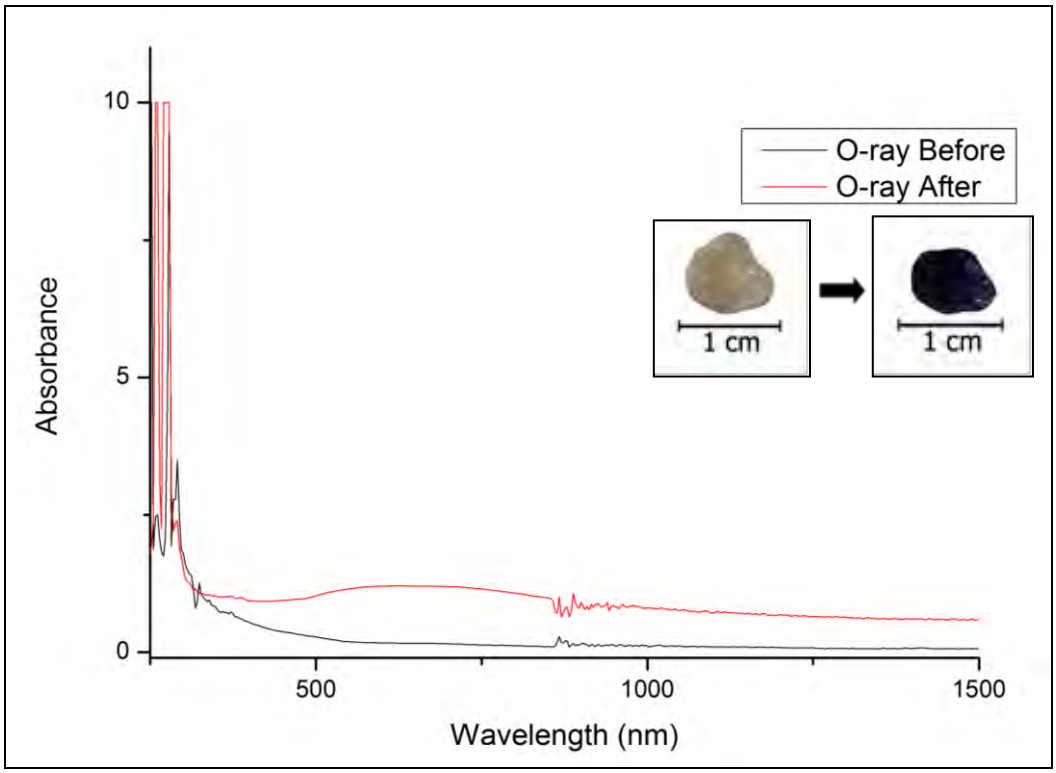


Fig.D51 UV-VIS-NIR absorption spectra of sample Y5, before and after heat-treatment

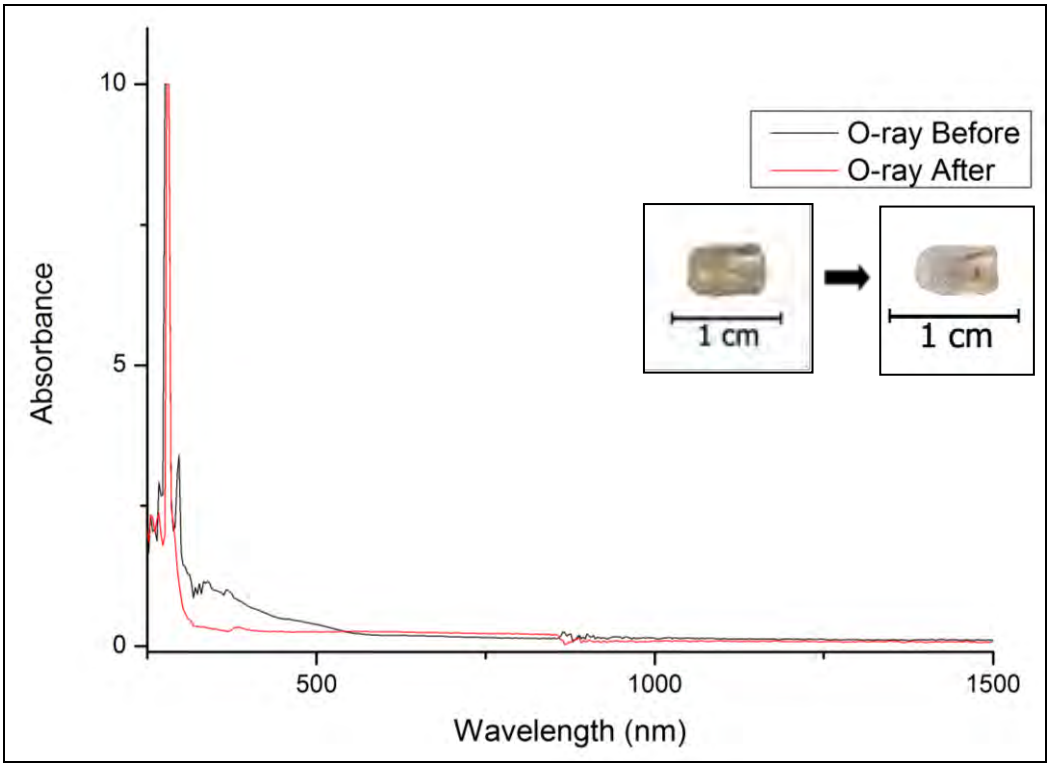


Fig.D52 UV-VIS-NIR absorption spectra of sample Y6, before and after heat-treatment

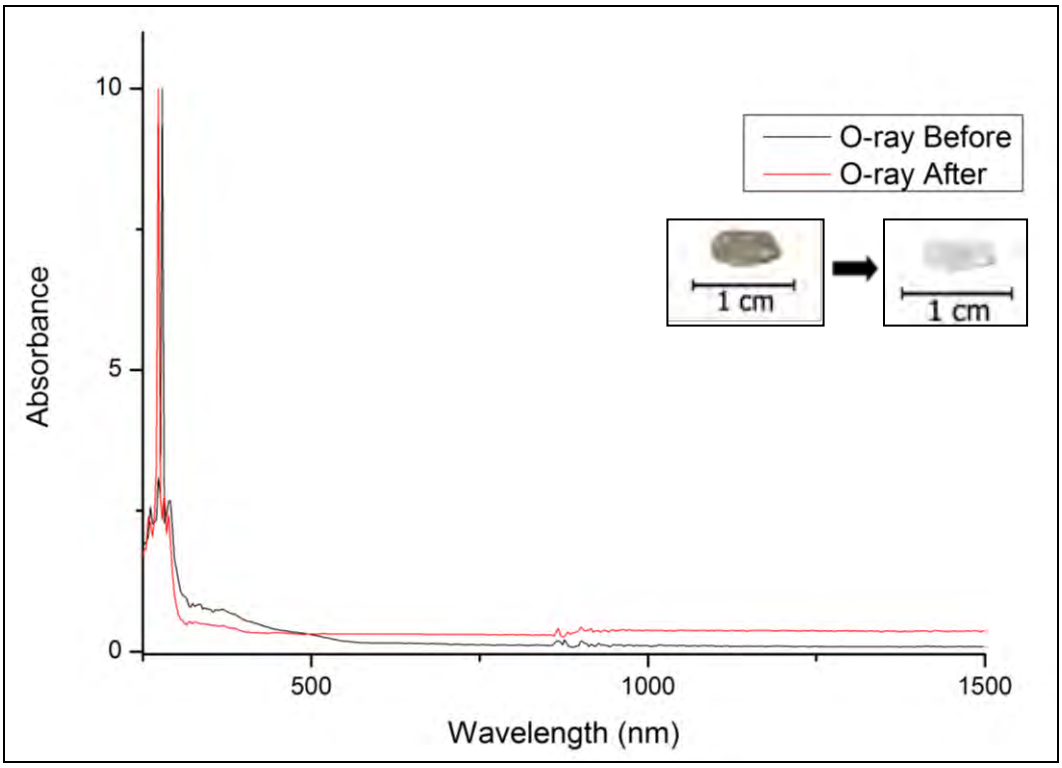


Fig.D53 UV-VIS-NIR absorption spectra of sample Y7, before and after heat-treatment

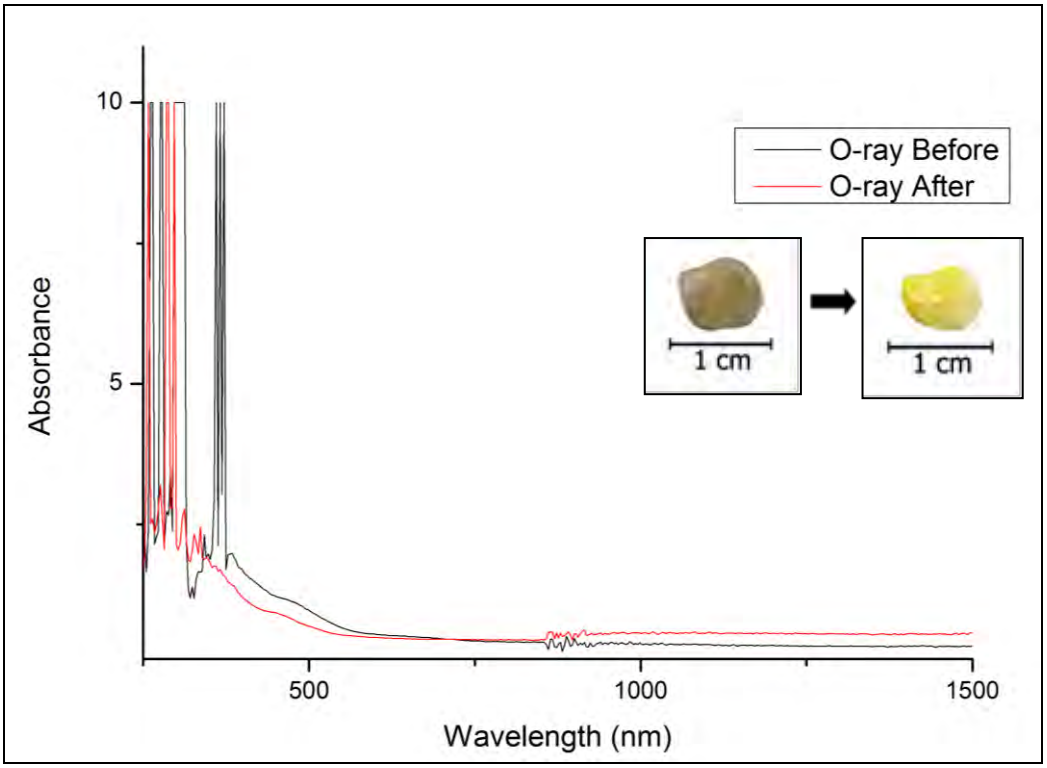


Fig.D54 UV-VIS-NIR absorption spectra of sample Y8, before and after heat-treatment

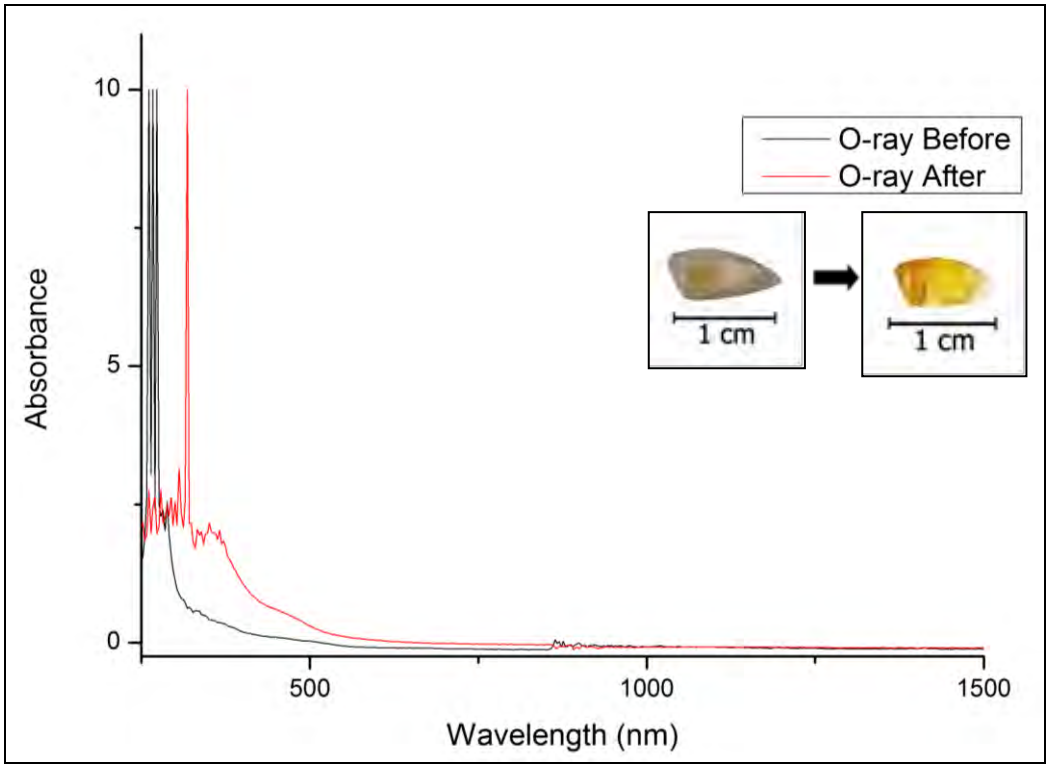


Fig.D55 UV-VIS-NIR absorption spectra of sample Y9, before and after heat-treatment

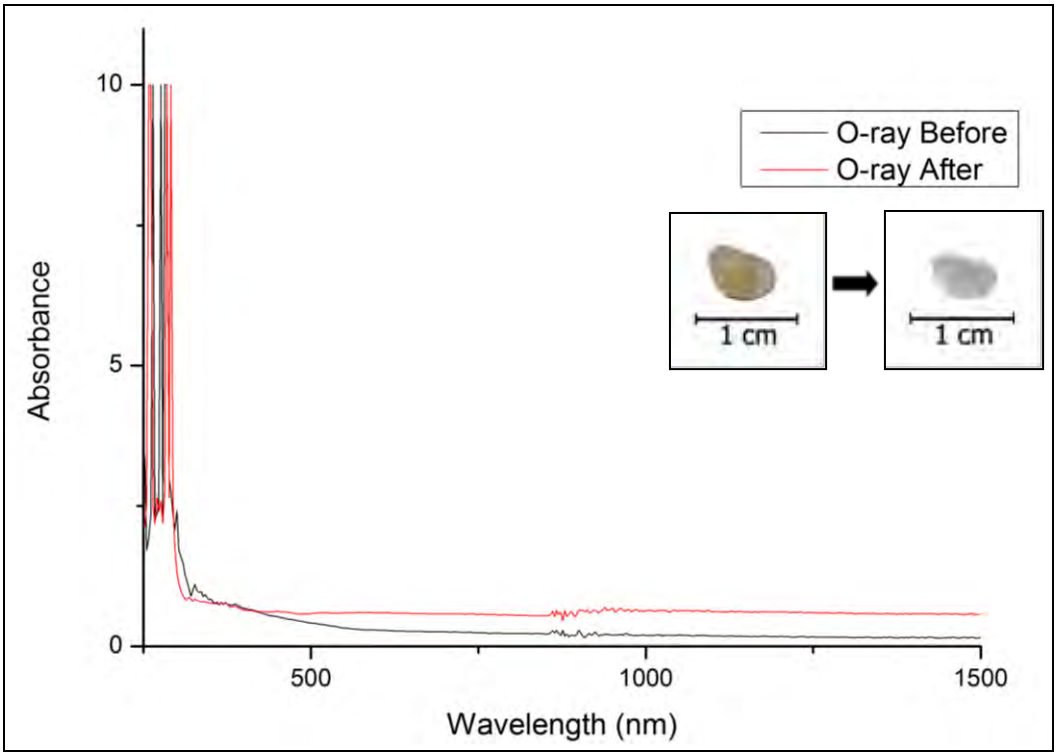


Fig.D56 UV-VIS-NIR absorption spectra of sample Y10, before and after heat-treatment

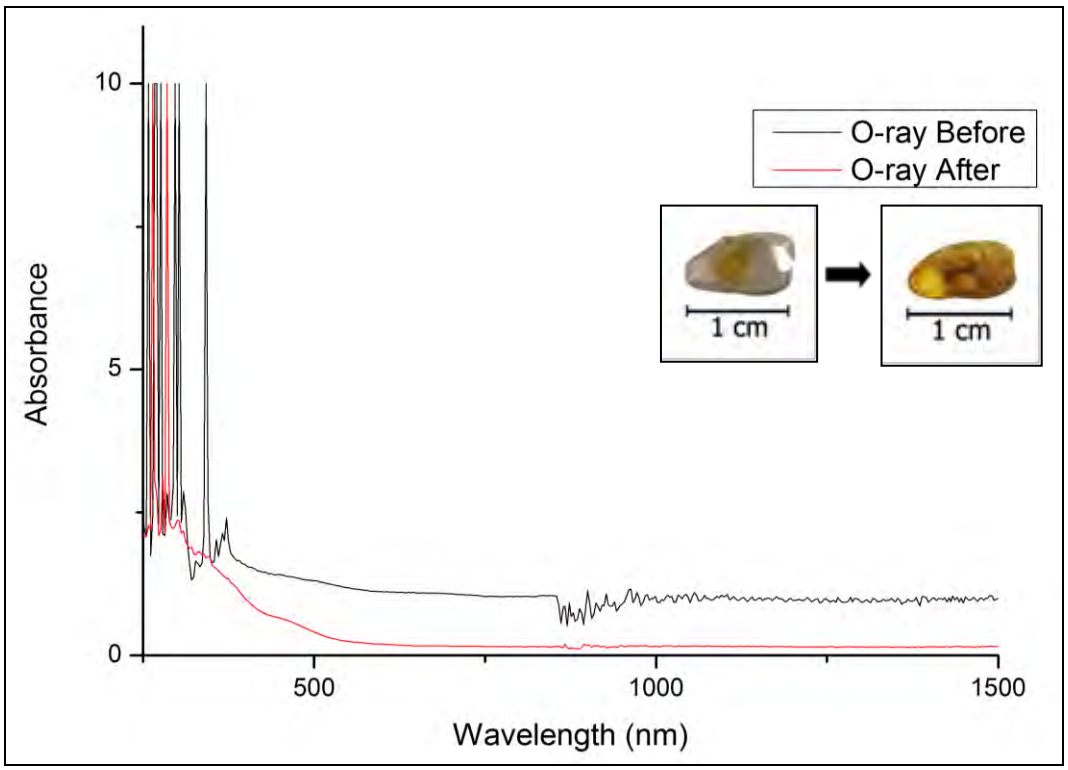


Fig.D57 UV-VIS-NIR absorption spectra of sample Y11, before and after heat-treatment

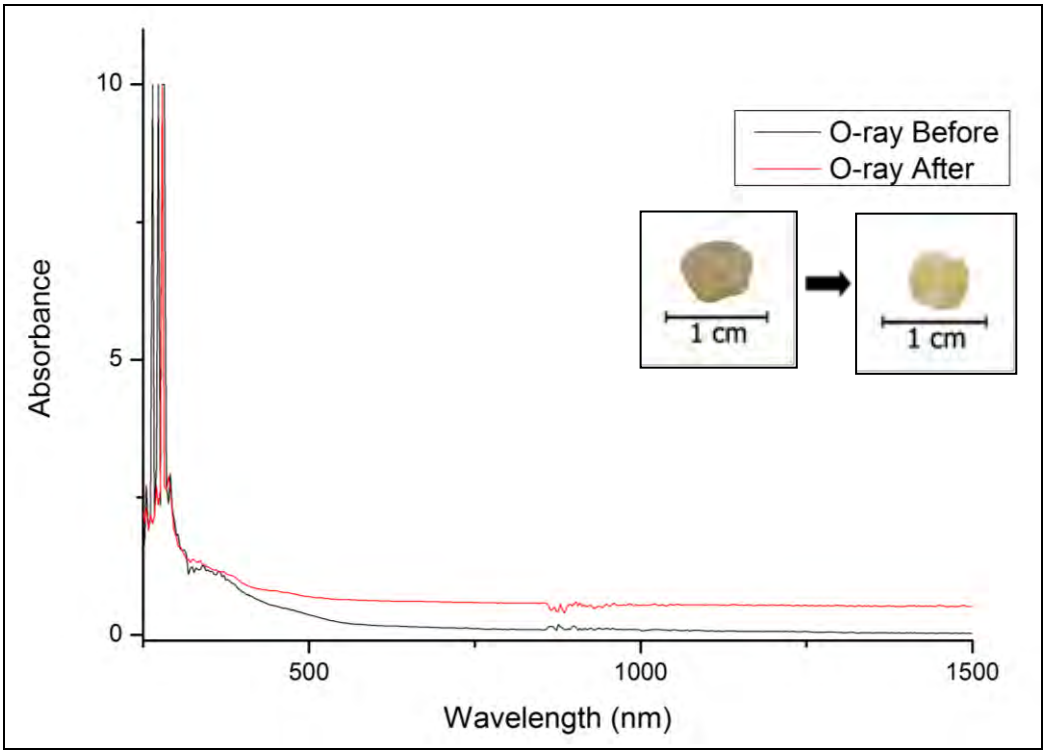


Fig.D58 UV-VIS-NIR absorption spectra of sample Y12, before and after heat-treatment

APPENDIX E

E. Fourier Transform Infraed (FTIR) spectra

The FTIR absorption spectra in 400-4000 cm^{-1} range of 29 rough sapphires were observed before and after treatment. The spectra showed a similar pattern and the representative spectra of samples are displayed in Figs. E1-E29.

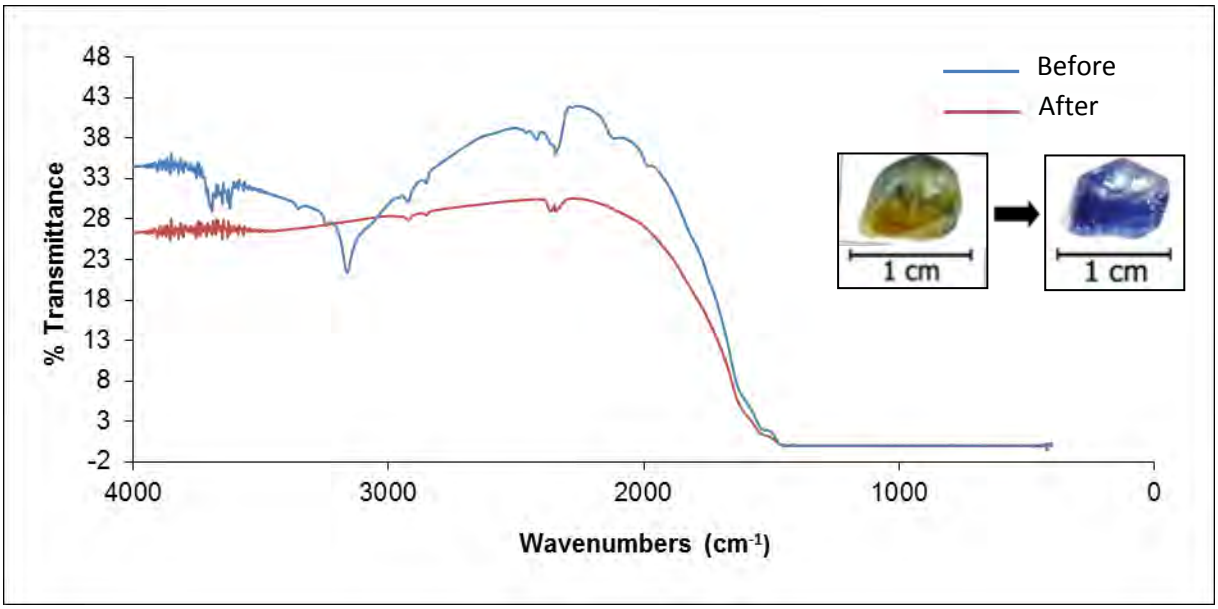


Fig.E1 FTIR absorption spectrum of sample B1, Deniyaya sapphires Group B

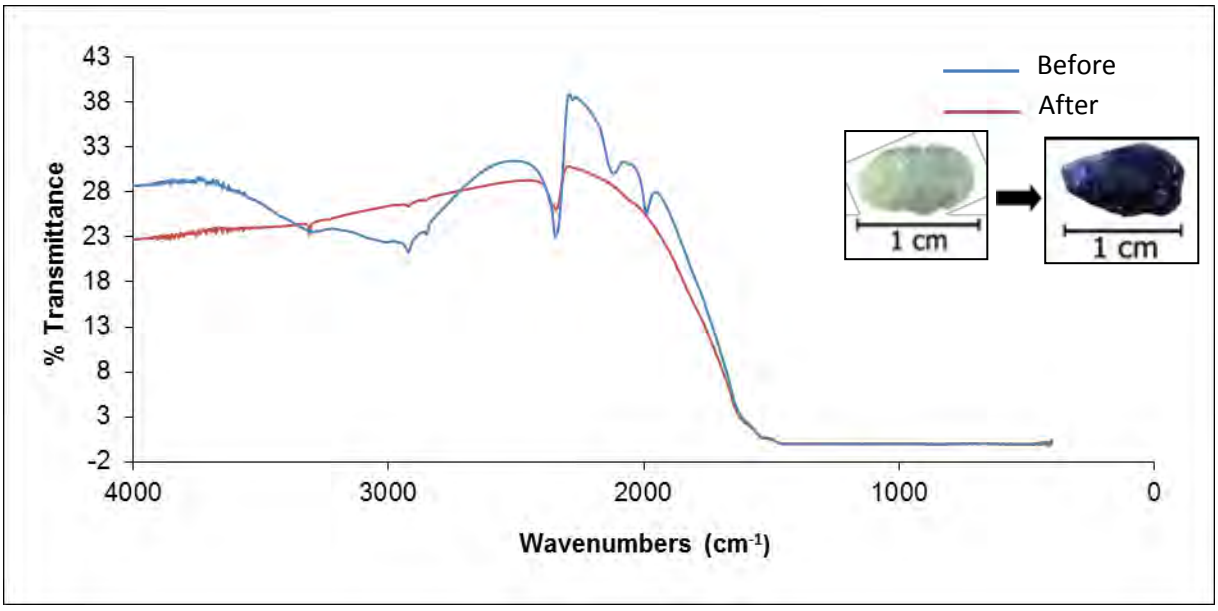


Fig.E2 FTIR absorption spectrum of sample B2, Deniyaya sapphires Group B

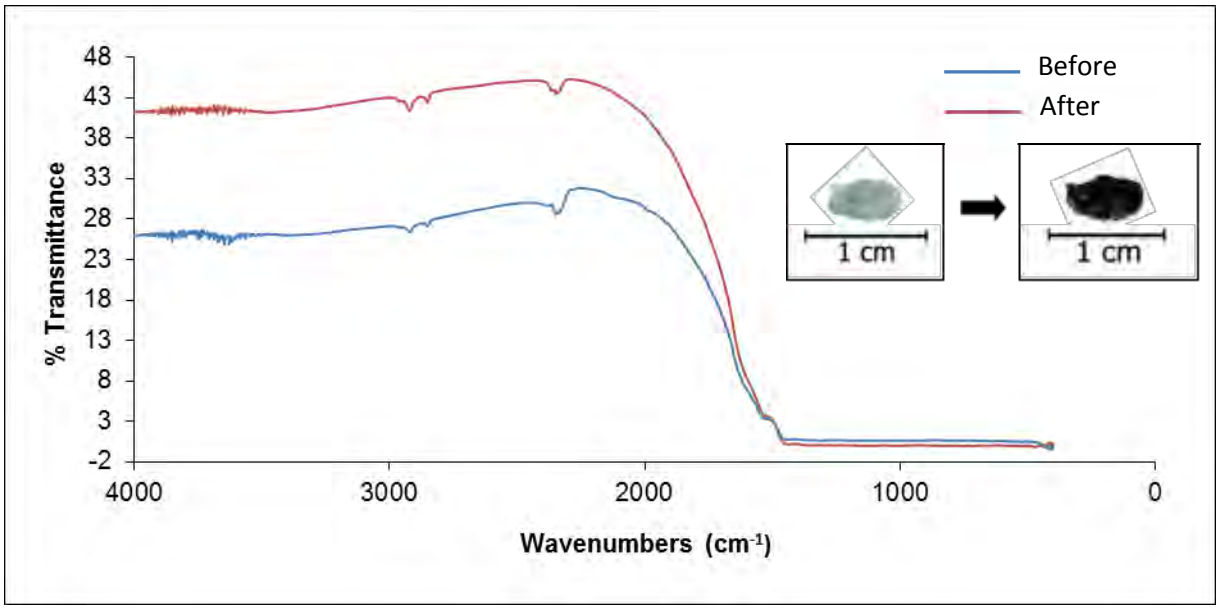


Fig.E3 FTIR absorption spectrum of sample B3, Deniyaya sapphires Group B

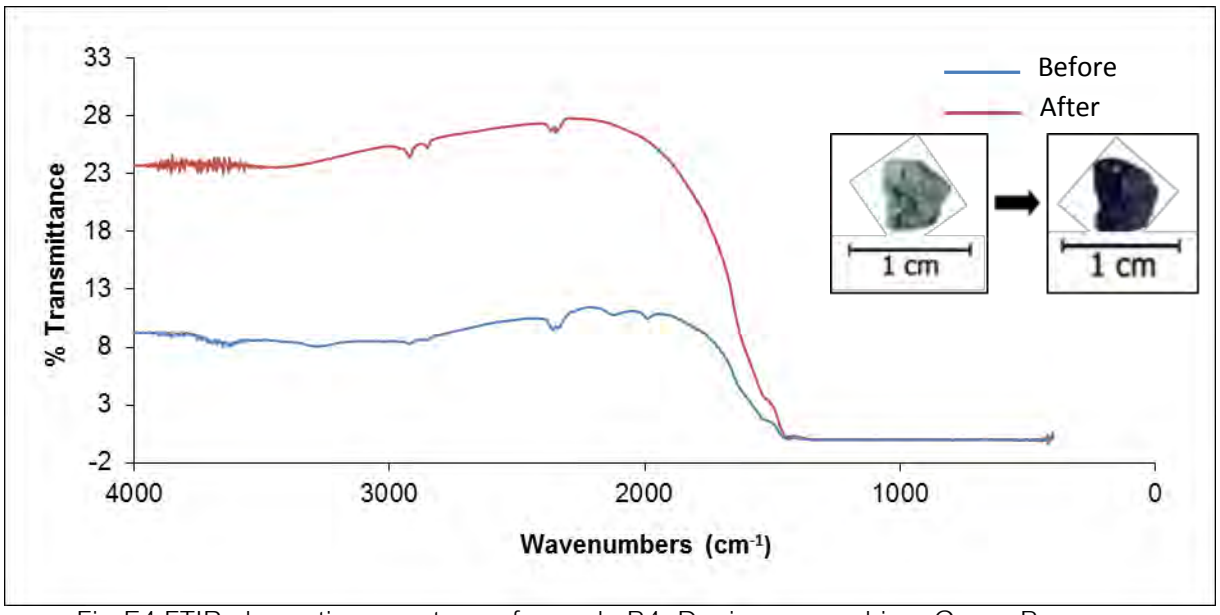


Fig.E4 FTIR absorption spectrum of sample B4, Deniyaya sapphires Group B

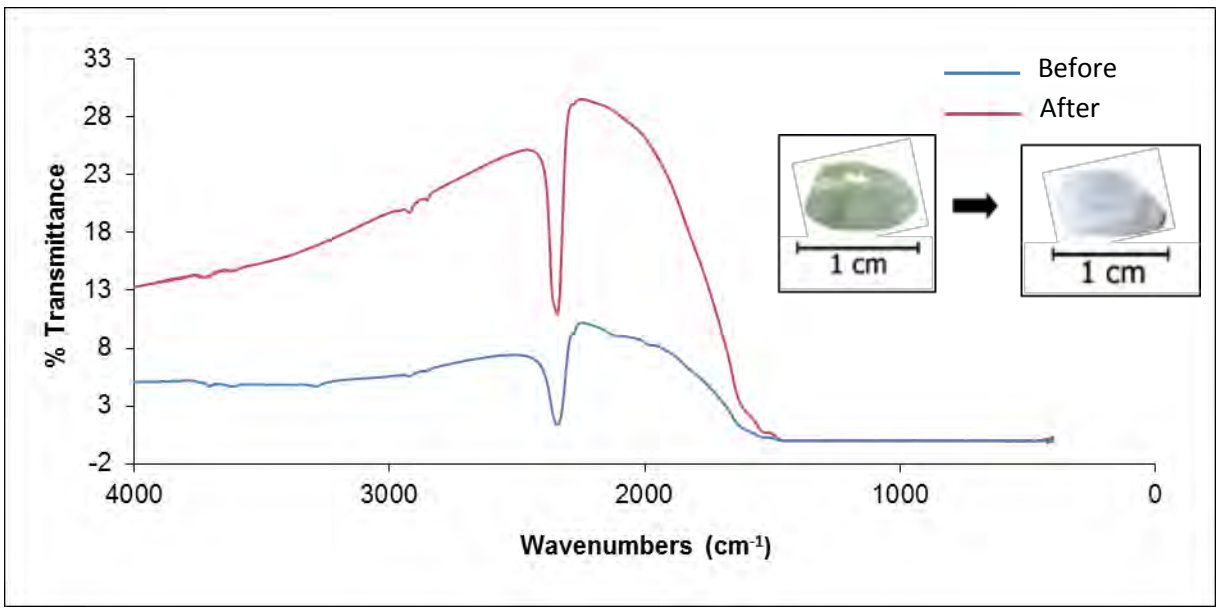


Fig.E5 FTIR absorption spectrum of sample B5, Deniyaya sapphires Group B

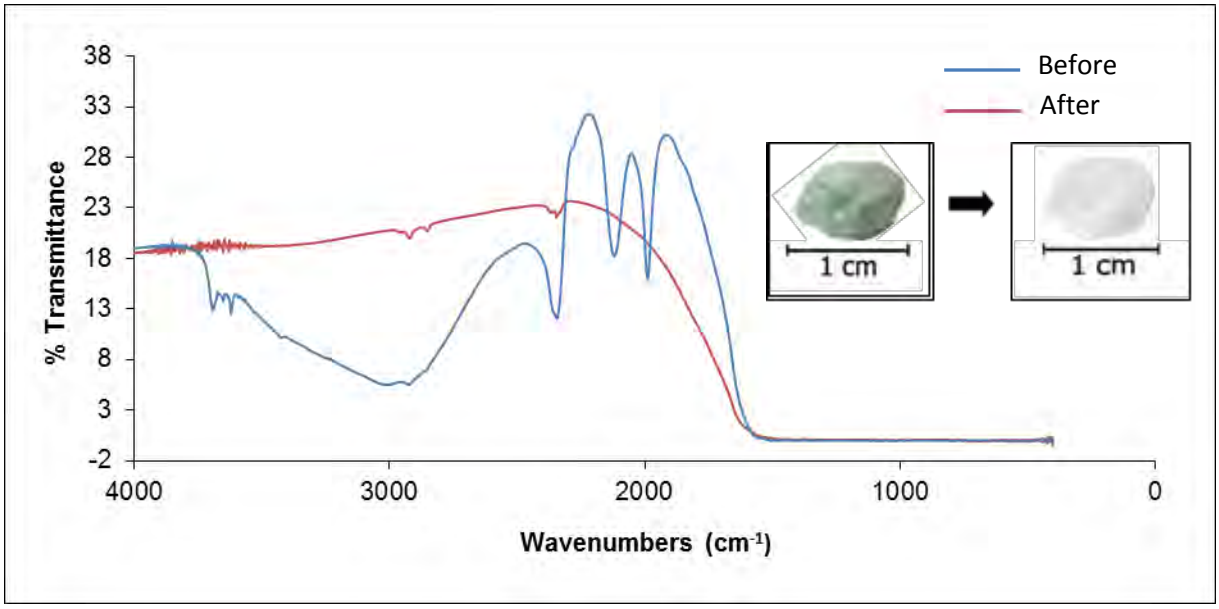


Fig.E6 FTIR absorption spectrum of sample B6, Deniyaya sapphires Group B

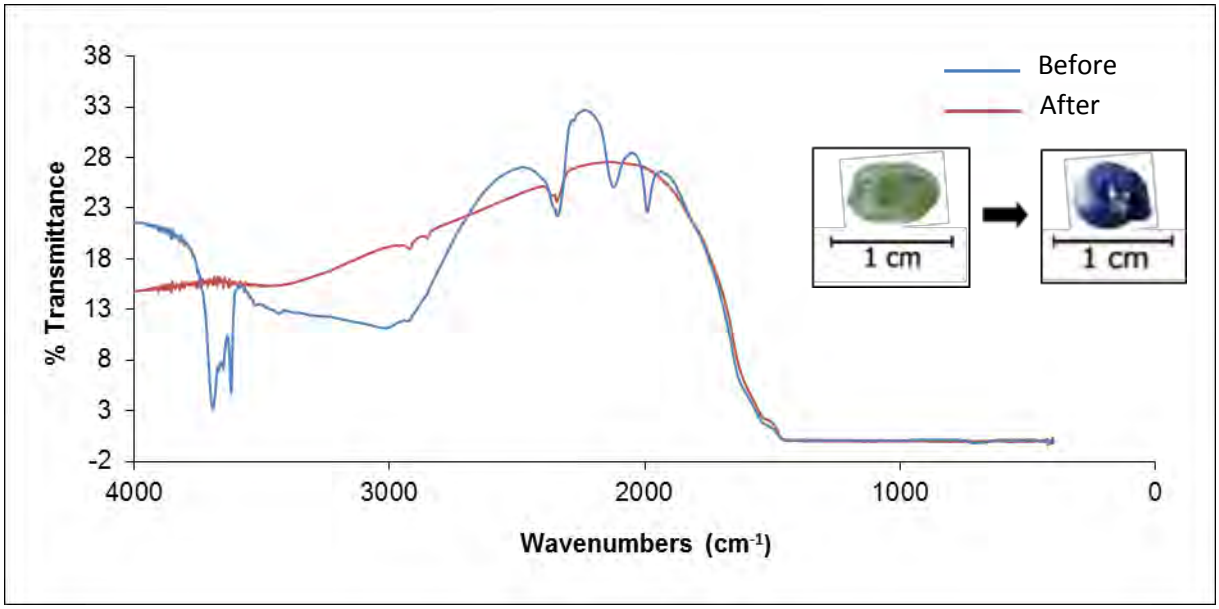


Fig.E7 FTIR absorption spectrum of sample B7, Deniyaya sapphires Group B

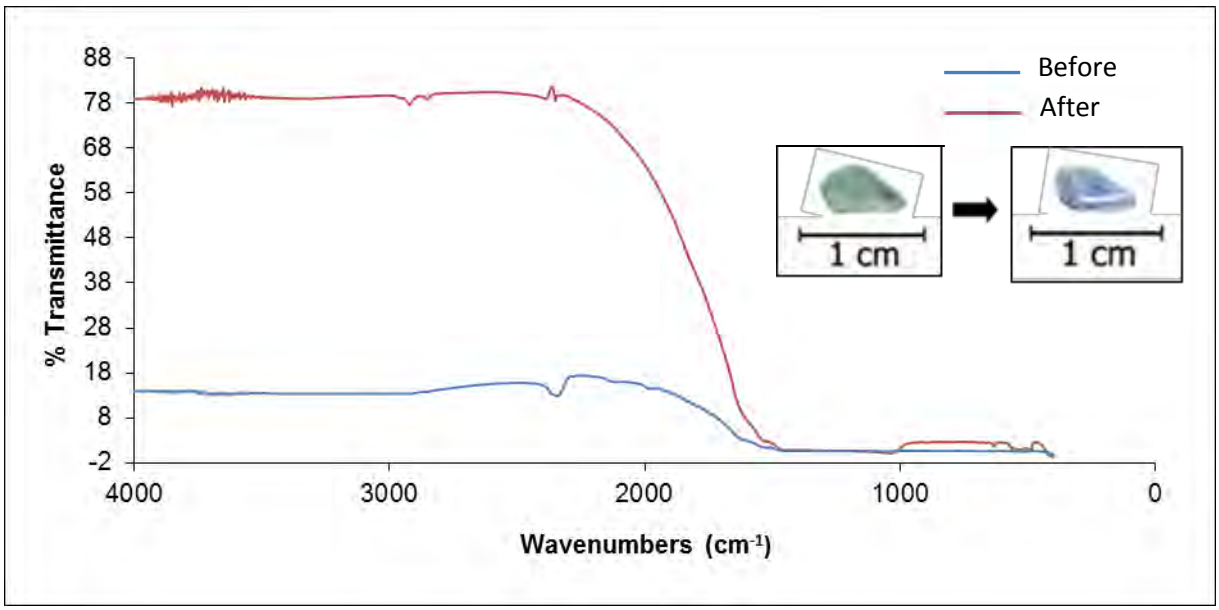


Fig.E8 FTIR absorption spectrum of sample C1, Deniyaya sapphires Group C

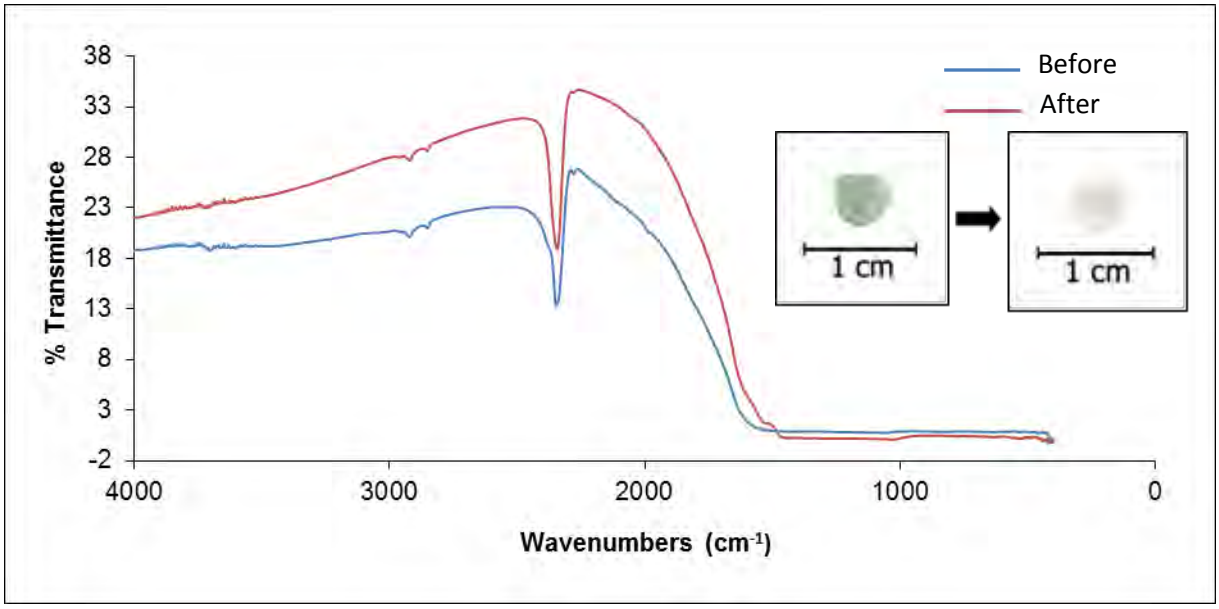


Fig.E9 FTIR absorption spectrum of sample C3, Deniyaya sapphires Group C

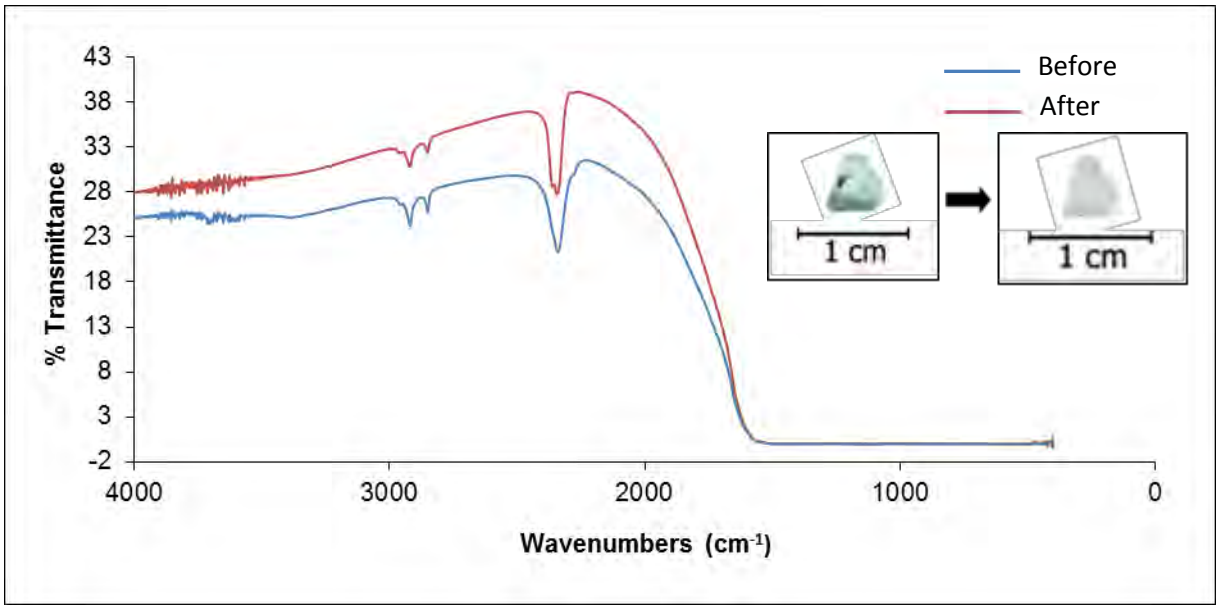


Fig.E10 FTIR absorption spectrum of sample C4, Deniyaya sapphires Group C

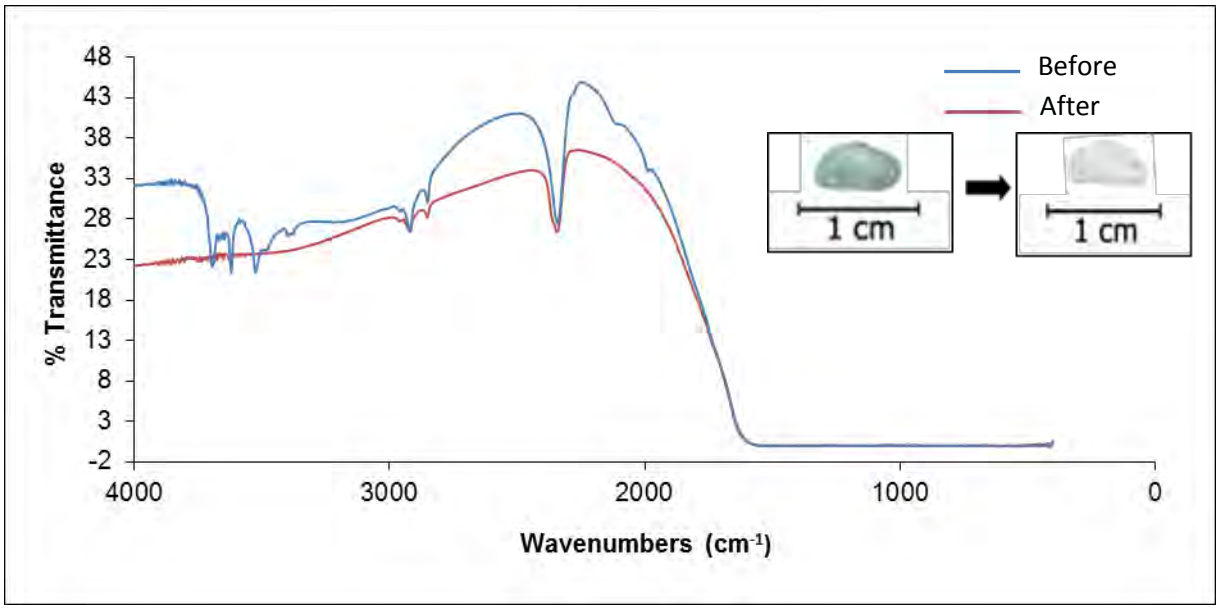


Fig.E11 FTIR absorption spectrum of sample C5, Deniyaya sapphires Group C

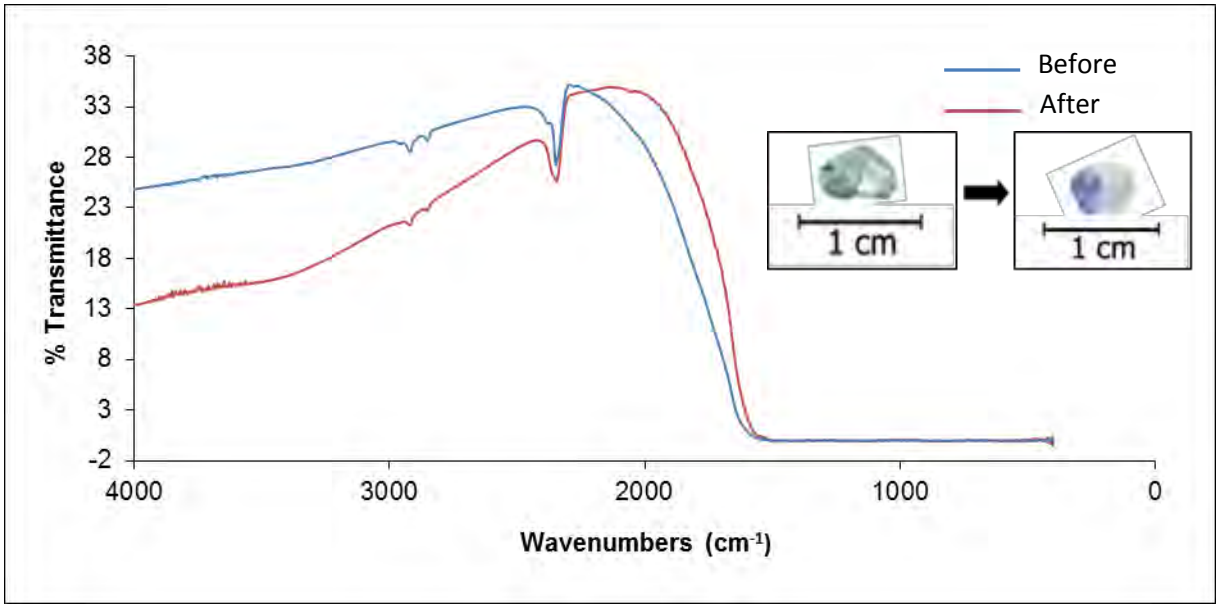


Fig.E12 FTIR absorption spectrum of sample C6, Deniyaya sapphires Group C

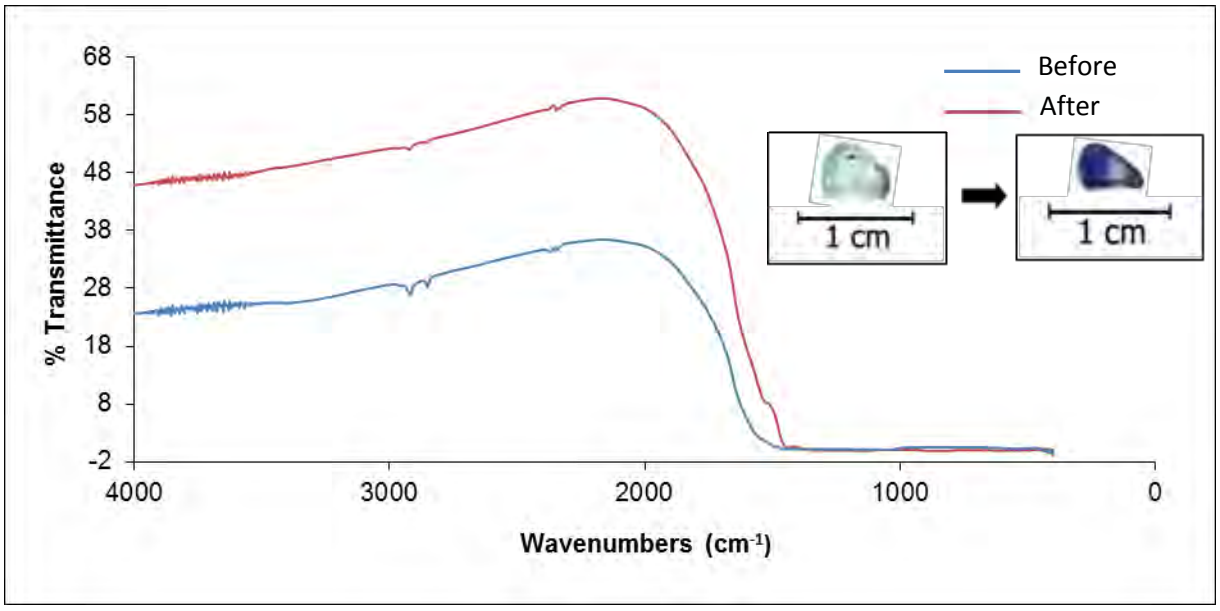


Fig.E13 FTIR absorption spectrum of sample C7, Deniyaya sapphires Group C

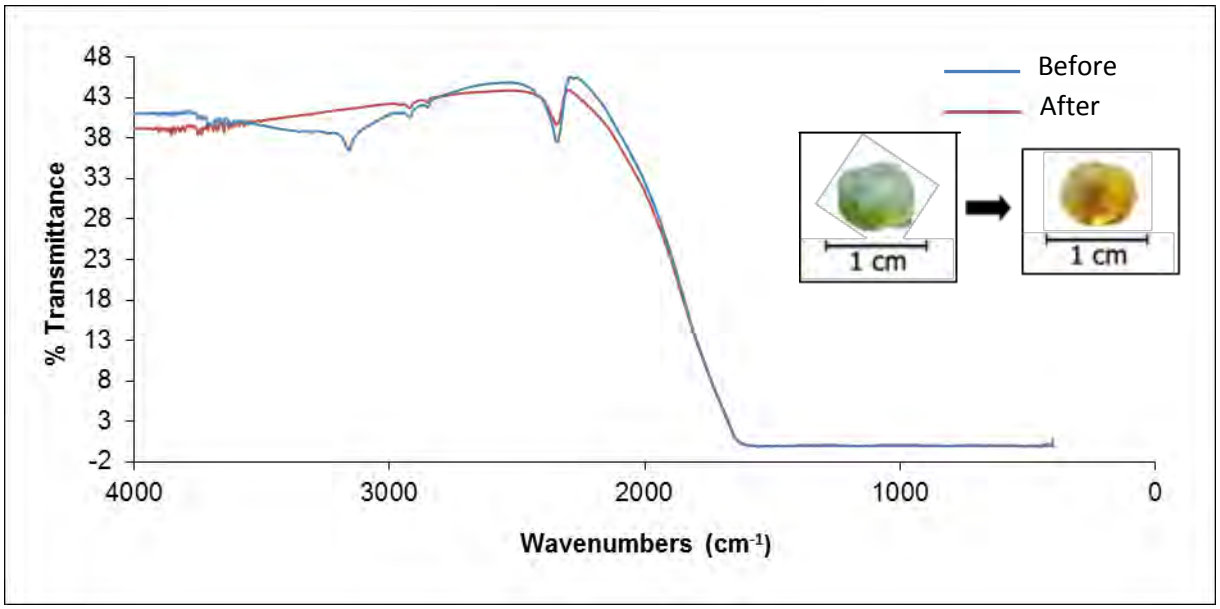


Fig.E14 FTIR absorption spectrum of sample C8, Deniyaya sapphires Group C

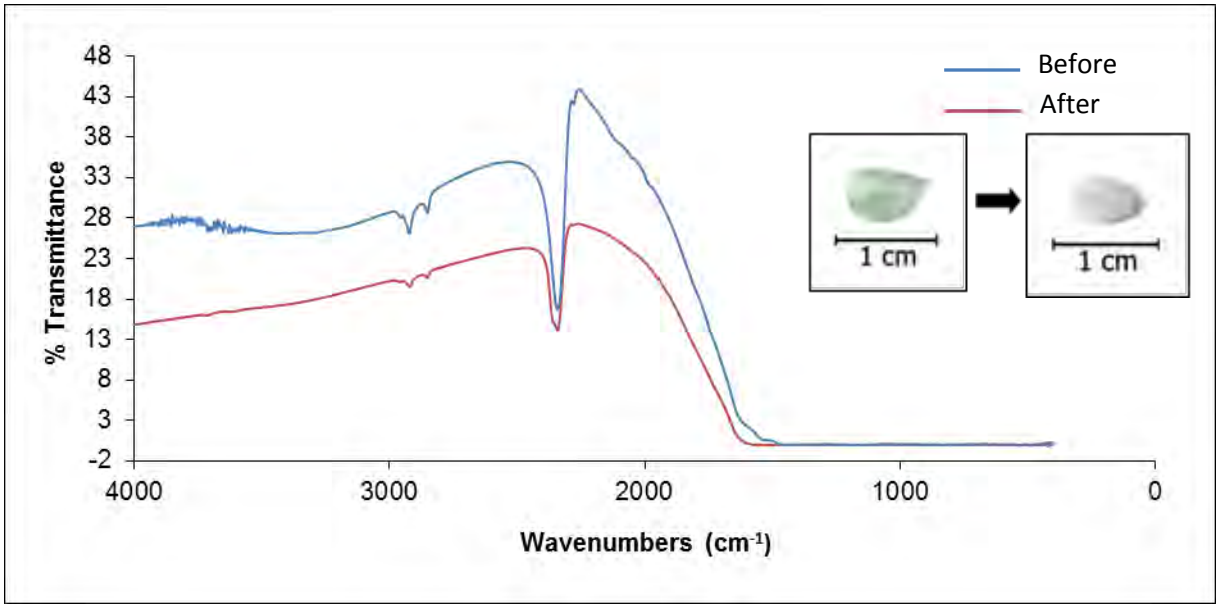


Fig.E15 FTIR absorption spectrum of sample C9, Deniyaya sapphires Group C

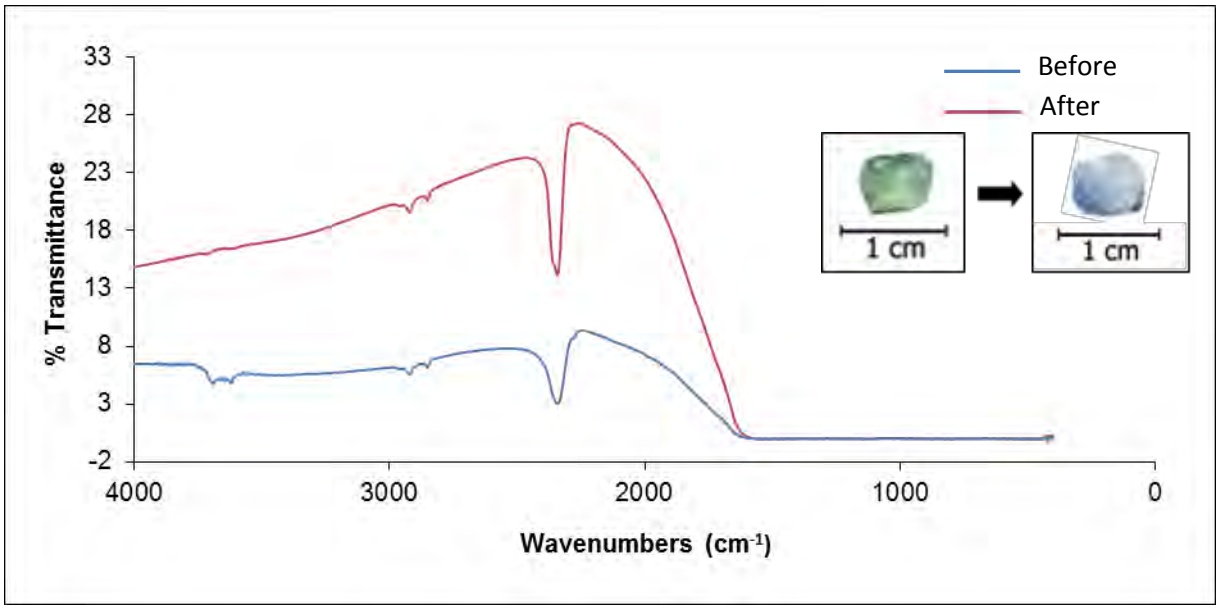


Fig.E16 FTIR absorption spectrum of sample C10, Deniyaya sapphires Group C

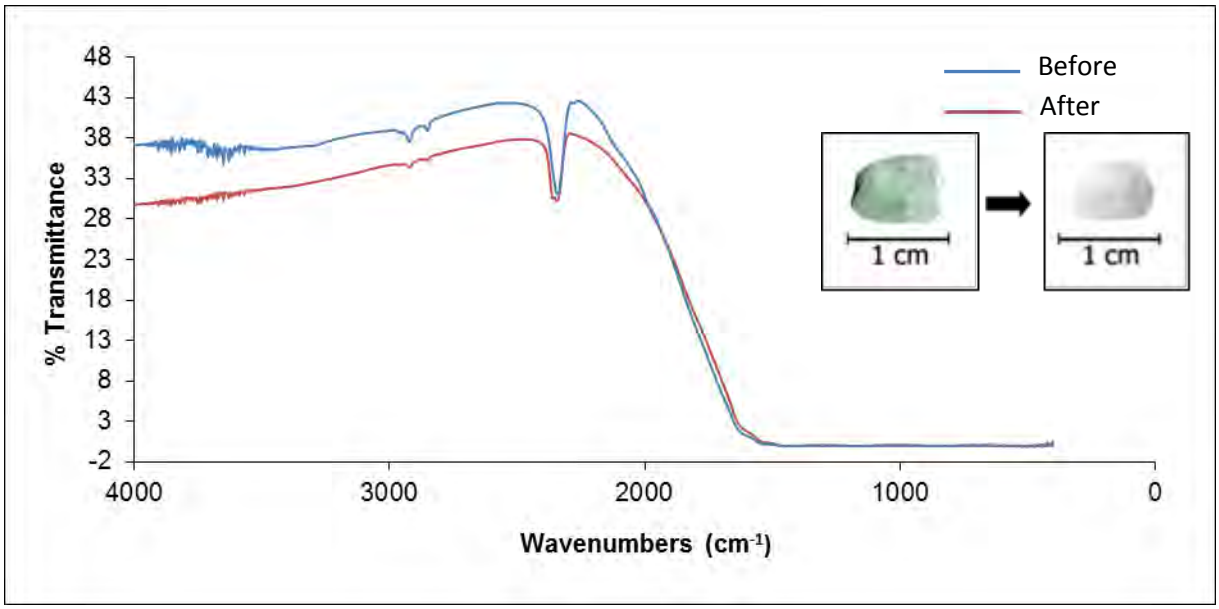


Fig.E17 FTIR absorption spectrum of sample C11, Deniyaya sapphires Group C

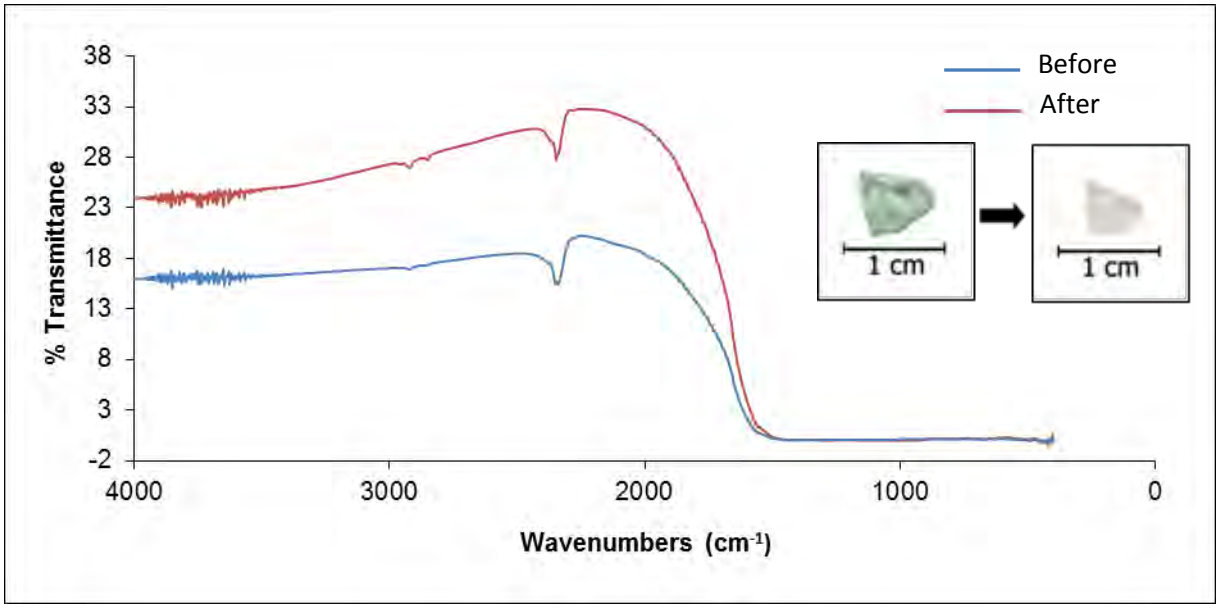


Fig.E18 FTIR absorption spectrum of sample C12, Deniyaya sapphires Group C

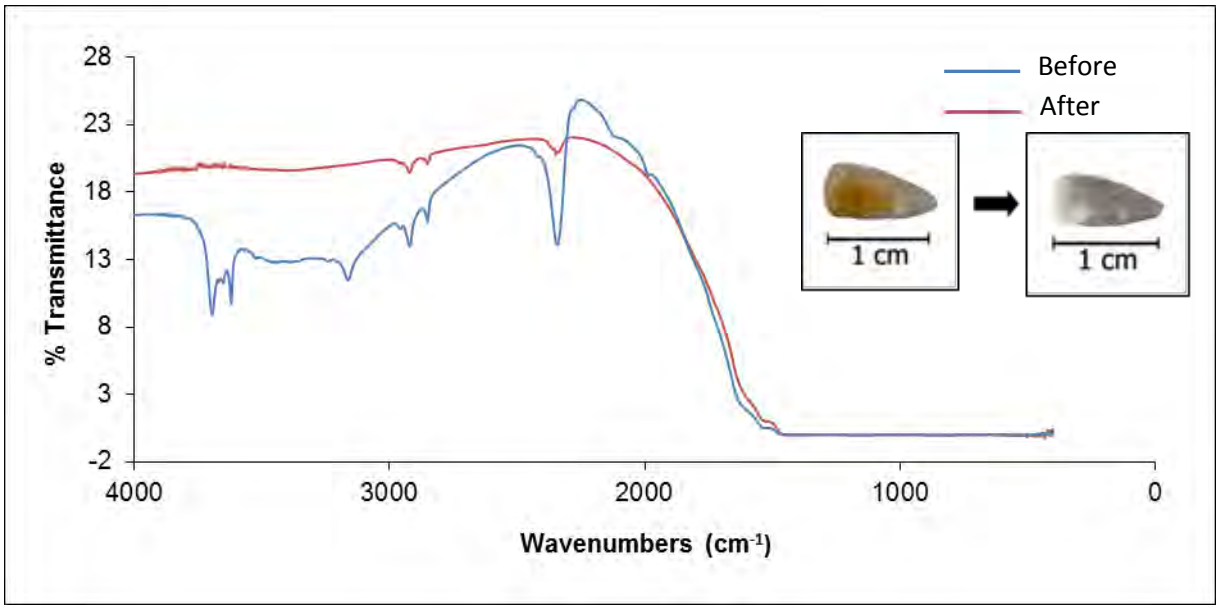


Fig.E19 FTIR absorption spectrum of sample Y2, Deniyaya sapphires Group Y

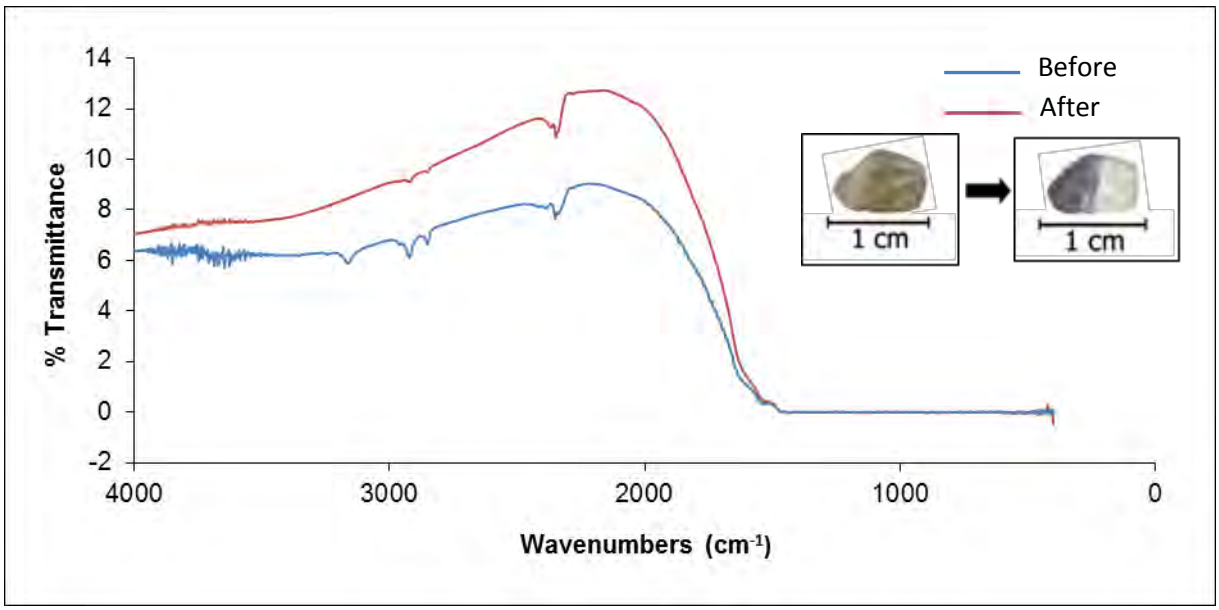


Fig.E20 FTIR absorption spectrum of sample Y3, Deniyaya sapphires Group Y

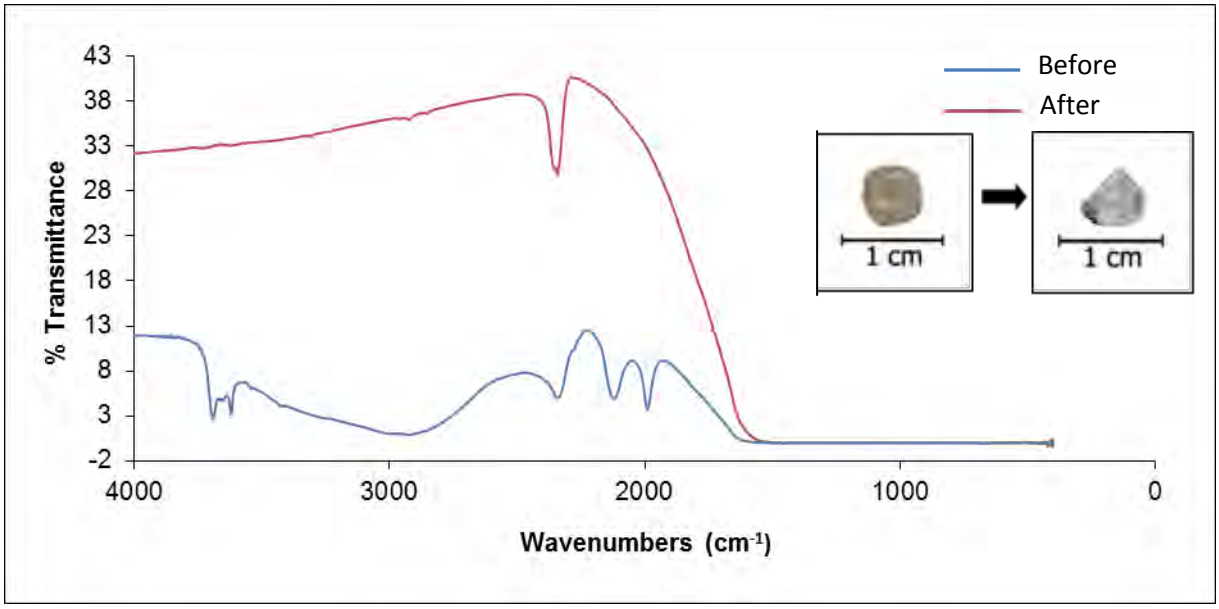


Fig.E21 FTIR absorption spectrum of sample Y4, Deniyaya sapphires Group Y

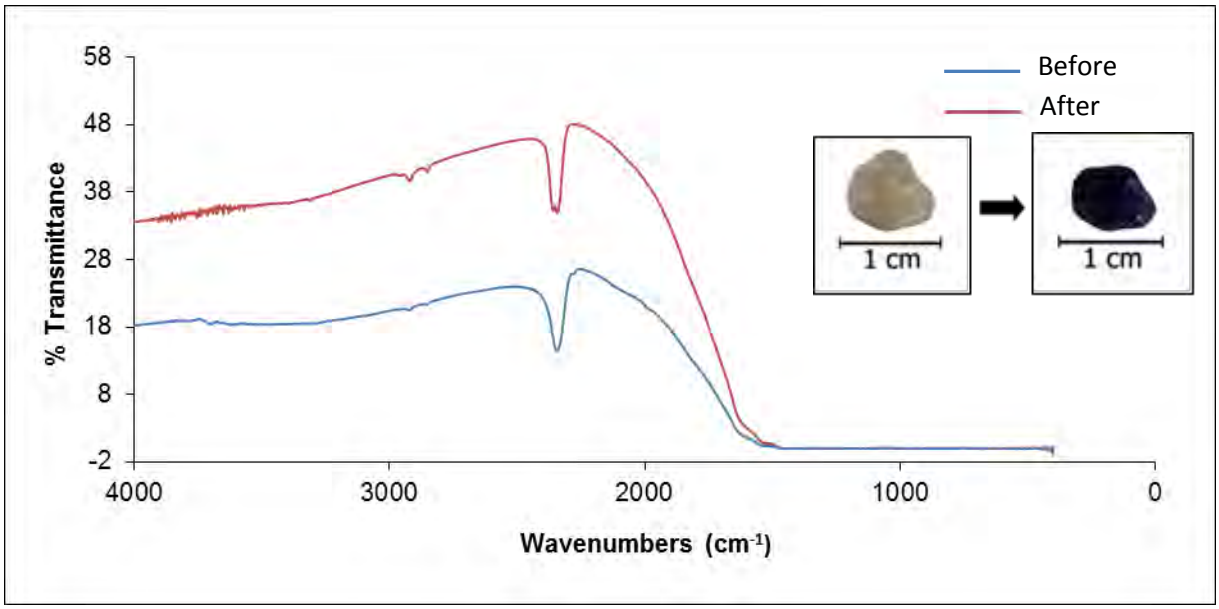


Fig.E22 FTIR absorption spectrum of sample Y5, Deniyaya sapphires Group Y

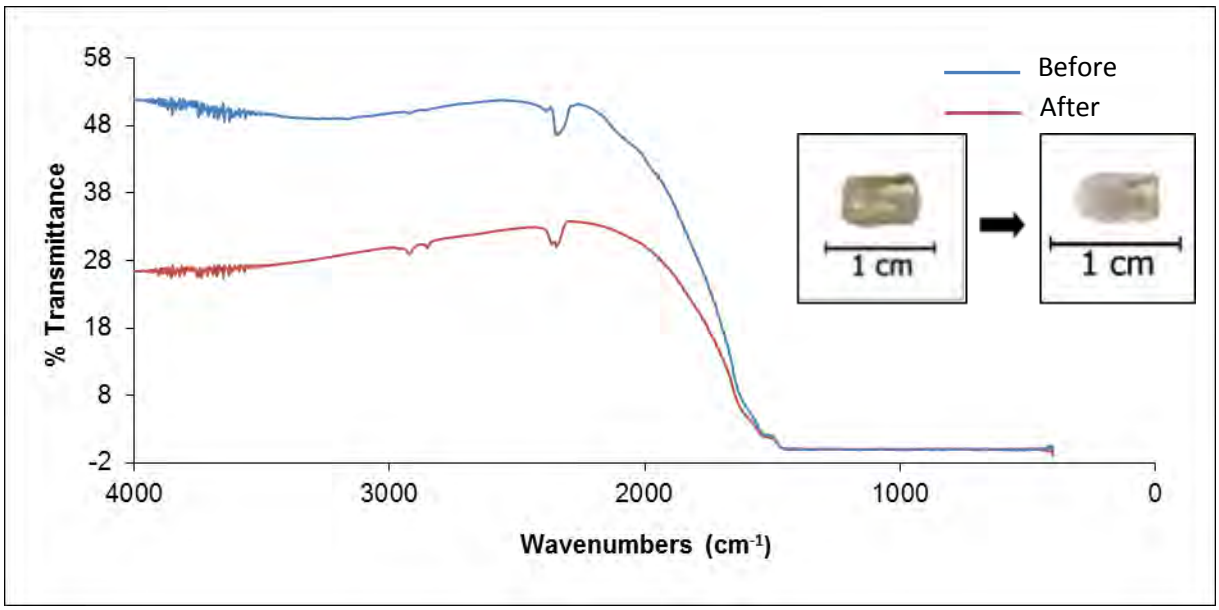


Fig.E23 FTIR absorption spectrum of sample Y6, Deniyaya sapphires Group Y

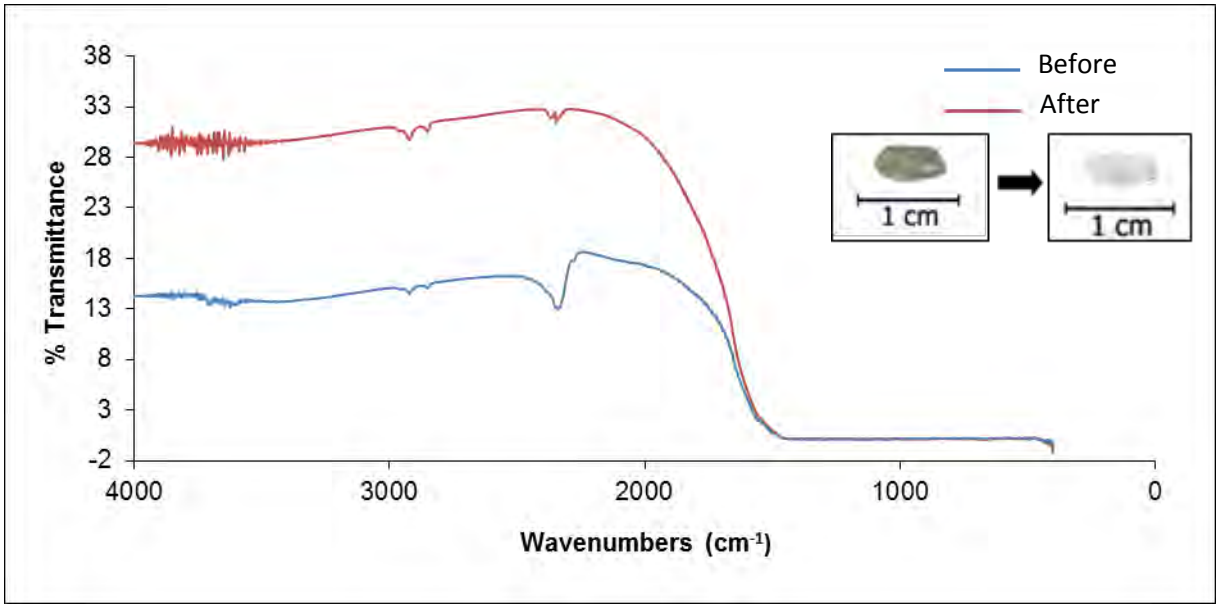


Fig.E24 FTIR absorption spectrum of sample Y7, Deniyaya sapphires Group Y

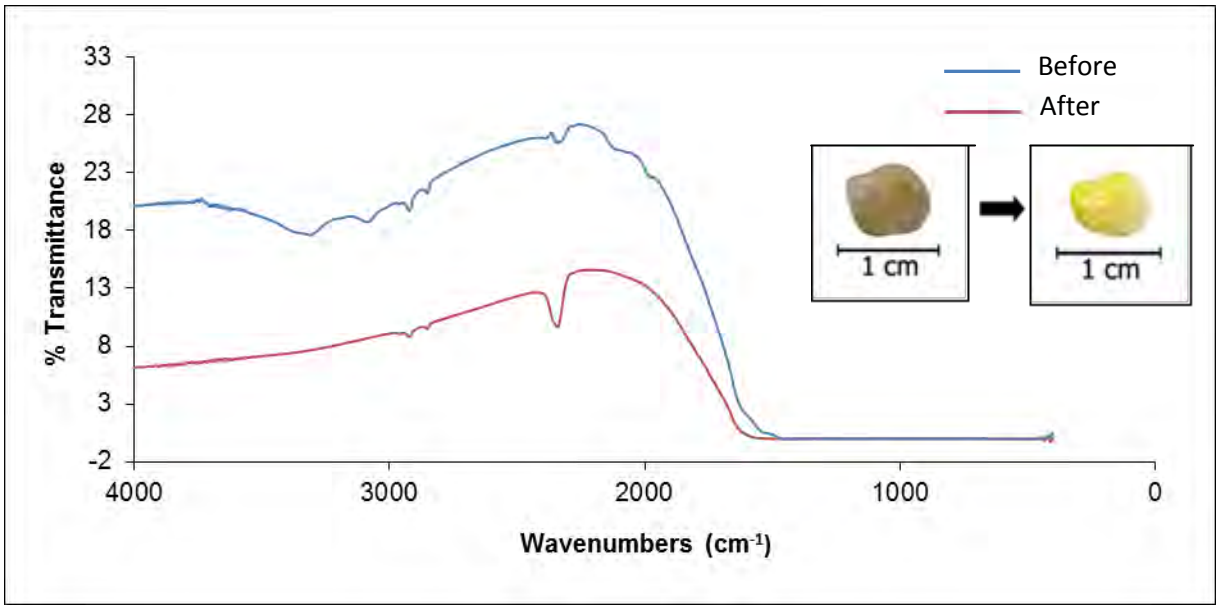


Fig.E25 FTIR absorption spectrum of sample Y8, Deniyaya sapphires Group Y

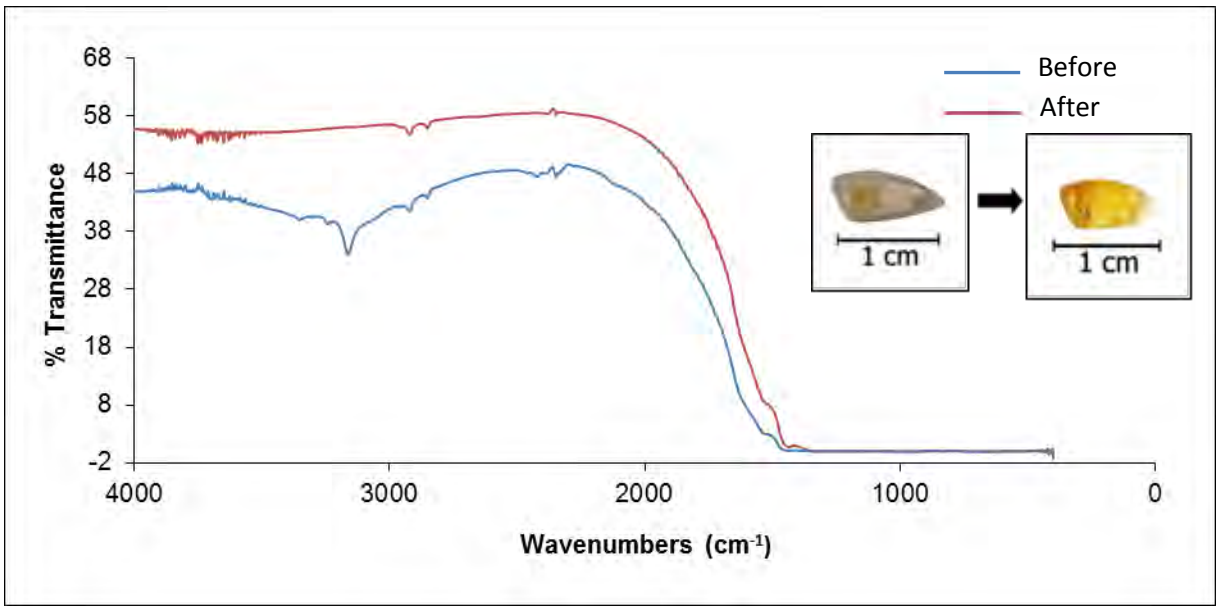


Fig.E26 FTIR absorption spectrum of sample Y9, Deniyaya sapphires Group Y

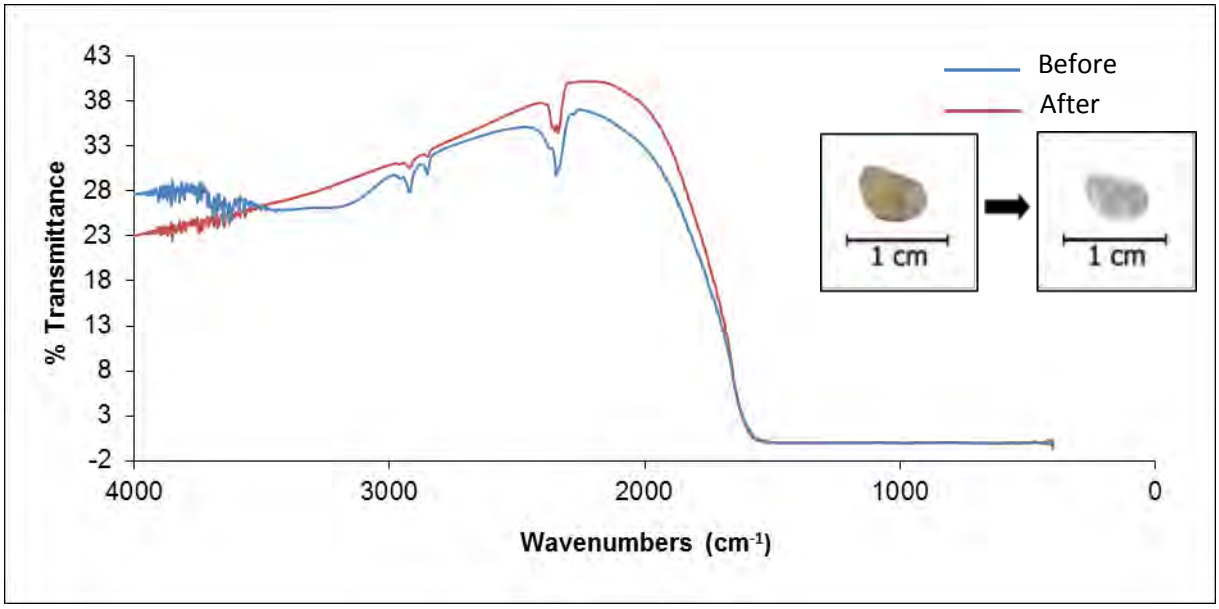


Fig.E27 FTIR absorption spectrum of sample Y10, Deniyaya sapphires Group Y

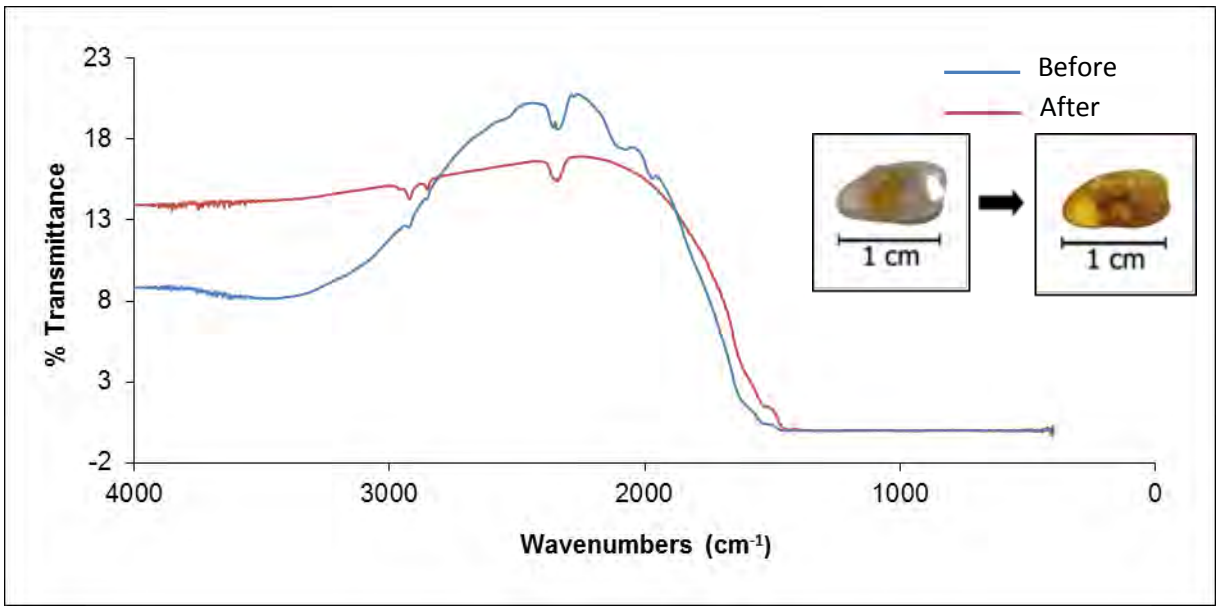


Fig.E28 FTIR absorption spectrum of sample Y11, Deniyaya sapphires Group Y

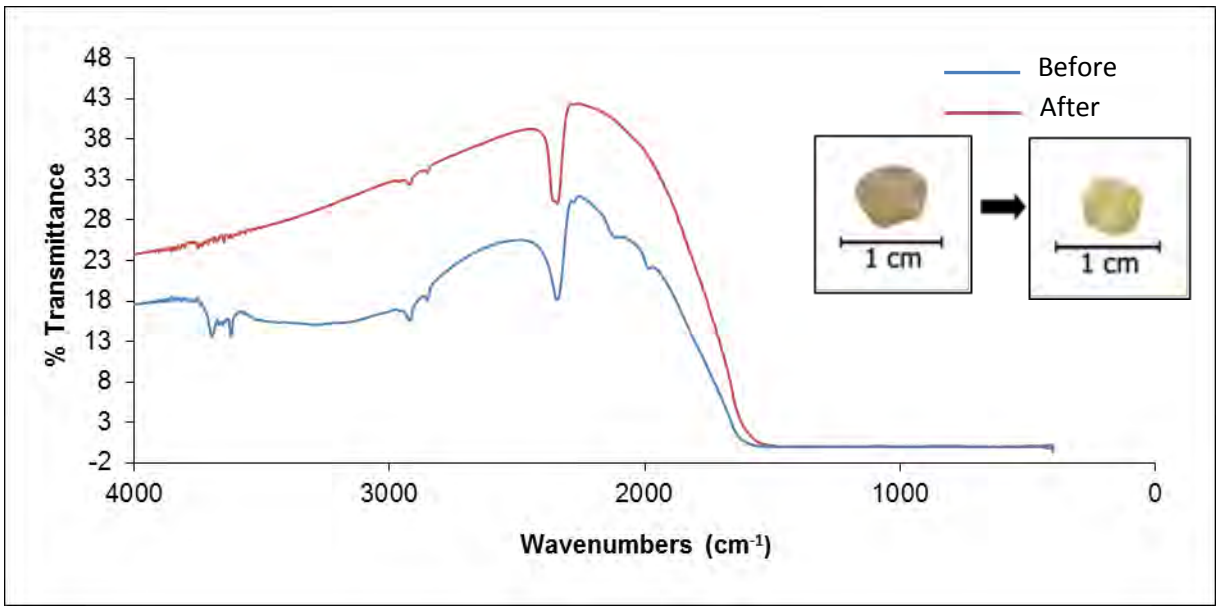


Fig.E29 FTIR absorption spectrum of sample Y12, Deniyaya sapphires Group Y