THE EFFECTS OF HEAT ON ZIRCON FROM KANCHANABURI

WATCHARAPORN PHOOTONG

A REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIRRMENT FOR THE DEGREE OF

THE BECHELOR OF
SCIENCE DEPARTMENT OF GEOLOGY CHULALONGKORN
UNIVERSITY
2010

Date of submit……/……./…….

Date of approval……/……/……

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(Assoc. Prof. Dr. Visut Pisutha-Arnond)

Senior project advisor

น.ส.วัชราภรณ์ ภู่ทอง : ผลของความร้อนต่อเพทายจากแหล่งกาญจนบุรี.
(THE EFFECTS OF HEAT ON ZIRCON FROM KANCHANABURI)
อ. ที่ปรึกษา: รศ.ดร. วิสุทธิ์ พิสุทธอานนท์, 58หน้า.

บทคัดย่อ

ในธรรมชาติเราสามารถพบเพทายสีน้ำตาลได้จากหลายแหล่ง เช่น จากแหล่งรัตนคีรี จากประเทศกัมพูชาซึ่งสามารถเผากลายเป็นเพทายสีฟ้า เหลือง และไร้สี ซึ่งจะเป็นที่นิยมมากกว่าสีดั้งเดิมในตลาดอัญมณี ดังนั้นการศึกษาผลจากการเผาเพทายจากแหล่งบ่อพลอย จังหวัดกาญจนบุรีด้วยความร้อนเพื่อให้สีต่างๆและคุณสมบัติอื่นๆจึงน่าสนใจเพราะยังไม่เคยมีผู้ใดศึกษามาก่อน

การศึกษานี้เราใช้ตัวอย่างจำนวน 35 ตัวอย่างจากแหล่งบ่อพลอย ซึ่งสามารถแบ่งออกเป็น 2 กลุ่มตามสี นั่นคือ กลุ่มสีน้ำตาลแดงถึงส้มเข้ม และกลุ่มสีส้มถึงน้ำตาลแดงอ่อน โดยทั้งสองกลุ่มมีค่าถ่วงจำเพาะเฉลี่ยประมาณ 4.569 และ 4.486 ซึ่งจัดเป็นเพทายชนิดสูง และตัวอย่างส่วนใหญ่จะไม่เรืองแสงภายใต้รังสีอุลตร้าไวโอเล็ตคลื่นสั้นและคลื่นยาว และลักษณะภายในที่พบ คือ มลทินของแข็ง ตำหนิแถบสี รอยแตกสมาน

ตัวอย่างทั้งหมดได้นำไปเผาที่อุณหภูมิ 900 องศาเซลเซียส ภายใต้สภาวะรีดักชั่น เป็นเวลา 3 ชั่วโมง หลังจากนั้นสีของตัวอย่าง ได้เปลี่ยนจากสีน้ำตาลถึงไร้สีเป็นไร้สี เทาเข้ม และสีม่วง ทั้งสองกลุ่ม วัดเสปกตรัมการดูดกลืนแสงยูวีซึ่งเดิมก่อนเผามีการดูดกลืนช่วง 600 นาโนเมตร ถึงช่วงยูวีซึ่งเกี่ยวข้องกับการเกิดสีน้ำตาลหรือศูนย์กลางสีได้หายไปหลังจากทำการเผาพลอยยดังกล่าว นอกจากนี้ยังสามารถ พบพีคของU^{5+}ที่ตำแหน่ง 1150 และ 1157 นาโนเมตรทั้งก่อนและหลังเผา นอกจากนี้ พบว่าโครงสร้างที่ถูกทำลายได้มีการปรับปรุงดีขึ้น โดยดูจากเสปกตรัมการดูดกลืนช่วงอินฟราเรดพบว่าพีคของ O-H stretching ซึ่งปรากฏช่วง 2800-3200 cm^{-1} หายไปหรือชัดเจนขึ้นหลังจากทำการเผา และพี คของ V_3(Si-O stretching) ซึ่งปรากฏในช่วง 1400-200 cm^{-1} ในบางตัวอย่าง มีความชัดเจนขึ้น นอกจากนี้รามานเสปกตรัม บอกถึงค่าเฉลี่ยพีคของ anti-SiO_4 stretching คือ 1007.23 cm^{-1}และ 1007.29 cm^{-1} ซึ่งจัดว่ามีความเป็นผลึกค่อนข้างสมบูรณ์หรือโดนทำลายไปเพียงเล็กน้อย โดย หลังจากทำการเผา ค่า V_3 มีค่าเฉลี่ยเพิ่มขึ้นเป็น 1007.67 cm^{-1} และ1007.46 cm^{-1} และค่าเฉลี่ยของ FWHM (Full with at Half Maximum)ก่อนเผาลดลงจาก 5.60cm^{-1} เป็น 5.46 cm^{-1} หลังเผา แสดงว่า การให้ความร้อนหรือการเผาสามารถปรับปรุงความเป็นผลึกให้สมบูรณ์ขึ้นได้

การวิเคราะห์เคมีด้วยเครื่อง LA-ICP-MS แสดงปริมาณธาตุต่างๆของเพทายจากแหล่งกาญจนบุรี เช่น Zr, Si, Hf, Th และ U เป็นต้น โดยกลุ่มสีน้ำตาลเข้มมีปริมาณธาตุ U น้อยกว่ากลุ่มสีน้ำตาลอ่อน และสูตรเคมีของเพทายจากแหล่งบ่อยพลอย อยู่ระหว่าง $ZrSiO_4$ และ $(Zr_{0.99},Hf_{0.01})SiO_4$

ภาควิชา ธรณีวิทยา

ปีการศึกษา2552

ลายมือชื่อนิสิต.....

ลายมือชื่อ อ.ที่ปรึกษา.....

4932722723 : MAJOR Geology

KEYWORDS : Heat treatment / Bo Phloi / Zircon

Watcharaporn Phootong: THE EFFECTS OF HEAT ON ZIRCON FROM KANCHANABURI.

ADVISOR: Assoc. Prof. Dr. Visut Pisutha-Arnond 58pp.

Abstract

The naturally occurring reddish brown zircon from many localities such as from Ratana Kiri, Cambodia can be heat-treated to blue, yellow and colorless which are more desirable in gem trade. It is therefore interesting to know and understand the effect of heat treatment on coloration and other properties of zircon from Amphoe Bo Phloi, Changwat Kanchanaburi which has not been investigated before.

Thirty five zircon samples from Bo Phloi were used in this study. The samples can be subdivided into 2 groups based on their color; dark reddish brown to orange brown and light orange and reddish brown. Their specific gravities average about 4.569 and 4.486 which fall into a high to intermediate-type zircon. The samples are mostly inert both under short and long wave UV. The dominant internal features are negative crystals, finger prints, color zones and fractures.

All samples were heat-treated at 900^{o}C in reduction condition for 3 hours. After treatment, the color mostly was changed from originally brown to colorless and some dark gray and violet in both groups. The UV-VIS-NIR absorption band from 600nm to UV range, which is related to brown color center or structure damaged by radioactive element, was disappeared after heating. Beside, peaks of U^{5+} appear at 1150 nm and 1157 nm both before and after heating. In addition, the structural damage appear to improve after heating as seen from FTIR absorption spectra; the O-H stretching peaks at 2800-3200 cm^{-1} disappear and some also sharper after heating. Beside, the Si-O stretching peaks at 1400-2000 $cm^{-1}$are sharper after heating. Furthermore, the Raman spectra of zircon samples before heating give the average V_3 (anti-symmetric SiO_4 stretching) values of 1007.23 cm^{-1} and 1007.29 cm^{-1} which represent a well crystalline

structure or slight degree of metamictization. After heat-treatment, the average V_3 values increase to 1007.67 cm^{-1} and 1007.46 cm^{-1} and the average FWHM (Full with at Half Maximum) values before heating decrease from 5.60 cm^{-1} to 5.46 cm^{-1}. Both values suggest that heat treatment can improve their structure.

The chemical analyzed by LA-ICP-MS shows the average contents of elements such as Zr, Si, Hf, Th and U etc. The dark brown group has lower U concentrations (average about 112.6 ppm) than that of the light brown group (average about 276.2 ppm). Their formulas vary from $ZrSiO_4$ to $(Zr_{0.99},Hf_{0.01})SiO_4$.

Department : Geology Student's Signature .....

Advisor's Signature .....

Academic Year : 2010

Acknowledgement

I thankfully acknowledge the contribution of my advisor, Assoc. Prof. Dr. Visut Pisutha-Arnond who helped me to reach my aim and also gave me good comments. In addition, he also improved and corrected my work literally. I also thank Assis. Prof. Dr. Sombat Yumuang and Assis. Prof. Dr.Thasinee Charoentitirat who are my committee for valuable suggestions.

I would like to thank the Geology Department, Chulalonglorn University Gem and Jewelry Institute of Thailand (GIT) for permission to use both basic and advanced instruments.

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CHAPTER I
INTRODUCTION

1.1 General Statement

Nowadays, The World has suffered from economic slowdown, but for the gem market, Thailand is still one of the international leaders especially for colored stones. We have many good craftsmanship and skills to produce high quality products. Gemstones are considered as luxury things for consumer. When the demands have been decrease dramatically, we have to increase market to other groups and the crucial thing is treatment. We need a treatment in order to improve gemstone's value acceptable in the market. The famous and good treatment is heat-treatment because it can improve color and makes gemstone clearer, and the important things are that heat treatment is acceptable. Color strikes eyes; we can treat gemstone by heating to make it better looking to catch consumers' eyes.

Despite corundum is the best seller colored stone in Thailand, zircon can be another choice for new consumers because of less price. We have to recommend another gemstone in order to increase new consumer's interest and the market too. Zircon is another good choice. We can treat zircon by heat treatment method to make it both clear and better color. We can develop zircon to the international trade comparable to corundum.

1.2 Problem Statement

From the study of Kitiphaisalnont (2004), Mongchamnankit et al. (2005), Thongnopkun et al. (2004), Klinkaew (2008), they found that brown zircons from Ratanakiri, Cambodia could be heat-treated to blue or colorless zircons and the causes of color before and after heat-treatment were also studies. During the course of sapphire mining at the Bo Phloi gem field, there were some zircon single crystals that were recovered along with sapphire and other heavy minerals. However, there has not been any similar work done on zircon from this gem field before. Therefore, it is interesting to find out the effects of heat treatment and the causes of color on the zircon from the Bo Phloi gem field for this project in order to compare with the result from other localities.

1.3 Objective

The objective of this study is to carry out heat treatment experiments on a group of zircon samples obtained from the Bo Phloi gem field of Kanchanaburi province in order to find the effect of heat on those stones and the causes of color both before and after heat treatment.

1.4 Hypothesis

1. Heat can change color of zircon.

2. Causes of color in zircon are related to defects and/or trace elements in crystal lattice.

1.5 Term Defined

1. Heat treatment: Heat treatment is a method intended to improve the color and/or clarity of a gemstone by placing the stone in high temperature furnace under controlled atmospheric condition. The method is commonly used to change or intensify the color of a gemstone and the color is usually permanent under normal wearing condition.
(http://jewelry.about.com/library/glossary/bldef_heat.htm)

2. Trace element: A chemical element required in minute quantities to maintain proper physical functioning.
(http://www.answers.com/topic/micromineral)

1.6 Literature Reviews

Thaephajan (2007) heat-treated yellow-brown to orange brown zircon samples from Khao Ploi Waen, Changwat Chanthaburi. After heat treatment at 1,000°C for two hours in reducing condition the brown zircon turned colorless. The Khao Ploi Waen zircon had a good potential for heat treatment and the change from yellow-brown to orange-brown was interpreted to be due to the structural damages or crystal defects from radioactive elements.

Klinkeaw (2008) studied zircon samples from Boh Kha, Cambodia. She suggested that UV-Vis absorption pattern of brown zircon samples was probably related to the structural damages or deflects in crystal structure (metamictization) caused by self-irradiation from radioactive elements such as U and Th. In fact, the spectra revealed prominent absorption peaks at 1109 and 1502 nm probably due to U^{5+}. After heat

treatment, the absorption in the UV to 600 nm (green-yellow region) disappeared and another broad absorption band centered at 650 nm was developed instead. After heat-treatment most samples showed a slight increase in both the peak positions of $\mathbf{V}_3$ (SiO_4) at 1008 cm^{-1} as well as their FWHM values. The increase of 1008 cm^{-1} peak position was interpreted due to the annealing of the structural damages or metamictization after heat-treatment whereas the increase of the FWHM values were suggested to be due to some structural expansion after high temperature heating.

Thongnopkun et al. (2007) heat-treated reddish brown zircons from Boh Kha, Cambodia in reducing conditions to about 900°C for two hours. The color of most of the treated stones changed to blue. The colors of the heat treated stones were turned to green blue. Before heat treatment, all reddish brown zircons revealed the absorption band at 490 nm and this band was disappeared after heat treatment. The obtained spectrum of heat treated blue zircon showed the new absorption at 680 nm which corresponding to U^{4+} absorption. After heat treatment, the band at 1107 nm and 1105 nm shifted to the longer wavelength. It was concluded that heat treatment could remove the radiation damage centers related to reddish brown color and restored the blue color with which zircon presumably originally crystallized.

General Properties of Zircon

Chemical composition	$ZrSiO_4$
Crystal system	Tetragonal
Transparency	Transparent to Translucent
Color	Colorless, blue, yellow, reddish brown, orange brown, orange red, yellowish brown, brown
Optical properties	Uniaxial positive to isotropic, double refraction
Refractive Index	1.757-1.779
Birefringence	Up to 0.059
Dispersion	High, 0.039
Specific gravity	3.9-4.7
Luster	Vitreous to sub-adamantine

Fracture	Conchoidal
Hardness	6-7.5

Type of Zircon

1. High type: Structure is normal and not significantly damaged by radiation. Color is blue or brown and colorless. Refractive index is 1.885-2.040 and birefringence is 0.059.

2. Intermediate type: Structure is partly damaged by radiation. Color is red or yellow, blue.

Refractive index is 1.845-1.935 and birefringence is 0.006-0.050.

3. Low or Metamict type: Structure is almost completely destroyed by radiation (metamictization). Color is green or green-yellow. Refractive index is 1.780-1.845 and birefringence is 0.002-0.005.

1.7 Scope of work

The scope of this project is the study of gemological properties of zircon from Bo Phloi gem field in Kanchanaburi before and after heat-treatment experiment by using both basic and advanced instruments.

1.8 Output

It is expected that the outputs from this study are the characteristics of Kanchanaburi zircon, the effect after heat treatment and causes of zircon's color.

CHAPTER II

METHODOLOGY

2.1 Method of study

The method of study can be summarized as the flow chart in Figure1-1. The works began by literature review of the previous works. Then a group of rough zircon samples were acquired from a reliable source. There are altogether 35 samples which could be subdivided into two groups based on color appearance. All 35 rough samples were given the code names, weighed and measured for specific gravity (SG) by a hydrostatic balance, and then photographed. The c-axis of rough samples was located by using a polariscope and crystal shape, and then they were cut and polished. After polishing samples, the samples were weighed and measured for SG again. In addition, we measured the dimension by a size measurement tool, described color. The fluorescence colors under short wave and long wave were recorded and photographed. The internal features will be observed under a gem microscope. Then the polished samples were measured their absorption characteristics by using UV-Vis-NIR, RAMAN and FTIR equipments.

Before heating, chemical compositions of those samples were determined by LA-ICP-MS. Then all samples were heated at 900 $^{\circ}$ C in reducing condition (N_2 atmosphere) for 2 hours in a Linn electrical furnace. The rate of temperature was controlled at about 4°C/minute.

After heat the samples, the physical, optical and chemical properties were recorded again by advanced equipments in order to compare and contrast them.

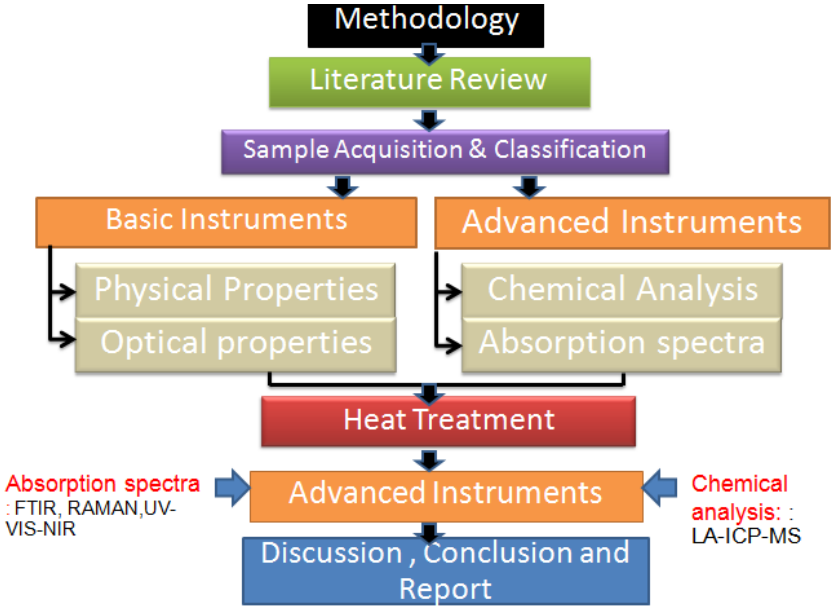


Figure1-1: Flow chart of methodology

2.2 Additional Background of Advanced Equipment being used in this study

2.2.1 UV-VIS-NIR Spectrophotometer

This equipment was used for studying of absorption in samples. The causes of color can be interpreted. Their results were shown as peaks which were indication of elements or radioactive elements which might be the causes of color. For this equipment, it generates wavelengths over Ultraviolet, visible light and near infrared and also expresses in nanometer. For this study, the Perkin Elmer UV-VIS-NIR Spectrophotometer at GIT was used.

2.2.2 Fourier Transform Infrared Spectrophotometer

This equipment was used for studying of sample bonding. It was needed in this study to represent the Si-O stretching and O-H stretching in order to indicate the structure of samples. Beside, the results can be additional information and was used with information in Raman part to describe the degree of metamictization. For this equipment, it generates the near to far infrared range. For this study, the Nicolet Fourier Transform Infrared Spectrophotometer at GIT was used.

2.2.3 Laser Raman Spectroscope

This equipment was used to indicate the degree of metamictization of the samples. The results at peak about 1008 cm^{-1} which is anti-symmetric SiO_4 stretching were needed. For this equipment, it is a powerful light scattering technique and also

diagnoses the structure in samples. For this study, the Renishaw Laser Raman Spectroscope at GIT was used.

2.2.4 High Temperature Furnace

This equipment was used for heating the samples at 900^{o}C in reduction state by feeding 99.99% N_2 for 3 hours and it was controlled at about 4^{o}C/minute. For this study, the Linn Electrical Furnace Model HT 1800 Plus VAC Bottom Loader at department of geology, Chulalongkorn University was used.

CHARPTER III

CHARACTERISTICS OF ZIRCON BEFORE TREATMENT

3.1 Samples

All 35 rough samples from Bo Phloi in Kanchanaburi province were studied both physical and chemical properties. For the physical properties, the samples are subhedral to anhedral single crystals, sub-adamantine to adamantine luster, mostly inert in shortwave and long wave UV; some of them contains many cracks, The samples can be divided into two groups based on their color appearance; Group KZ1 is dark reddish brown to orange brown (Figure 2-1) and Group KZ2 is light orange to reddish brown (Figure 2-3). Colors of most samples are not homogeneous.

Group KZ1: Dark reddish brown to orange brown after polishing

Figure 2-1: Zircon samples from Bo Phloi in Kanchanaburi Province after cut open and polished two sides parallel to the c axis, showing dark reddish brown to orange brown color of Group KZ1

Example of Zircon Samples group KZ1 compare between before and after polishing.

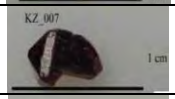
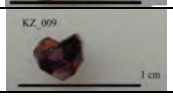
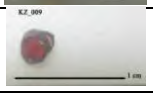
Before polishing	After polishing
	
	
	

Figure2-2: Zircon samples of Group KZ1 showing original rough and after cut open.

Group KZ2: Light orange to reddish brown after polishing

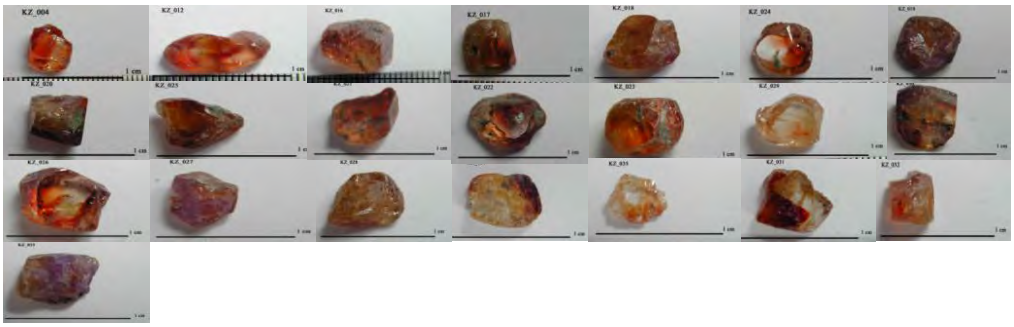


Figure2-3: Zircon samples from Bo Phloi Kanchanaburi Province after cut open and polished on two sides parallel to the c axis showing light orange to reddish brown color of Group KZ2.

Example of Zircon sample group KZ2 compare between before and after polishing.

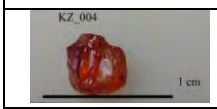
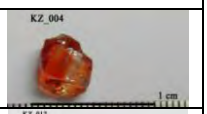
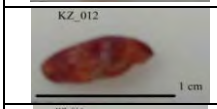
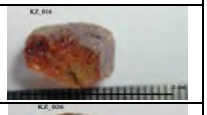
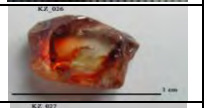
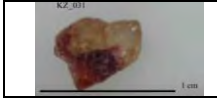
Before polishing	After polishing
	
	
	
	
	
	

Figure 2-4: Zircon samples of Group KZ2 showing original rough and after polishing.

3.2 Basic gemological properties of Bo Phloi zircon

The physical properties and optical properties of Bo Phloi zircon are shown in Table1-1 for Group KZ1 in Table1-2 for Group KZ2

Table1-1: Basic properties of Group KZ1 (**dark reddish brown to orange brown**)

No.	Sample	Wt. (ct.)	SG	Dimension (mm)	Color (visual)	GIA color code	Fluorescence	
							SW	LW
1.	KZ_001	1.468	4.615	6.15*6.31*3.10	Reddish brown	RO7/3	inert	inert
2.	KZ _002	0.701	4.692	3.71*4.52*2.76	Reddish brown	R8/2	inert	inert
3.	KZ _003	1.659	4.282	5.12*5.01*4.99	Reddish brown	RO6/4, RO4/3	inert	inert
4.	KZ _005	1.058	4.353	5.27*4.83*3.09	Reddish brown	RO8/2, RO7/4	inert	inert
5.	KZ _006	1.715	4.655	4.75*6.15*4.71	Reddish brown	RO8/3	inert	inert
6.	KZ _007	0.700	4.628	4.61*3.04*3.03	Reddish brown	OR8/3	inert	inert
7.	KZ _008	0.361	4.591	3.85*3.73*1.33	Reddish brown	RO/OR8/2	inert	inert
8.	KZ _009	0.416	4.502	3.50*3.85*3.91	Orange brown	RO7/3	inert	inert
9.	KZ _010	0.455	4.710	2.38*3.07*3.87	Orange brown	RO/OR6/3	inert	inert
10.	KZ _011	0.429	4.519	4.14*4.52*1.82	Orange brown	RO/OR6/3	inert	inert
11.	KZ _013	1.538	4.581	4.44*4.37*5.59	Reddish brown	R8/2	inert	inert
12.	KZ _014	0.581	4.672	3.82*2.04*4.44	Reddish brown	R8/2RO/OR8/2	inert	inert
13.	KZ _015	0.583	4.596	3.40*4.84*1.88	Reddish brown	R/8/2	inert	inert

Table1-2: Basic properties of Group KZ2 (**light orange to reddish brown**)

No.	Sample	Wt. (ct.)	SG	Dimension (mm)	Color(visual)	GIA color code	Fluorescence	
							SW	LW
1.	KZ_004	1.067	4.624	4.94*4.60*2.44	Orange	YO5/5, YO2/3	red	Purple red
2.	KZ_012	0.714	4.666	2.85*8.13*2.15	Orange	YO6/4, OY2/3	inert	inert
3.	KZ_016	1.539	4.595	4.66*6.46*4.68	Orange	YO6/3, OY2/3	inert	inert
4.	KZ_017	1.054	4.595	3.48*4.01*2.38	Orange	YO5/5, OY2/3	inert	inert
5.	KZ_018	1.407	4.664	4.88*4.06*4.44	Reddish brown	Y4/3, R3/2	inert	inert
6.	KZ_019	0.923	3.497	6.35*5.25*3.46	Reddish brown	R5/1, YO3/3	inert	Purple red
7.	KZ_020	0.722	4.727	5.85*2.56*6.39	Reddish brown	OY2/5, R8/2	Red	inert
8.	KZ_021	0.773	4.458	3.13*5.04*3.93	Orange	YO5/4, OY2/3	inert	inert
9.	KZ_022	1.279	4.571	3.56*5.78*2.83	Orange	YO5/5, OY2/3	inert	inert
10.	KZ_023	1.536	4.558	4.04*6.19*4.59	Orange	YO5/5, OY2/3	inert	Purple red
11.	KZ_024	0.495	4.621	4.32*4.88*1.79	Orange	OY2/3, YO6/4	inert	inert
12.	KZ_025	1.089	4.597	5.90*4.02*3.34	Orange	YO2/3, OR7/4	inert	inert
13.	KZ_026	2.184	4.648	7.86*3.64*5.87	Orange	YO6/4, YO3/3	inert	inert
14.	KZ_027	0.652	3.743	4.73*2.09*5.42	Reddish brown	R5/1	inert	Purple red
15.	KZ_028	1.332	4.606	4.34*3.01*7.39	Orange brown	Y4/3, RO6/5	inert	inert
16.	KZ_029	0.934	4.705	4.05*2.74*6.24	Orange brown	OY2/3	inert	inert

17.	KZ _030	1.647	4.638	5.61*6.16*3.90	Yellowish orange	OR8/3, Y2/2	Red	inert
18.	KZ _031	0.911	4.546	1.88*5.10*6.40	Yellowish red	Y2/2, YO6/4	inert	inert
19.	KZ _032	0.642	4.692	3.62*3.10*4.12	Yellowish orange	OY2/3, RO4/3	inert	Purple red
20.	KZ _033	1.027	3.775	5.94*2.36*5.81	Reddish brown	S/PR6/3, Y4/3	inert	Purple red
21.	KZ _034	0.995	4.647	4.79*2.34*6.89	Yellowish red	Y2/2, OR8/3	Red	inert
22.	KZ _035	0.252	4.523	1.10*4.63*4.12	Yellowish orange	YO2/3	inert	inert

Table2-1: Summary of basic properties of zircon from Bo Phloi in Kanchanaburi Province.

No.	Sample ID.	Wt. (ct.)	SG.	Fluorescence		Color (visual)
				SW	LW	
1.	Group KZ1	0.897	4.569	Inert	Inert	Dark Orange brown, reddish brown
2.	Group KZ2	1.053	4.486	inert	inert	Light Orange, Yellowish orange, orange brown, reddish brown

3.3 Internal Characteristics

All samples were studied under a gemological microscope and the internal features were photographed. The dominant internal features in zircon from Bo Phloi are cracks, fingerprints, fluid inclusions and negative crystals. Growth or color zones are obvious in some samples. Moreover, many characteristics of negative crystal and doubling effect can be obvious. They are shown in Figures 3-1 to 3-5.

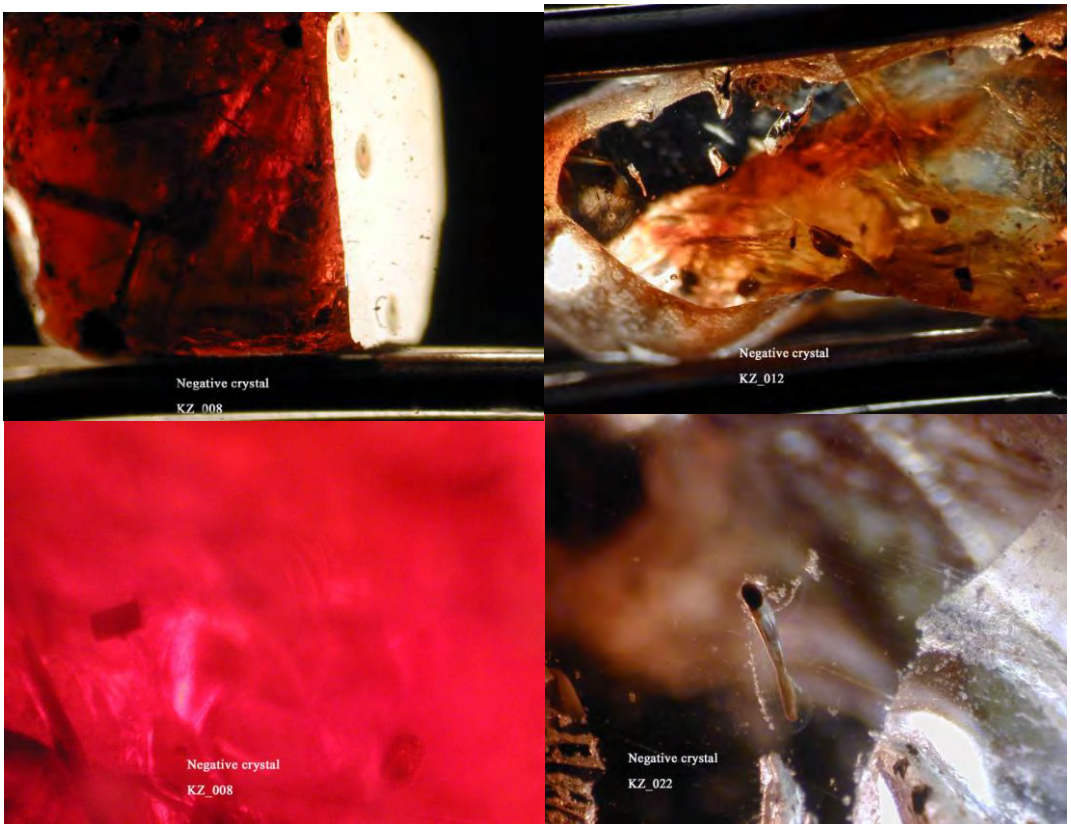


Figure 3-1: Negative cylinder crystal and oblong crystal

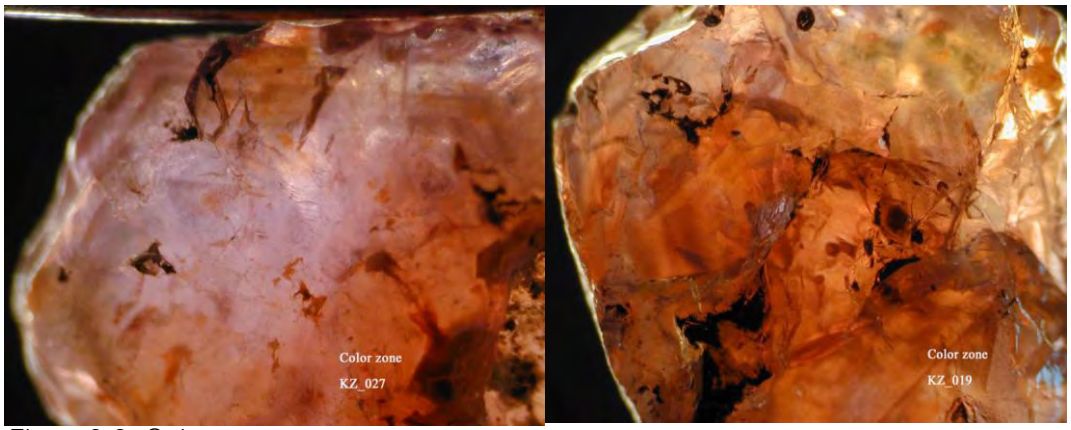


Figure3-2: Color zone

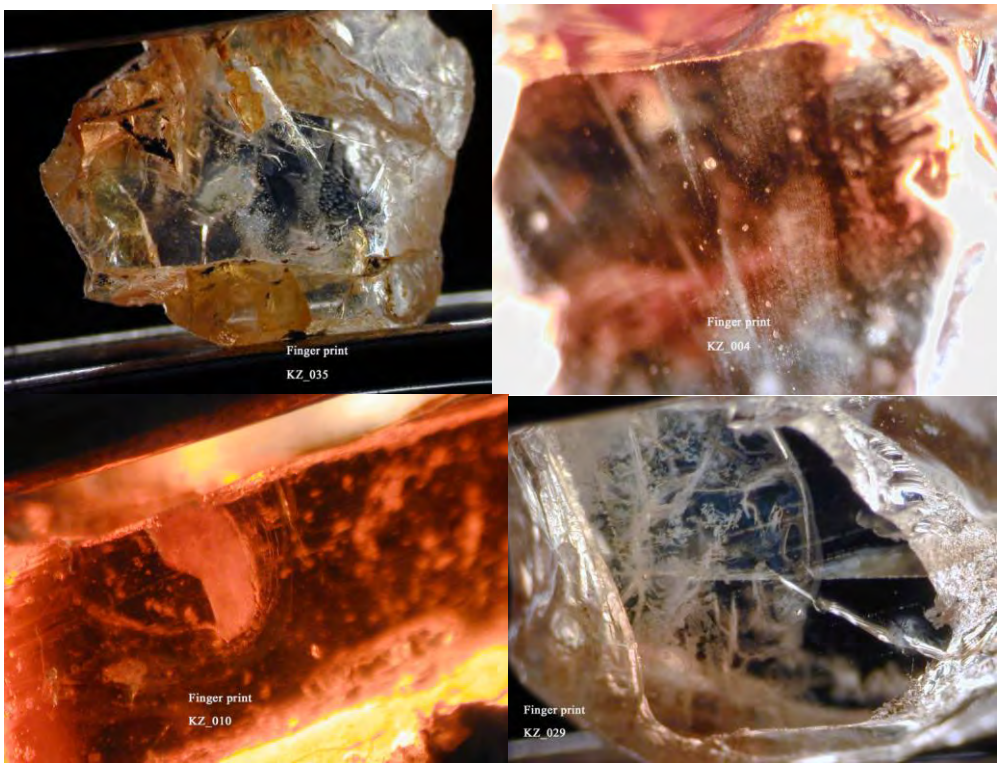


Figure3-3: Fingerprints

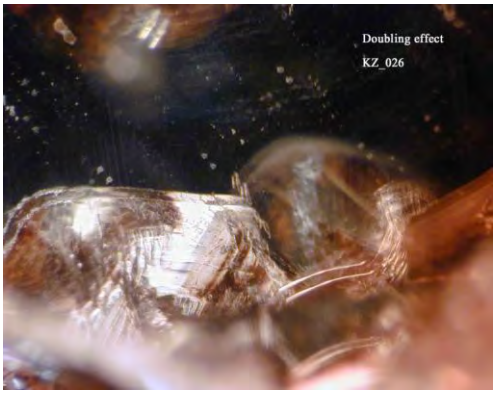


Figure3-4: Doubling effect

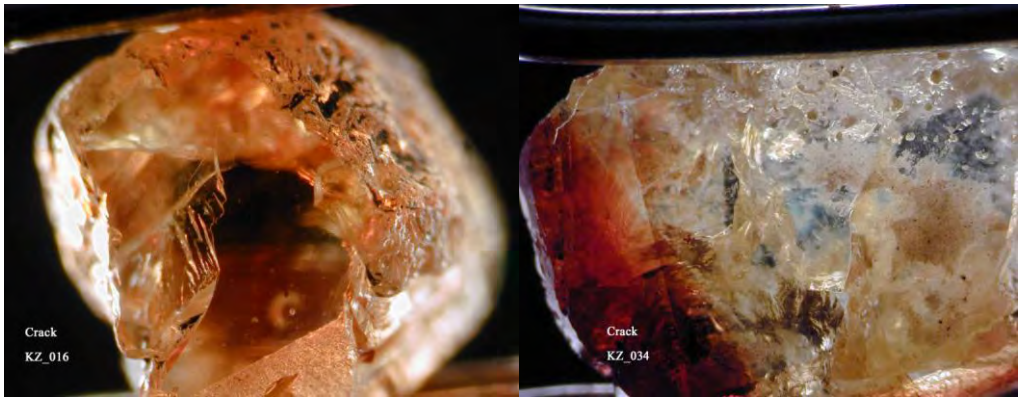
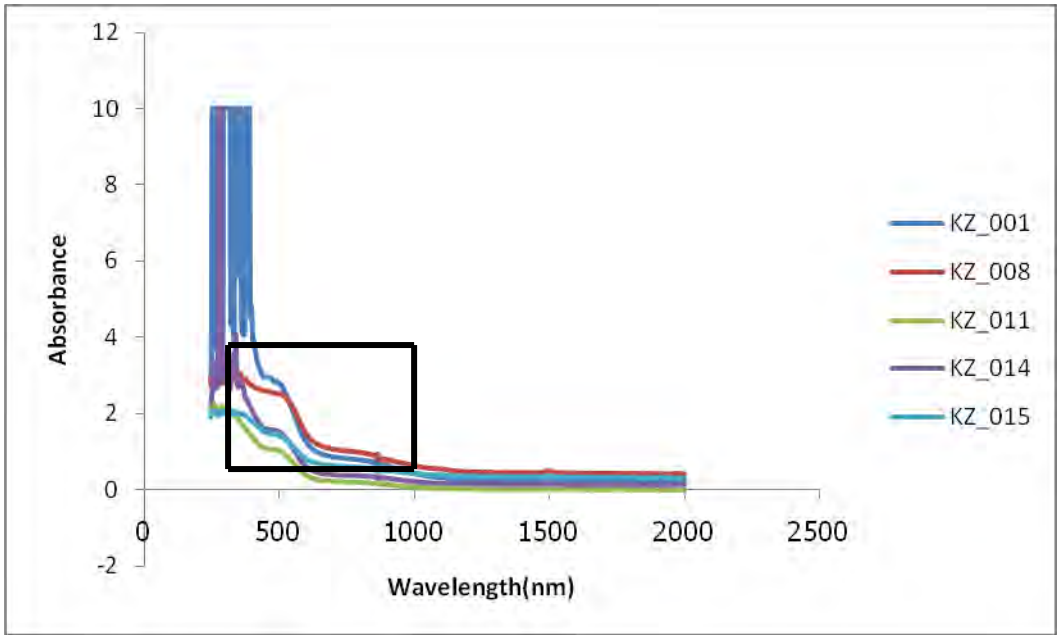


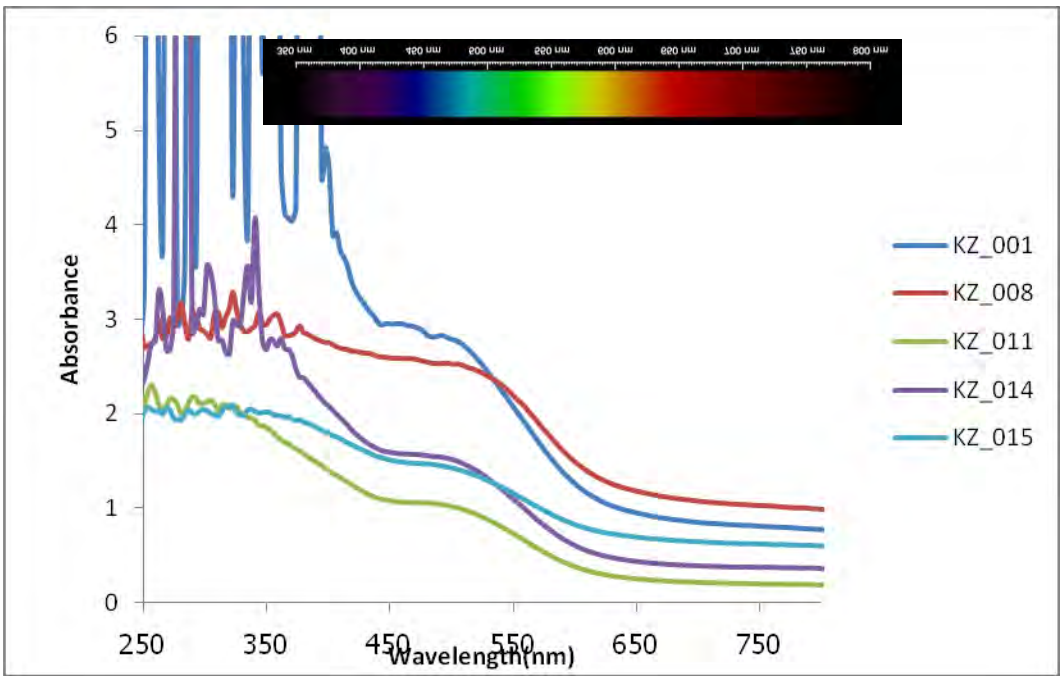
Figure3-5: Cracks or fractures

3.4 UV-VIS-NIR Absorption Spectra

Ten samples were recorded for UV-VIS-NIR absorption spectra between 250-2000nm for both O-Ray and E-Ray in order to study their absorption. As seen in Figures 4-1 and 4-2, both show the increase the absorption from 600 nm to UV range and they have shoulder at 500 nm. It represents dark reddish brown and orange brown colors. Moreover, there are 2 peaks at about 1150 nm and 1550 nm which probably are related to U^{5+} (อรุณีและคณะ, 2550). The U^{5+} can self-irradiate and cause the defect in crystal structure. As a result it is probably the cause of brown color. This part will be discussed later.

The U^{5+} peaks of both groups show at about 1113 and 1510 nm. They cause from self-irradiation and conform well to the results from FTIR.


12
10
8
6
4
2
0
-2
Absorbance
0
500
1000
1500
2000
2500
Wavelength(nm)
KZ_001
KZ_008
KZ_011
KZ_014
KZ_015


6
5
4
3
2
1
0
Absorbance
250
350
450
550
650
750
Wavelength(nm)
KZ_001
KZ_008
KZ_011
KZ_014
KZ_015

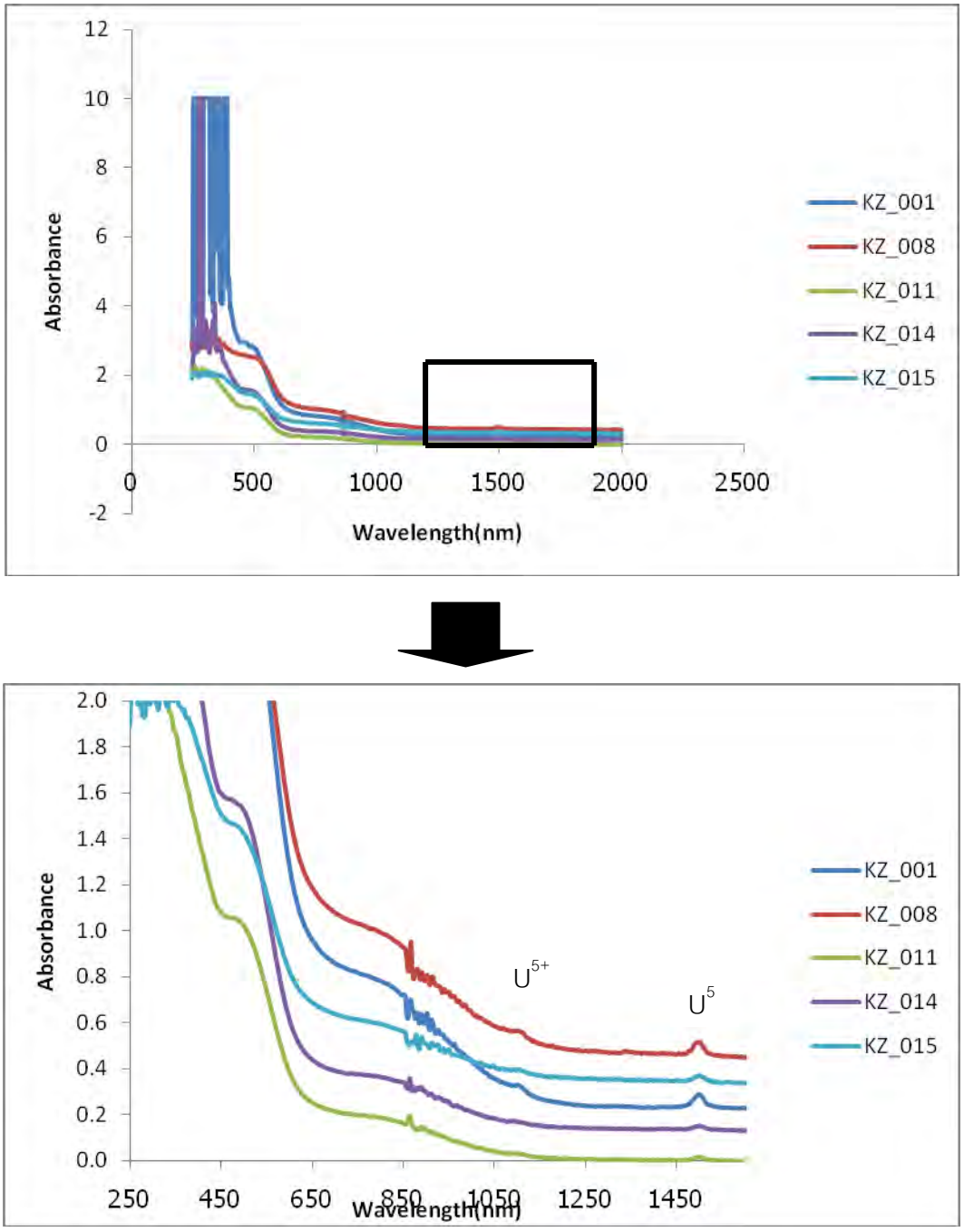
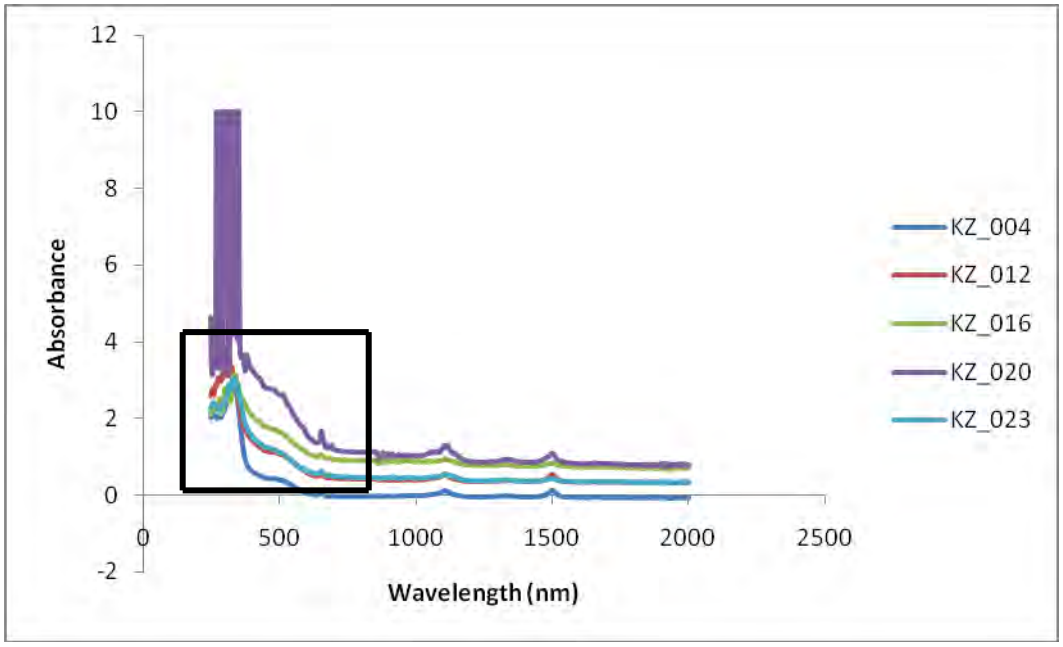
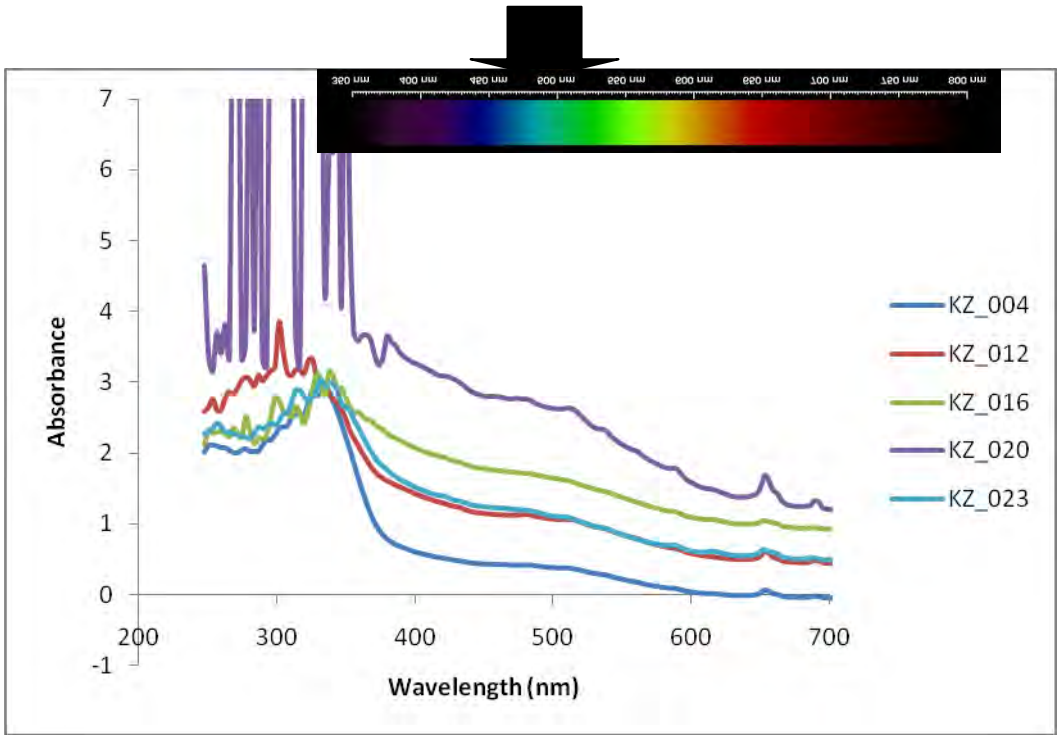


Figure 4-1: UV-VIS-NIR absorption spectra of O-Ray of Group KZ1 (dark reddish brown to orange brown) before heating.


12
10
8
6
4
2
0
-2
Absorbance
0
500
1000
1500
2000
2500
Wavelength (nm)
KZ_004
KZ_012
KZ_016
KZ_020
KZ_023


7
6
5
4
3
2
1
0
-1
Absorbance
200
300
400
500
600
700
Wavelength (nm)
KZ_004
KZ_012
KZ_016
KZ_020
KZ_023

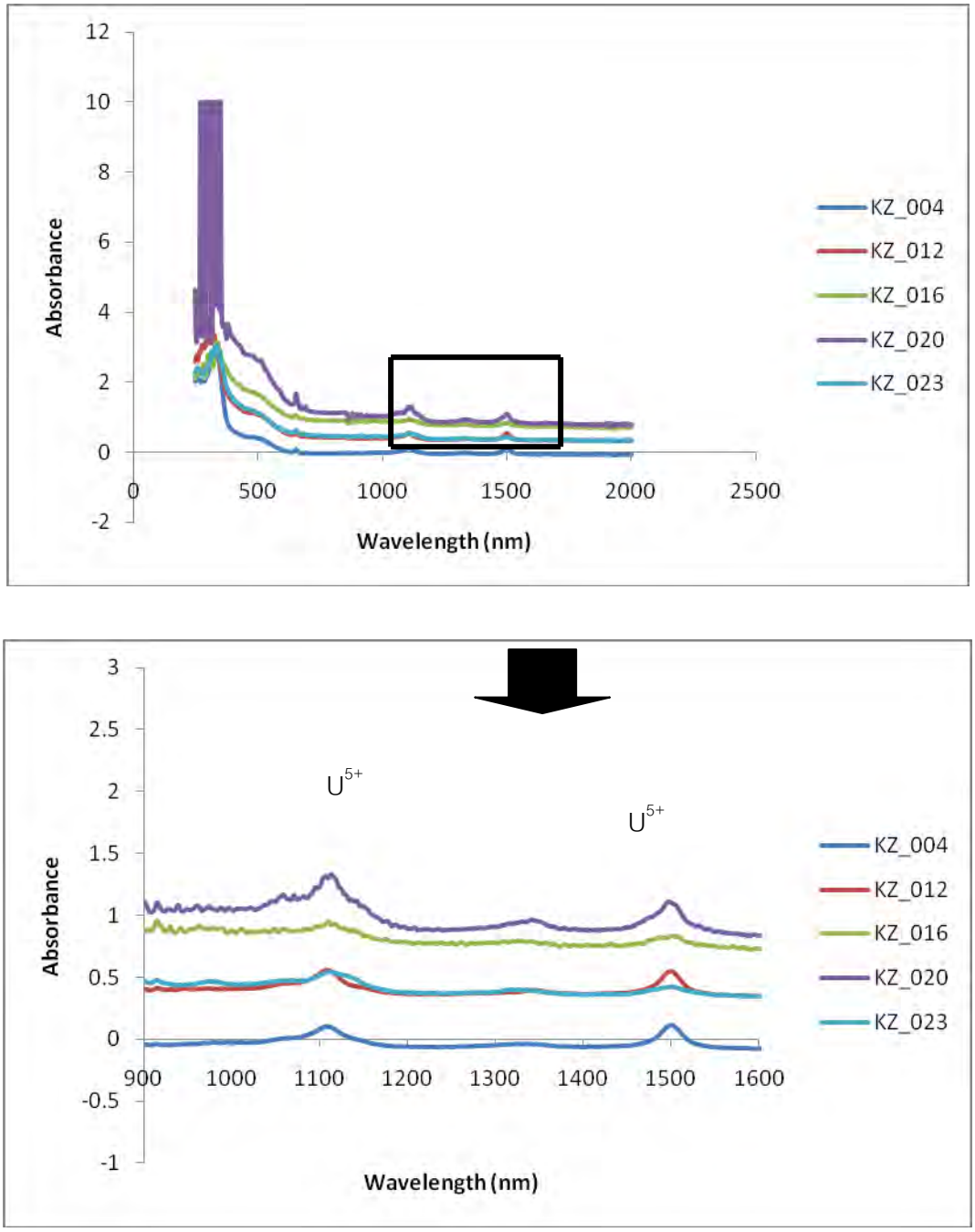


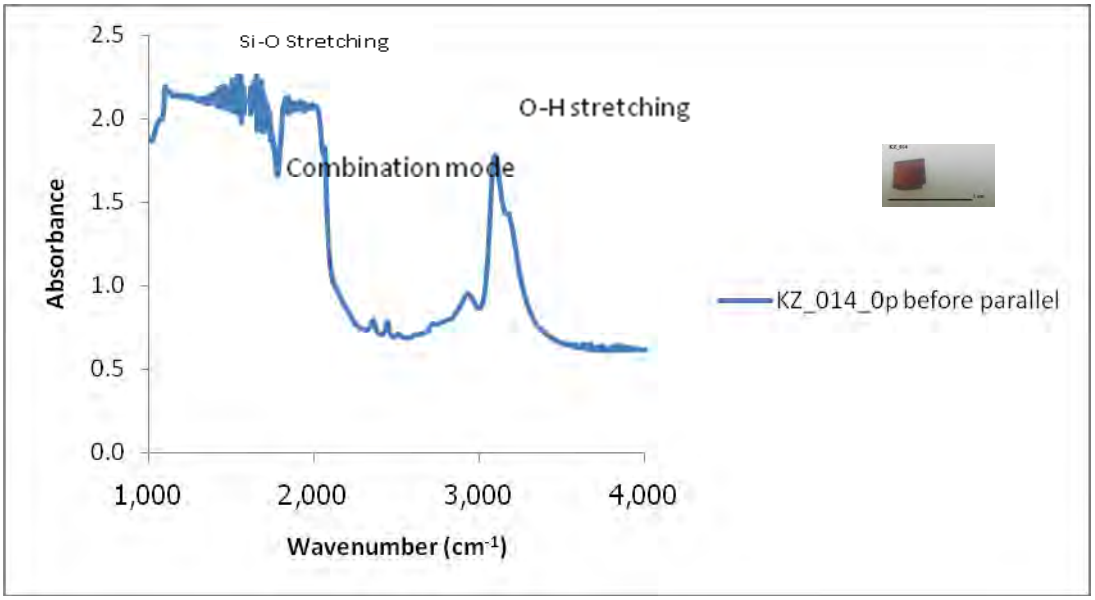
Figure 4-2: UV-VIS-NIR absorption spectra for O-Ray of Group KZ2 (light orange to reddish brown) before heating.

3.5 Fourier Transform Infrared (FTIR) spectra

Fifteen samples were measured with the FTIR before heat in order to study about structure of zircon such as O-H stretching, Si-O stretching and combination group. The samples were measured both parallel c-axis and perpendicular c-axis because Si-O stretching is better observed when recorded perpendicular c-axis and O-H stretching is better observed when recorded parallel to c-axis (Woodhead et al., 1991).

From Woodhead et al. (1991) and Zhang et al., (2002), Si-O stretching can be estimated the degree of metamictization. Peak of Si-O stretching shows at about 1400-2000 cm^{-1}. If the peak is broadband, degree of metamictization will be high. In contrast, if the peak is sharp, zircon is well crystalline or fewer defects. In addition, OH group is abundant in metamict zircon.

As seen in Figures 5-1 and 5-2, both show peaks of Si-O stretching at 1400-2000cm^{-1} and O-H stretching at 2800-3200 cm^{-1}. The Si-O stretching peaks of Group KZ2 are somewhat sharper than those of Group KZ1. Moreover, the peaks of OH group of Group KZ1 are better defined that those of Group KZ2 but all of peaks still indicate a well crystalline structure.



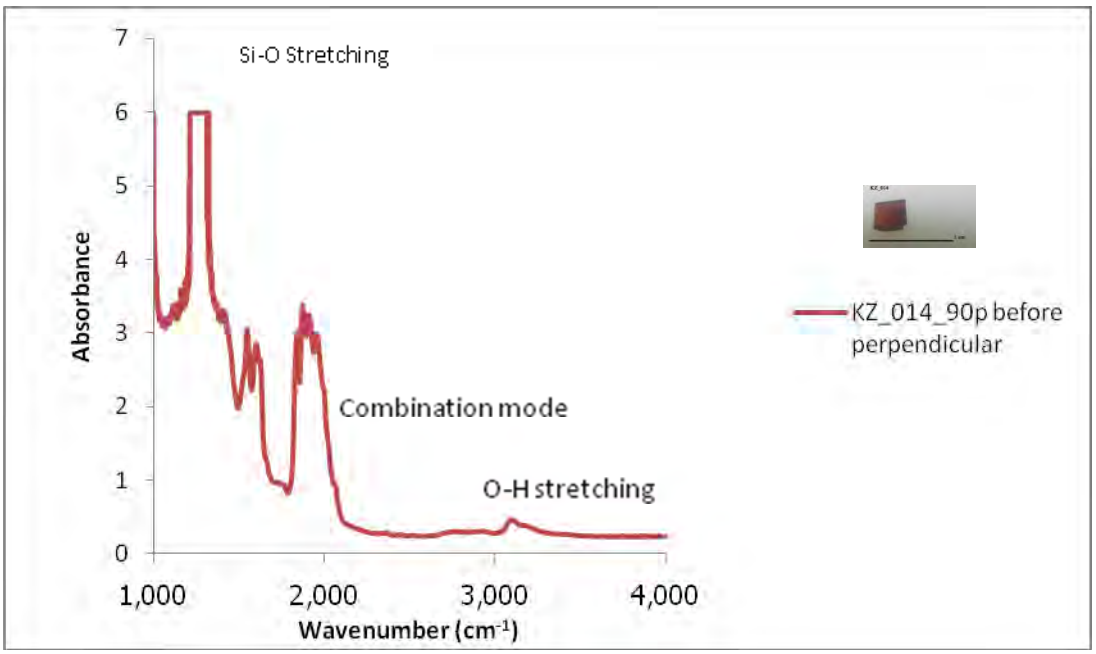
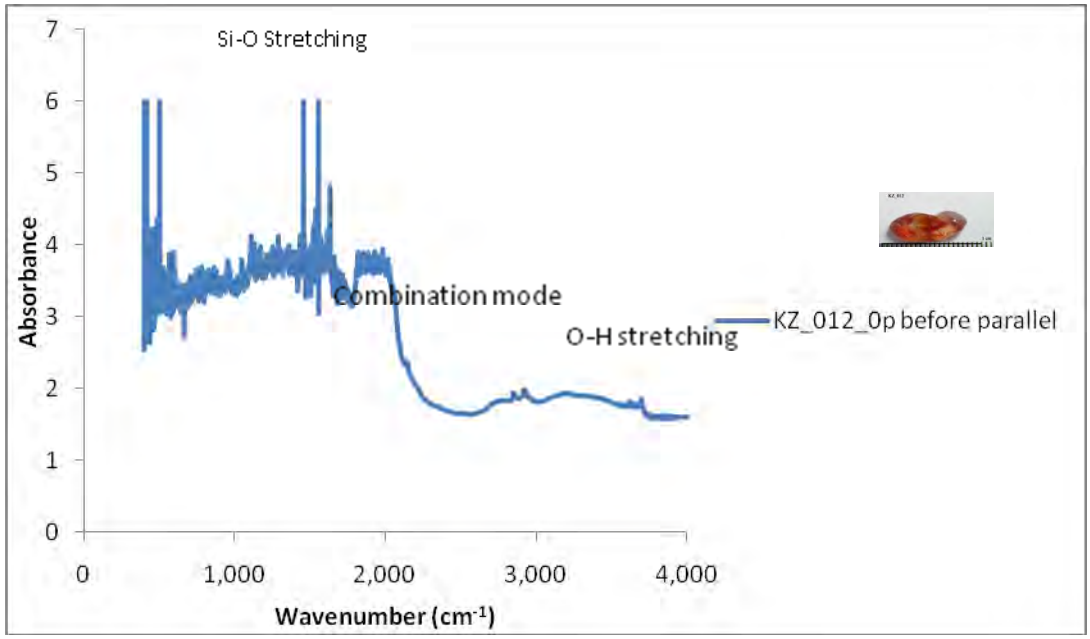


Figure 5-1: The FTIR absorption spectrum of Group KZ1 before heating.



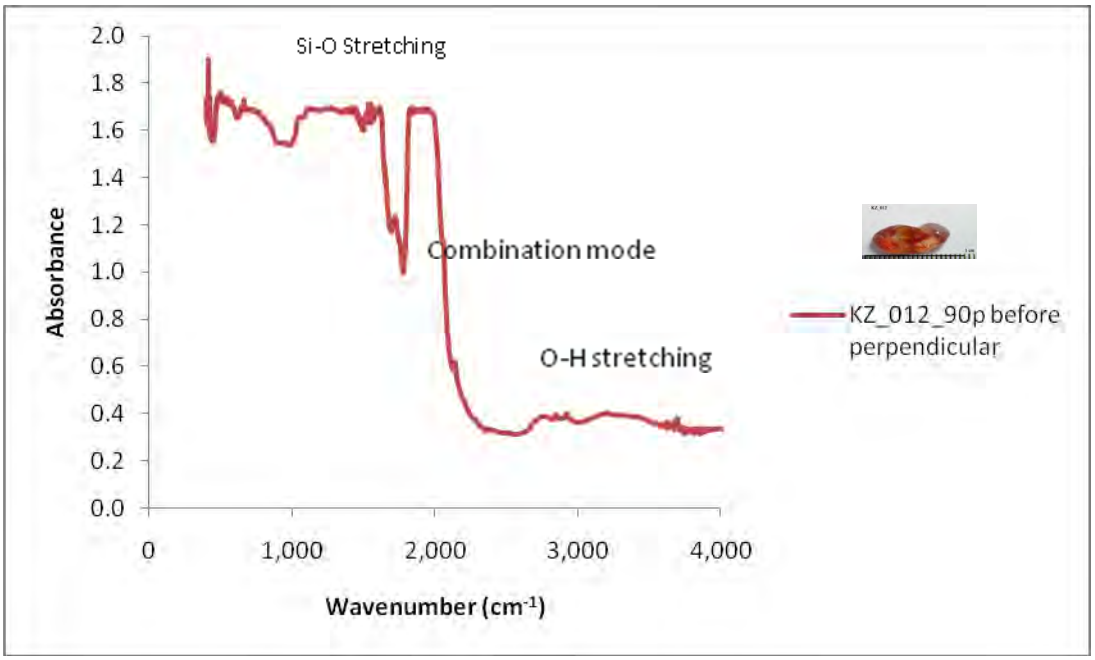


Figure 5-2: The FTIR absorption spectrum of Group KZ2 before heating.

3.6 Raman Spectrum

Twenty samples were measured for Raman spectra before heating in 0-3500 cm^{-1} range (Figures 6-1 and 6-2). Raman spectrums not only help identify mineral species but, in the case of zircon, can also help indicate the degree of metamictization of the zircon structure. The samples were measured parallel to c-axis because peak at 1008 cm^{-1} which is anti-symmetric SiO_4 stretching (V_3) will be disappeared if the samples are measured perpendicular c-axis. V_3 is crucial for indication of degree of metamictization. A well crystalline zircon usually has V_3 at 1008-1009 cm^{-1}. In contrast, a metamict zircon has V_3 less than about 1000 cm^{-1}. Furthermore, if full width at half maximum (FWHM) of V_3 is considered, a well crystalline zircon has FWHM about 2-3 cm^{-1} and metamict zircon has FWHM more than 100 cm^{-1}. In addition, the others are V_1 at about 970 cm^{-1} is symmetric SiO_4 stretching, V_2 at about 440 cm^{-1} is symmetric SiO^4 bending and V_4 at about 357 cm^{-1} is lattice mode.(Dawson et al., 1971) and (Nasdala et al., 1995)

As seen from Tables 3-1 and 3-2, Group KZ1 has V_3 peak about 1007 cm^{-1} and FWHM about 5 cm^{-1} whereas Group KZ2 has V_3 peak about 1007 cm^{-1} and FWHM about 5.6 cm^{-1}.

As shown in Figure 6-3, the FWHM of anti-symmetric SiO_4 stretching peaks (V_3) Group KZ1 and Group KZ2 are overlapping at about 1007-1008 cm^{-1}. So both groups still remain well crystalline structures with minor defects or destruction from self-irradiation.

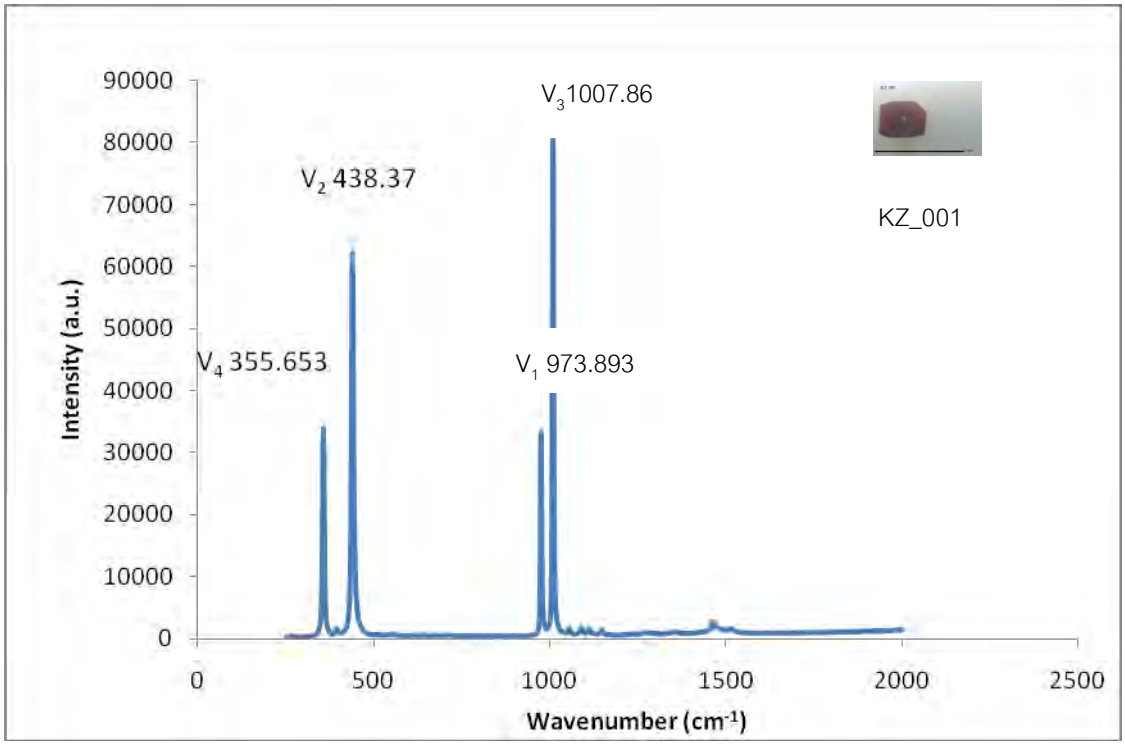


Figure 6-1: Raman spectra of Group KZ1 before heating.

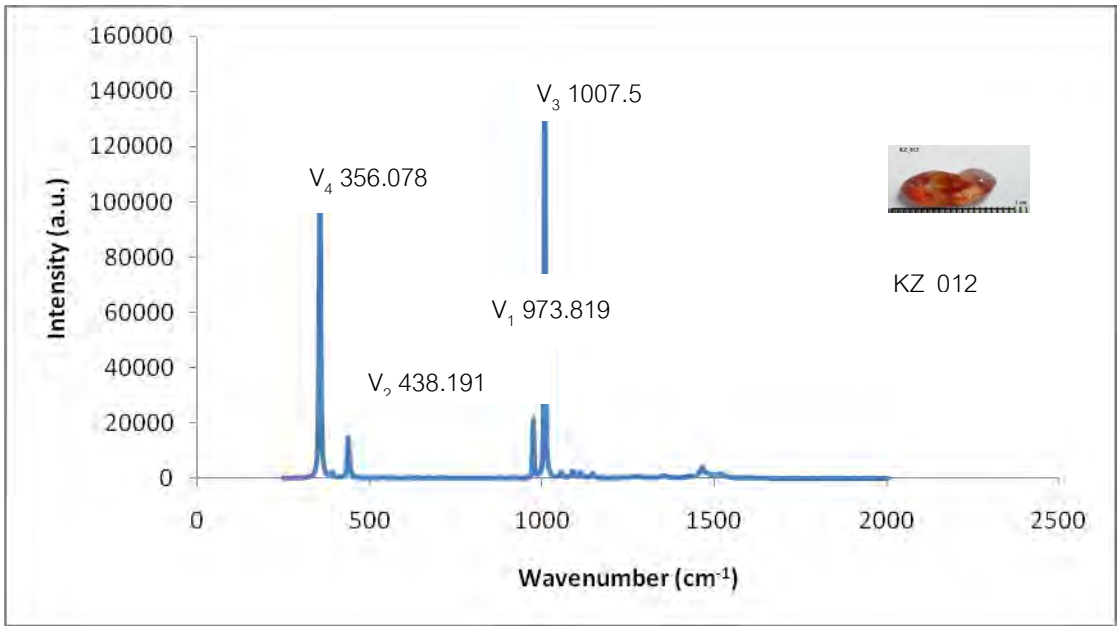


Figure 6-2: Raman spectrum of Group KZ2 before heating.

Table 3-1: Peak position of V_3 (anti-symmetric SiO_4 stretching) and their FWHM values of Group KZ1.

Group1	V_3 (cm^{-1})	FWHM(cm^{-1})
KZ_001	1006.86	4.35
KZ_005	1006.95	4.64
KZ_007	1008.01	6.10
KZ_008	1007.76	6.73
KZ_010	1007.02	4.90
KZ_011	1007.17	4.48
KZ_013	1007.61	4.45
KZ_014	1007.53	4.71
KZ_015	1008.28	4.61
Average	1007.47	5.00

Table 3-2: Peak position of V_3 (anti-symmetric SiO_4 stretching) and their FWHM value of Group KZ2.

Group2	V_3 (cm^{-1})	FWHM(cm^{-1})
KZ_004	1007.34	5.32
KZ_012	1007.5	4.68
KZ_016	1007.59	4.95
KZ_017	1006.59	7.19
KZ_018	1006.71	6.42
KZ_021	1007.69	4.79
KZ_022	1007.02	4.83
KZ_024	1007.6	4.84
KZ_026	1007.37	6.32
KZ_035	1007.5	6.67
Average	1007.29	5.60

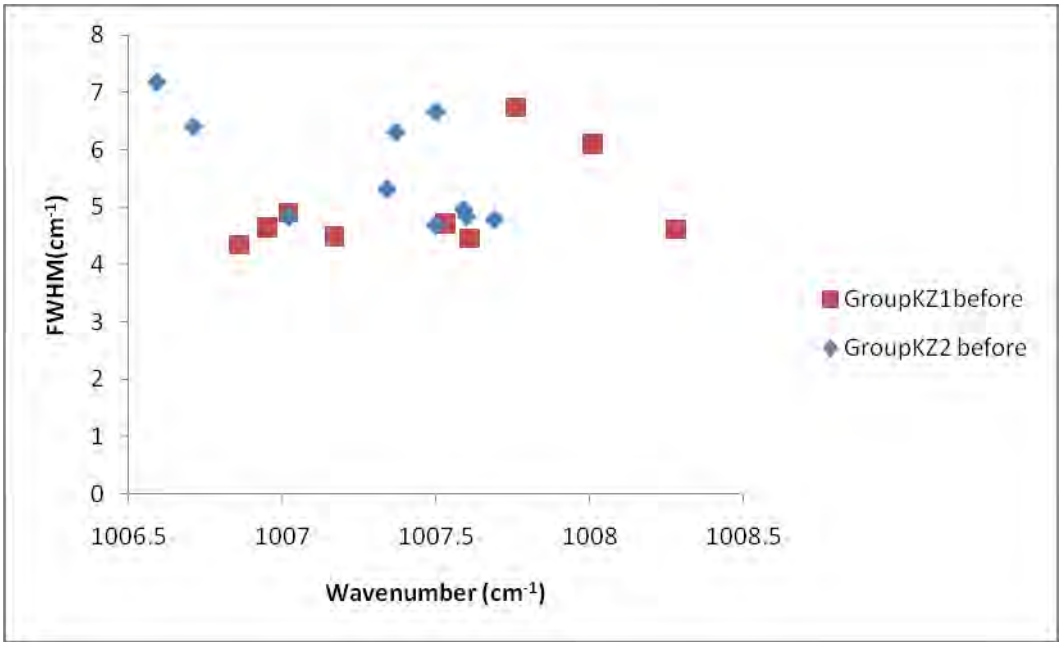


Figure 6-3: Comparison of FWHM of anti-symmetric SiO_4 stretching peaks (V_3) of Group KZ1 and Group KZ2 before heating.

CHARPTER IV

CHARACTERISTICS OF ZIRCON AFTER TREATMENT

4.1 Samples

All thirty-five zircon samples from Bo Phloi were heated in a graphite crucible at 900^{o}C in reduction condition (pure N_2 atmosphere) for 3 hours. After heating the samples of Group KZ1changed from original dark reddish brown and orange brown to colorless (Figure7-1) while those of Group KZ2 turned from original light reddish to orange brown to colorless, light violet and dark gray (Figure 7-2).

Group KZ1: colorless

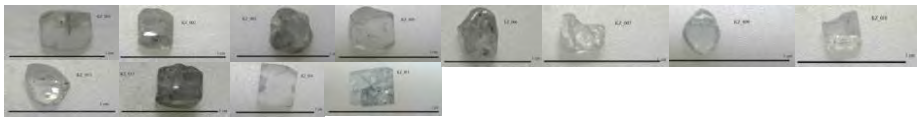


Figure 7-1: Zircon samples after heat treatment from Bo Phloi in Kanchanaburi Province, showing colorless and dark gray.

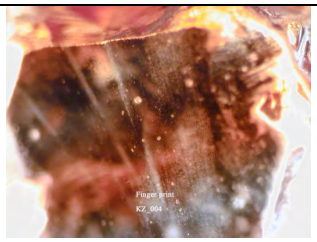
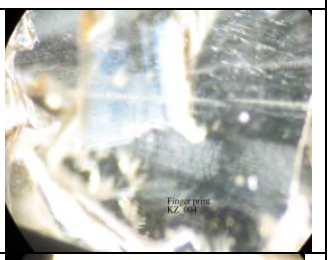
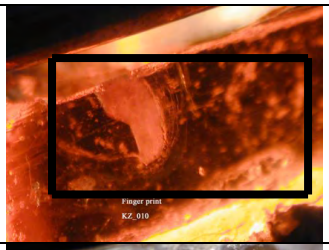
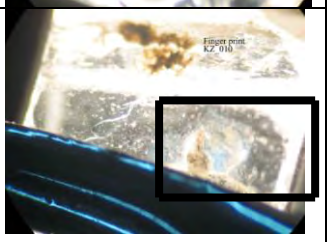
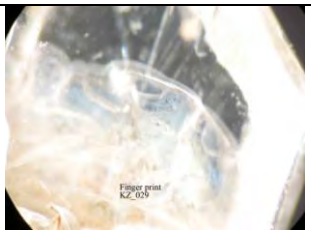
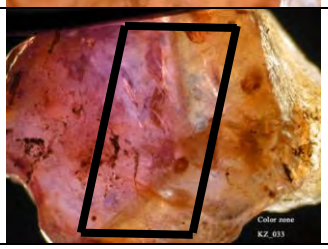
Group KZ2: colorless, dark gray and violet

Figure 7-2: Zircon samples from Bo Phloi Kanchanaburi Province after heat treatment showing colorless, dark gray and violet.

4.2 Internal characteristics

The internal characteristics such as fingerprints, color zones, negative crystals are still remaining. But some parts of color zone were disappeared as seen in Table 4-1.

Table 4-1: Comparison of Inclusions in Bo Phloi zircon samples before and after heating at 900°C.

Type of inclusion	Before heating	After heating
Fingerprints		
Fingerprints		
Fingerprints		
Negative crystals		
Color Zones		

4.3 UV-VIS-NIR Absorption Spectra

Ten heated samples were recorded for UV-VIS-NIR absorption spectra for both E-Ray and O-Ray between 250-2000 nm. As seen in Figures 8-1, they show no absorption in visible range and shoulder at 350 nm which corresponds well to the colorless characteristic after heating. This suggests that the reddish brown and orange brown coloration of both groups are related to color center or structure defects that can be removed by annealing at high temperature. In addition, after heating, two peaks at 1121 nm and 1508 nm (Figure 8-2), which are related to U^{5+}(Thongnopkun et al., 2007), are still at the same positions as before heating.

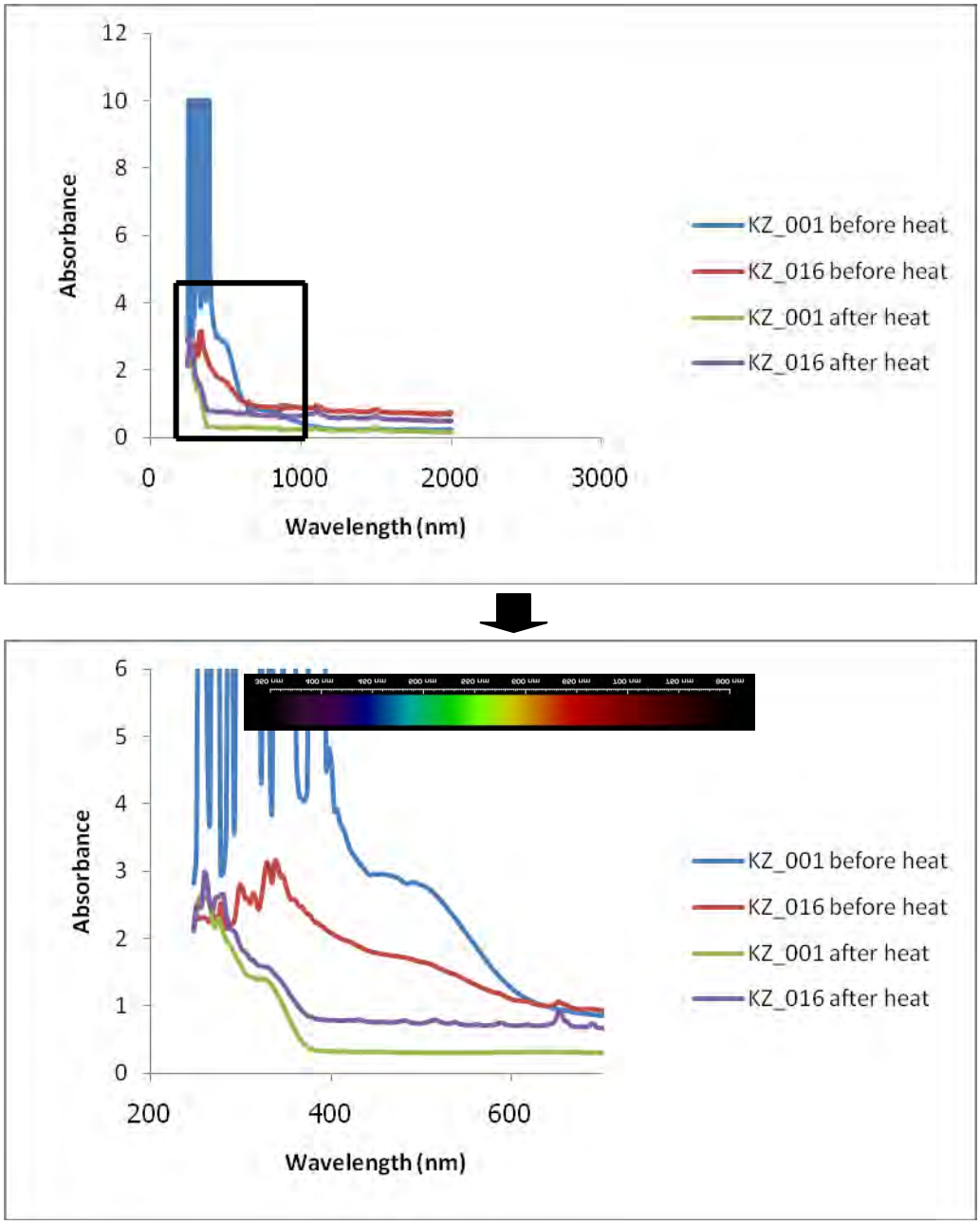


Figure 8-1: Comparison of UV-VIS-NIR absorption spectra of zircon samples (Group KZ1; KZ_001 and Group KZ2; KZ_016) recorded before and after heating.

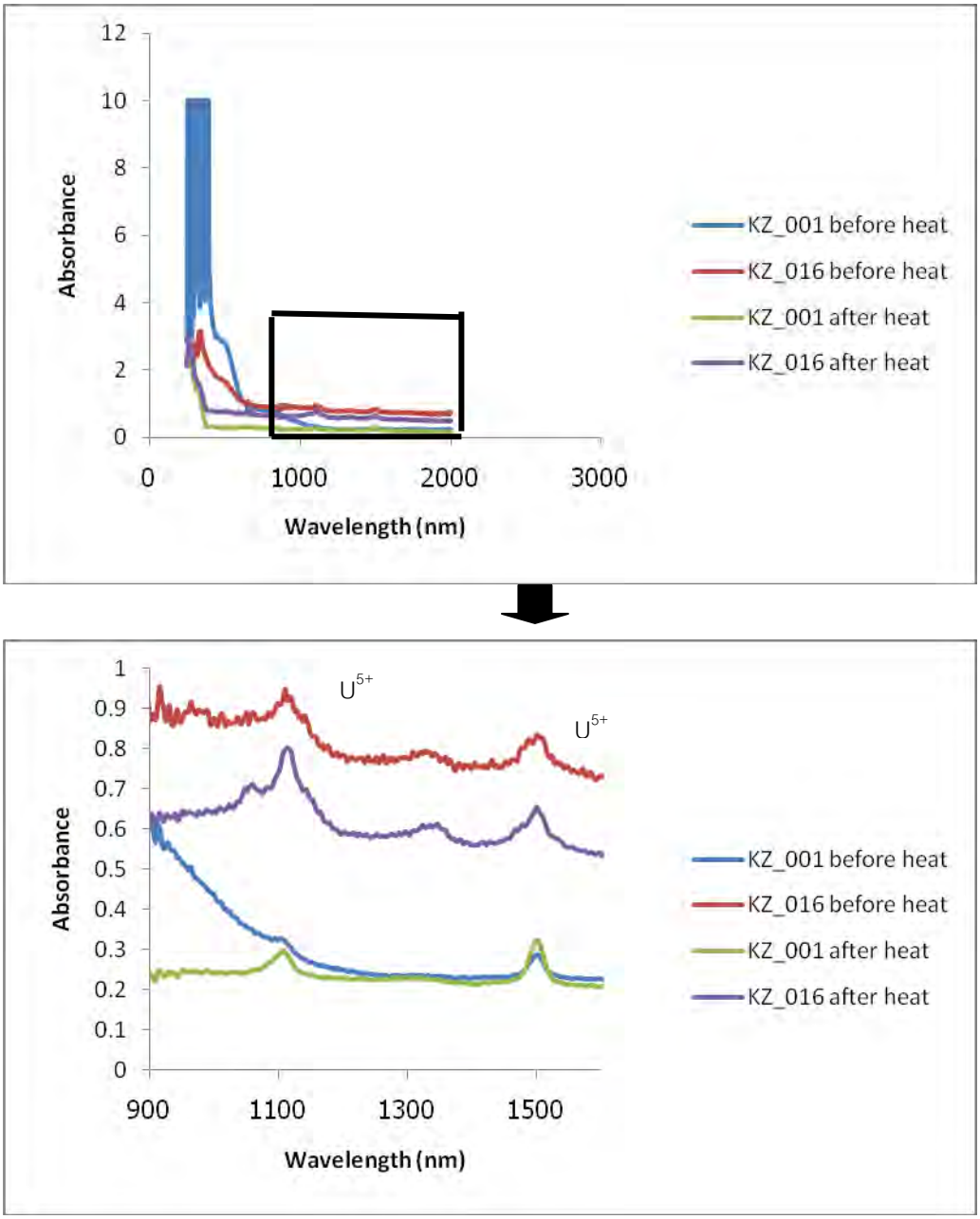


Figure 8-2: Comparison of UV-VIS-NIR absorption spectra of U^{5+} peak on zircon samples (Group KZ1; KZ_001 and Group KZ2; KZ_016) recorded before and after heating.

4.4 Fourier Transform Infrared (FTIR) spectra

Fifteen heated samples were measured for FTIR absorption spectra in order to compare and study about O-H group and Si-O stretching. The samples were measured parallel and perpendicular to c-axis.

As seen in Figures 9-1, the peak of O-H stretching (about 3000-3300 cm^{-1}) before heating is more board brand than that after heating which is the result of the heat effects. The heat treatment makes zircon rearrange their structures. Some of O-H group was probably removed and structures are better. Moreover, as seen in Figures 9-2, the peaks of Si-O stretching (1400-2000 cm^{-1}) after heat is not clearer than the peaks before heat so it is not significantly represent well structures. However, the removing of O-H stretching is represented well crystalline.

The sharp peaks at 3385 and 3420 cm^{-1} are O-H species which are in Si-occupied and Si-vacant tetrahedral, respectively. The sharp peak represents low degree of metamictization. In contrast, the board band peak at 3600-3400 cm^{-1} represents metamict zircon or low zircon and intermediate zircon. (Geister et al., 2003)

After heating both groups have better structures than before heating and all samples are well structure or low degree of metamictization.

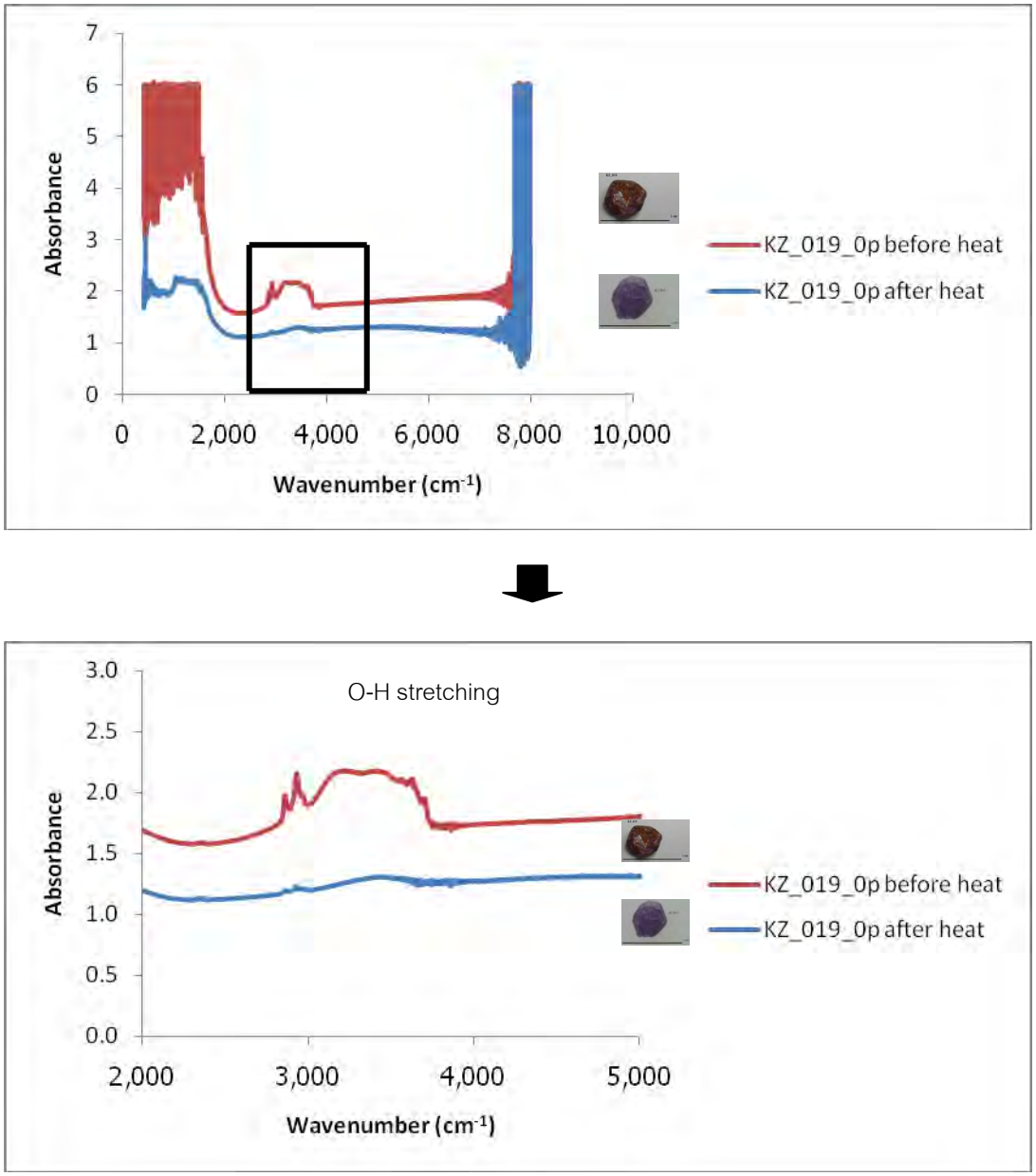


Figure 9-1: Comparison of FTIR absorption spectra of a zircon sample (Group KZ2; sample KZ_019) measured parallel to c-axis before and after heating at 900°C

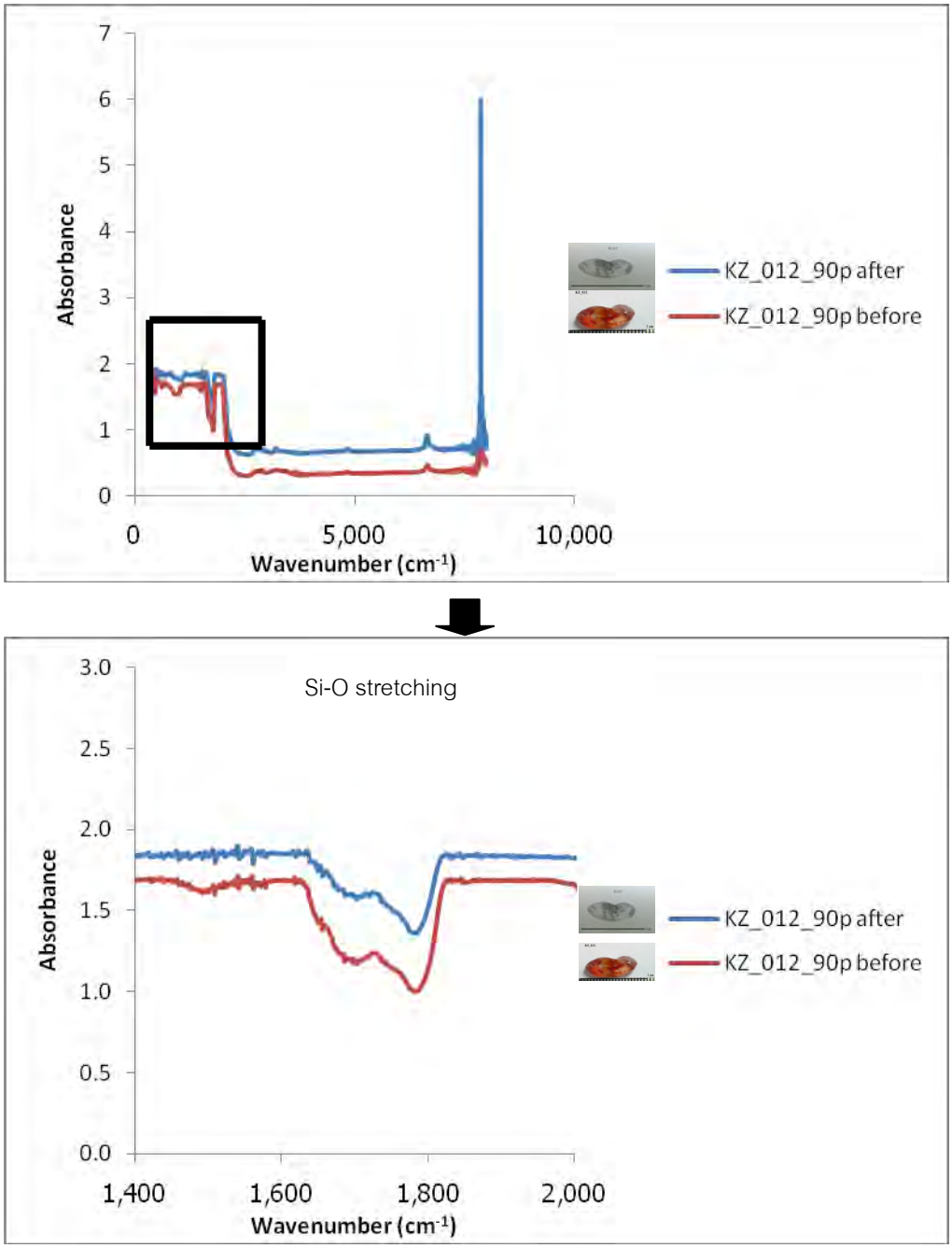


Figure 9-2: Comparison of FTIR absorbance spectra of a zircon sample (Group KZ2; sample KZ_012) measured perpendicular to c-axis before and after heating at 900°C

4.5 Raman spectrum

Twenty heated samples were also measured for Raman spectrum in order to compare with those before heating and to analyze the degree of metamictization and recrystallization .

If the peaks after heating at 1008 cm^{-1} (V_3, Si-O stretching) and 973 cm^{-1} (V_1, Si-O stretching) are higher and sharper than those before heating, it suggests a better structure after heating (Zhang, 2000). Moreover, the peaks at 1008 cm^{-1} and 973 cm^{-1} are related to U and Th in zircon, if the peaks shift to high wavenumber, ratio of U:Th will change that result from charge transfer in structure.(Vance and Mackey, 1975,1978)

As seen in Figures 10-3 and 10-4, and Tables 5-1, the V_3 values of both groups increase toward 1008 cm^{-1} and FWHM values of both groups decrease after heating. The average V_3 value of Group KZ1 before heating is 1007.23 cm^{-1} and the average FWHM value of V_3 is 4.83 cm^{-1} while the average V_3 value of after heating is 1007.67 cm^{-1} and the average FWHM value of V_3 is 4.69 cm^{-1}. The average V_3 value of Group KZ2 before heating is 1007.28 cm^{-1} and the average FWHM value of V_3 is 5.52 cm^{-1} while that of after heating is 1007.46 cm^{-1} and the average FWHM value of V_3 is 5.46 cm^{-1}. Therefore, heat treatment can improve strutural damage to some extend.

As seen in Tables 5-2, V_1 values of both groups increase slightly. The average V_1 value of Group KZ1 before heating is 973.95 cm^{-1} while that of after heating is 974.13 cm^{-1}. The average V_1 value of Group KZ2 before heating is 973.65 cm^{-1} whereas that after heating is 973.79 cm^{-1} .

Table5-1: Comparison peak positions of V_3 (anti-symmetric SiO_4 stretching) and their FWHM values of both Group KZ1 and Group KZ2 samples after heating.

Group KZ1	Before heating		After heating		Group KZ2	Before heating		After heating	
	$V_3(cm^{-1})$	FWHM (cm^{-1})	$V_3(cm^{-1})$	FWHM (cm^{-1})		$V_3(cm^{-1})$	FWHM (cm^{-1})	$V_3(cm^{-1})$	FWHM (cm^{-1})
KZ_001	1006.86	4.35	1007.70	4.61	KZ_012	1007.34	5.32	1006.88	5.31
KZ_005	1006.95	4.35	1007.78	4.51	KZ_016	1007.50	4.69	1007.41	6.42
KZ_007	1006.95	4.65	1007.53	5.03	KZ_017	1007.59	4.96	1007.72	5.66
KZ_009	1007.76	6.74	1007.60	4.67	KZ_018	1006.59	7.19	1007.34	6.21
KZ_011	1007.02	4.91	1007.27	4.48	KZ_021	1006.71	4.79	1007.63	4.72
KZ_013	1007.17	4.48	1008.37	5.22	KZ_022	1007.69	4.83	1007.34	5.05
KZ_014	1007.61	4.46	1007.46	5.87	KZ_024	1007.60	4.84	1007.68	4.84
KZ_015	1007.53	4.46	1007.61	3.13	KZ_035	1007.50	6.67	1007.67	5.49
Average	1007.23	4.83	1007.67	4.69	Average	1007.29	5.60	1007.46	5.46

Table5-2: Comparison peak positions of V_1 (symmetric SiO_4 stretching) and their FWHM values of both Group KZ1 and Group KZ2 samples after heating.

Group KZ1	Before heat		After heat		Group KZ2	Before heat		After heat	
	$V_1(cm^{-1})$	FWHM (cm^{-1})	$V_1(cm^{-1})$	FWHM (cm^{-1})		$V_1(cm^{-1})$	FWHM (cm^{-1})	$V_1(cm^{-1})$	FWHM (cm^{-1})
KZ_001	973.62	4.28	974.07	4.15	KZ_012	973.81	4.30	973.78	4.39
KZ_005	973.81	4.30	973.823	4.45	KZ_016	973.85	4.28	973.75	4.68
KZ_007	973.85	4.28	973.96	4.39	KZ_017	973.14	4.71	973.90	4.63
KZ_009	973.14	4.43	973.98	4.39	KZ_018	973.28	4.43	973.53	4.78
KZ_011	973.28	4.30	973.86	4.47	KZ_021	973.87	4.30	974.00	4.80
KZ_013	973.87	4.54	974.72	4.68	KZ_022	973.83	4.54	973.96	4.63
KZ_014	973.83	4.32	973.84	4.46	KZ_024	973.85	4.32	974.00	4.37
KZ_015	973.85	4.32	974.18	4.60	KZ_035	973.72	4.52	973.86	4.53
Average	973.64	4.35	974.05	4.45	Average	973.67	4.43	973.85	4.60

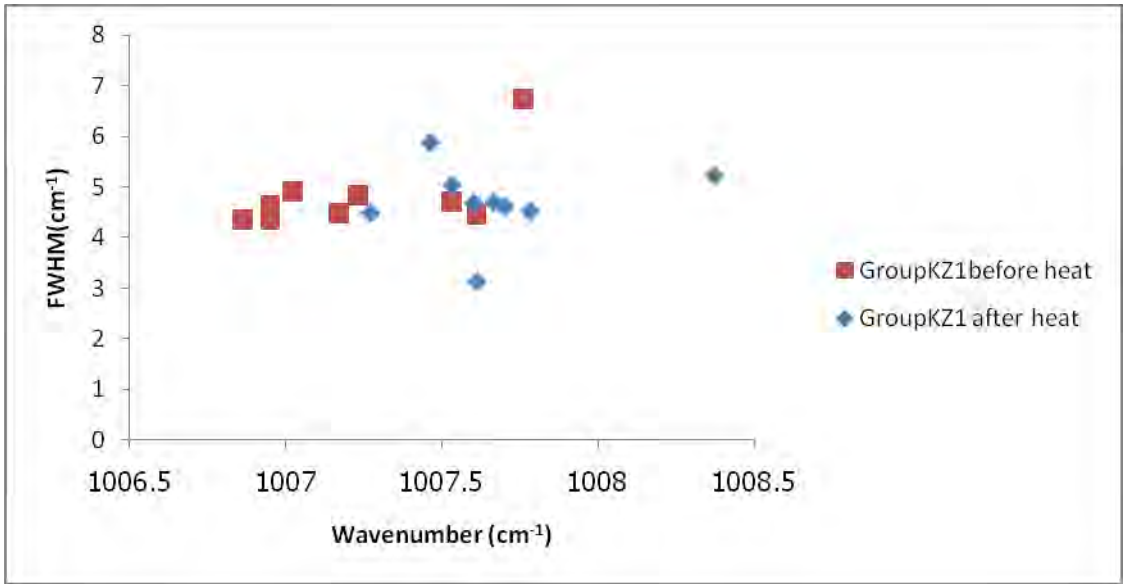


Figure10-3: Comparison of V_3 and FWHM of Group KZ1 samples after heating which show lower degree of metamictization after heating.

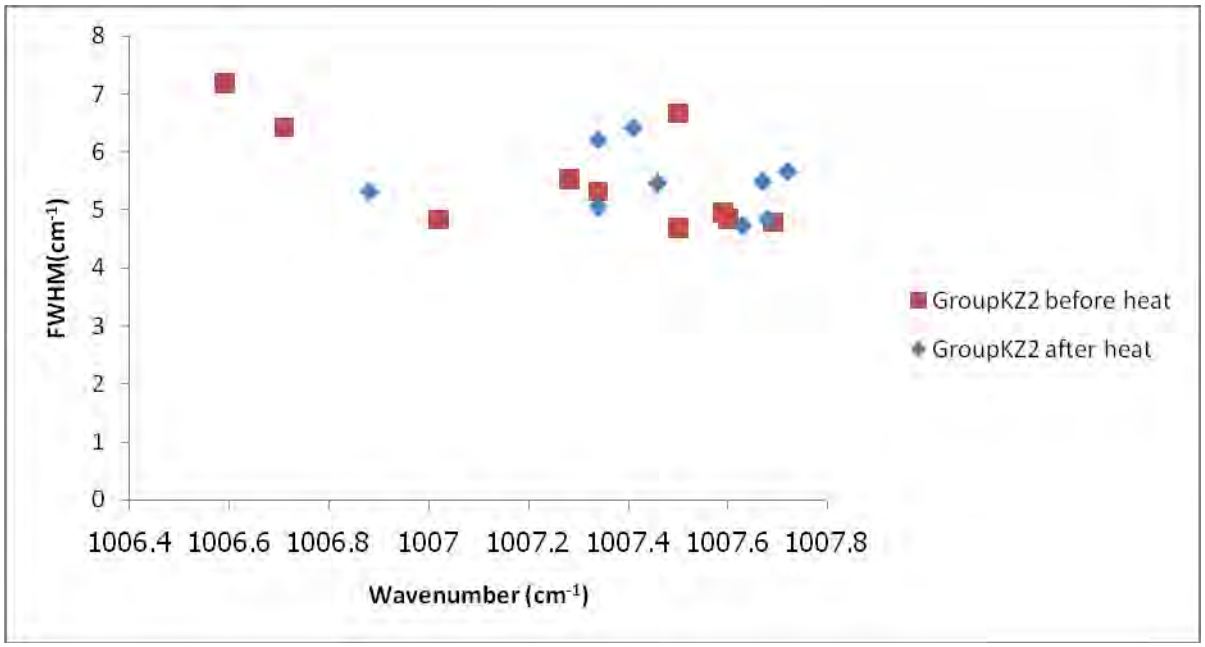


Figure10-4: Comparison of V_3 and FWHM of Group KZ2 samples after heating which show lower degree of metamictization after heating.

CHAPTER V

CHEMICAL ANALYSIS

Twelve samples from Bo Phloi were analyzed by LA-ICP-MS in order to study about major, minor and trace element. Those probably involve causing of color in zircon and also defecting in structure. This quantitative analysis was displayed in Table 6-1 and 6-2 which major element is Zr, minor element is Hf and trace elements are radioactive elements such as U and Th. Each sample was analyzed in 3 spots and then averaged in ppm.

The concentrations of radioactive elements (U and Th) were displayed in Table 6-3. For the group KZ1 which its original color is dark reddish brown to orange brown before heating contains the lowest of uranium content. In contrast, group KZ2 which its original color is light orange to reddish brown contains the highest of uranium content and also the thorium content. The results correspond to degree of metamictization. For the group KZ1, the average specific gravity is about 4.6 which is high type or undamaged whereas the average specific gravity of group KZ2 is about 4.5 which is intermediate type or slightly damaged. Moreover, the results correspond to the result of Raman spectra section which represent that group KZ1 has narrow range of V_3 (anti-symmetric SiO_4) which represent better crystalline than group KZ2.

The concentrations of U or Th are related to the color of zircon. If zircon has original dark color, it would have high U or Th content and after heating it would turn to blue color which corresponds to U and Th content. In contrast, the light color zircon will have less U or Th than dark color zircon. (อรุณีและคณะ, 2550)

As seen in Table 6-4, the Bokha zircon and Ratanakiri zircon which have original brown color, those turned to blue color after heating in reduction condition (Kitiphaisalnont, 2004) and (Klinkeaw, 2551) whereas the Khao Phloi Wean zircon turned to colorless even though there are higher U content than Ratanakiri zircon (Thaephajan, 2550). The Bo Phloi zircon samples contain higher U content than Ratanakiri zircon but after heating they changed to colorless.

For Bo Phloi zircon, the cause of color is self-radiation of U or Th and it also corresponds to degree of metamictization which group KZ1 has lower degree of metamictization than group KZ2. However, the dark color Bo Phloi zircon is lower U

content and also lower degree of metamictization than the light color Bo Phloi zircon, so the further study is needed to find out the relation of U or Th concentration and degree of metamictization. In addition, the colorless of Bo Phloi zircon after heating may result of low U and Th concentrations.

Table 6-1: Summary of chemical contents (ppm) of Group KZ1 analyzed by LA-ICP-MS

Elements	KZ_001	KZ_002	KZ_003	KZ_005	KZ_006	KZ_014	KZ_015
Si29	152599.2	150511.2	146432.9	148732.1	143869.5	139327.2	144468.8
Zr90	486364.7	486364.4	486364.7	486364.7	486364.6	486364.5	486364.6
Hf178	5689.0	8254.8	6557.4	5930.8	5309.6	5712.4	5969.7
Mg24	0.8	1.1	1.3	1.0	1.2	39.1	5.8
Al27	0.7	4.6	2.4	0.8	3.1	2.0	1.6
P31	56.0	121.0	59.1	62.4	63.2	48.5	65.8
Sc45	109.8	138.8	107.5	100.7	102.0	92.5	91.59
Ti47	617.7	726.6	583.0	568.5	580.3	509.9	496.6
Fe57	0	2.3	0	0	0	0	0
Y89	294.7	782.6	431.3	430.3	583.3	301.7	281.6
Nb93	4.8	12.2	5.8	4.8	4.2	3.6	3.3
La139	0	0.2	0.0	0	0	0	0
Ce140	3.7	8.0	4.6	4.3	4.1	3.5	3.9
Ta181	1.0	4.7	1.8	1.5	1.3	0.9	1.0
Pb206	0.5	0.8	0.3	0.3	0.2	0.2	0.2
Th232	42.7	153.4	89.6	82.3	79.4	36.2	41.8
U238	65.0	261.2	142.1	120.1	85.5	57.4	57.1
Total %	64.6	64.7	64.1	64.2	63.7	63.3	63.8

Table 6-2: Summary of chemical contents (ppm) of Group KZ2 analyzed by LA-ICP-MS

Elements	KZ_012	KZ_017	KZ_021	KZ_029	KZ_032	KZ_034	KZ_035
Si29	144978.5	148690	142616.5	145025.6	144650.7	137649	132816.7
Zr90	486364.5	486364.5	486364.5	486364.5	486364.6	486364.6	486364.6
Hf178	9923.0	10924.8	8049.5	10734.7	9919.1	9928.6	10182.3
Mg24	5.3	0.3	1.8	2.0	31.0	3.8	6.0
Al27	105.2	133.0	85.9	66.1	86.6	54.7	147.3
P31	563.2	1277.1	333.9	885.7	537.3	741.3	873.9
Sc45	284.1	518.5	241.0	319.8	275.1	168.9	345.0
Ti47	740.9	701.4	742.2	685.7	635.4	441.1	420.4
Fe57	0	0	0	4.8	0	0	8.9
Y89	1349.6	2630.1	555.7	2325.0	1070.3	2082.6	1892.0
Nb93	9.0	9.6	6.7	5.1	4.2	6.7	5.1
La139	0.9	0	0.1	0.3	0	0	0
Ce140	5.7	1.5	1.0	2.0	1.1	2.7	1.2
Ta181	3.6	4.5	1.1	2.8	1.7	2.7	2.1
Pb206	2.0	3.0	0.5	2.8	0.9	1.4	1.4
Th232	133.5	302.3	39.3	253.7	72.3	151.8	111.2
U238	283.1	633.8	70.4	407.6	175.9	321.6	273.0
Total %	64.5	65.2	63.9	64.7	64.4	63.8	63.4

Table 6-3: Comparison of U and Th concentration (ppm) between Group KZ1 and Group KZ2

Group KZ1	**U**	**Th**	**Group KZ2**	**U**	**Th**
KZ_001	65.0	42.7	KZ_012	283.1	133.5
KZ_002	261.2	153.4	KZ_017	633.8	302.3
KZ_003	142.1	89.6	KZ_021	70.4	39.3
KZ_005	120.1	82.3	KZ_029	175.9	253.7
KZ_006	85.5	79.4	KZ_032	175.9	72.3
KZ_014	57.4	36.2	KZ_034	321.6	151.8
KZ_015	57.1	41.8	KZ_035	273.0	111.2
Average	112.6	75.1	**Average**	276.2	152.0

Table 6-4: Comparison the amount of uranium in zircon from Ratanakiri by NAA analysis (Kitiphaisalnont,2004) and heat-treated colorless zircon from Khao Phloi Wean by EPMA analysis (Thaephajan,2007) and heat-treated blue zircon from Bokha by EPMA analysis (Klinkeaw, 2008) and unheated brown zircon from Bo Phloi by LA-ICP-MS analysis.

Sample	Uranium in sample (ppm)
Ratanakiri;unheat brown zircon	52.19 ± 3.5
Ratanakiri; heat-treated colorless zircon	38.11 ±1.38
Ratanakiri; heat-treated blue zircon	60.51±5.11
Khao Phloi Wean;heat-treated colorless zircon (average)	163.75
Bokha; heat-treated blue zircon	587.64
Bo Phloi; unheated brown zircon (average)	194.4

As seen in Table 6-5, for some of Bo Phloi zircons, Zr were replaced by Hf in their structure $(Zr_{0.99},Hf_{0.01})SiO_4$ but mostly were not replaced and still be $ZrSiO_4$ in chemical formula.

Table 6-5: Chemical formulas and concentrations of Si, Zr and Hf (atom mole) on zircon from Bo Phloi by LA-ICP-MS analysis.

Samples	Formula	No. of Atom of		
		Zr	Hf	Si
KZ_001	$ZrSiO_4$	1.00	0.00	0.98
KZ_002	$(Zr_{0.99},Hf_{0.01})SiO_4$	0.99	0.01	0.99
KZ_003	$ZrSiO_4$	1.00	0.00	0.98
KZ_004	$ZrSiO_4$	1.02	0.00	0.95

KZ_005	$ZrSiO_4$	1.01	0.00	0.98
KZ_006	$ZrSiO_4$	1.01	0.00	0.98
KZ_008	$ZrSiO_4$	1.01	0.00	0.98
KZ_009	$ZrSiO_4$	1.01	0.00	0.98
KZ_010	$ZrSiO_4$	1.01	0.00	0.98
KZ_011	$ZrSiO_4$	1.01	0.00	0.98
KZ_012	$ZrSiO_4$	1.00	0.00	0.98
KZ_013	$ZrSiO_4$	1.01	0.00	0.98
KZ_014	$ZrSiO_4$	1.01	0.00	0.98
KZ_015	$ZrSiO_4$	1.01	0.00	0.98
KZ_016	$ZrSiO_4$	1.00	0.00	0.98
KZ_017	$ZrSiO_4$	1.00	0.00	0.97
KZ_018	$ZrSiO_4$	1.00	0.00	0.97
KZ_020	$ZrSiO_4$	1.00	0.00	0.97
KZ_021	$ZrSiO_4$	1.00	0.00	0.97
KZ_022	$ZrSiO_4$	1.00	0.00	0.97
KZ_023	$ZrSiO_4$	1.00	0.00	0.97
KZ_024	$ZrSiO_4$	1.00	0.00	0.97
KZ_025	$ZrSiO_4$	1.00	0.00	0.97
KZ_026	$ZrSiO_4$	1.00	0.00	0.97
KZ_028	$ZrSiO_4$	1.00	0.00	0.97

KZ_029	$ZrSiO_4$	1.00	0.00	0.97
KZ_030	$ZrSiO_4$	1.00	0.00	0.97
KZ_031	$(Zr_{0.99},Hf_{0.01})SiO_4$	0.99	0.01	0.99
KZ_032	$ZrSiO_4$	1.00	0.00	0.97
KZ_034	$ZrSiO_4$	1.00	0.00	0.97
KZ_035	$ZrSiO_4$	1.00	0.00	0.97

CHAPTER VI
CONCLUSION

6.1 Characteristics of zircon before heating

6.1.1 The zircon samples from Bo Phloi can be sundivied into 2 groups based their color appearance; Group KZ1 is dark reddish brown to orange brown and Group KZ2 is light orange to reddish brown. Beside, their color are not homogeneous. Most of the samples are inert in short wave and long wave UV, subhedral to anhedral, sub adamantine to adamantine luster and the average SG values of both groups are 4.569 (Group KZ1) and 4.486 (Group KZ2) which represent high to intermediate type of zircon.

6.1.2 The dominant internal features in zircon from Bo Phloi are cracks, fingerprints, negative crystals which mostly are tube-shape and color zones.

6.1.3 The UV-VIS-NIR spectra of zircon samples from Bo Phloi before heating show the increase of the absorption from 600 nm to UV range which represents dark reddish brown to orage brown color. They probably relate to self irridiation of radioactives or color center which damage structure. Moreover, there are peak at 1150 nm and 1550 nm which are related to U^{5+}.

6.1.4 The FTIR absorption spectra of zircon samples from Bo Phloi before heating show O-H stretching peaks about 2800-3200 cm^{-1} and Si-O stretching peaks about 1400-2000 cm^{-1}. Both peaks are moslty quite sharp which indicate a well crystalline structure.

6.1.5 The Raman spectra of zircon samples from Bo Phloi before heating give the average V_3 value of 1007.23 cm^{-1} and the average FWHM value of 4.83 cm^{-1} for the Group KZ1 whereas for the Group KZ2 the average V_3 value is 1007.29 cm^{-1} and the average FWHM value is 5.60cm^{-1}, all represent low degree of metamictization.

6.2 Characteristics of zircon after heating

6.2.1 The zircon samples after heat at 900^{o}C in reduction condition (pure N_2 atmosphere) for 3 hours changed to mostly colorless, some dark gray and violet.

6.2.2 The dominant internal features after heat are still remaining the same except some part of color zone was disappeared.

6.2.3 The UV-VIS-NIR absorption spectra of Bo Phloi zircon samples after heat show no absorption in visible range which represents the colorless color (or the orignal dark brown to orange brown disappeared). Furthermore, this suggest the heat treatment at 900^{o}C in reduction condition for 3 hours can remove color center. In addition, the U^{5+} at 1150 nm and 1557 nm are still remaining.

6.2.4 The FTIR absorption spectra of Bo Phloi zircon samples after heating show disappearance and sharp of the O-H stretching peak at 2800-3200 cm^{-1} and some of the Si-O stretching peak is clearer and sharper than before heat. This also suggests that heating of zircon at 900 ^{o}C in reduction condition for 3 hours can improve their structures.

6.2.5 The Raman spectra of Bo Phloi zircon samples after heating show the average V_3 values of 1007.67cm^{-1} for Group KZ1 and 1007.46cm^{-1} ofrGroup KZ2 which increase after heating, and the average FWHM values of 4.69cm^{-1} for Group KZ1 and 5.46cm^{-1} for Group KZ2 which decrease after heating. These results relate to improvement of structure damage or the crystals have better structure.

6.2 Chemical analysis by LA-ICP-MS

The concentrations of U and Th were related to causes of brown color and also degree of metamictization. For this study, The average U content of Group KZ1 is 112.6 ppm and Group KZ2 is 276.2 ppm and the average Th content of Group KZ1 is 75.1ppm and 152.0 ppm for Group KZ2. The high concentration of U in Group KZ1 may suggest that Group KZ1 might have been subjected to higher degree of metamictization than Group KZ2 which are coresponding to their SG and Raman spectra, but the relation of their colors and U contents were not not clear, so the furthur study is needed to find out. Beside, Hf can replace Zr in some samples and both groups have same formular which mostly are $ZrSiO_4$ and some are $(Zr_{0.99},Hf_{0.01})SiO_4$.

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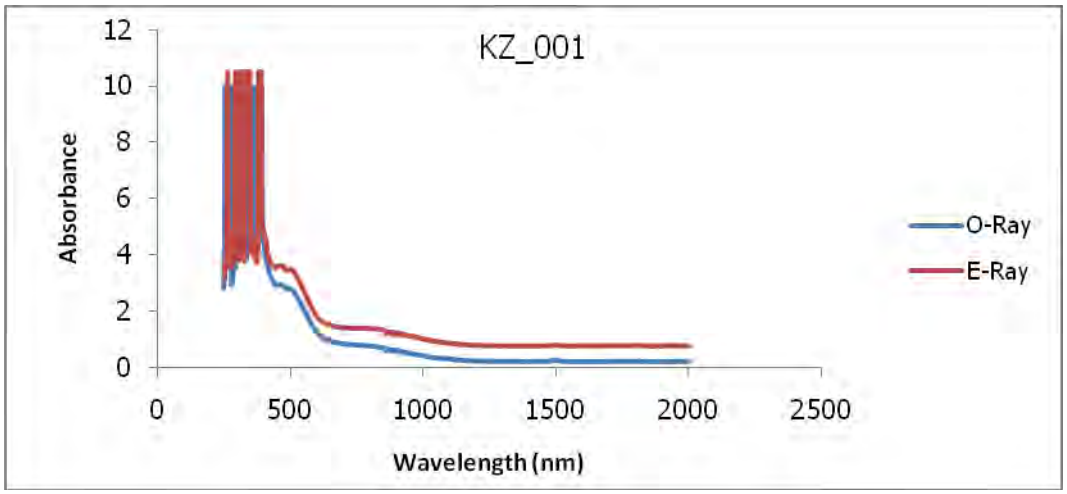
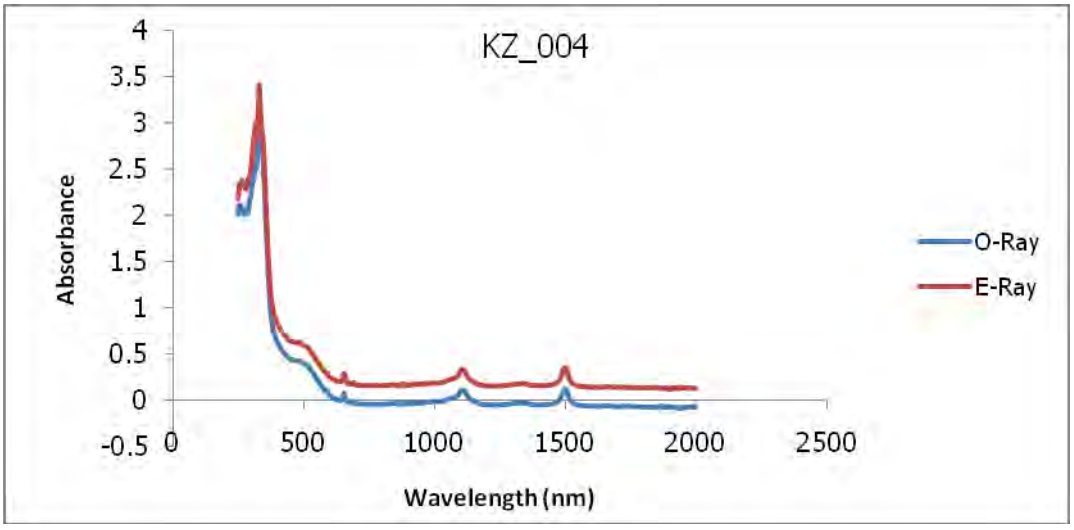
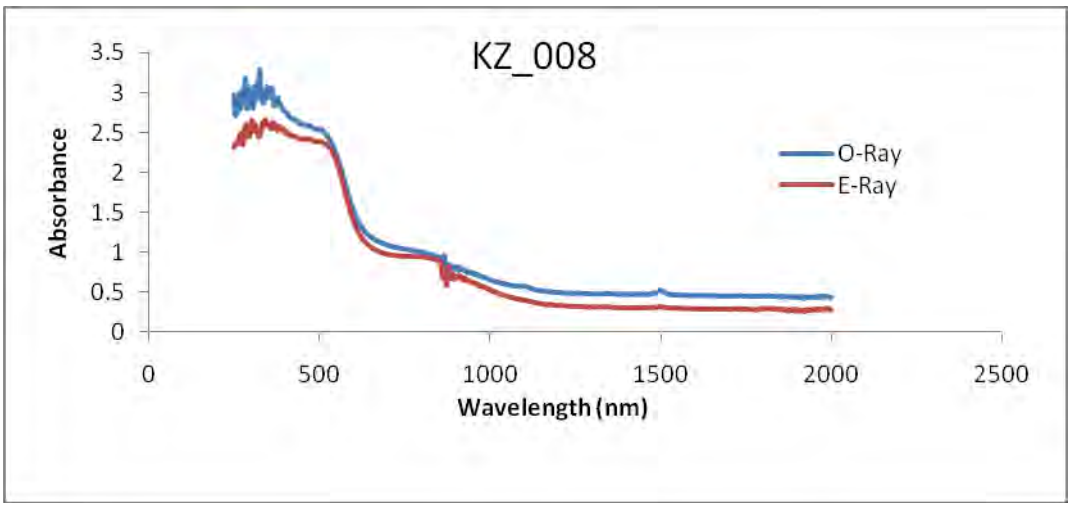
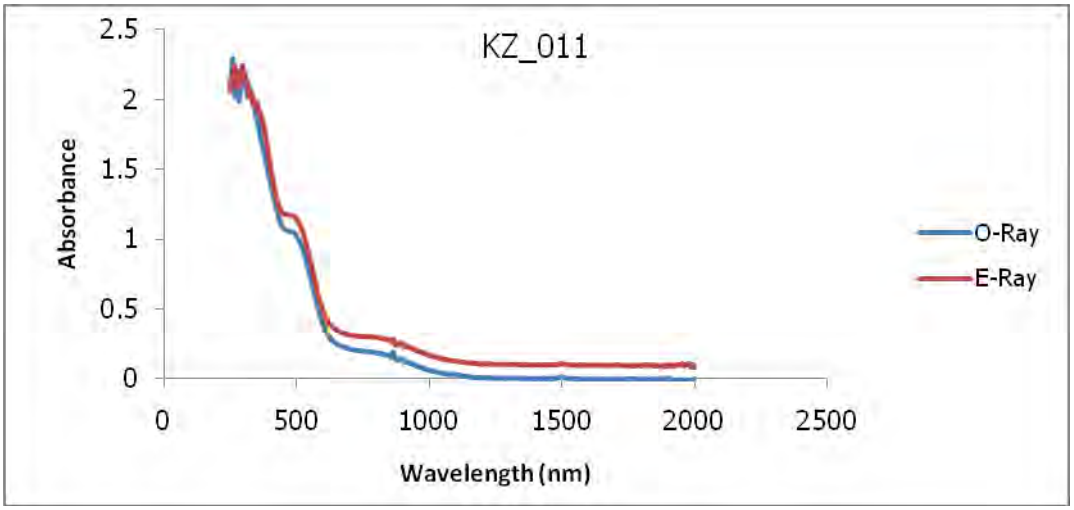
Appendix A

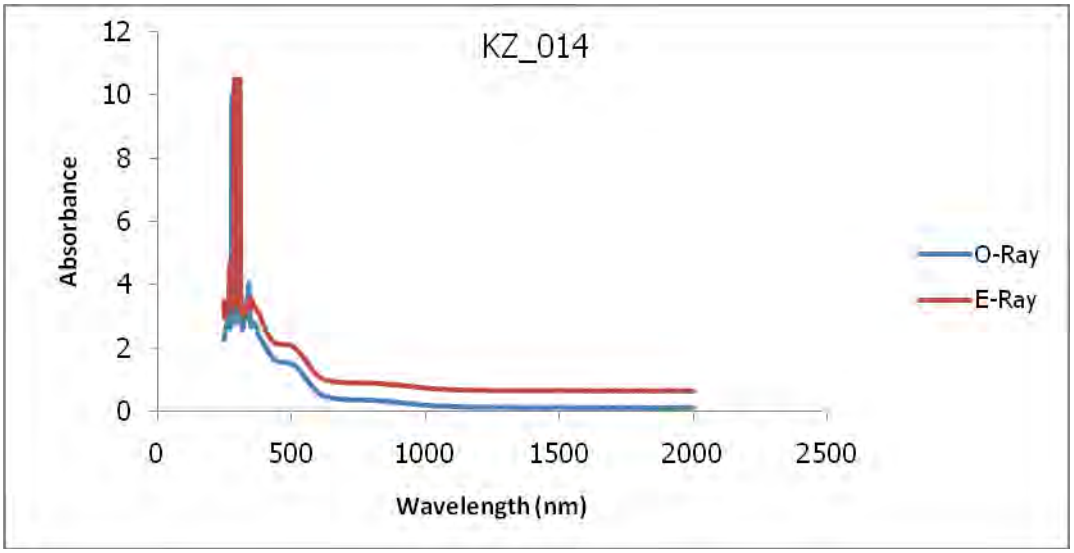
Showing all the UV-VIS-NIR spectra recorded before treatment

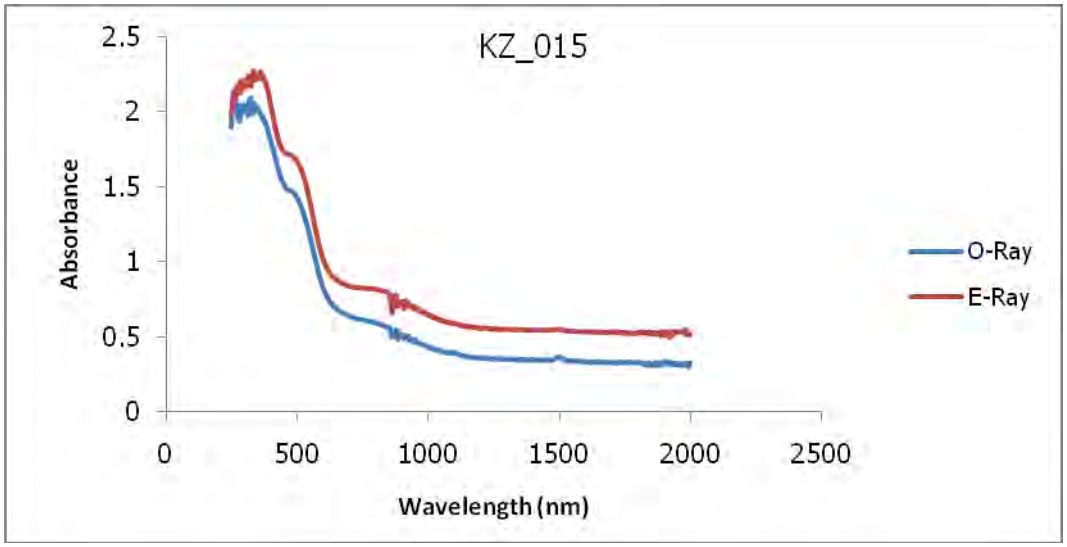


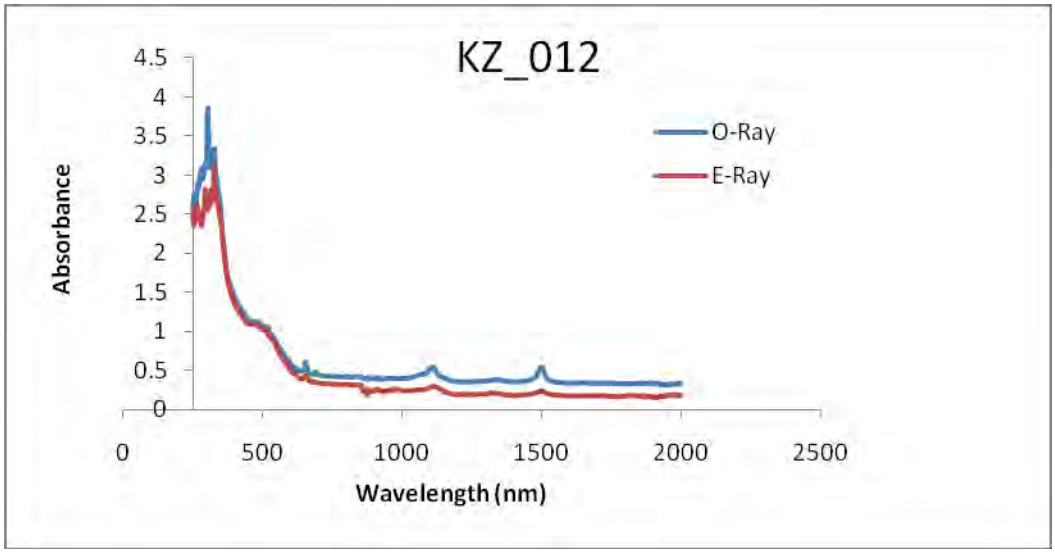


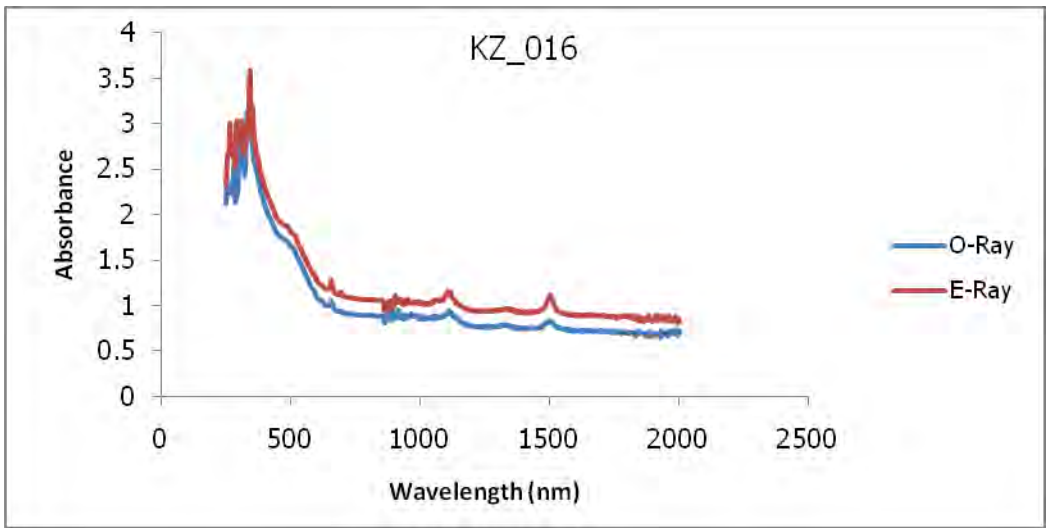


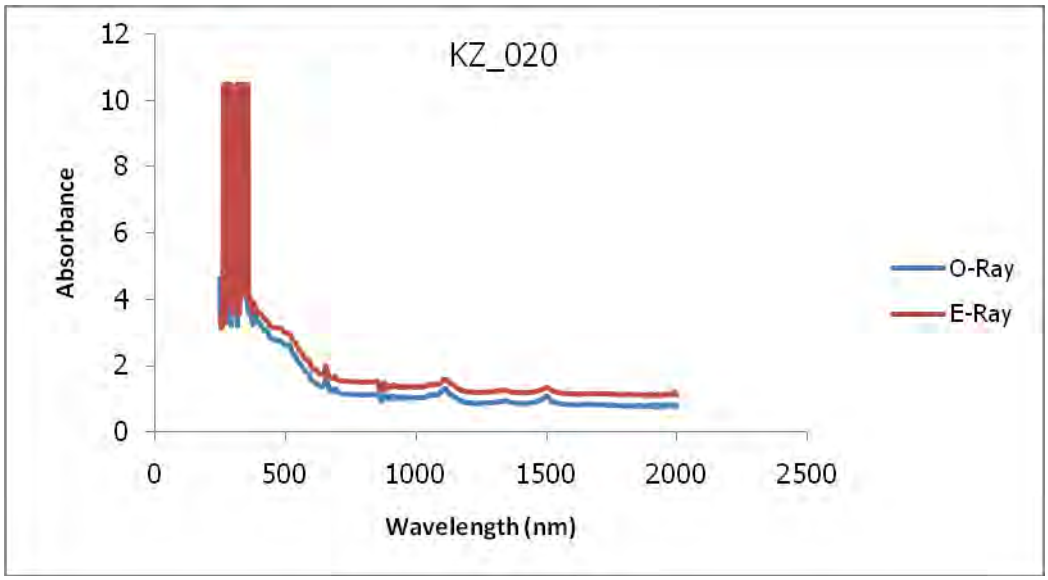

KZ_011
Absorbance
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500
Wavelength (nm)
O-Ray
E-Ray

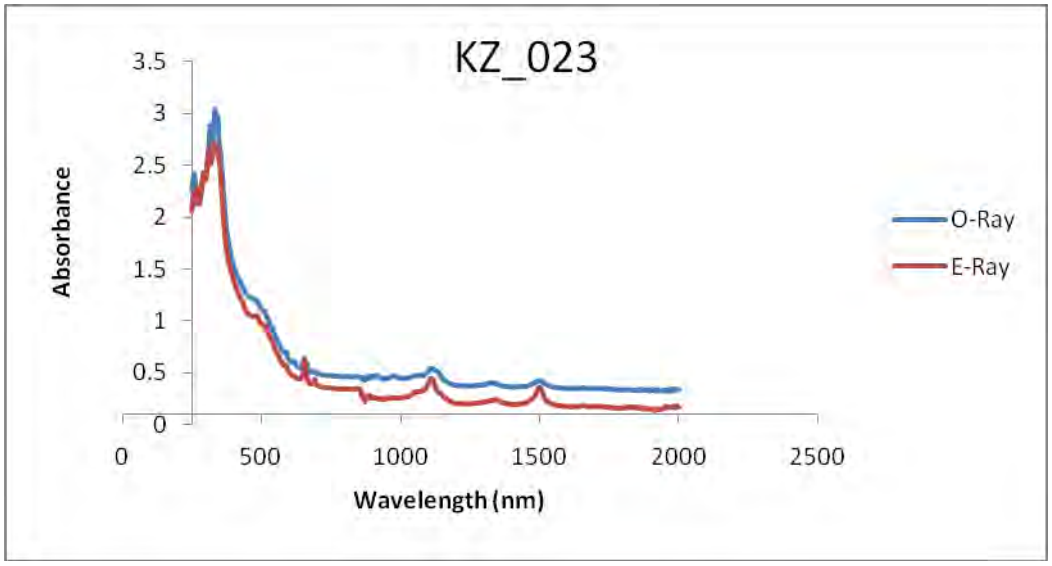

KZ_014
Absorbance
12
10
8
6
4
2
0
0
500
1000
1500
2000
2500
Wavelength (nm)
O-Ray
E-Ray


KZ_015
Absorbance
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500
Wavelength (nm)
O-Ray
E-Ray

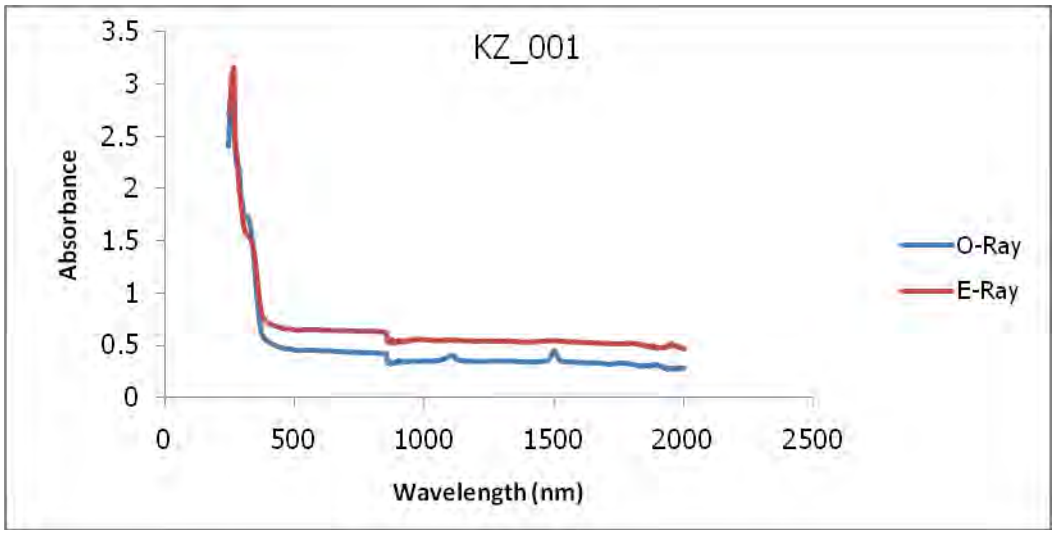

KZ_012
Absorbance
Wavelength (nm)
O-Ray
E-Ray
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500

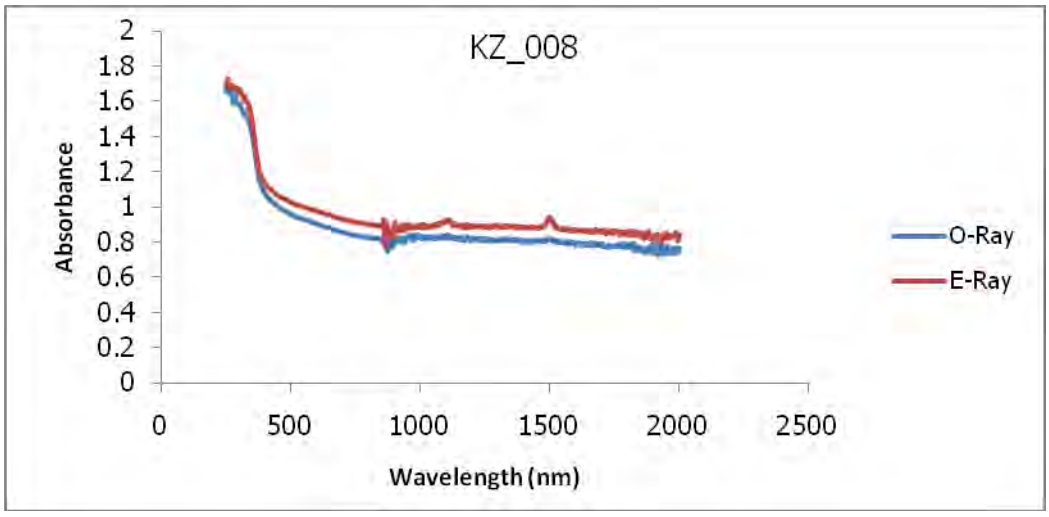

KZ_016
Absorbance
Wavelength (nm)
O-Ray
E-Ray
4
3.5
3
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500

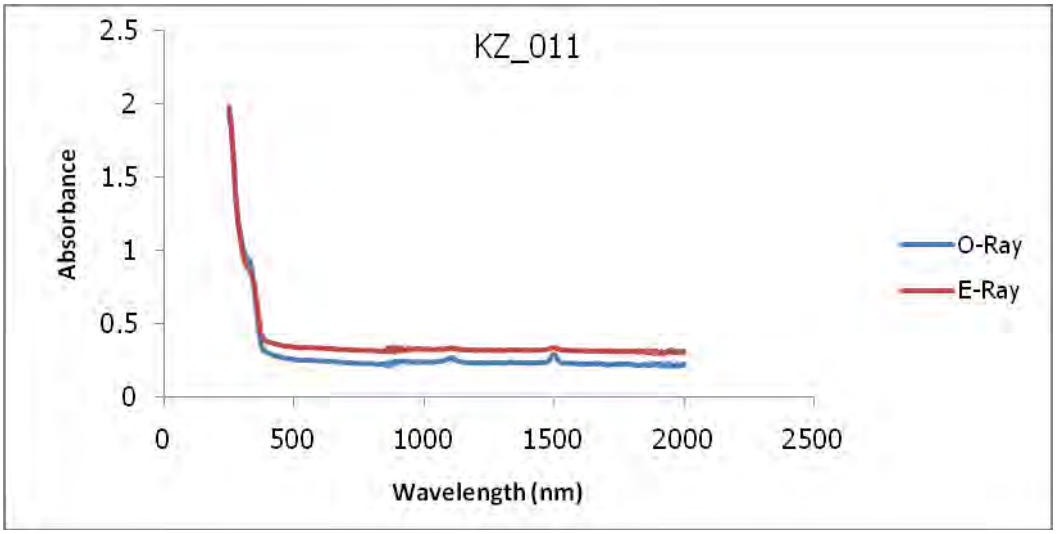

KZ_020
Absorbance
Wavelength (nm)
O-Ray
E-Ray
12
10
8
6
4
2
0
0
500
1000
1500
2000
2500

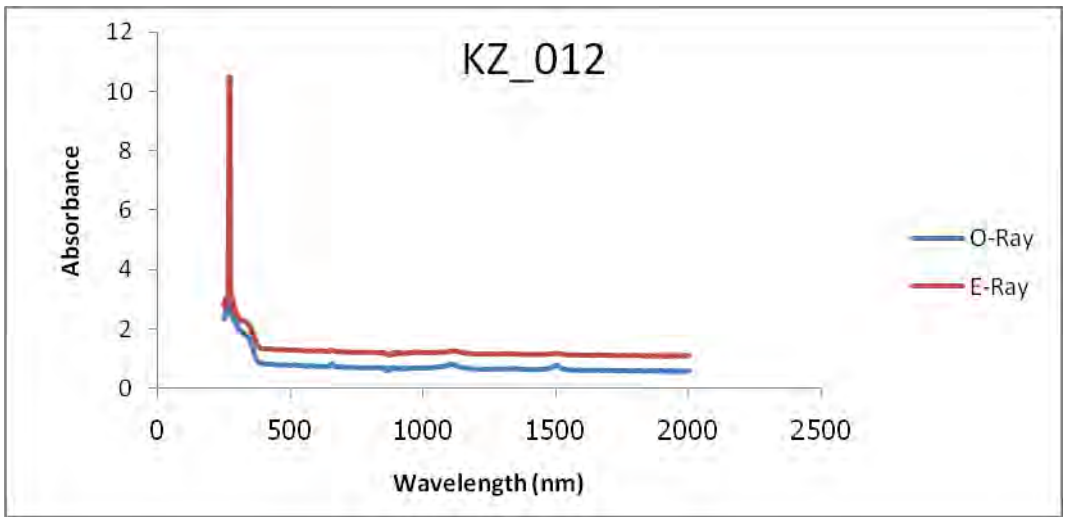


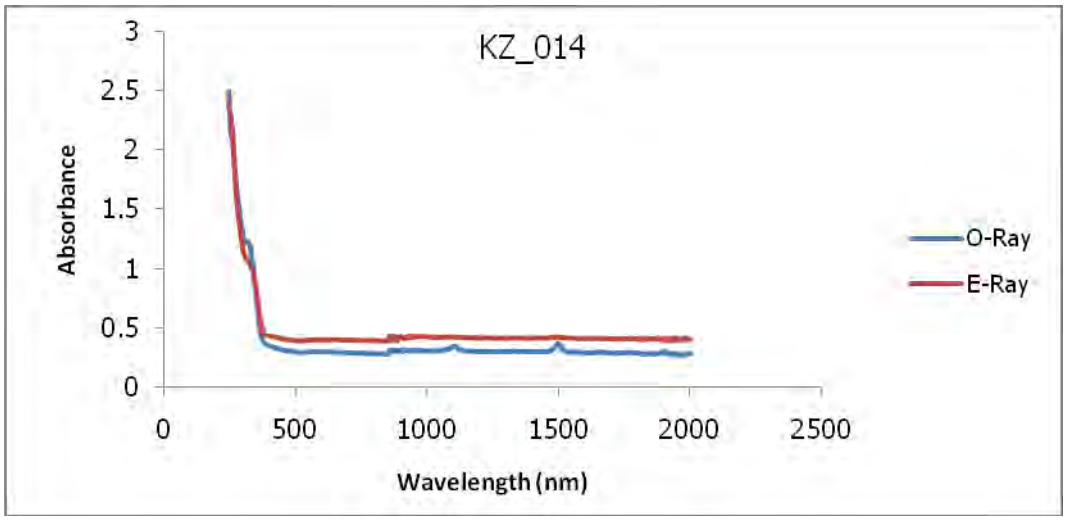
Showing all the UV-VIS-NIR spectra recorded after treatment

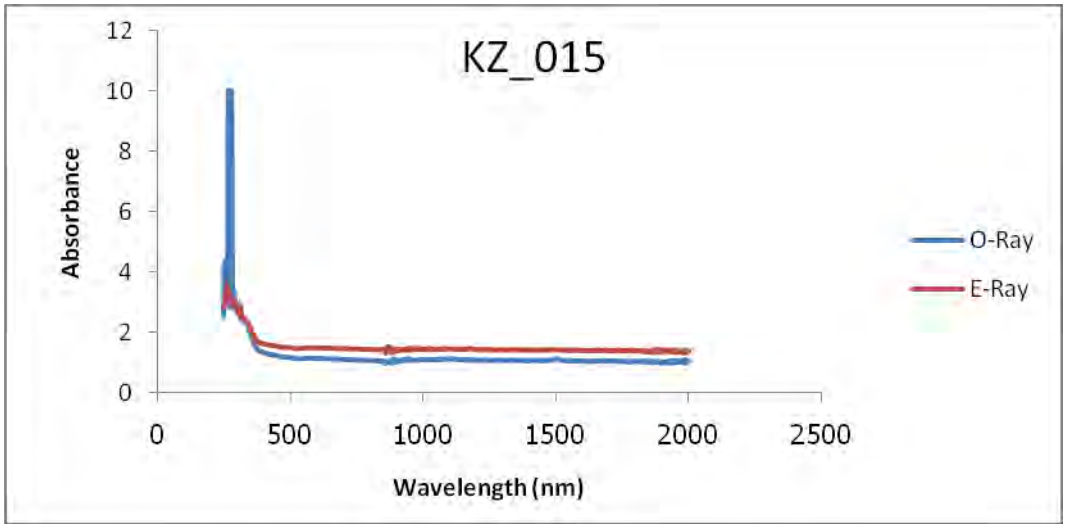


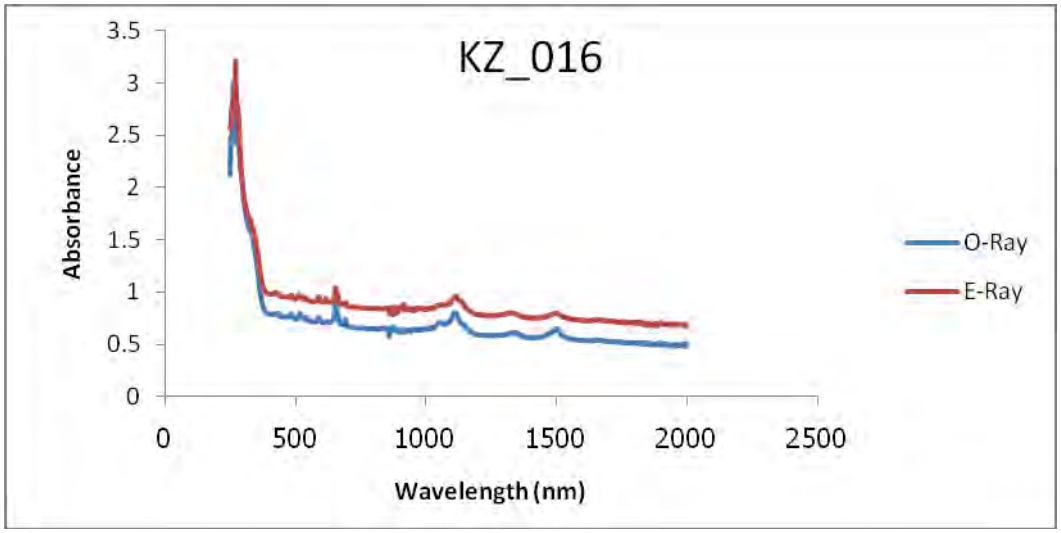


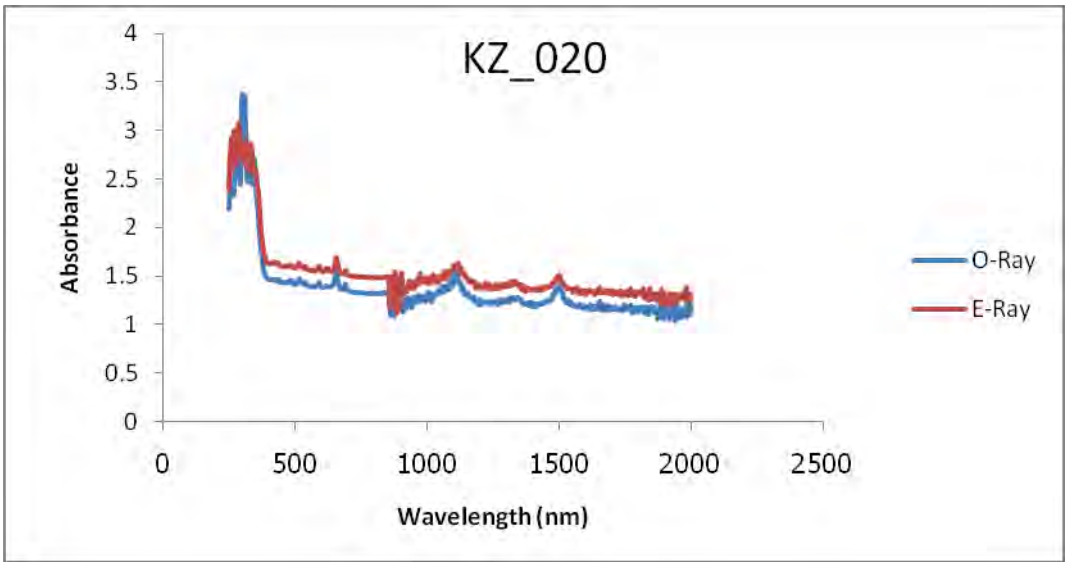

KZ_011
Absorbance
Wavelength (nm)
O-Ray
E-Ray
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500

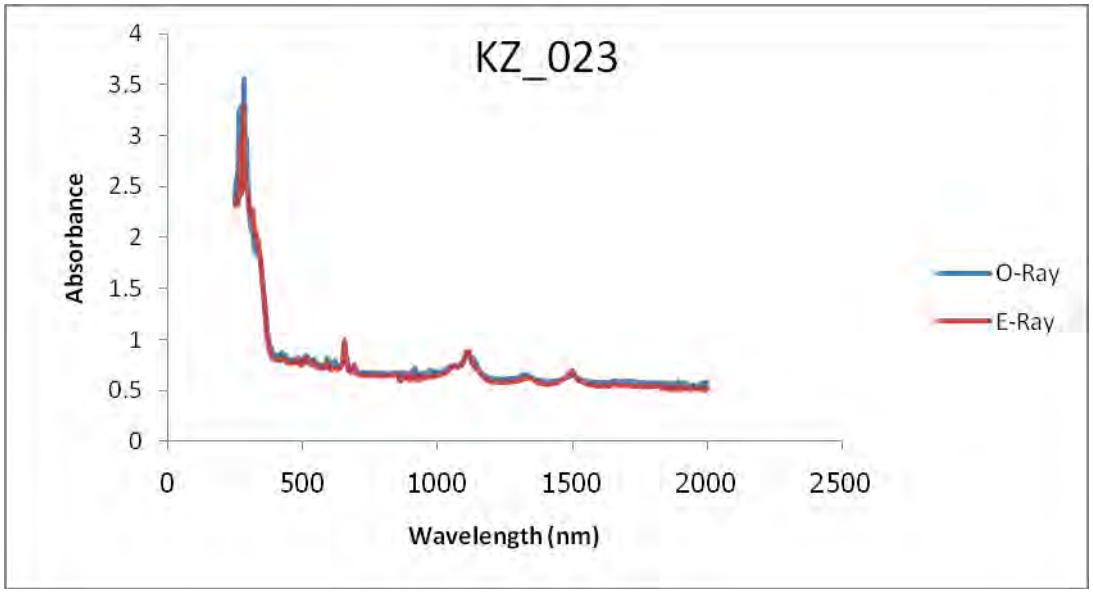

KZ_012
Absorbance
Wavelength (nm)
O-Ray
E-Ray
12
10
8
6
4
2
0
0
500
1000
1500
2000
2500

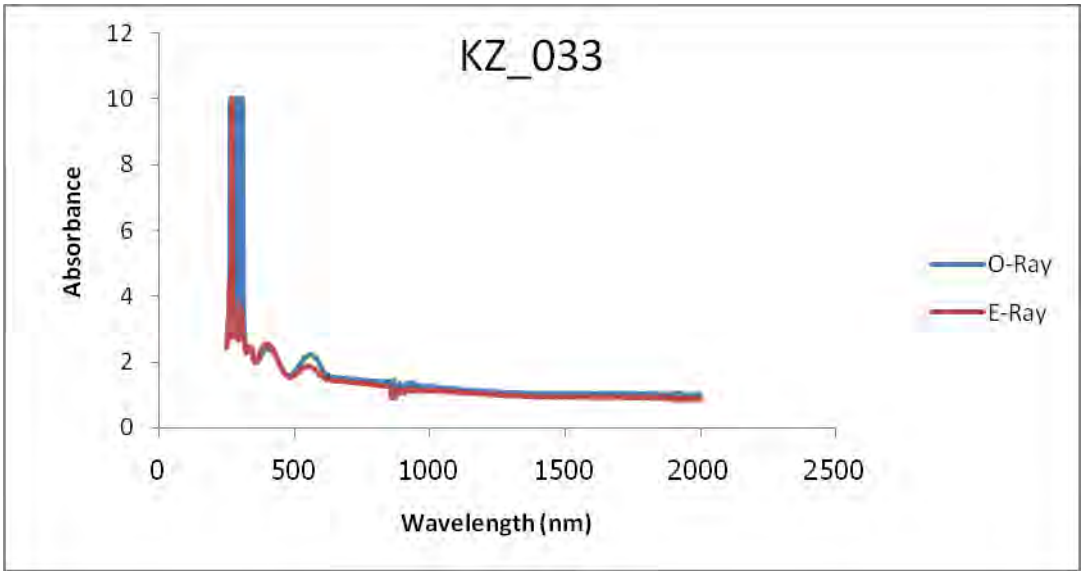

KZ_014
Absorbance
Wavelength (nm)
O-Ray
E-Ray
3
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500


KZ_015
Absorbance
Wavelength (nm)
O-Ray
E-Ray
0
2
4
6
8
10
12
0
500
1000
1500
2000
2500


KZ_016
Absorbance
Wavelength (nm)
O-Ray
E-Ray
0
0.5
1
1.5
2
2.5
3
3.5
0
500
1000
1500
2000
2500

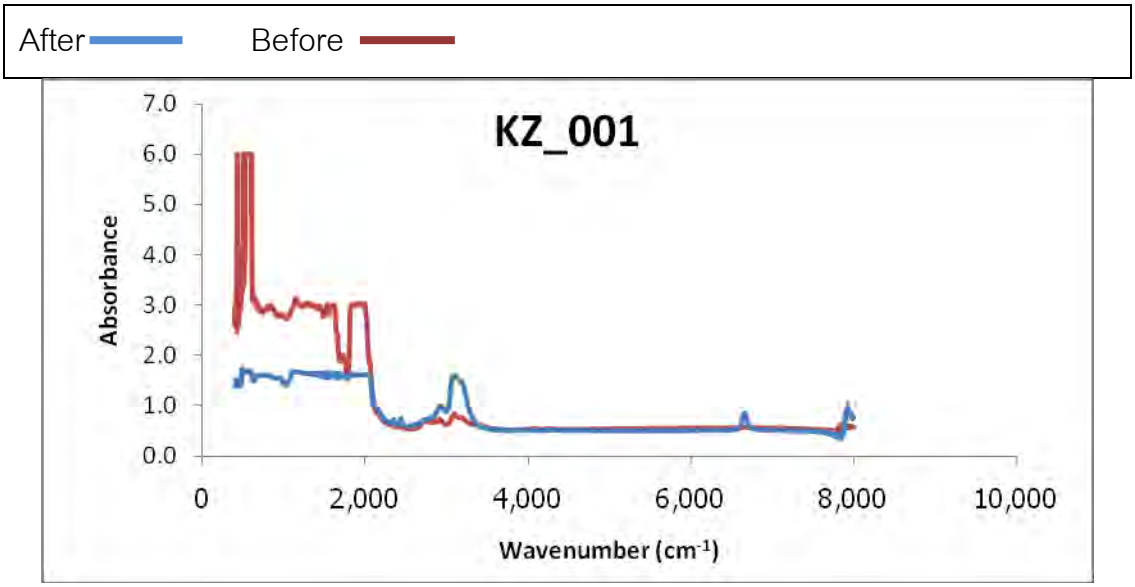

KZ_020
Absorbance
Wavelength (nm)
O-Ray
E-Ray
0
0.5
1
1.5
2
2.5
3
3.5
4
0
500
1000
1500
2000
2500

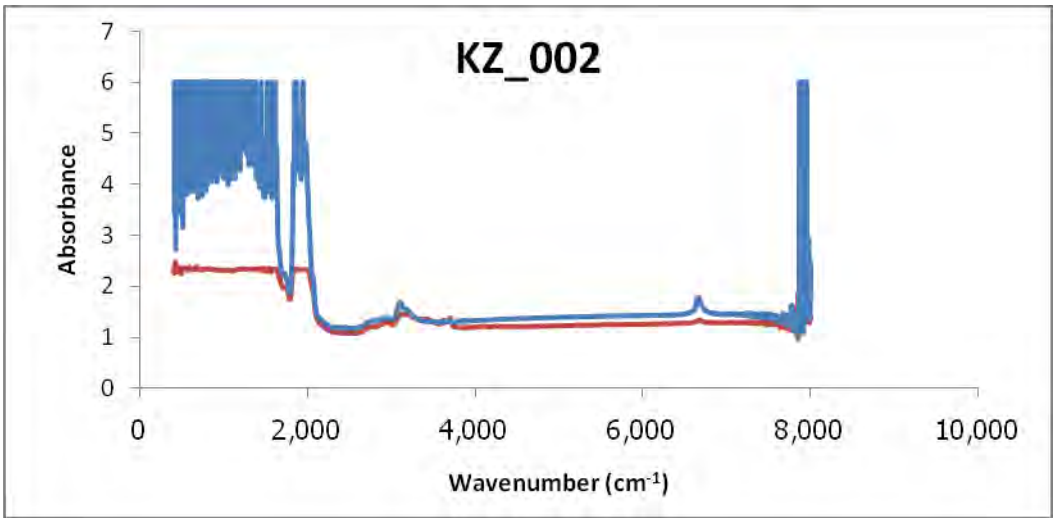

KZ_023
Absorbance
Wavelength (nm)
O-Ray
E-Ray
0
0.5
1
1.5
2
2.5
3
3.5
4
0
500
1000
1500
2000
2500

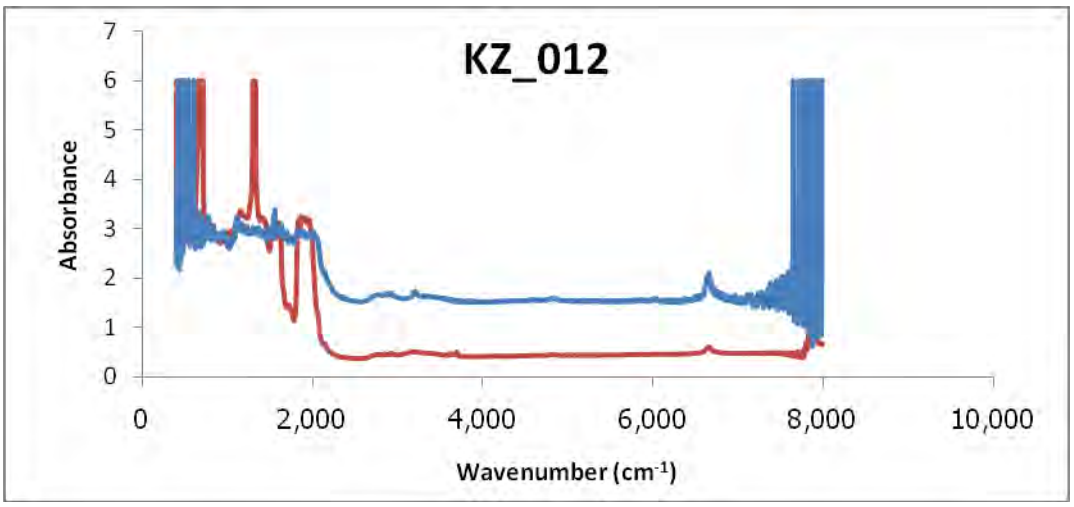

KZ_033
Absorbance
Wavelength (nm)
O-Ray
E-Ray
0
2
4
6
8
10
12
0
500
1000
1500
2000
2500

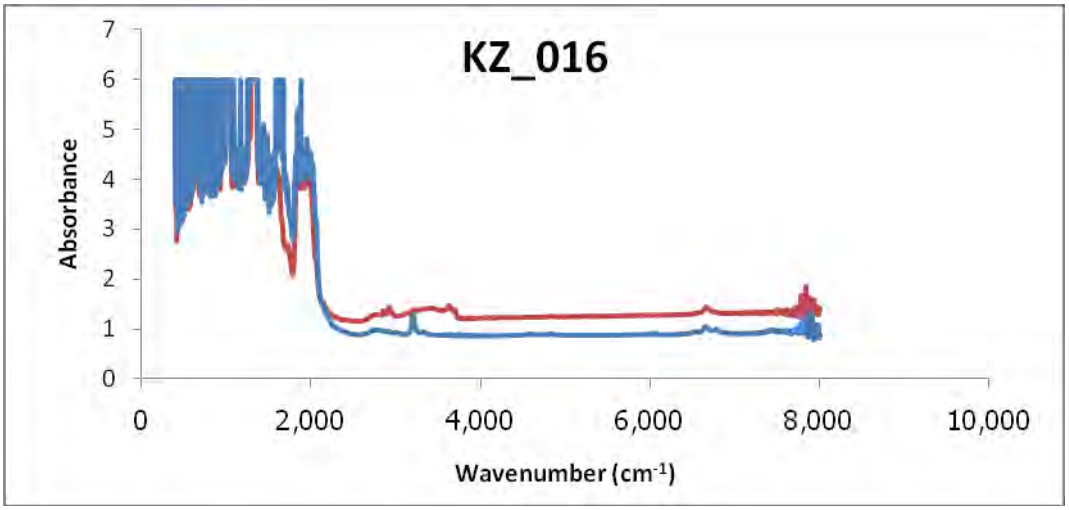
Appendix B

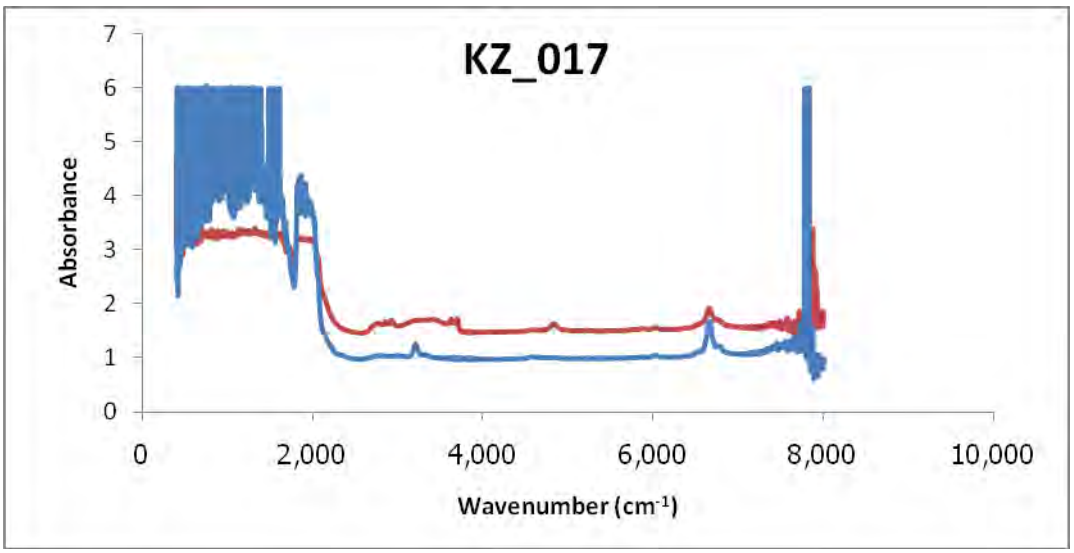
Showing all the FTIR spectra recorded before and after treatment

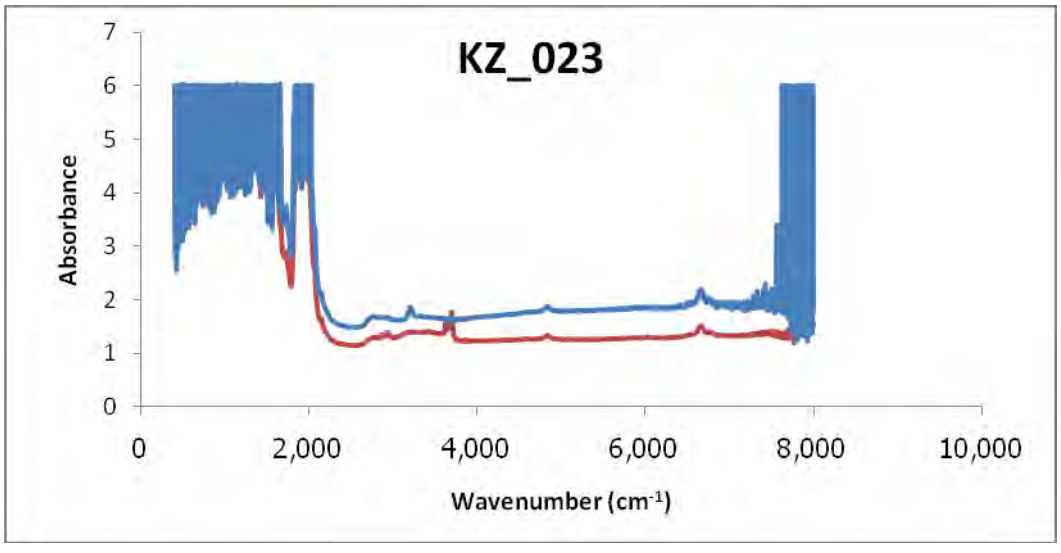






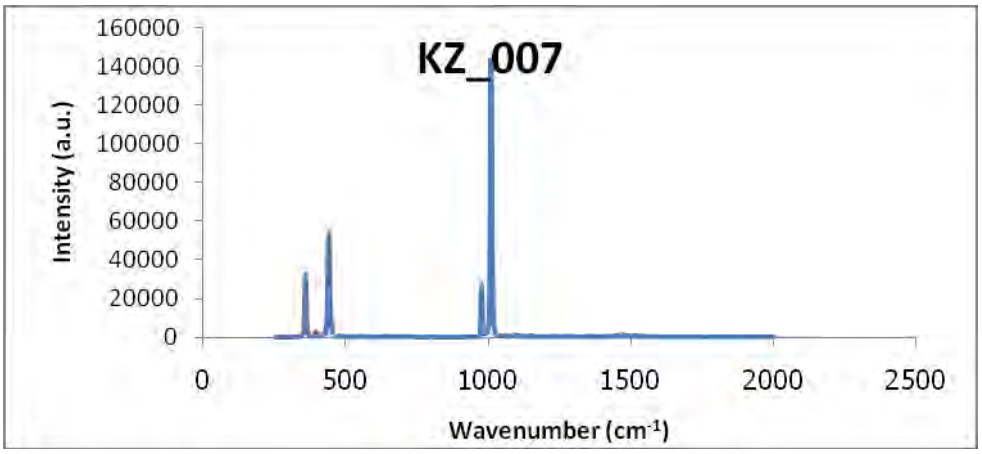

KZ_016
Absorbance
0
1
2
3
4
5
6
7
0
2,000
4,000
6,000
8,000
10,000
Wavenumber (cm-1)

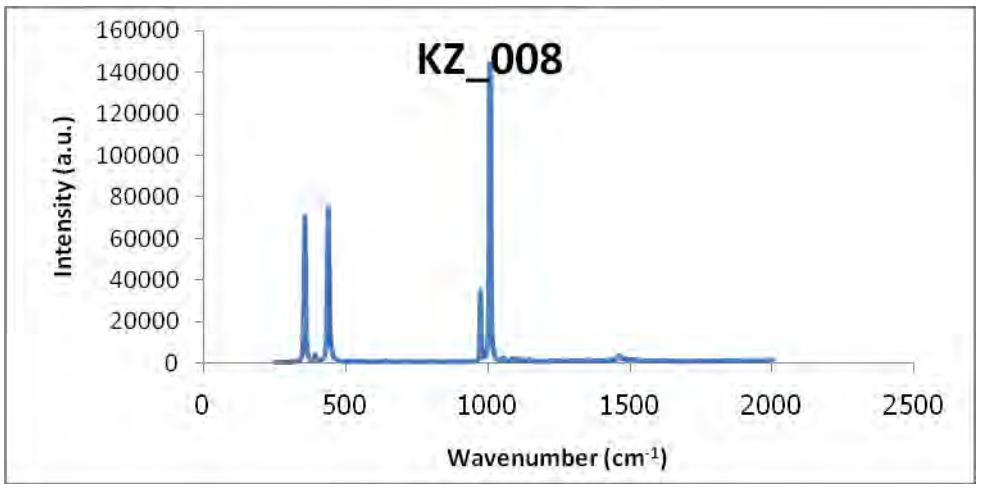

KZ_017
Absorbance
0
1
2
3
4
5
6
7
0
2,000
4,000
6,000
8,000
10,000
Wavenumber (cm-1)

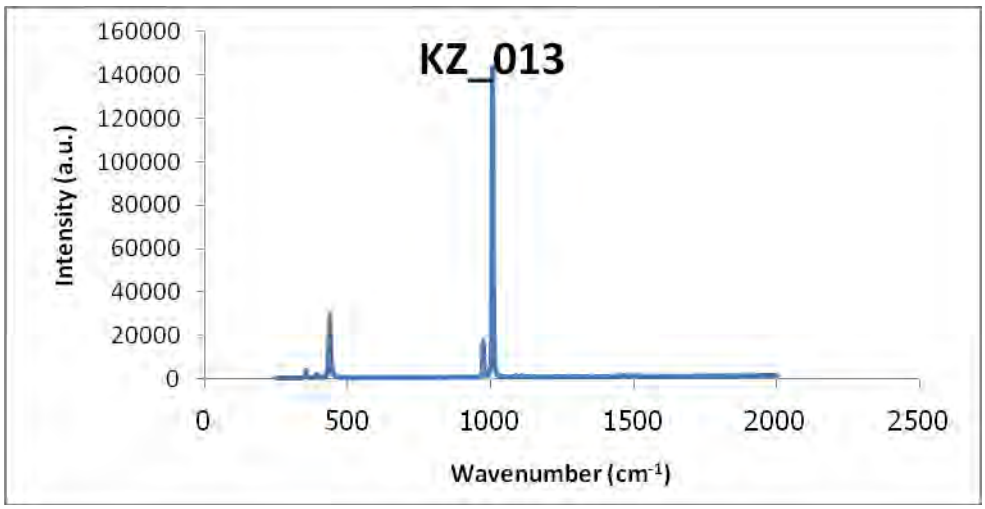

KZ_023
Absorbance
0
1
2
3
4
5
6
7
0
2,000
4,000
6,000
8,000
10,000
Wavenumber (cm-1)

Appendix C

Showing all the Raman spectra recorded before heat-treatment.







Showing all the Raman spectra recorded after heat-treatment.