

CHAPTER V

EXPERIMENTAL HEAT TREATMENT

5.1 Introduction

Seven groups of blue sapphires (totally 45 samples) have been inspected physical and optical properties before heating experiment; these properties were reported in the former chapters. All cleaned samples were subsequently placed into alumina crucible for heating in Linn electrical furnace, model HT 1800 Plus VAC Bottom Loader (Figure 5.1) at Department of Geology, Faculty of Science, Chulalongkorn University. The furnace consists of a heating chamber attached with bottom-side sample loader. U-shaped rods of molybdenumdisilicide (MoSi_2) are used as heating element. A pair of heating are hung on the top of chamber. Heating steps and soaking temperatures are automatically controlled using preset programs. The reducing atmosphere in the chamber is controlled by feeding nitrogen (N_2) gas through out the heating and cooling processes. Different maximum temperatures were set and planed to heat the same groups of sample. These samples were initially heated at the lowest temperature, then the higher temperatures have been increased progressively in each step of experiment. In addition, most characteristics and properties were continuously observed in each heating step. This procedure is intended to find the optimum conditions for heat treatment of these sapphires. Changes of properties and characteristics during heating are present in this chapter.

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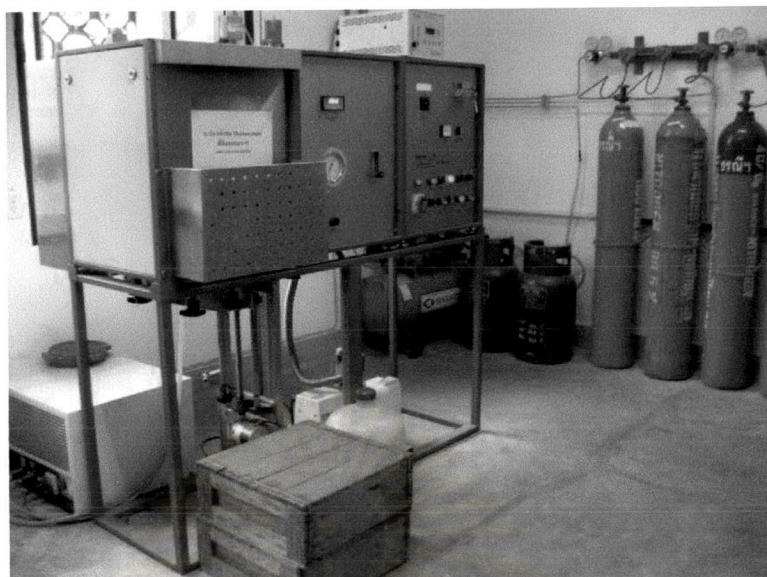


Figure 5.1 Linn electrical furnace, model HT 1800 Plus VAC Bottom Loader, engaged for this study is based at the Department of Geology, Faculty of Science, Chulalongkorn University.

5.2 Heating Cycle

Successive segments (e.g. heat-up, soaking and cool-down) are set in every heating processes. The cleaned samples were heated at 4 different maximum temperatures (1000 °C, 1200 °C, 1400 °C and 1650 °C) for 3 hours soaking time under reducing atmosphere. Heat-up segment was started from room temperature to maximum temperature. Rate of temperature increment was controlled at about 4 °C/minute for all heating steps. Soaking segment means period that the maximum temperature is sustained. In each heating, the soaking time was set at 3 hours. Cool-down segment was decreasing temperature from soaking segment at maximum temperature to room temperature. The cool-down rate was programmed at approximately 3 – 4 °C/minute. These segments were applied with consistent rates in all heating cycles, in which they have been operated individually from the lowest temperature (1000 °C) to the highest temperature (1650 °C). All sapphire samples were observed every time after heating in each cycle. Results of the experiment are compared and present below.

5.3 Effect of Heating Experiment on Color Appearance

The GIA GemSet was used to compare color codes between unheated and heated sapphires. Results of comparison are shown in Table 5.1. Figures 5.2 to 5.8 reveal color appearance of sapphire before and after step-heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C, respectively. Details of each sample groups are described below.

Dark blue sapphires: Color appearances of dark blue samples before and after step-heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C are displayed in Figures 5.2. Most of dark blue samples lost some blue shade after burning at 1000 °C under reducing atmosphere and colors were still unchanged after heating experiment at 1200 °C. However, blue colors in some samples were developed again after the maximum temperature reached to 1400 °C and they are continuously intensified at 1650 °C (see sample numbers IDB1, IDB4, IDB5 and IDB6). It is significant to note that many dark blue samples have lost the blue shade after heating at 1000 °C and their blue shades never came back again (see samples IDB2, IDB3, DB1, DB2, DB3, DB4 and DB5).

Medium blue sapphires: Color appearances of medium blue samples before and after step-heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C are displayed in Figures 5.3. Most of medium blue samples were lightened after burning at 1000 °C under reducing atmosphere and their pale colors were still unchanged after heating experiment at 1200 °C. A few samples (IMB3, IMB5 and MB4) turned partly blue colors again after heating at 1400 °C and intense blue colors were also developed at 1650 °C burning. Many medium blue samples (IMB1, IMB2, IMB4, MB1, MB3, MB6 and MB9) lost the blue shades after heating and their blue colors were not returned after step-heating.

Very light blue sapphires: Very light blue samples and their colors before and after heating experiments at 1000 °C, 1200 °C, 1400 °C and 1650 °C are revealed in Figures 5.4. Very light blue samples were almost turned colorless after burning at 1000 °C under reducing atmosphere and these colors were still unchanged after heating at 1200 °C. Many samples were able to developed blue colors again after the treatment

was operated at 1400 °C. In addition, blue zones were developed at 1650 °C in a few samples (IVLB1, IVLB2 and VLB1), whereas blue components in whole grains of a few samples (IVLB5, VLB2 and VLB4) were intensified at this temperature. Some very light blue samples (IVLB3, VLB3, VLB5, VLB6 and VLB7) have lost the blue shade and became colorless after step-heating.

Milky, very light blue sapphires: Untreated colors of milky, very light blue sapphires and their colors after step-heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C are displayed in Figure 5.5. Most samples appeared to be unchanged in their colors after experiments at 1000 °C and 1200 °C. Most samples (MVLB3, MVLB5, MVLB7 and MVLB8) have shown blue shades after heated at 1400 °C and they yielded even more intense blue at 1650 °C. Sample MVLB6 become colorless with blue zone after the end of experiment.

Dark violet sapphires: The group of dark violet sapphires appeared to have been changed obviously since heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C. Their natural colors and treated colors are presented in Figures 5.6. The dark violet samples, which showed color change effect, have lost their purplish coloration and color change effect since heating at 1000 °C under reducing atmosphere. After heating at 1200 °C, their colors were still similar to those treated at 1000 °C. The bluish shades were developed significantly after heating at 1400 °C and 1650 °C (see samples DV1 and DV2).

Medium violet and light violet sapphires: The medium and light violet sapphires also yielded different colors after heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C. The medium violet group seemed to be obviously developed (Figures 5.7), however, the light violet sapphires still gave slightly different colors at each step of heating (Figure 5.8). Blue components in medium violet sapphires were mostly lightened after experiments at 1000 °C and 1200 °C and they were partly developed again at 1400 °C and 1650 °C.

Most violet samples have lost their purplish coloration after 1000 °C heating under reducing atmosphere. Their colors were still unchanged after they were

heated up to 1200 °C and 1400 °C, respectively. Some samples were developed bluish color after heating at the highest temperature of 1650 °C (see samples DV1, DV2, MV3 and LV1 in Figures 5.6 – 5.8).

Table 5.1 Color codes of sapphires before heating and after heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C in comparison with GIA GemSet (List of hue, tone and saturation terms for describing gem color was shown in Appendix I).

Sample No	Hue Tone Saturation				
	Unheat	Heat 1000°C	Heat 1200°C	Heat 1400°C	Heat 1650°C
Dark blue					
IDB 1	BV6/5 + RV5/3 * V 6/5 + P 4/3	P6/3 + P4/3 + V5/5	BP 4/4 + P 3/4 + BV 5/4	V 7/4 + BP3/3	BV 7/4 + RB 7/5 + BP 2/3
IDB 2	V 6/4 + RP 5/3 * V 6/5 + rP8/3	< RP 8/3	BP 4/4 + P 3/4	P 6/3	P 6/3
IDB 3	BV5/4 + RP5/3 * V 6/5 + rP8/3	BP 6/3 + RP 5/3	BP 6/3 + RP 5/3	BP6/3 + RP5/3	BP 6/3 + RP 5/3
IDB 4	BV 6/5	BV 6/4 + V 5/5	BV 8/3	BV 7/4	VB 7/5 + V 6/5
IDB 5	BV 6/5	VB 4/4	VB 7/3	BV 7/4	> V 6/5
IDB 6	BV 6/5	B 3/1 + BV 5/5	BV2/3 + BV4/5	BV5/5 + B2/2	BV 7/4 + VB 7/5
DB 1	BV 6/5	BV 4/3	BV 5/4	BV 5/4	BV 4/3
DB 2	BV 6/4 * V 7/4	V 3/2	V 3/2	V 4/3	V 4/3
DB 3	BV 6/5	BV2/3 + BV4/5	BV5/5 + BV6/4	BV 5/5	BV 7/4
DB 4	BV 7/4 + V 7/4 *V 7/4	P 6/3	BP 6/3	P 6/3	BP 3/3 + V 3/2
DB 5	V 6/4 * V 6/5	P 4/3	RP 5/3	P 6/4	BP 7/4 + vP 5/3
Medium blue					
IMB 1	BV 5/4	B 2/2	B 3/1	vSLGB 2/2	B 2/2
IMB 2	BV5/4 + BV4/5	B 3/1	B 3/1 + bV 2/3	vSLGB 2/2 + B 2/2	bV 4/3 + B 3/1
IMB 3	BV 8/3	gB 2/2	vslgB 3/3	vSLGB 3/3	B 6/2
IMB 4	BV 5/5 + B 2/2	vslgB 2/2	vslgB 2/2	B 3/1	B 3/1 + B 5/2
IMB 5	BV 4/5	B 3/1	B 3/3	bV 3/4	bV 7/4

Table 5.1 (continued)

Sample No	Hue Tone Saturation				
	Unheat	Heat 1000 ⁰ C	Heat 1200 ⁰ C	Heat 1400 ⁰ C	Heat 1650 ⁰ C
Medium blue (continued)					
MB 1	bV 2/3	vslgB 2/2	vslgB 2/2	B 3/1	B 3/1
MB 3	bV 4/3	< B 2/2	B 3/1	B 3/1	B 3/1
MB 4	bV 3/4	B 2/2 + bV 3/4	B 2/2 + bV 3/4	bV5/4 + B3/1	vB 7/5 + B 3/1
MB 6	bV 5/4	< B 2/2	B 3/1	B 3/1	B 3/1
MB 9	bV 4/3	P 2/1 + V 3/2	bV 3/4 + P 3/4	bV5/5 + bP2/3	bV 7/4 + bP 2/3
Very light blue					
IVLB 1	B 2/2	< B 3/1	< vslgB 2/2	B 2/2	B 3/1 + bV 3/4
IVLB 2	B 3/3	B 3/1	< vslgB 2/2	B 3/1	B 3/1 + vB 5/3
IVLB 4	vB 4/3	B 3/1	B 3/1	vslgB 2/2	B 4/2
IVLB 5	B 3/3	B 3/1	B 3/1	bV8/3 + B4/2	bV 6/4
VLB 1	B 3/1	<< Y 2/2	colorless	bV3/4 + B3/1	bV 3/4 + B 3/1
VLB 2	bV 2/3	B 3/1	B 2/2 + bV 3/4	BV5/4	vB 7/5 + V 6/5
VLB 3	bV 2/3	< B 3/1	colorless	< B 3/1	B 3/1
VLB 4	bV ¾	B 3/1	B 2/2	bV8/5 + B2/2	bV 5/4 + B 3/1
VLB 5	bV 2/3	B 3/1	B 3/1	< B 3/1	B 3/1
VLB 6	bV ¾	<< B 3/1	colorless	< B 3/1	< B 3/1
VLB 7	B 3/1	colorless	colorless	< B 3/1	< B 3/1
Milky, very light blue					
MVLB 3	B 2/2	colorless	< YG/GY 2/1	vB 4/3	B 7/4
MVLB 5	B 3/1	colorless	<< B 3/1	bV3/4 + B3/1	B 4/2 + bV 7/4
MVLB 6	B 3/1 + V 2/2	colorless	<< B 3/1	< B 3/1	B 2/2
MVLB 7	B 3/1	colorless	<< B 3/1	vB4/3 + V5/2	bV 7/4
MVLB 8	B 3/1	colorless	<< B 3/1	B3/3 + bV3/4	B 2/2 + bV 5/5
Dark violet					
DV 1	V 6/4 + rP4/4 * V6/4 + P6/4	PR/PR 5/3 + PR/RP 6/3	rP 3/4 + rP 5/3	P 6/3 + rP 3/4	P 6/3 + rP 4/4
DV 2	bP5/5 + P6/4 * bP 6/5	PR/RP 8/2	P 6/4	P 6/4	P 6/4
DV 3	bP5/5 + P6/4 * bP 6/5	PR/RP 6/3	rP 5/3	RP 5/3	rP 5/3

Table 5.1 (continued)

Sample No	Hue Tone Saturation				
	Unheat	Heat 1000°C	Heat 1200°C	Heat 1400°C	Heat 1650°C
Medium violet					
MV 1	V 4/3 * bP /6/5	P 3/1	P 3/1	P 3/1	P 2/1
MV 3	V 4/4 * bP 6/3	P 3/1	P 3/1	BP 2/3	P 6/3 +V 5/2
Light violet					
LV 1	V 2/2	<< PR/RP 2/1	colorless	<< P 2/1	B 2/2
LV 2	V 2/2	PR/RP 2/1	< P 2/1	P 2/1	P 2/1
LV 3	V 2/2	< PR/RP 2/1	< P 2/1	P 2/1	< P 2/1

*under incandescence light

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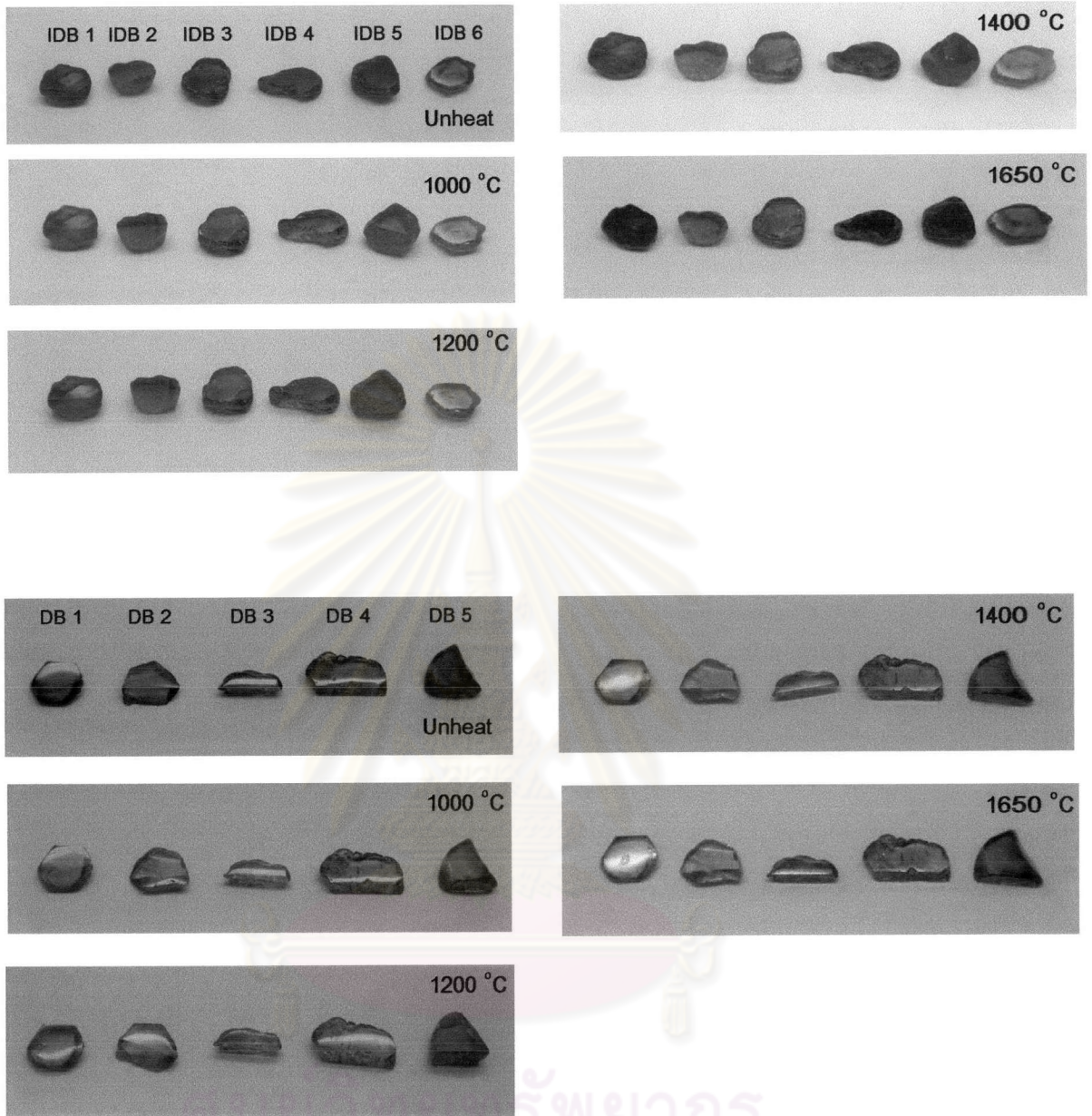


Figure 5.2 Comparison between initial colors and colors after heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C in dark blue sapphires.



Figure 5.3 Natural colors of medium blue sapphire samples and their changes after heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C, respectively.

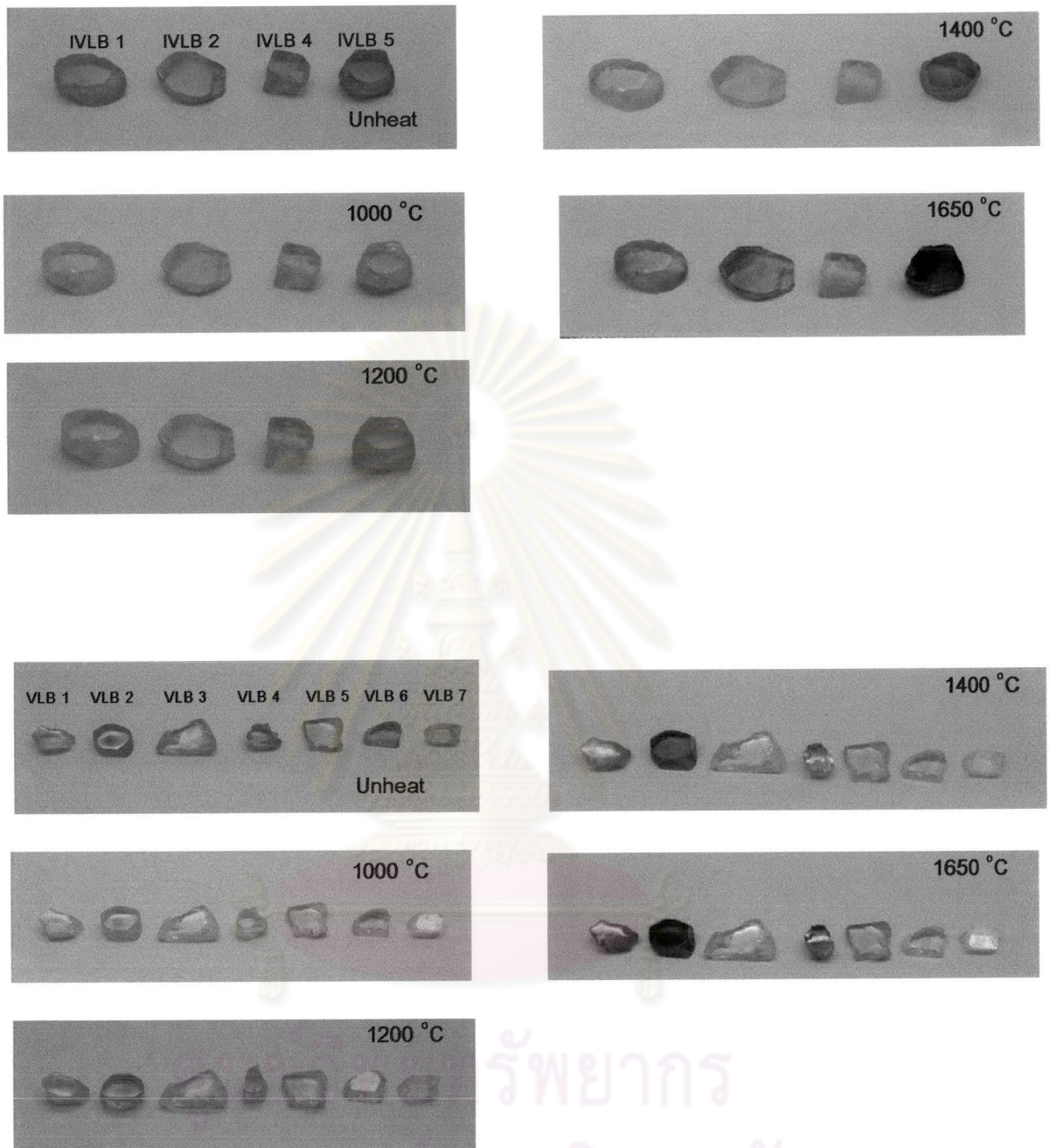


Figure 5.4 Very light blue sapphires and their colors before and after burning at 1000 °C, 1200 °C, 1400 °C and 1650 °C.

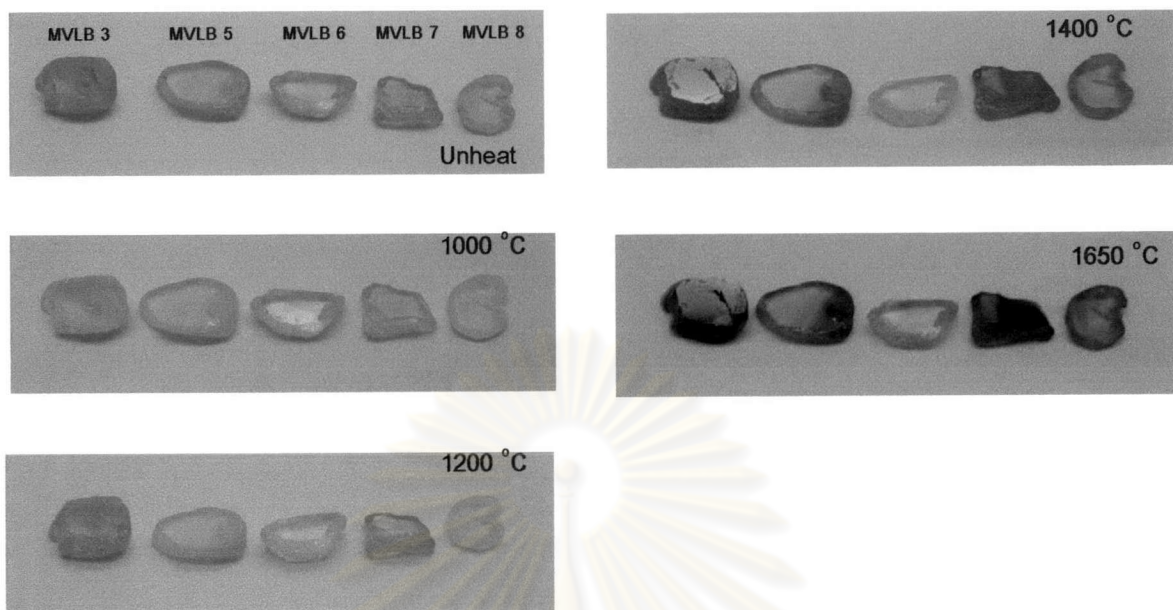


Figure 5.5 Changing in colors of milky, very light blue sapphires from unheated stones to heated stones at 1000 °C, 1200 °C, 1400 °C and 1650 °C, respectively.

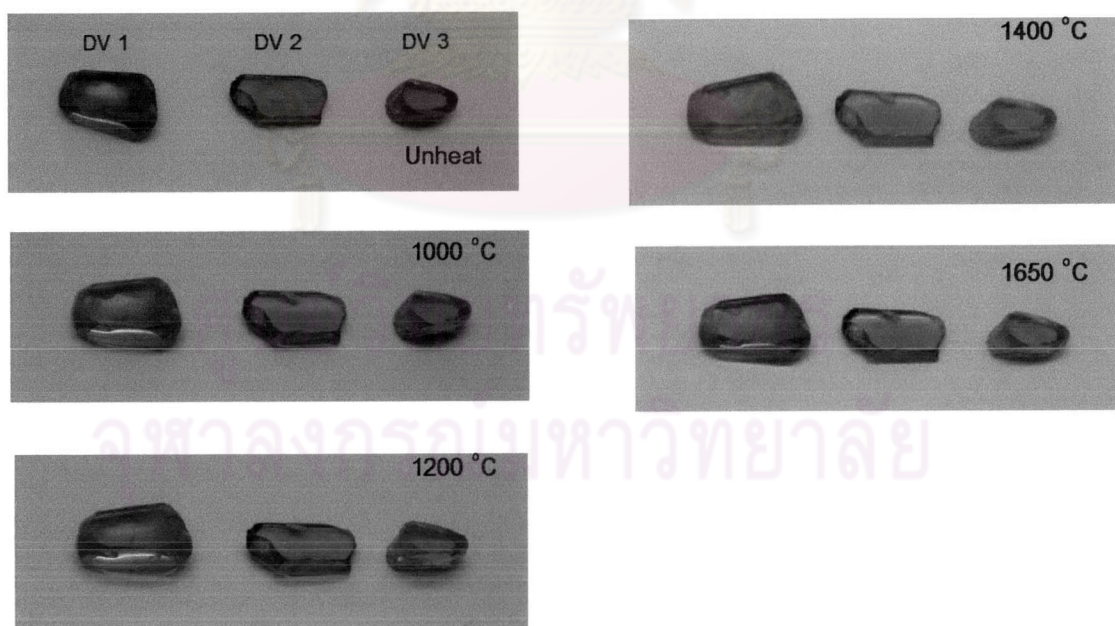


Figure 5.6 Color appearances in dark violet sapphires comparing between unheated stones and heated stones at 1000 °C, 1200 °C, 1400 °C and 1650 °C.

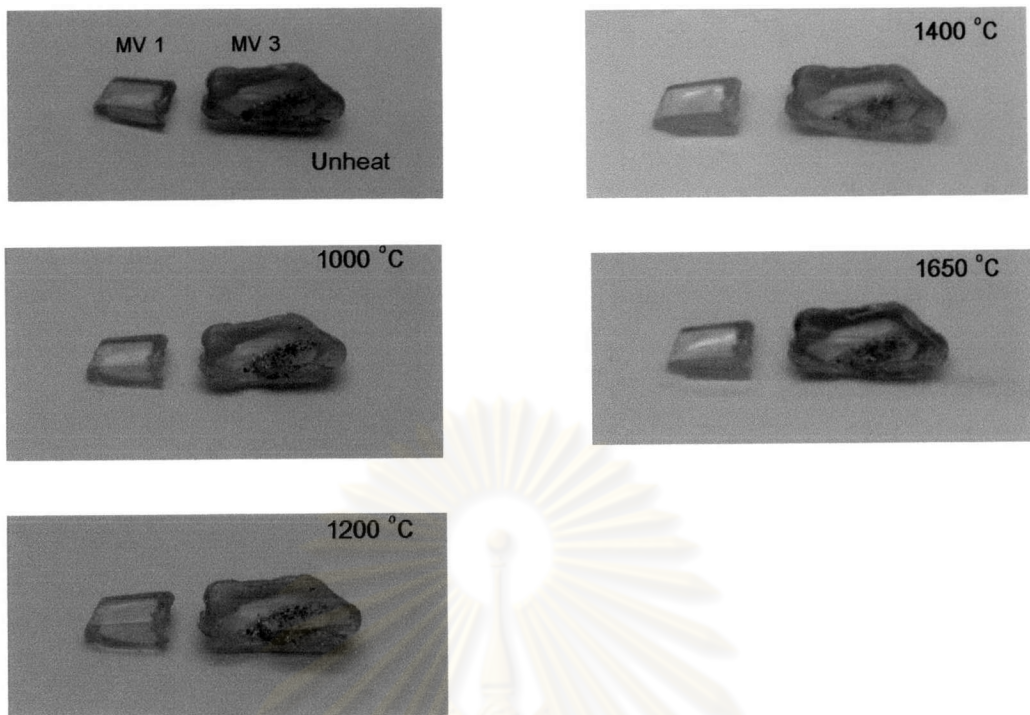


Figure 5.7 Color appearance in medium violet sapphires, comparing between unheated stones and heated stones at 1000 °C, 1200 °C, 1400 °C and 1650 °C.

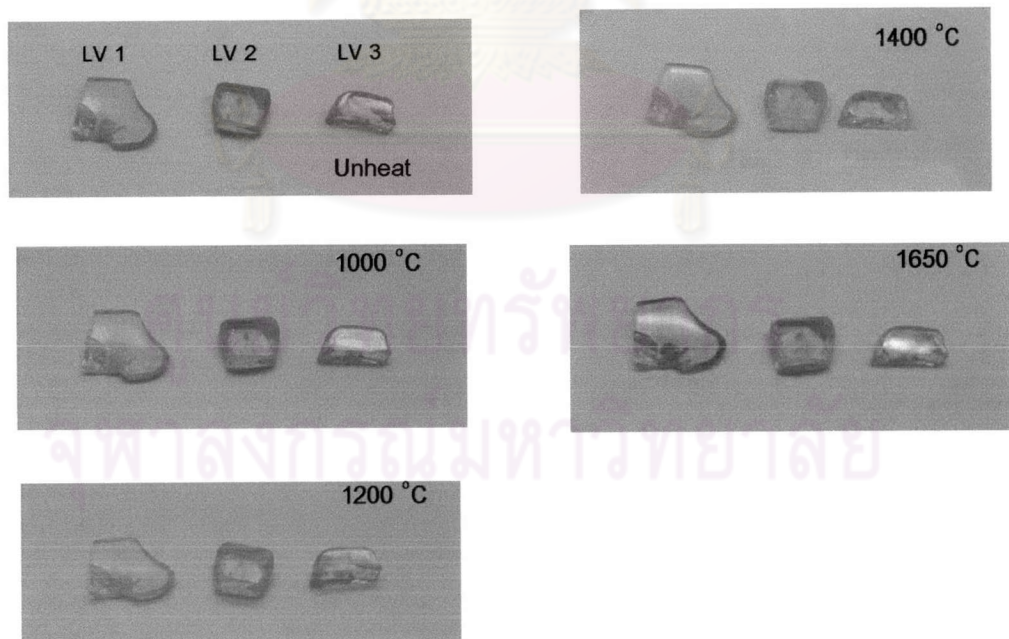


Figure 5.8 Color appearance in light violet sapphires showing very slightly different in color during the experiment.

5.4 Effect of Heat Treatment on Internal Characteristics

As reported in chapter 3, several kinds of internal features have been observed in most sapphire groups. They are characterized by some mineral inclusions, healed fractures, tubes and color zones. These internal features have been distinguished and documented throughout the heating experiments at 1000 °C, 1200 °C, 1400 °C and 1650 °C. Changes of these internal characteristics are reported below.

Zircon inclusions are usually colorless and often show slight development of tension discs even in the unheated stones. The crystals were however altered into a whitish crystals after heat-treating at 1000 °C. Moreover, the tension discs were enlarged at higher temperatures (Figure 5.9). However, some zircon crystals were still unchanged after step heating at 1000°C and 1200°C, but decomposed to whitish crystals after treating at 1400°C and 1650°C (Figure 5.10). Besides, some zircon clusters have been gradually changed after step-heating from 1000°C to 1650°C, whereas the tension discs were expanded significantly at higher temperatures (Figure 5.11).

Apatite inclusions were generally decomposed after heating up to 1000 °C. Small tension discs were developed after heat-treating at 1200 °C and they were expanded progressively at higher temperatures (Figure 5.12).

Fluid - healed fractures or cracks, so called fingerprints, were commonly found in the host corundums. They can be observed within both unheated and heated stones. In some sapphire samples, fingerprints were developed and widened gradually after step heating from 1000°C to 1650°C (Figure 5.13).

Rutile needles, that were normally discovered in the unheated sapphire samples from the study area, appeared to have been altered at high temperatures especially at 1400 °C and 1650 °C (Figure 5.13). These temperatures may imply dissolution temperatures or eutectic temperature between TiO_2 of rutile inclusions and Al_2O_3 of corundum host.

In addition, it should be noted that recrystallizations were somehow occurred on the surface of some samples after heating at high temperature (1650 °C) (Figure 5.14).



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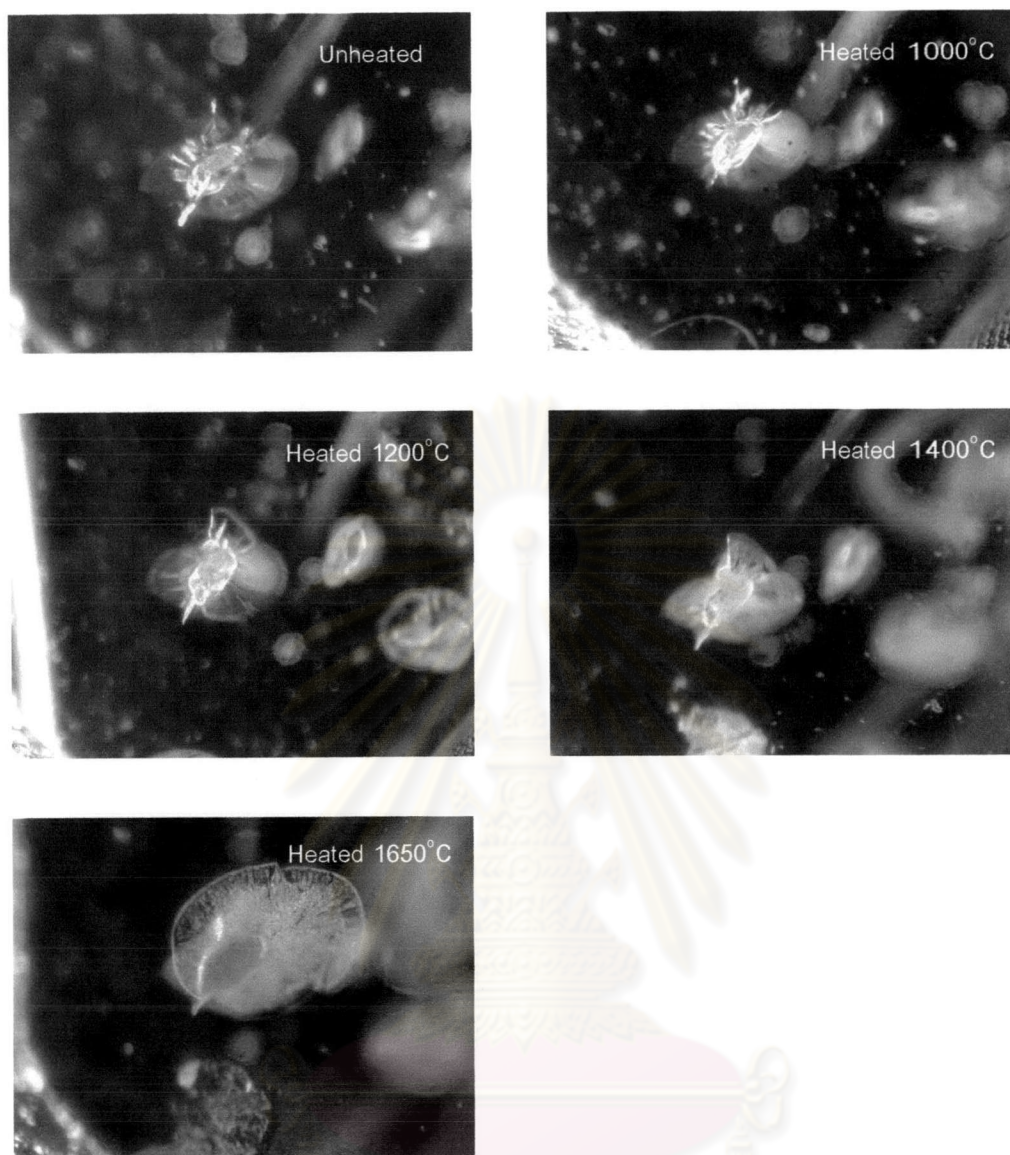


Figure 5.9 Zircon inclusions with tension discs before and after heat-treatment. After step heating from 1000°C to 1650°C under reducing atmosphere, they were gradually changed. The crystals turned whitish and were obviously enclosed by tension discs (sample no. LV 2; about 70 times magnification).

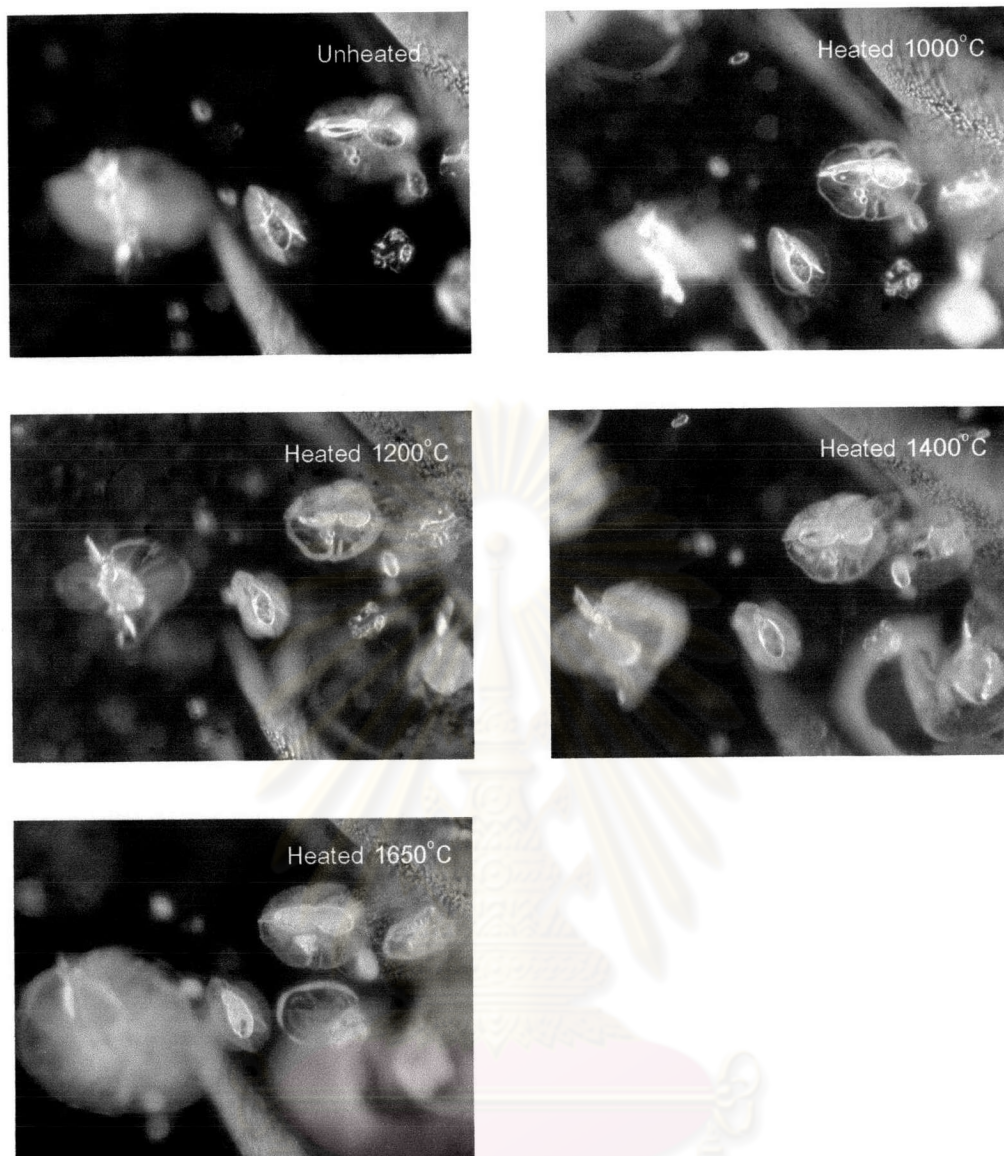


Figure 5.10 Zircon inclusions with tension discs before and after heating experiments. After step-heating from 1000°C to 1650°C under reducing atmosphere, they were slightly changed. The tension disc surrounding crystals were obviously expanded and zircon crystals were also decomposed after heat-treating at 1400°C to 1650°C (sample no. LV 2; about 70 times magnification).

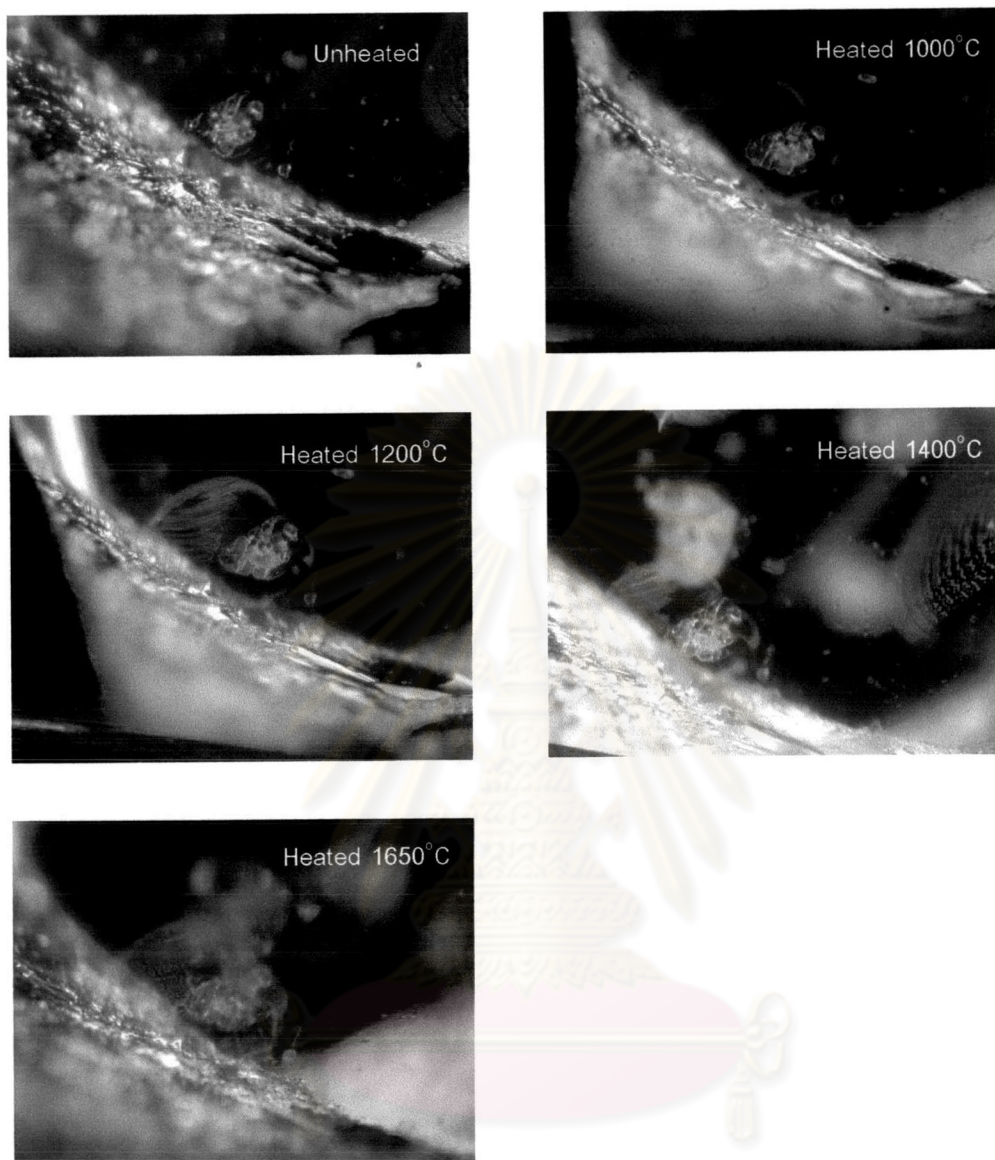


Figure 5.11 Showing zircon clusters before and after heating experiments. After step-heating from 1000°C to 1650°C under reducing atmosphere some zircon crystals in the clusters were slightly changed. The tension discs appeared to have been more extensive at higher temperatures (sample no. LV 2, about 70 times magnification).

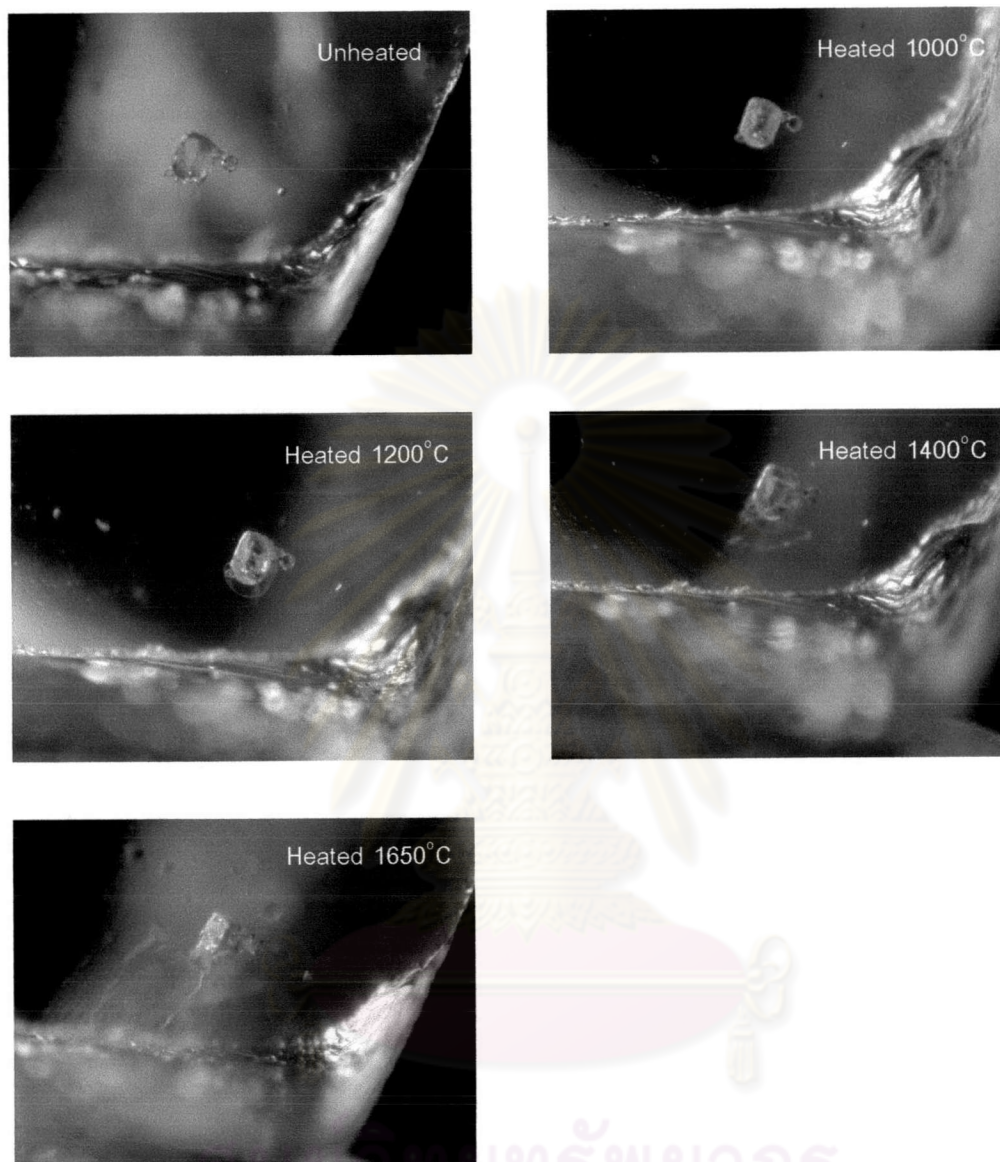


Figure 5.12 Showing an apatite inclusion before and after heating experiments. After step-heating from 1000°C to 1650°C under reducing atmosphere, the apatite crystal was slightly altered into whitish material with surrounding tension disc (sample no. IMB 4, about 70 times magnification).

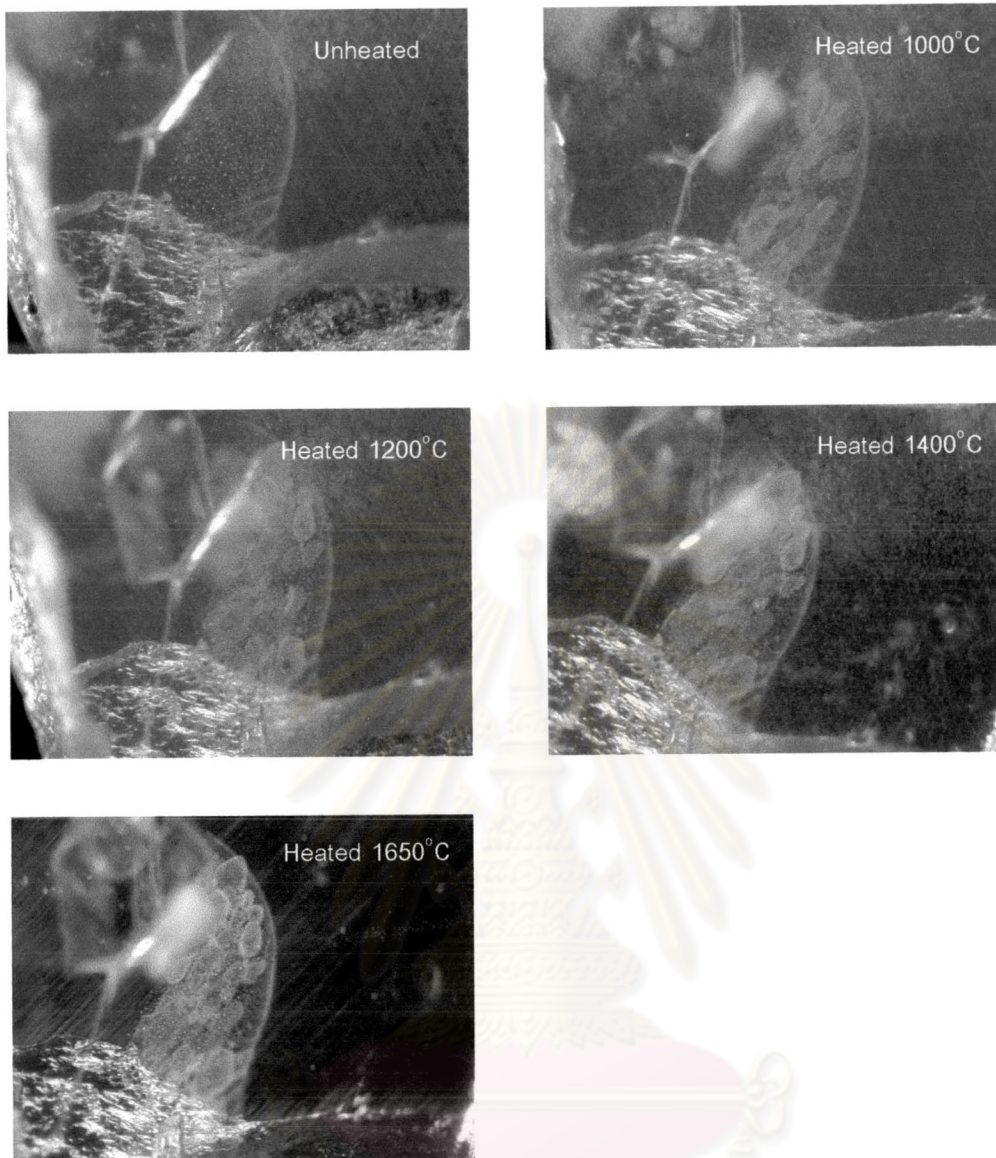


Figure 5.13 Showing development of fingerprints after step heating from 1000°C to 1650°C under reducing atmosphere. The fingerprints were gradually expanded. In addition, rutile needles intersecting at 60°/120° angles were still unchanged after heating at 1000°C and 1200°C, They were partially dissolved into the host sapphire generating dot-like pattern after heating at 1400°C. Eventually, they were dissolved completely at 1650°C (sample no. IVLB 2, about 45 times magnification).

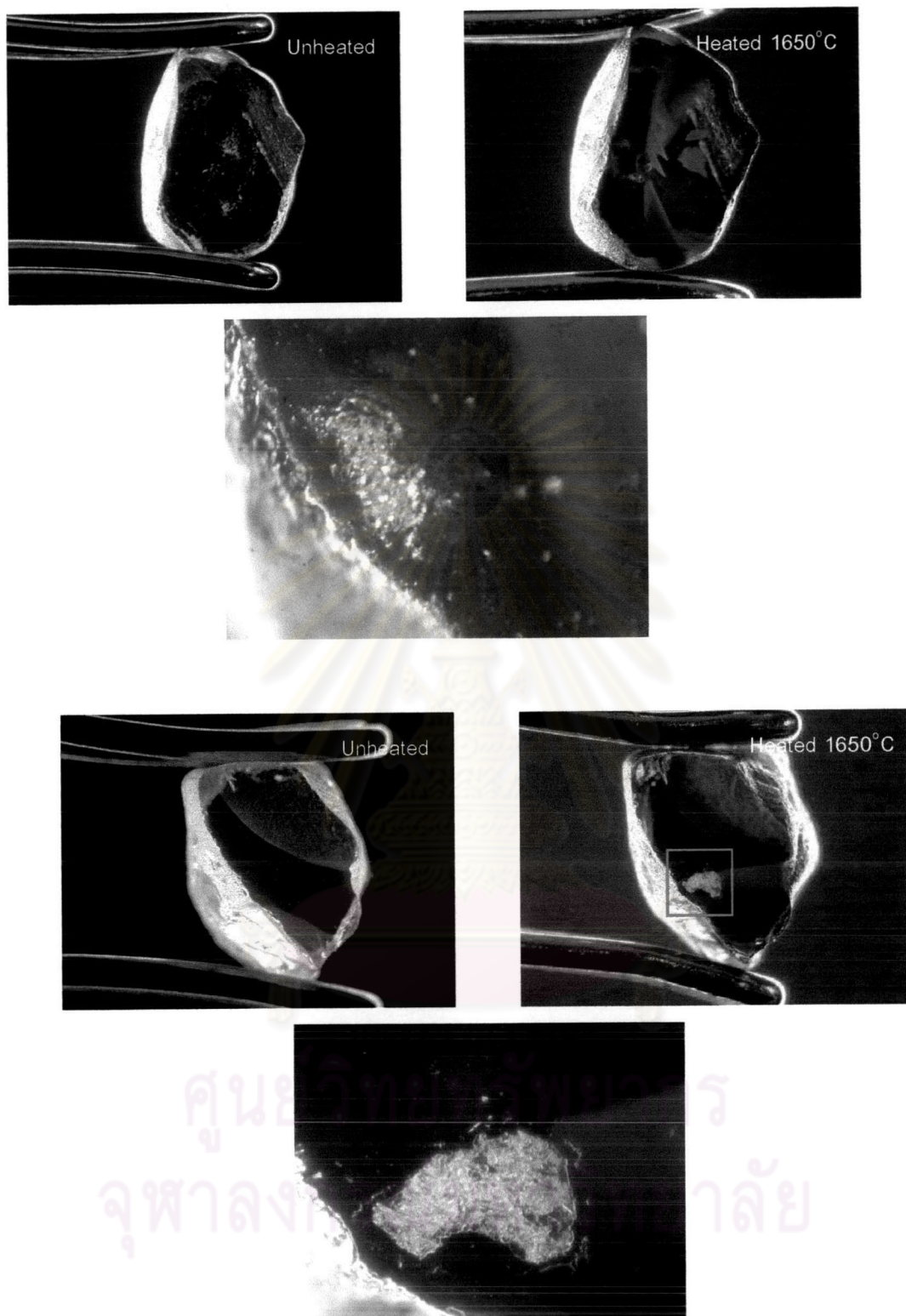


Figure 5.14 Showing areas of recrystallization developed after heating at 1650°C under reducing atmosphere (sample no. IDB 1 and IMB 5, about 70 times magnification).

5.5 UV-VIS-NIR spectra

Absorptions of light in the ranges of ultraviolet (UV), visible light (VIS) and near infrared (NIR), effect directly the color appearances of sapphires as well as those of other gemstones. Hence UV-VIS-NIR absorption spectra of sapphire samples before and after step-heating would give important information on the causes of colors and their changes after heating. UV-VIS-NIR spectra of 7 sapphire groups were measured before heating experiments, subsequently, absorption spectra were consistently detected at the same points after each step of heating experiments (e.g. 1000 °C, 1200 °C, 1400 °C and 1650 °C). Some selected spectra are displayed in Figures 5.15 to 5.20 and more samples are shown in Appendix III. The absorption spectra of a natural stone before experiment and after heating at 1000 °C, 1200 °C, 1400 °C and 1650 °C were usually overlained in the same diagrams for comparison; however, these spectra are somehow different in the baseline levels which may be caused by a slightly different condition during each measurement. Consequently, comparison could not be straight forward. Technique of spectrum subtraction were therefore considered to solve this problem. Spectra of unheated stones were subtracted by absorption spectra occurred after experiments at 1000 °C, 1200 °C, 1400 °C and 1650 °C, respectively. Then these results reveal directly differences between absorption of initial samples and those of heated samples at each step of experiment. The remaining peaks in the positive area indicate that absorptions in heated stones are relatively less than those in unheated stones, whereas, reverse peaks located in the negative area apparently reflect more intensive absorption in the heated stones.

The UV-VIS-NIR spectra of most studied groups (e.g. dark blue, medium blue, very light blue and milky, very light blue sapphires) showed $\text{Fe}^{2+}/\text{Ti}^{4+}$ intervalance charge transfer (IVCT) band at 562 to 704 nm with highest peak at about 588 nm (Figures 5.15 to 5.19). Additional peaks caused by iron (Fe^{3+}) at 388 nm also show in Figures 5.15 to 5.19. $\text{Fe}^{3+}/\text{Fe}^{3+}$ ion pair absorption at 450 nm can be observed in some samples (Figure 5.17). Heights of absorption bands and absorption peaks are obviously related to color intensities of stones.

Figure 5.15A, color of dark blue sample (IDB6) was changed from dark blue before heating to pale blue after heating at 1000°C. Its blue color was slightly recovered after heating up to 1200°C and 1400°C; eventually, dark blue color appeared again after heating at 1650°C. The residue spectra after subtraction (Figure 5.15B) show a board band about 562 nm to 704 nm, which corresponds to $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT (Häger, 2001).

Figures 5.16A, color of medium blue sapphire sample (IMB 5) was changed to very light blue after 1000°C heat and it still remained the same color after burning up to 1200°C. Blue color started to be recovered after heating up to 1400°C and deeper blue component was finally developed at 1650°C. The remaining spectra after subtraction between before and after step heating show a board band of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT at about 562 nm to 704 nm (Figure 5.16B).

Some medium blue sapphires have lost their colors after heating at 1000°C (Figure 5.17A) and blue component was not able to appear even temperature in creasing to 1650°C. The residue spectra after subtraction (Figure 5.17B) show board band peak at about 704 nm, which also corresponds to $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT.

Figure 5.18A shows UV-VIS-NIR spectra of very light blue sapphire (IVLB 5) between before and after step heating, which its color was changed from very light blue to almost colorless after heating at 1000°C. Blue color have been intensified continuously after step heating from 1200°C to 1650°C. The remaining spectra after subtraction between before and after step heating show board band of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT at 562 - 704 nm (Figure 5.18B).

UV-VIS-NIR spectra between before and after step heating of milky, very light blue sapphire (sample MVLB 7) in Figure 5.19A show the same color of stone before heating and after heating at 1000°C to 1200°C. Blue color was slightly developed after heating at 1400°C and more intense blue shade appeared after heating 1650°C. The remaining spectra after subtraction between before and after step heating show a board band of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT at 588 nm (Figure 5.19B).

Comparisons of absorption spectra between natural color and treated color as revealed in Figures 5.15 to 5.19 indicate clearly that the main cause of blue component in these samples is $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT, showing broad band of absorption at between 562 and 704 nm. This absorption band is significantly increased when blue shade is intensified; in contrast, it appears to have been decreased when blue color is lightened. Consequently, subtracted spectra would remain $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption band when the blue component is lightened after heating; otherwise reversed band in negative area is present when blue component is intensified after heating. Most information clearly show that blue color appears to have been developed with more intensive than the initial color after heating at 1650 °C. However some samples start to have deeper blue at 1400 °C (Figure 5.19). Other absorption peaks (e.g. Fe^{3+} at 388 nm and $\text{Fe}^{3+}/\text{Fe}^{3+}$ at 450 nm) have not been likely changed during heating experiment (see Figures 5.15 – 5.19).

Causes of colors in violet to pink shades of sapphires are significantly effected by Cr^{3+} in octahedral site of crystal lattice. The absorption peaks of Cr^{3+} at about 405 – 410 nm and 555 – 560 nm are usually present in most sapphires appearing violet to pink shades (Figure 5.20). Some sapphires showing color change effect may contain absorption peaks of Cr^{3+} in combination with $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT bands. However, $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption bands in these sapphires are rather weak and low intensive; therefore they may be influenced and overlaid mostly by Cr^{3+} peaks at about 555 nm – 560 nm; besides, tails of $\text{Fe}^{2+}/\text{Ti}^{4+}$ absorption bands partially extend to 704 nm then these absorption bands would be recognized (see Figure 5.20A).

As shown in Figure 5.20A, the color of sample MV1 was changed from medium violet before heating to very light pink after heating at 1000°C and still be the same color even it was heated up to 1650°C. Absorption spectra are obviously dominated by Cr^{3+} components with additional absorption peaks of Fe^{3+} at 388 nm (Figure 5.20A), which they are mostly disappeared after subtraction (see Figure 5.20B). The result indicates likely that concentrations of both Cr^{3+} and Fe^{3+} have not been effected by high temperature burning under reducing atmosphere. In addition, sign of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT absorption is slightly observed, particularly in unheated color (Figure

5.20A) and it is rapidly decreased and eventually absent after the heating, while blue shade in the stone is significantly lightened. It is very crucial to note that all violet sapphires with presenting color change effect were lost this valuable characteristic after heating up to 1000 °C.



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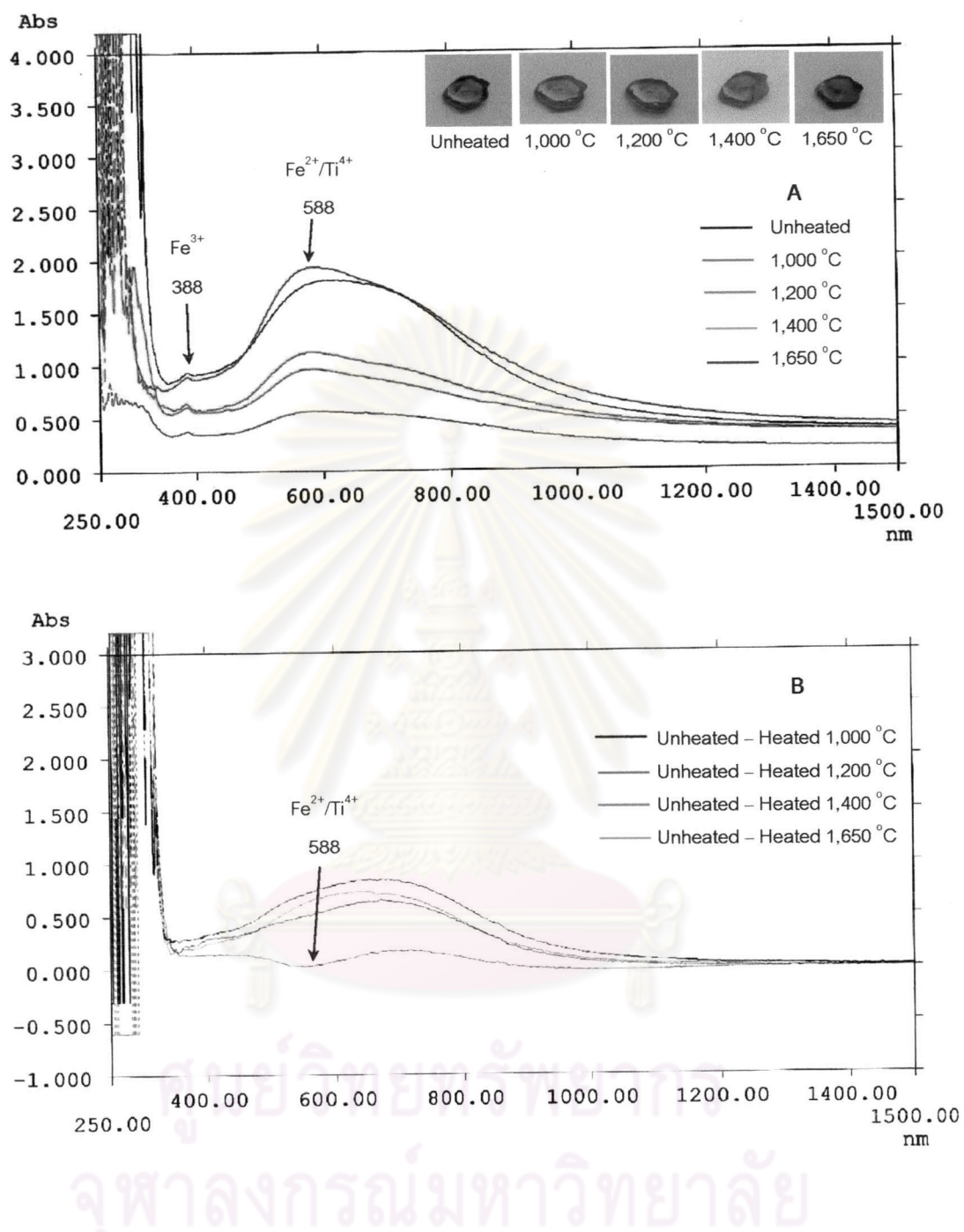


Figure 5.15 Typical UV-VIS-NIR absorption spectra of a dark blue sapphire (sample no. IDB 6) on the vibration plane perpendicular to the c-axis (o-ray). (A) The observed spectra of unheat dark blue sapphire before experiment and after step heating from 1000°C to 1650°C, respectively. (B) The remaining spectra resulted from subtraction between the spectrum of the unheated natural stone and each of the spectrum earned from each step of heating.

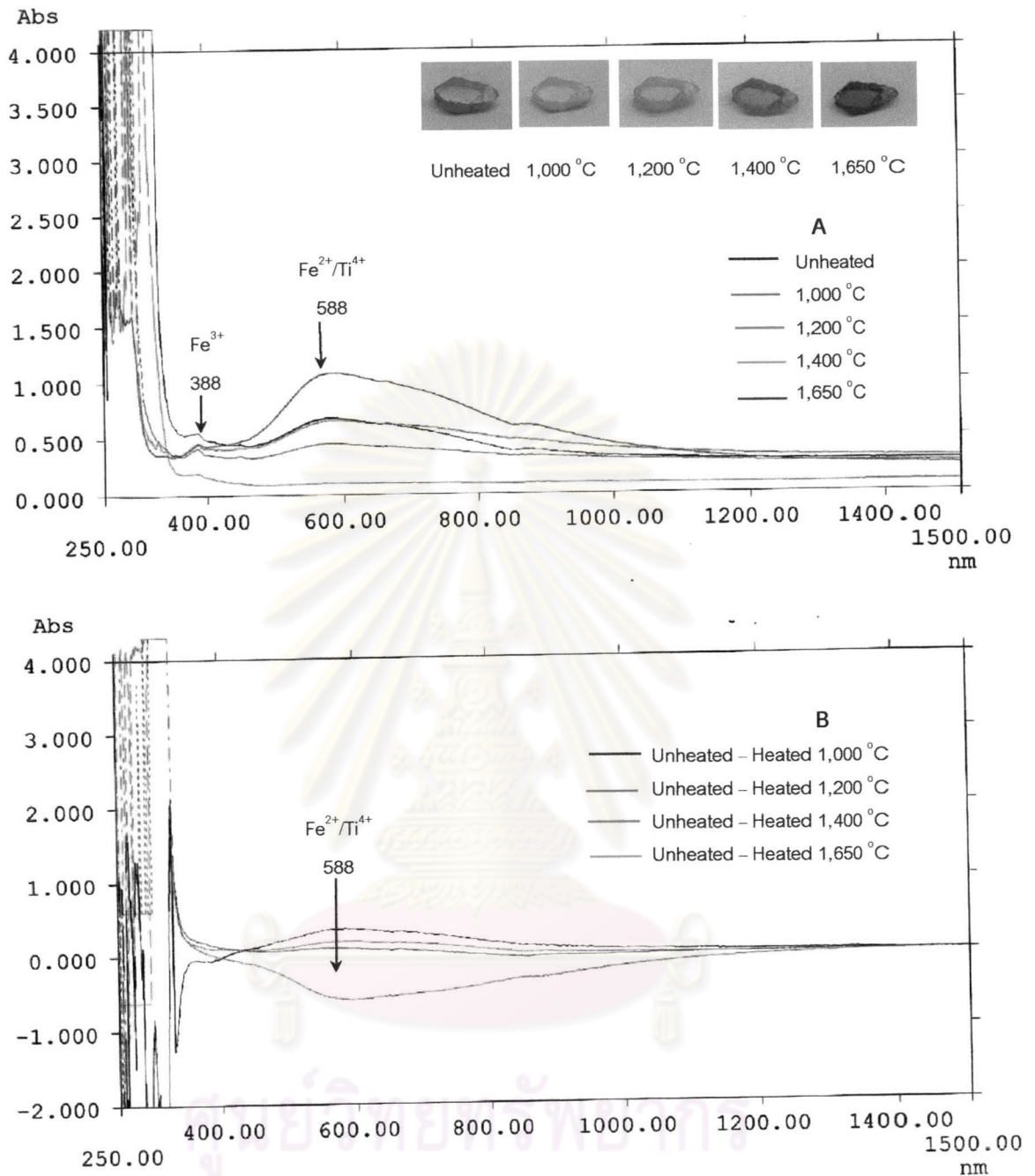


Figure 5.16 Typical UV-VIS-NIR absorption spectra of a medium blue sapphire (sample no. IMB 5) on the vibration plane perpendicular to the c-axis (o-ray). (A) The raw spectra of unheat dark blue sapphire before experiment and after step heating from 1000°C to 1650°C, respectively. (B) The residue spectra resulted from subtraction between the spectrum of the unheated natural stone and each of the spectrum earned from each step of heating.

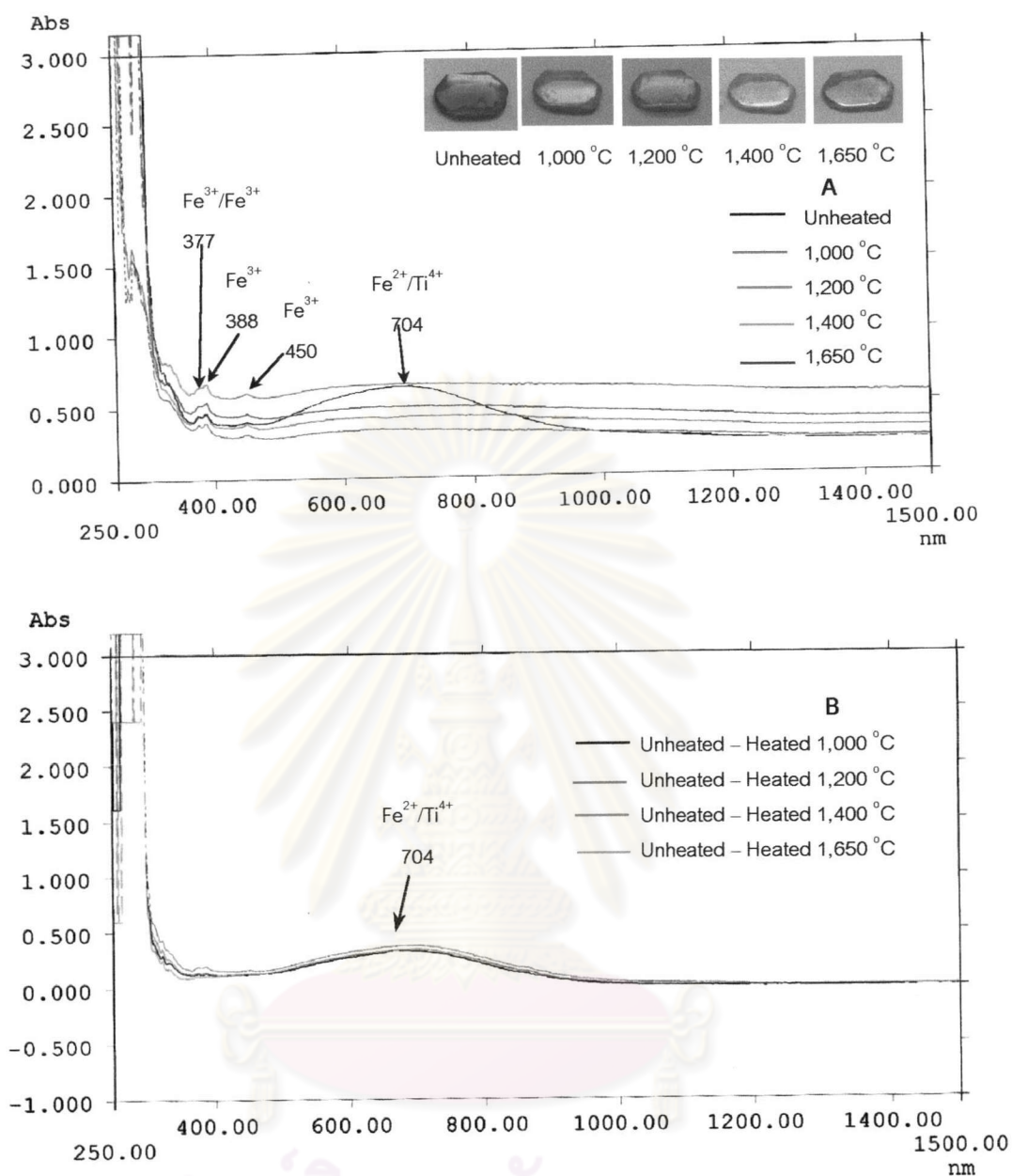


Figure 5.17 Typical UV-VIS-NIR absorption spectra of a medium blue sapphire (sample no. MB 6) on the vibration plane perpendicular to the c-axis (o-ray). (A) The raw spectra of unheated dark blue sapphire before experiment and after step heating from 1000 °C to 1650 °C, respectively. (B) The remaining spectra resulted from subtraction of the spectrum of the unheated natural stone and each of the spectrum earned from each step of heating.

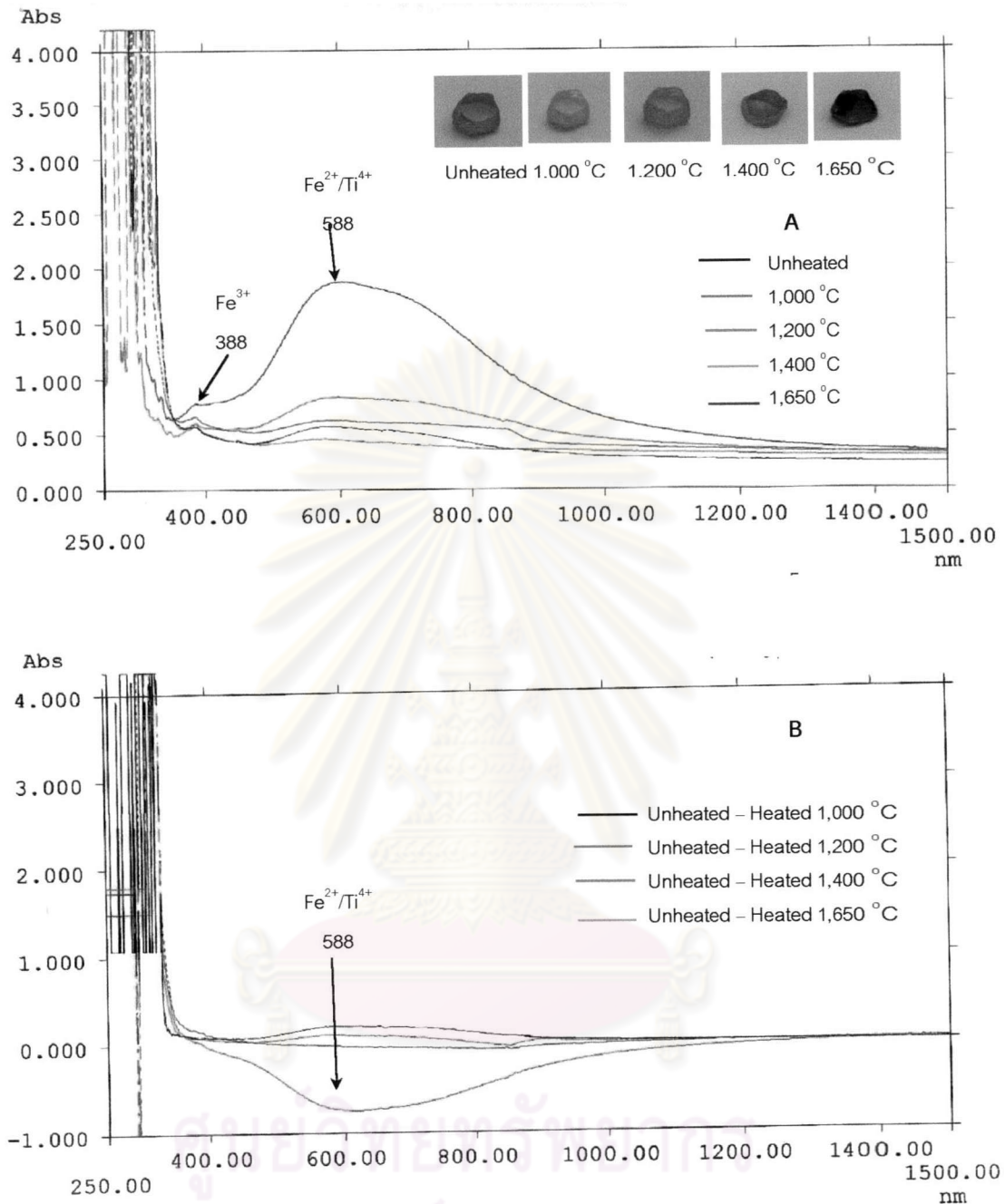


Figure 5.18 Typical UV-VIS-NIR absorption spectra of a very light blue sapphire (sample no. IVLB 5) on the vibration plane perpendicular to the c-axis (o-ray). (A) The raw spectra of unheated dark blue sapphire before heating and after step heating from 1000 °C to 1650 °C, respectively. (B) The remaining spectra resulted from subtraction between the spectrum of the unheated natural stone and each of the spectra earned from each step of heating.

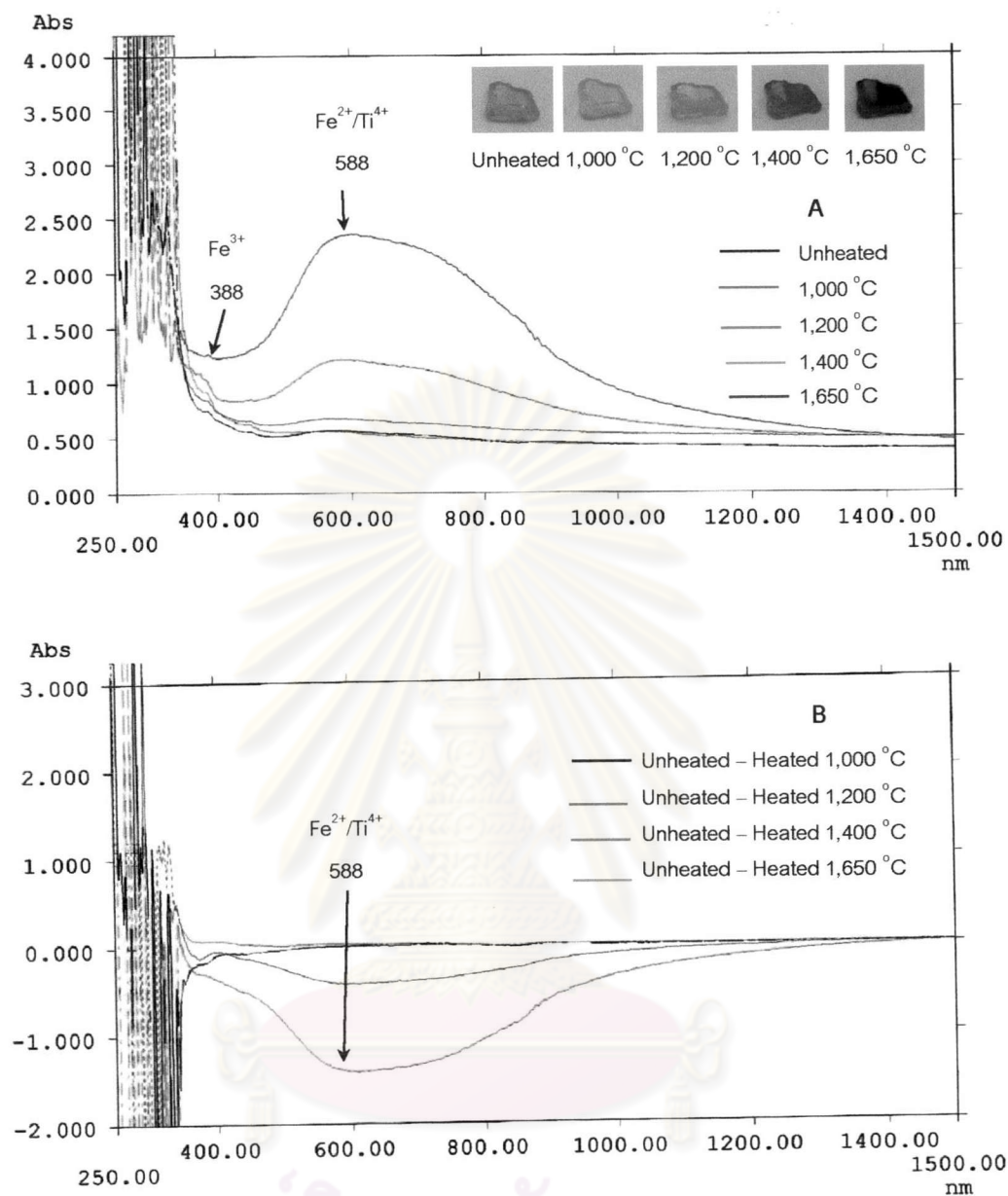


Figure 5.19 Typical V-VIS-NIR absorption spectra of a milky, very light blue sapphire (sample no. MVLB 7) on the vibration plane perpendicular to the c-axis (o-ray). (A) The raw spectra of unheated dark blue sapphire before heating and after step heating from 1000 °C to 1650 °C, respectively. (B) The remaining spectra resulted from subtraction between the spectrum of the unheated natural stone and each of the spectrum earned from each step of heating.

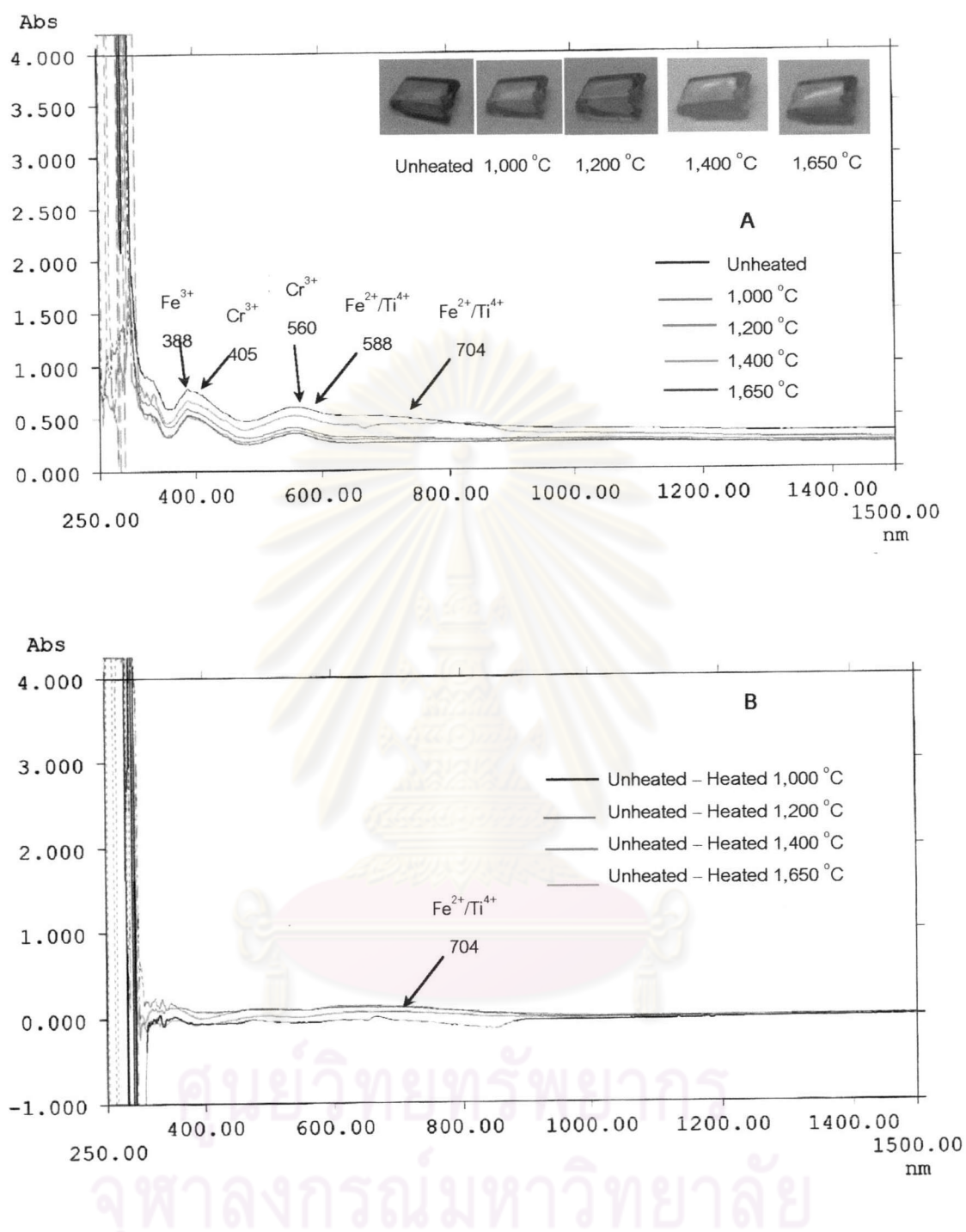


Figure 5.20 Typical UV-VIS-NIR absorption spectra of a medium violet sapphire (sample no. MV 1) on the vibration plane perpendicular to the c-axis (o-ray). (A) The raw spectra of unheated dark blue sapphire before treatment and after step heating from 1000°C to 1650°C, respectively. (B) The remaining spectra resulted from subtraction between the spectrum of the unheated natural stone and each of the spectrum earned from each step of heating.

5.6 FTIR spectra

Volynet et al. (1972) and Baran (1991), cited in Smith (1995) discovered and reported the structural bonding of OH groups in corundum. They have been recorded in verneuil synthetics of various colors and compositions, hydrothermal synthetic rubies and also natural corundums such as Sri Lanka rubies, Montana sapphires and Mong Shu rubies. Volynet et al. (1972) has indicated that hydrogen atoms are typically incorporated within the structure of corundum as a charge compensation mechanism. They may bound to various trace transitional metal ions, occupying interstitial sites between two oxygen atoms (O^{2-}) or may also be trapped by cation vacancies. These information lead to detection of corundums that have been treated at high temperature, in which oxygen and hydrogen may be allowed to diffuse into the crystals. Therefore, heat-treated corundum are assumed to have higher concentration of these gases and in turn presenting in form of their interaction. Systematic measurements were taken place for all samples before the experiment and after each step of heating. Collection of these FTIR spectra may be used as database to recognize heated corundum from unheated one; however, a lot more analytical data would be required and experimented to develop the conclusive criteria.

Representatives of FTIR spectra of sapphire samples before experiment and after step heat-treatment are shown in Figures 5.21 to 5.27, whereas all FTIR spectra collected in this study are displayed in Appendix II. In general, all sapphires show absorption patterns of H_2O at $3900 - 3400\text{ cm}^{-1}$, patterns of C-H stretching at $2926 - 2918$ and $2862 - 2860\text{ cm}^{-1}$, and patterns of CO_2 at $2365 - 2360$ and $2360 - 2340\text{ cm}^{-1}$ respectively. Among these peaks, O-H stretching peak at about 3309 cm^{-1} is the most crucial for consideration of high temperature treatment; this is because the other peaks are possibly effected by contamination of the stone. For examples, peaks of H_2O and CO_2 may be involved by vapor and air surrounding the sample, whereas C-H stretching peaks would indicate organic oil film coated on the surface. Volynet et al. (1972) suggested that O-H stretching peak could be appeared and intensified after heating up corundum at high temperatures. Therefore, only O-H stretching peaks will be considered below.

An unheated dark blue sapphire sample (IDB 4) showed a small O-H stretching peak at 3309 cm^{-1} that was rapidly increased after heating at $1000\text{ }^{\circ}\text{C}$ and $1200\text{ }^{\circ}\text{C}$ but it was abruptly decrease after heating up to $1400\text{ }^{\circ}\text{C}$ and $1650\text{ }^{\circ}\text{C}$ (Figure 5.21). The medium blue sapphire sample (IMB 2) appeared to have no O-H stretching peak at 3309 cm^{-1} in the unheated state as well as after each step of heating experiment (Figure 5.22).

Sapphire samples (VLB 4) of very light blue group has no O-H stretching peak either in unheated state or after heated state at $1000\text{ }^{\circ}\text{C}$. This peak was created slightly after heating at $1200\text{ }^{\circ}\text{C}$ and $1400\text{ }^{\circ}\text{C}$. However, it was disappeared again after heating up to $1650\text{ }^{\circ}\text{C}$ (Figure 5.23). Milky, very light blue sapphire samples (MVLB 8) was also absent in O-H stretching peak before undertaking heat treatment and it still showed similar FTIR patterns after burning at $1000\text{ }^{\circ}\text{C}$ and $1200\text{ }^{\circ}\text{C}$. The O-H stretching peak only appeared when the stone was heated at $1400\text{ }^{\circ}\text{C}$. It was to disappeared again after heating up to $1650\text{ }^{\circ}\text{C}$ (Figure 5.24). The O-H stretching peak of a dark violet sapphire sample (DV 2) revealed before undertaking experiment and still remained after heating at $1000\text{ }^{\circ}\text{C}$. The O-H stretching peak was however totally removed after heating up to $1200\text{ }^{\circ}\text{C}$ and it was still disappeared even temperature was risen to $1650\text{ }^{\circ}\text{C}$ (Figure 5.25). A medium violet sapphire sample (MV 1) has no O-H stretching peak in FTIR spectra both in the unheated state and after step heating from $1000\text{ }^{\circ}\text{C}$ to $1650\text{ }^{\circ}\text{C}$ (Figure 5.26). An unheated light violet sapphire sample (ILV 2) showed O-H stretching peak at 3309 cm^{-1} but it was disappeared after step heating from $1000\text{ }^{\circ}\text{C}$ to $1650\text{ }^{\circ}\text{C}$ (Figure 5.27).

These results clearly demonstrate the uncertainty uncertain effect of high temperature effect on occurrence of O-H stretching peak in FTIR spectra. Some samples contain O-H stretching peaks in their natural condition which may decrease rapidly or disappear after step heating experiments. On the contrary, the O-H stretching peaks may not occur in some natural stones but they can be developed in some stages of heating; and destroyed later at higher heating temperatures, especially at $1650\text{ }^{\circ}\text{C}$. A few sapphire samples appear to have no O-H stretching peaks in their natural condition as well as throughout all step heating experiments. Based on this study, FTIR spectra

are unlikely to be used as a good evidence to indicate high temperature treatment of corundum. The application of this kind of information for gem testing should be undertaken with great cares, particularly in aspect of heat treatment.



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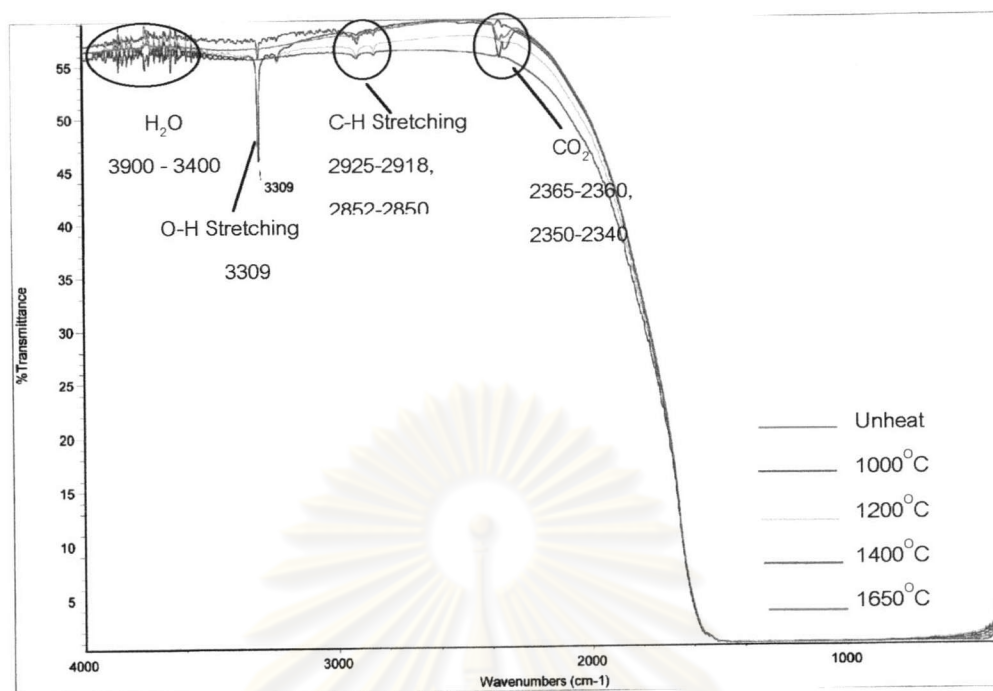


Figure 5.21 FTIR spectra of a dark blue sapphire (IDB 4) before the experiment and after step heating from 1000 °C to 1650 °C.

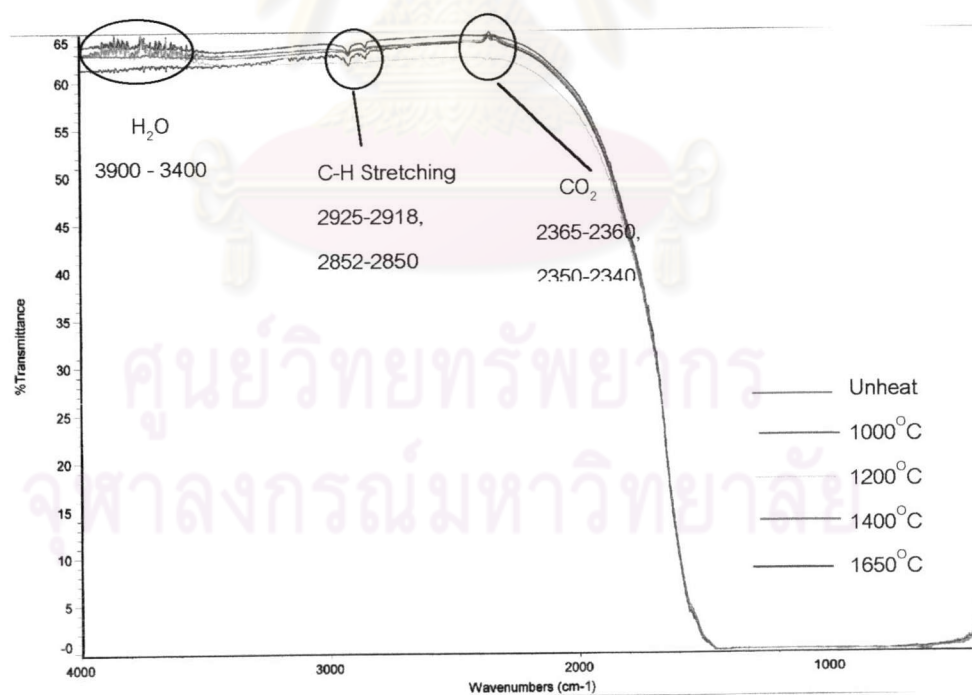


Figure 5.22 FTIR spectra of a medium blue sapphire (IMB 2) before the experiment and after step heating from 1000 °C to 1650 °C.

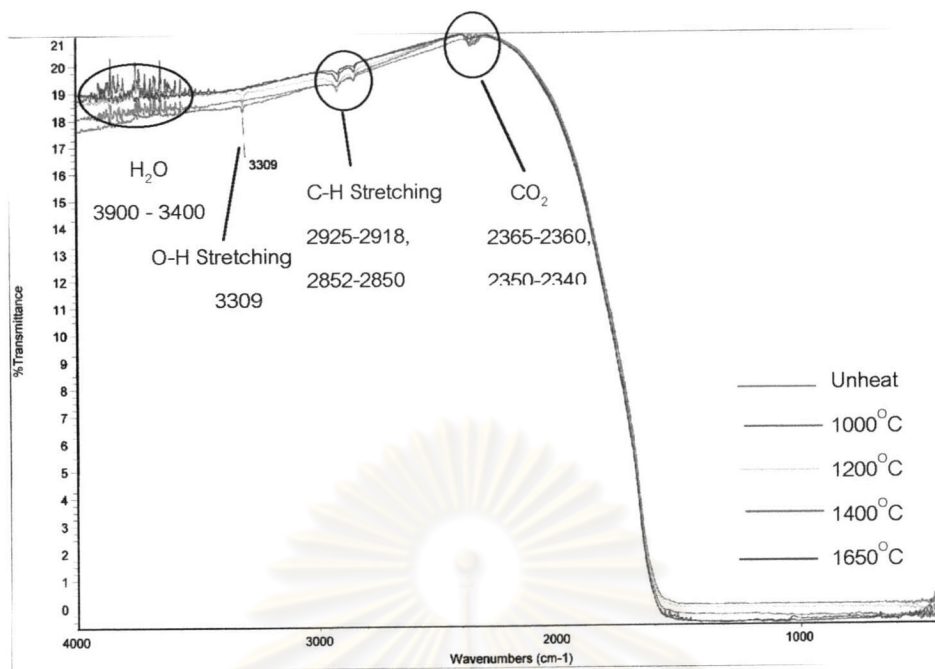


Figure 5.23 FTIR spectra of a very light blue sapphire (VLB 4) before the experiment and after step heating from 1000 °C to 1650 °C.

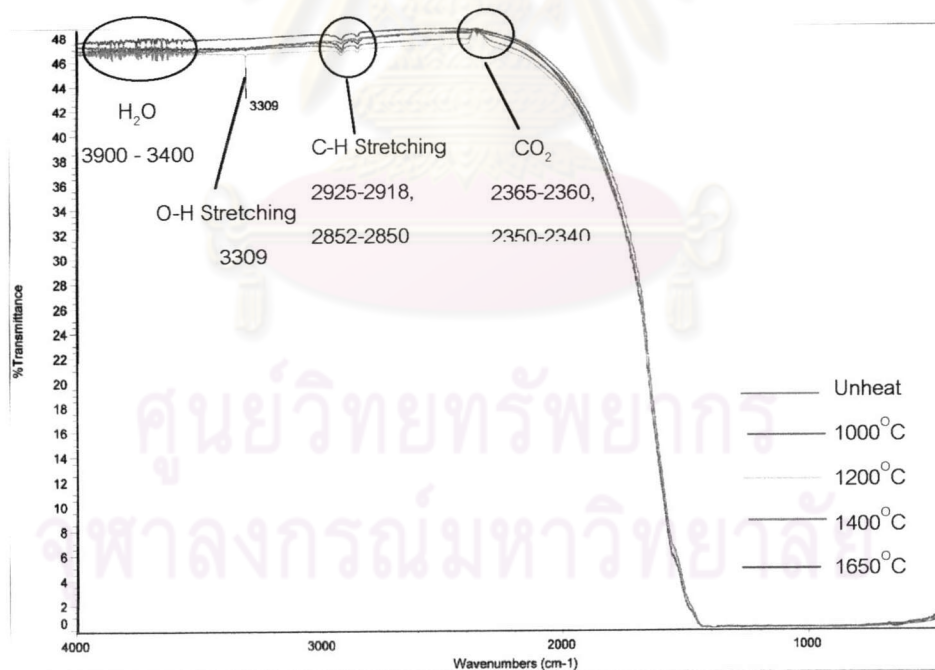


Figure 5.24 FTIR spectra of a milky, very light blue sapphire (MVLB 8) before the experiment and after step heating from 1000 °C to 1650 °C.

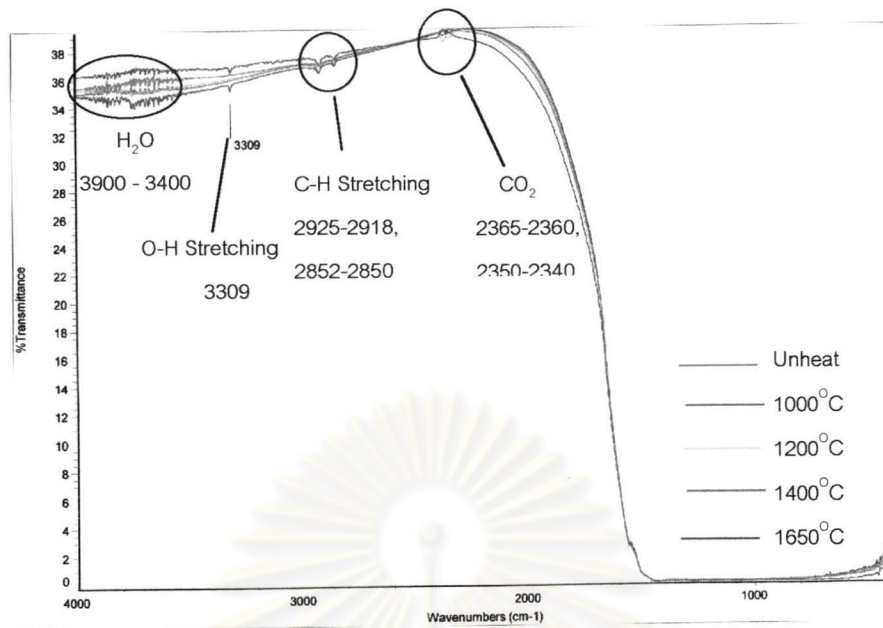


Figure 5.25 FTIR spectra of a dark violet sapphire (DV 2) before the experiment and after step heating from 1000 °C to 1650 °C.

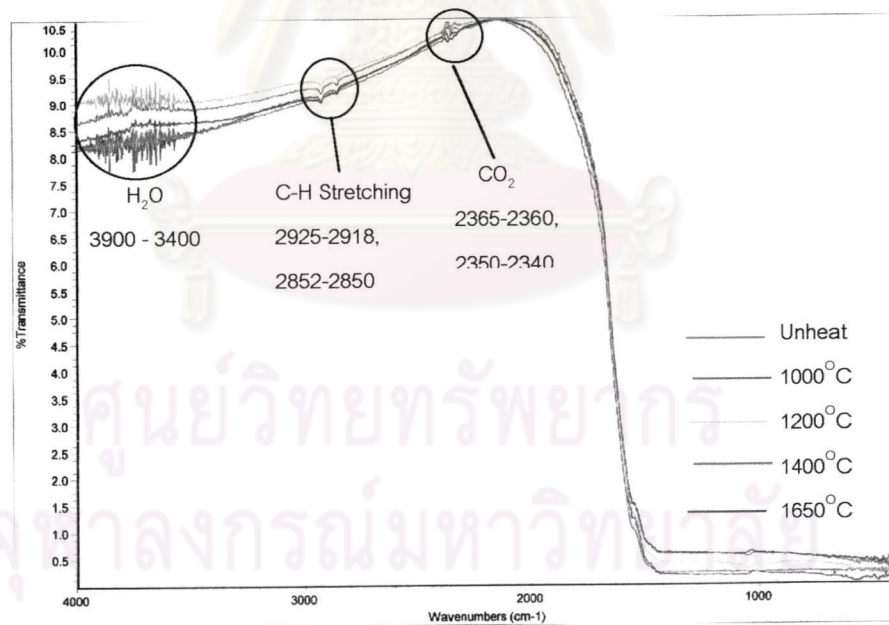


Figure 5.26 FTIR spectra of a medium violet sapphire (MV 1) before the experiment and after step heating from 1000 °C to 1650 °C.

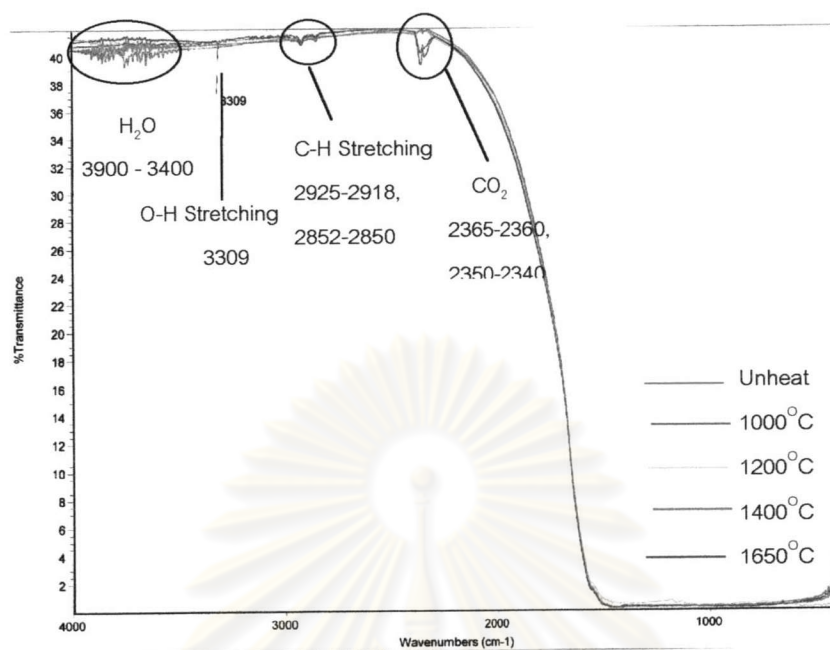


Figure 5.27 FTIR spectra of a light violet sapphire (LV 2) before the experiment and after step heating from 1000 °C to 1650 °C.

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