CHAPTER IV

ABSORPTION SPECTRA

4.1 Cause of color

Nassau (1978), Fritsch et al. (1987) and GAGTL (2001) reported about the causes of colors in gemstones such as crystal field theory, charge transfer or molecular orbital theory, band theory and physical optics. Causes of color in corundum can be explained by two theories as:

4.1.1 Crystal field theory can explain two types of color in corundum, one is caused by transition metals and the other is produced by color centers. The predominantly ionic crystals in corundum may contain dispersed transition ions with unpaired electrons such as Cr^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$). The three unpaired electrons in 3d shell can interact with visible light as to produce absorption and color in ruby.

The unpaired electron which produced color by light absorption into excited states does not have to be located on the transition element ion; under certain circumstances it can be located on a crystal defect such as a missing ion. This can be the cause of color centers which created yellow color in yellow sapphire (Nassau, 1978).

4.1.2 Metal – metal charge transfer: In blue sapphire, with both Fe and Ti trace elements, each of the impurity ions can exist in two valence states, and therefore in two combinations:

$$Fe^{2+} + Ti^{4+} \rightleftharpoons Fe^{3+} + Ti^{3+}$$

A single electron can be transfer from the Fe to the Ti by light absorption and back again. The transition from Fe^{2+} + Ti^{4+} to Fe^{3+} + Ti^{3+} involves the absorption of energy, producing a broad intense absorption band at the red end of the spectrum and resulting in the deep blue color. Another charge transfer process involving only Fe as: Fe^{2+} + Fe^{3+} and Fe^{3+} + Fe^{2+} can also occur, this process produces absorption only in the infrared in sapphire (Nassau, 1978).

As basis of the molecular structure and chromophoric element contained in structure, spectroscopic methods are applied to investigate corundum samples and their colors. The absorption spectra over UV-VIS-NIR range and transmission spectra covering near to far infrared region of 45 samples were observed before heating and after each step of heating.

4.2 UV-VIS-NIR Absorption Spectra

UV-VIS-NIR Spectrophotometer contains a light source generating wavelengths over the range of ultraviolet (UV), visible light (VIS) and near infrared (NIR). Absorption spectra are detected with photocell and then signal is transferred to display on monitor. UV-VIS-NIR Spectroscopy gives information about the absorption spectra in this range, which in turn may related to electron transitions of trace elements or other structural defects in sapphires. The absorption patterns of UV-VIS-NIR region in this study were measured using Hitachi UV-VIS-NIR Spectrophotometer, model U-4001 (Figure 4.1) based at the Gem and Jewelry Institute of Thailand (GIT).

Figure 4.1 Hitachi UV-VIS-NIR Spectrophotometer (Model U-4001) at GIT

The oriented sample was fixed in the middle of a black plate with 0.25 mm diameter slit and placed in a cell holder. Each sample was measured twice:

perpendicular to c-axis for ordinary ray (o ray) and parallel to c-axis for extraordinary ray (e ray). A polarizing filter was used to obtain the o-ray and e-ray. The absorption spectra of the sapphires were examined between 250 and 1500 nanometers (nm) with spectral resolution of 2 nm.

Typical examples of the UV-VIS-NIR spectra of unheated sapphires are displayed in Figures 4.2 to 4.9. All absorption peaks are related to transition ions (e.g. Cr^{3+}, Fe^{2+}, Ti^{4+}or V^{3+}). Blue sapphires usually show Fe^{3+}/Fe^{3+} pairs absorption peaks at 377 and 450 nm, Fe^{3+} absorption peaks at 388 nm and Fe^{2+}/Ti^{4+} absorption peaks at about 588 nm. Typical blue color is caused by Fe^{2+}-O-Ti^{4+} intervalence charge transfer (IVCT) process (Themelis, 1992). The intensity of blue color is directly related to the strength of Fe^{2+}/Ti^{4+} IVCT absorption band, (see Figures 4.2 to 4.5). The blue sapphires with color-change effect show additional Cr^{3+} absorption peaks at 412 and 694 nm apart from Fe^{2+}/Ti^{4+} absorption peaks at 588 nm (Figure 4.3).

Violet sapphires with color-change effect show Cr^{3+} absorption peaks at 412, 555 and 694 nm, Fe^{3+}/Fe^{3+} pairs absorption peaks at 377 and 450 nm, Fe^{3+} absorption peaks at 388 nm and Fe^{2+}/Ti^{4+} absorption peaks at 588 nm (Figures 4.7 and 4.8).

Violet sapphires without color-change effect show absorption peaks similar to those of the violet sapphires with color-change effect; however Fe^{3+}/Fe^{3+} peak is disappear (Figure 4.9). Schmetzer et al. (1980) cited in Fritsch and Rossman (1988) reported a particular range of concentration of Cr^{3+} and/or V^{3+} in octahedral coordination is the cause of color-change effect in corundum.

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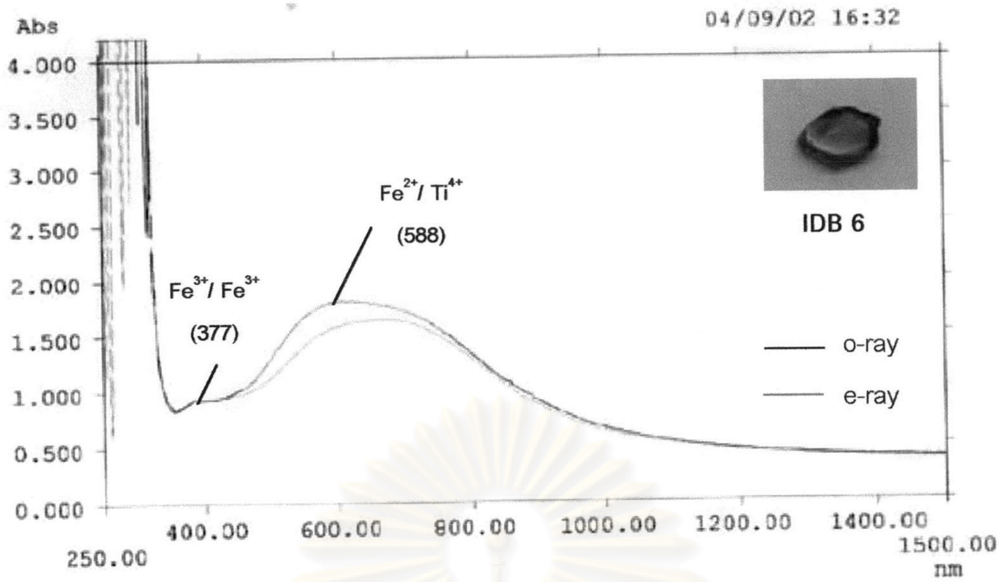

Figure 4.2 UV-VIS-NIR spectra of unheated dark blue sapphire from Ilakaka-Sakaraha, Madagascar

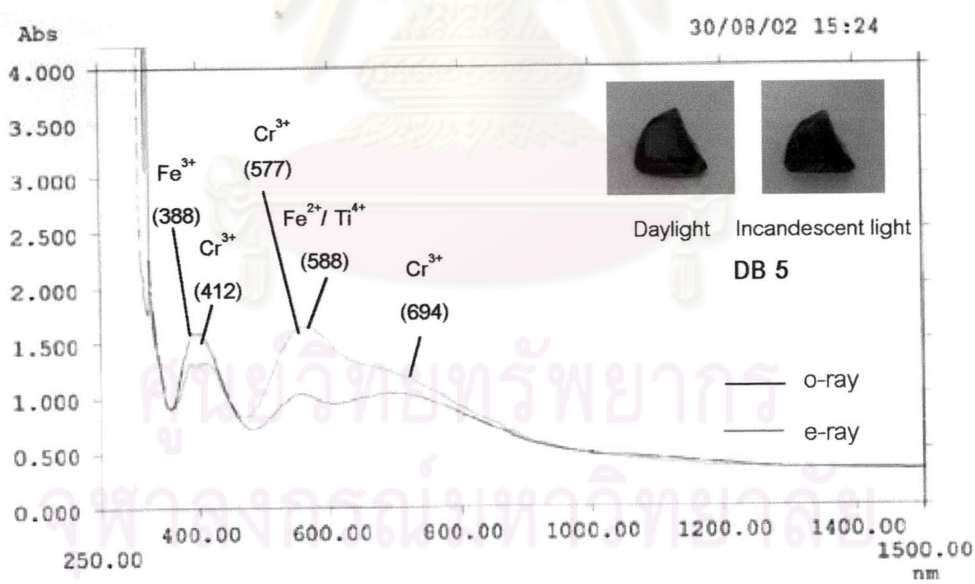

Figure 4.3 UV-VIS-NIR spectra of unheated dark blue sapphire with color-change effect from Ilakaka-Sakaraha, Madagascar

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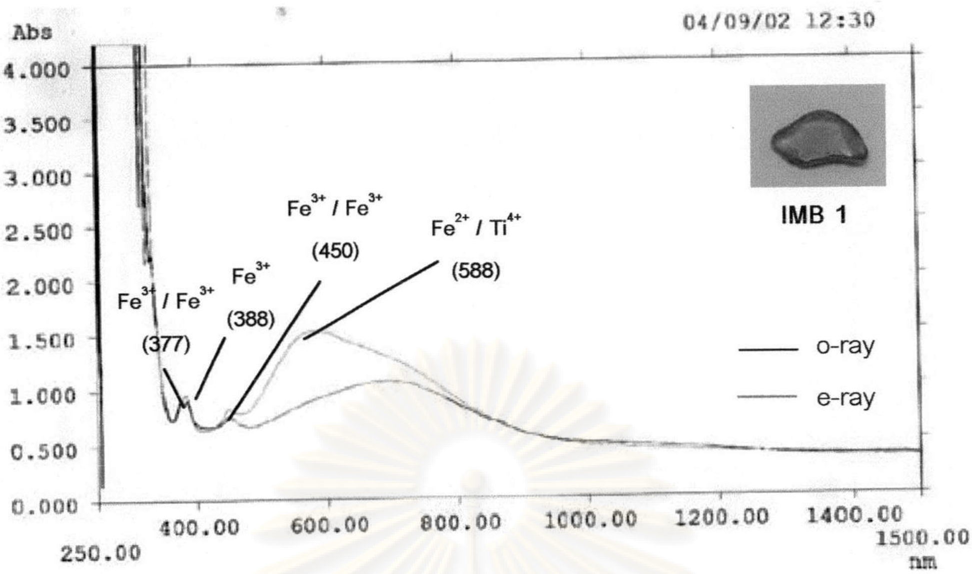

Figure 4.4 UV-VIS-NIR spectra of unheated medium blue sapphire from Ilakaka-Sakaraha, Madagascar

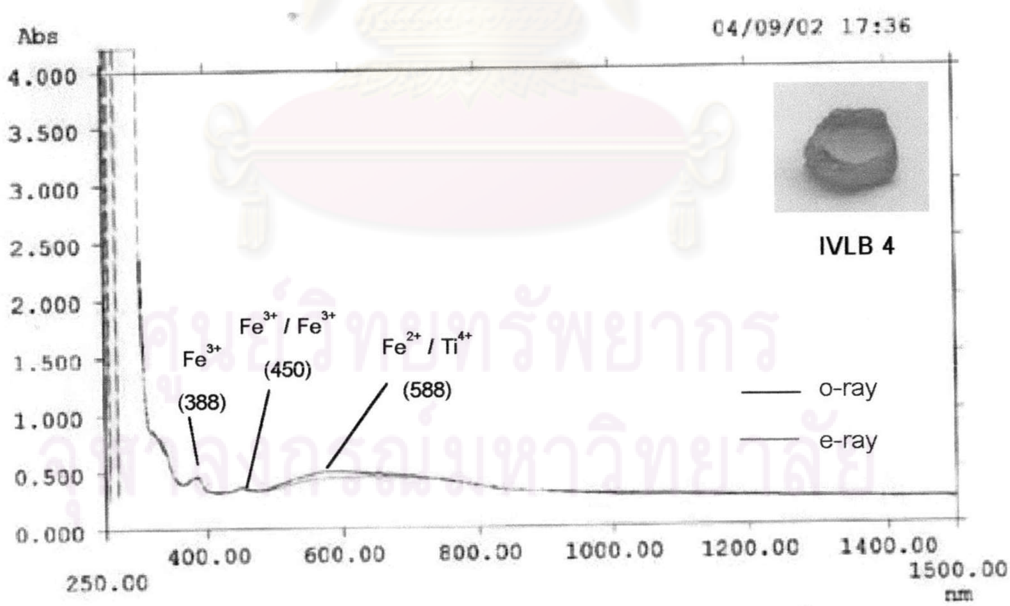

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Figure 4.5 UV-VIS-NIR spectra of unheated very light blue sapphire from Ilakaka-Sakaraha, Madagascar

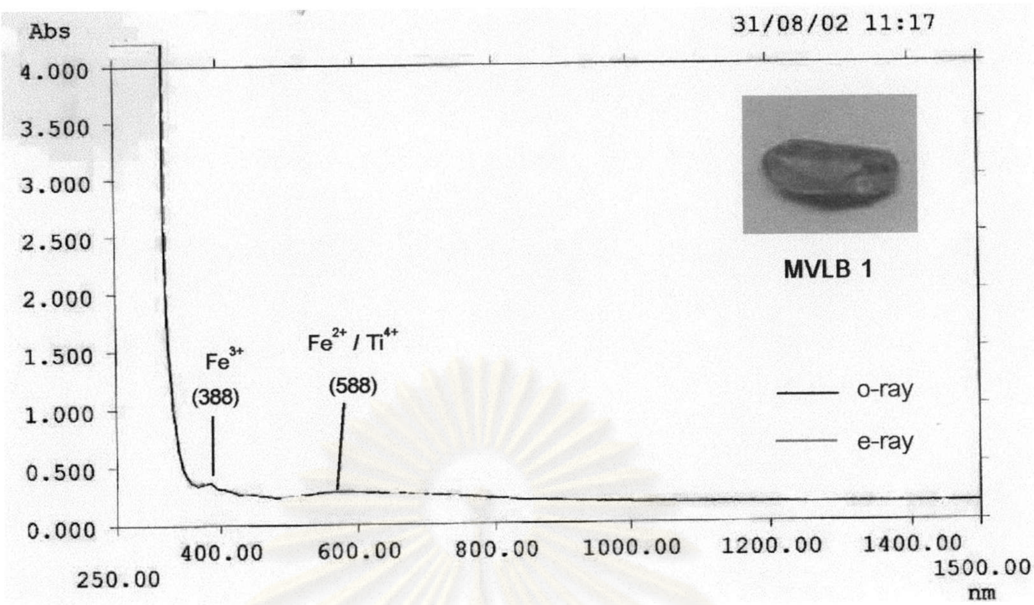

Figure 4.6 UV-VIS-NIR Spectra of unheated milky-very light blue sapphire from Ilakaka-Sakaraha, Madagascar

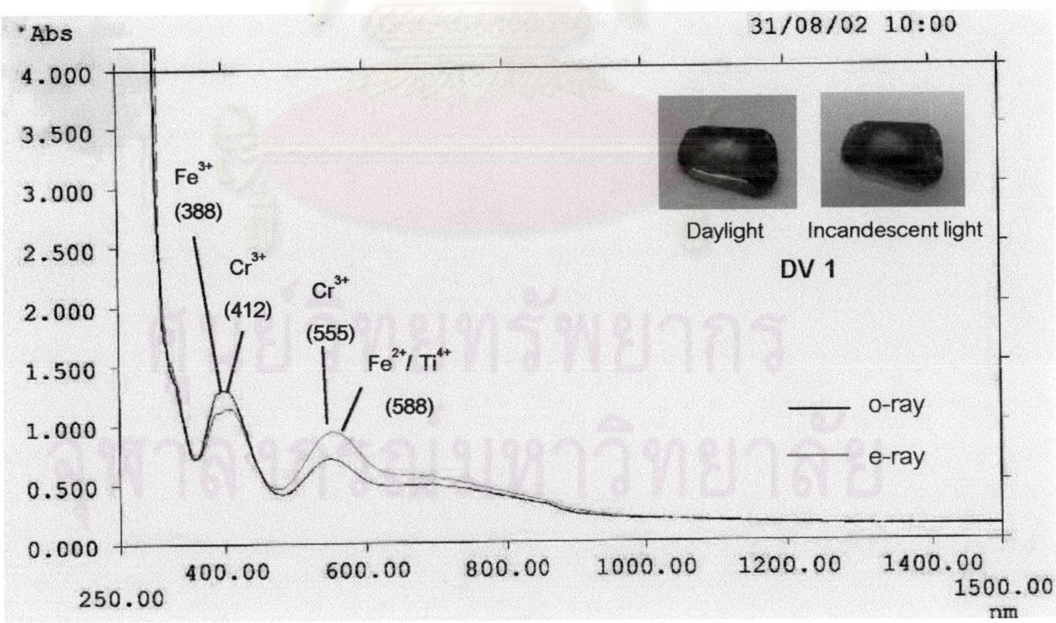

Figure 4.7 UV-VIS-NIR Spectra of unheated dark violet sapphire with color-change effect from Ilakaka-Sakaraha, Madagascar

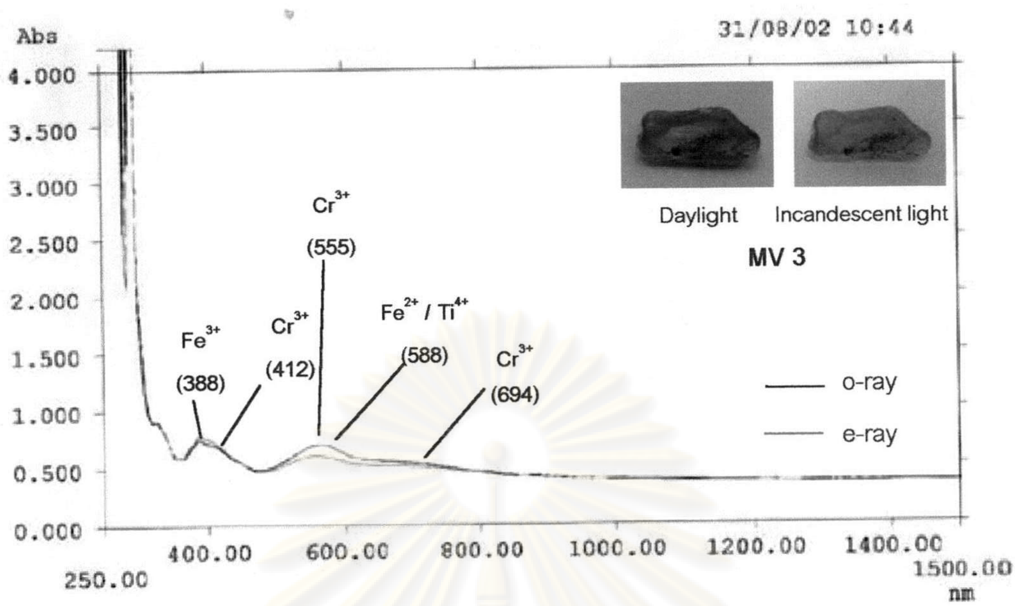

Figure 4.8 UV-VIS-NIR Spectra of unheated medium violet sapphire with color-change effect from Ilakaka-Sakaraha, Madagascar

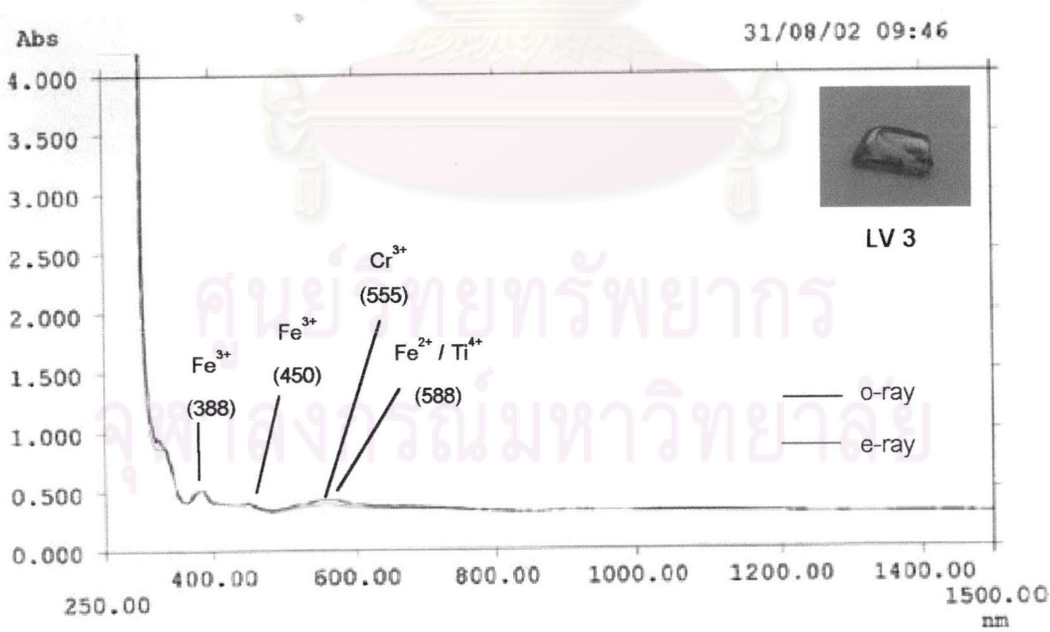

Figure 4.9 UV-VIS-NIR Spectra of unheated light violet sapphire from Ilakaka-Sakaraha, Madagascar

4.4 Fourier Transform Infrared (FTIR) Spectra

Fourier Transform Infrared (FTIR) spectrometer can be used for recording the absorption or transmission spectra in the range of near to far infrared. The infrared spectra give information about the structures and bonding in mineral specimen. The transition responsible for IR band is related to molecular vibrations (stretching or bending of bonds) (Field et al., 2002). The infrared absorption is caused by structural vibration determined by bond lengths and bond angles between atoms (Yan et al., 1995). Measuring of transmission spectra in mid infrared range (400 – 4000 cm^{-1} wavenumber) was carried out using Nicolet FTIR Spectrophotometer (model NEXUS 670) at GIT (Figure 4.10).

Forty-five polished samples were examined in the near - to mid – infrared spectral region. Each sample was fixed placed in the middle of a plate with 0.3 mm diameter slit and placed in the cell holder. Single IR beam was allowed to pass through the sample to detector. The infrared spectrum of corundum is dominated by absorption resulting from Al-O stretch frequencies (Smith, 1995).

Figure 4.10 Fourier Transform Infrared (FTIR) Spectrophotometer (Nicolet model NEXUS 670 belong to GIT)

The infrared spectrum is indication of vibration energy levels in atomic structure of the sapphire samples. FTIR spectra of some unheated blue sapphires from Ilakaka-Sakaraha were displayed in Figures 4.11 to 4.17. They show absorption peaks at 3900 – 3400 cm^{-1} caused by moisture (H_2O), 2925 – 2918 and 2852 – 2850 cm^{-1} resulted from C-H stretching, 2365 – 2360 and 2350 – 2340 cm^{-1} due to CO_2 (Smith, 1995). Some samples also show very weak absorption peaks of O-H stretching at 3309 cm^{-1} (Volynets et al., 1972).

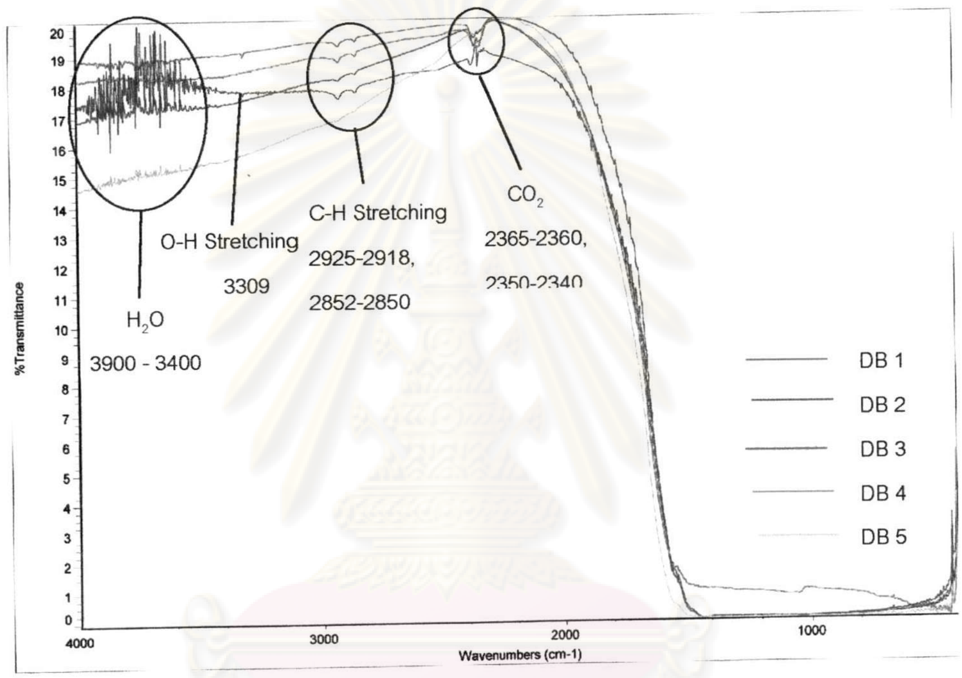

Figure 4.11 FTIR Spectra of unheated dark blue sapphires

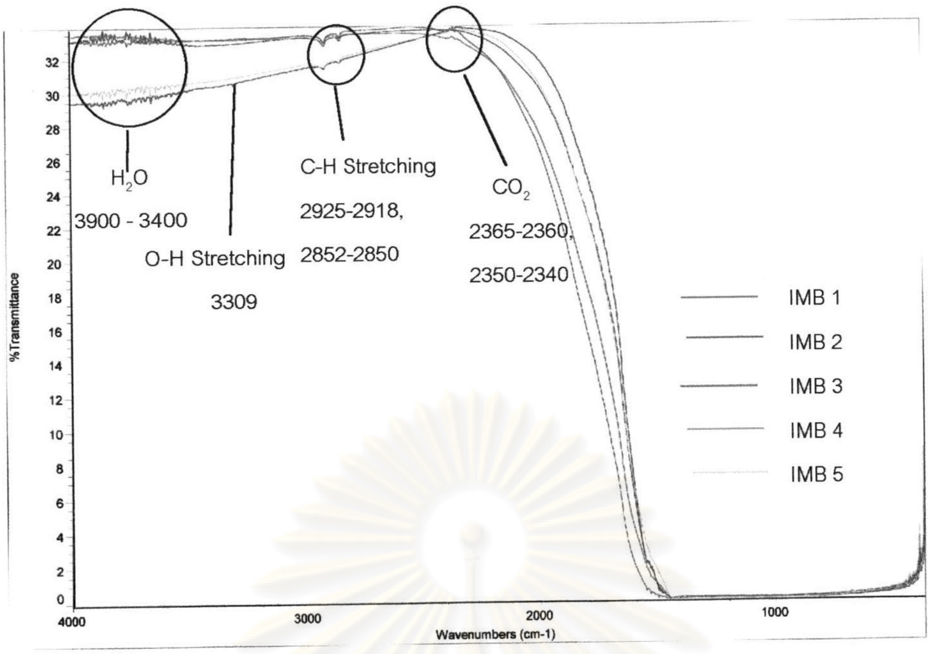

Figure 4.12 FTIR Spectra of unheated medium blue sapphires

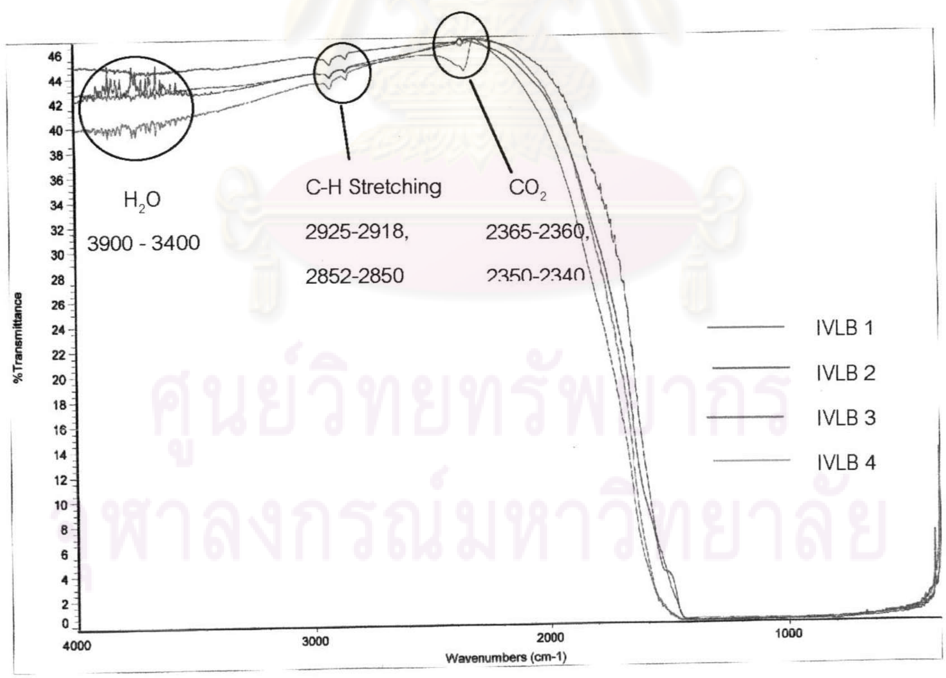

Figure 4.13 FTIR Spectra of unheated very light blue sapphires

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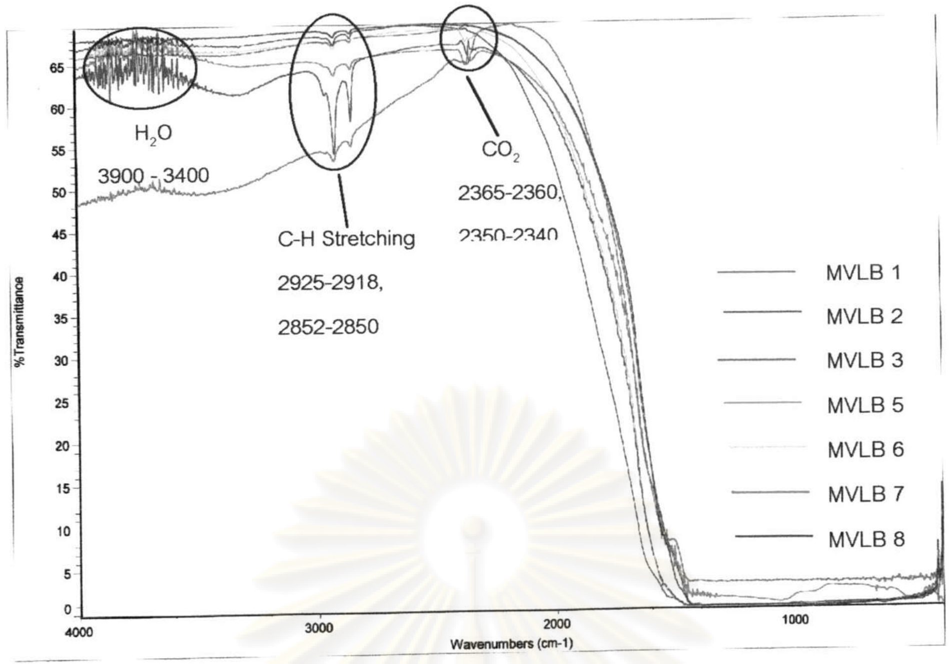

Figure 4.14 FTIR Spectra of unheated milky very light blue sapphires

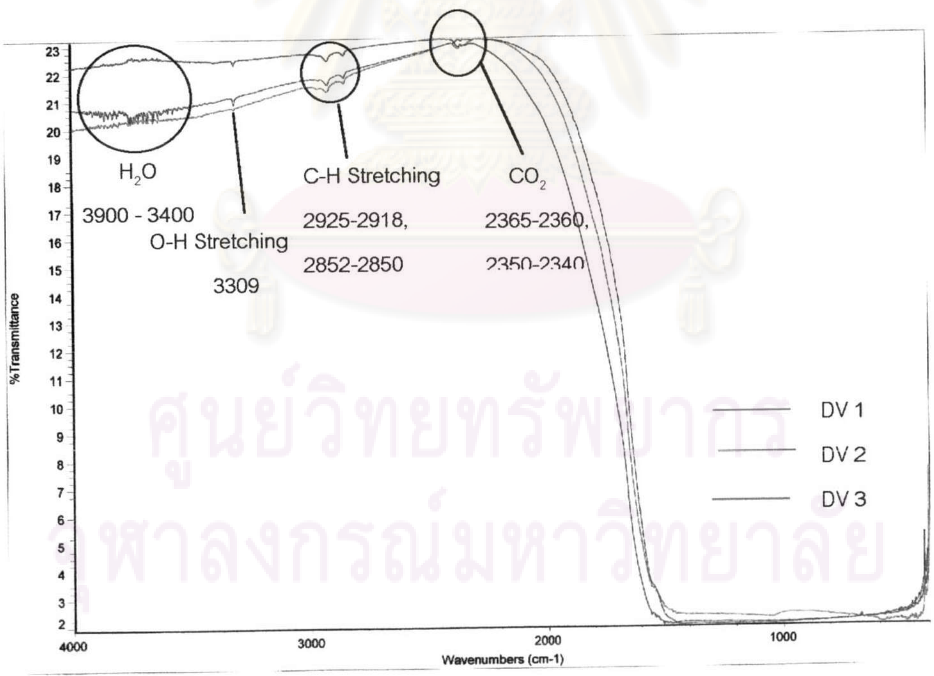

Figure 4.15 FTIR Spectra of unheated dark violet sapphires

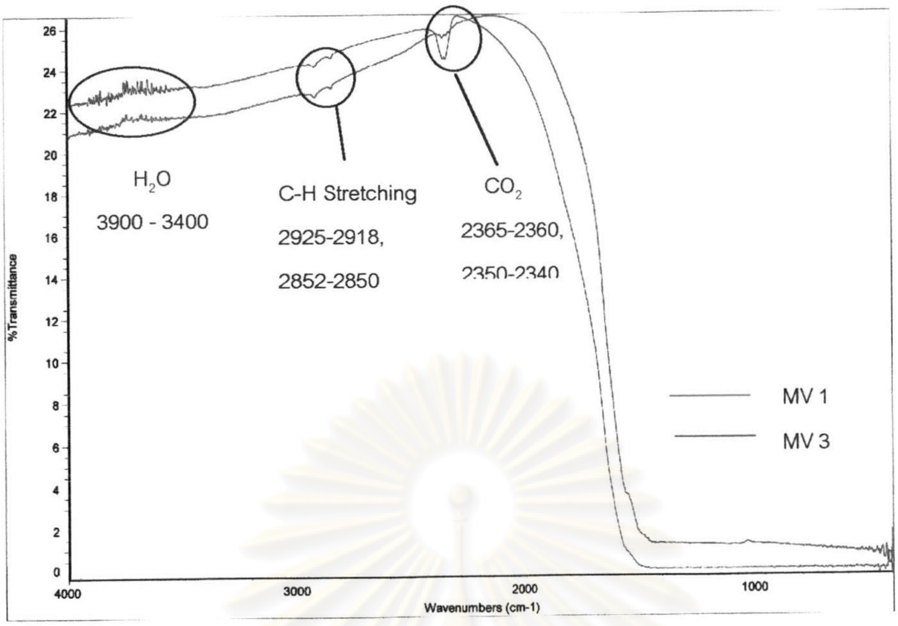

Figure 4.16 FTIR Spectra of unheated medium violet sapphires

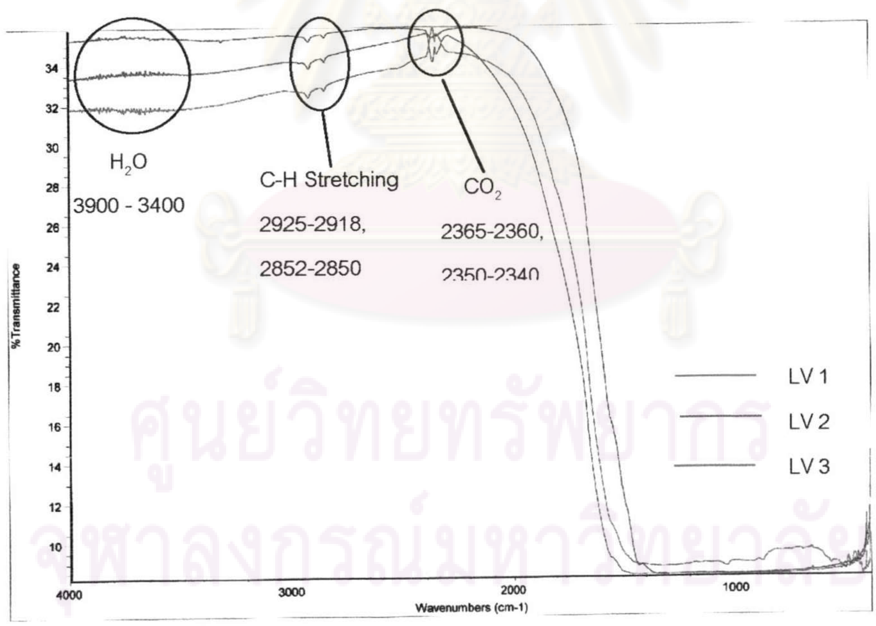

Figure 4.17 FTIR Spectra of unheated light violet sapphires

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