

Spectroscopic properties for identifying sapphire samples from Ban Bo Kaew, Phrae Province, Thailand

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Abstract. Gemstone commercial is a high revenue for Thailand especially ruby and sapphire. Moreover, Phrae is a potential gem field located in the northern part of Thailand. The studies of spectroscopic properties are mainly to identify gemstone using advanced techniques (e.g. UV-Vis-NIR spectrophotometry, FTIR spectrometry and Raman spectroscopy). Typically, UV-Vis-NIR spectrophotometry is a technique to study the cause of color in gemstones. FTIR spectrometry is a technique to study the functional groups in gem-materials. Raman pattern can be applied to identify the mineral inclusions in gemstones. In this study, the natural sapphires from Ban Bo Kaew were divided into two groups based on colors including blue and green. The samples were analyzed by UV-Vis-NIR spectrophotometer, FTIR spectrometer and Raman spectroscopy for studying spectroscopic properties. According to UV-Vis-NIR spectra, the blue sapphires show higher $\text{Fe}^{3+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ absorption peaks than those of green sapphires. Otherwise, green sapphires display higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ absorption peaks than blue sapphires. The FTIR spectra of both blue and green sapphire samples show the absorption peaks of $-\text{OH}$, $-\text{CH}$ and CO_2 . The mineral inclusions such as ferrocolumbite and rutile in sapphires from this area were observed by Raman spectroscopy. The spectroscopic properties of sapphire samples from Ban Bo Kaew, Phrae Province, Thailand are applied to be the specific evidence for gemstone identification.

1. Introduction

Ban Bo Kaew is a sapphire potential area, located in Phrae Province, Northern Thailand, which related to basaltic rock [1]. Sapphire is an inorganic mineral consisting of aluminium oxide (Al_2O_3) and other trace elements, for example, Fe, Ti, Cr, etc. There are various colors of Phrae sapphire including green, black and blue.

The colors of sapphire are mainly caused by an interaction of trace elements. The blue color of blue sapphire predominantly causes by the defected-color center of Fe^{3+} and Ti^{4+} mixed acceptor states [2]. Moreover, the intervalence charge transfer process (IVCT) between Fe^{2+} and Fe^{3+} as trace elements in sapphire structure also helpful represents blue color. Some Fe^{3+} ions replacing some Al^{3+} ions cause yellow color. In addition, the combination of blue and yellow coloration produces green color [3]. Some mineral inclusions can be applied to indicate the sapphire origin. For instance, iron-oxide mineral inclusions (e.g. hematite, goethite etc.) in sapphires are mainly found in sapphire from the basaltic origin [4].

Fourier transform infrared (FTIR) spectroscopy is a technique to study the functional groups on the sapphire samples. UV-Vis-NIR spectrophotometry is the analysis to detect the absorption peaks of

trace elements which can be applied to study the cause of color in minerals. Raman spectroscopy shows the specific Raman scattering of each sample to indicate the mineral inclusions in the gemstone.

In this study, the spectroscopic properties for sapphires identification were measured by UV-Vis-NIR spectrophotometer, FTIR spectrometer, and Laser Raman spectroscopy.

2. Experiment

Blue and green sapphire samples were collected from Ban Bo Kaew, Phrae Province, Thailand as shown in figure 1. The samples were cut and polished for preparing to spectroscopic experiments. FTIR spectra of the samples were carried out by FTIR spectrometer (NEXUS 470 model) at Department of Physics, Faculty of Science, Kasetsart University in the range of 400 cm^{-1} to 4000 cm^{-1} with 32 numbers of scan and 4 cm^{-1} spectral resolution. UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 900 model) at Department of Earth Sciences, Faculty of Science, Kasetsart University have recorded the absorption spectra from 200 nm to 1400 nm. The mineral inclusions in sapphire samples were observed by Nikon gemological microscope on the dark filed illuminator with Dino-eye microscope eye-piece camera (AM423x model). Raman spectroscopy (Nicolet 6700 Model) at the Gem and Jewelry Institute of Thailand (GIT) was applied to indicate the mineral inclusions. UV-Vis-NIR spectra and FTIR spectra of sapphire samples were undergone normalization and background subtraction process by Igor Pro software to compare the absorption peaks among blue and green sapphire samples.



Figure 1a. Blue sapphire sample from Ban Bo Kaew, Phrae Province, Thailand.



Figure 1b. Green sapphire sample from Ban Bo Kaew, Phrae Province, Thailand.

3. Results and discussion

There are the internal features of sapphire samples showing the mineral inclusions such as ferrocolumbite (figure 2a), rutile (figure 2b), zircon and feldspar.



Figure 2a. Ferrocolumbite mineral inclusion (60x magnification).



Figure 2b. Rutile mineral inclusion (40x magnification).

Typically, the mineral inclusions of sapphire samples from Ban Bo Kaew were identified by Raman spectroscopy as ferrocolumbite, rutile, zircon, and feldspar. These mineral inclusions are consistent with GIT database as shown in figure 3. For rutile mineral inclusion in a blue sapphire sample from this area, it could be observed that this rutile inclusion contains with high iron oxide showing as iron stain caused by the weathering process.

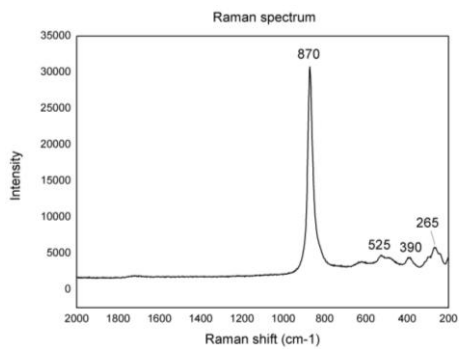


Figure 3a. Raman spectrum of ferrocolumbite in sapphire samples.

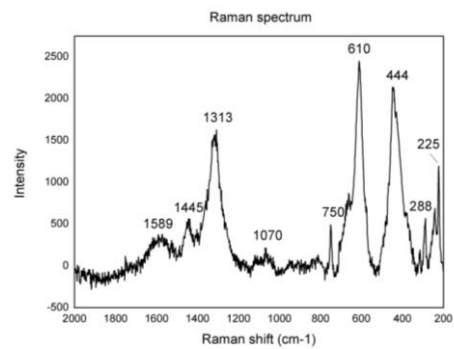


Figure 3b. Raman spectrum of rutile in sapphire samples.

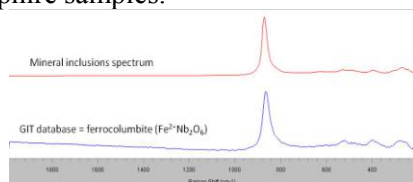


Figure 3c. Raman spectrum of ferrocolumbite in sapphire samples compared to GIT database.

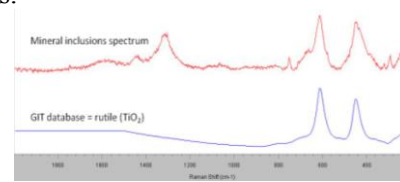


Figure 3d. Raman spectrum of rutile in sapphire samples compared to GIT database.

The FTIR spectra of both blue and green sapphire samples from Ban Bo Kaew deposit display the similar absorption peaks of -OH at 3309 cm^{-1} , -CH at 2925 and 2855 cm^{-1} and absorption of CO_2 at 2345 cm^{-1} [5] as shown in figure 4. These functional groups are the significant absorption peaks evidencing to the unheated natural sapphires.

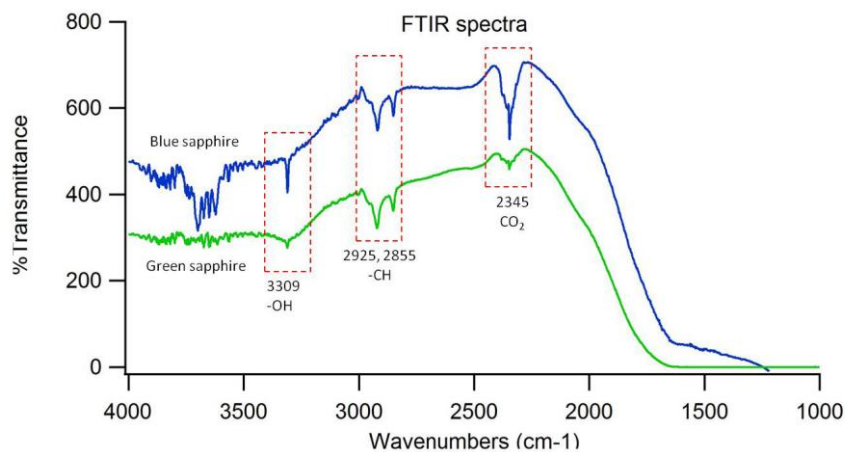


Figure 4. FTIR spectra of blue and green sapphire samples from Ban Bo Kaew, Phrae Province.

UV-Vis-NIR spectra of sapphire samples from this area show the absorption peaks of $\text{Fe}^{3+}/\text{Fe}^{3+}$ at 377 nm , Fe^{3+} at 388 nm , and $\text{Fe}^{3+}/\text{Fe}^{3+}$ at 450 nm . For mix acceptor states, $\text{Fe}^{3+}/\text{Ti}^{4+}$ are found at 575 nm , and 710 nm and $\text{Fe}^{2+}/\text{Fe}^{3+}$ pairs at 860 nm corresponding to other researches [2] as shown in figure 5. The intensity of each peak is related to the cause of colors in sapphire samples. For blue sapphire, it shows high intensity of $\text{Fe}^{3+}/\text{Ti}^{4+}$ peaks and very low $\text{Fe}^{3+}/\text{Fe}^{3+}$ peaks whereas green sapphire shows high $\text{Fe}^{3+}/\text{Fe}^{3+}$ and some $\text{Fe}^{3+}/\text{Ti}^{4+}$ peaks as the mixture between yellow and blue to produce green color. In addition to $\text{Fe}^{3+}/\text{Fe}^{3+}$ showing different frequencies (377 nm , 450 nm), it could be caused by the homonuclear intervalence charge transfer between Fe^{3+} pairs. One of Fe^{3+} ion was

located in ground state and another Fe^{3+} ion was initially found in excited state and the electron particle could be systematically moved between both Fe^{3+} pairs [6]. Furthermore, the $\text{Fe}^{3+}/\text{Ti}^{4+}$ mix acceptor states also show two different frequencies (575 nm, 710 nm) because Fe^{3+} and Ti^{4+} were located in ground state. Therefore, it is a defect color center and it requires one electron from valence band to create as $\text{Fe}^{3+}/\text{Ti}^{3+}$ or $\text{Fe}^{2+}/\text{Ti}^{4+}$ for stability in the structure referring to [2].

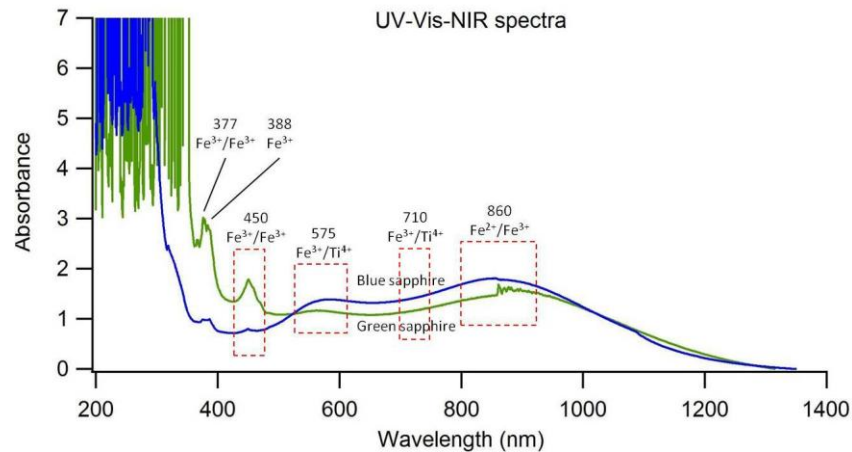


Figure 5. UV spectra of blue and green sapphire samples from Ban Bo Kaew, Phrae Province.

4. Conclusion

The sapphires from Ban Bo Kaew deposits show blue and green colors. The predominantly mineral inclusions of sapphire from this area are ferrocolumbite, zircon, feldspar, and rutile with high iron oxide impurity. The spectroscopic properties including FTIR, UV-Vis-NIR and Raman spectra could be applied to indicate the geographical origin of sapphire samples from Ban Bo Kaew, Phrae Province, Thailand and to create the database of sapphire from Phrae Province.

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