

GEMOLOGICAL AND SPECTROSCOPIC PROPERTIES OF BLUE SAPPHIRES FROM DEN CHAI DISTRICT, PHRAE PROVINCE

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Abstract

The total of 30 rough samples of very dark, low transparency, or uneven-coloured blue sapphire from basaltic affiliated gem field of Den Chai district, Phrae province, Thailand, were studied to characterize the gemological and spectroscopic properties. The specific gravity ranges from 3.86 to 4.20 (average 3.97) and refractive index are $n_e = 1.762\text{--}1.768$ and $n_o = 1.770\text{--}1.775$ respectively. Inclusions are negative crystals, gas bubbles, fingerprint, rhombohedral parting and mineral inclusions. Some of them show a characteristic fixed six-rayed star-shaped growth zoning or Trapiche. Spectroscopic methods using UV-VIS-NIR analysis shows prominent peaks of Fe^{3+} in the ultraviolet region at 376 nm, as well as in the visible region at 450 nm of $\text{Fe}^{3+}/\text{Fe}^{3+}$ pair. The absorption band of $\text{Fe}^{2+}/\text{Ti}^{4+}$ Intervalence Charge Transfer (IVCT) between 550 and 750 nm and increasing absorption of $\text{Fe}^{2+}/\text{Fe}^{3+}$ IVCT towards the near infrared (maximum in the region between approximately 870 to 890 nm) which is typically found in sapphire from basaltic sources. The FTIR results show C/O, C/H and Ti/OH absorption peaks at 2350, 2846, 2915, and 3309 cm^{-1} respectively. The chemical composition analysis using PIXE shows relatively high FeO content and traces of Ti, V, Cr, and Ga that indicates the basaltic origin of these sapphires.

Keywords: Corundum, sapphire, gem deposit

Introduction

Blue sapphire is one of the classic precious gemstones of all time in corundum variety. The corundum deposits of Thailand were found in great abundance in the northern, northeastern,

eastern and western part of the country. Among these deposits, Phrae - Sukhothai is accounted for 10–15% of the overall corundum source of Thailand⁶ and is the only one

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economic deposit in the north (Saraphanchotwitthaya, 2008).

By comparison to the other gem fields in Kanchanaburi, Chantaburi and Trat where are huge reservation and suitable for large machinery mining, the localities of Phrae-Sukhothai are smaller scales and only suitable for primitive pit or small tool mining. However, during the last 2 decades, many specialists and reports reveal that most corundum deposits in Thailand are decreasing and really finished completely. Recently, the Department of Mineral Resources geologist reports the machinery scale corundum mining in Phrae-Sukhothai is on operation. This is a pleasure that there still has high potential corundum production in northern Thailand and may be the clue of new corundum deposit (Saraphanchotwitthaya, 2008).

The Phrae gem deposits are located in Den Chai district, Phrae province. The geology of the area is of Carboniferous-Permian rocks overlain by basalt flows. All of the deposits in Phrae province occur in stream alluvial. The thickness of the corundum-bearing layer varies from 50 cm to 1 m. The majority (around 90%) of Phrae-Sukhothai sapphire occurs in various shades of blue with a small amount of green, yellow and star sapphire. Ruby is rarely found (Vichit, 1992).

Methods

The total of 30 rough samples of low quality, very dark, low transparency, or uneven-coloured blue sapphire (0.39–6.27 ct) from basaltic affiliated gem field of Den Chai district, Phrae province, Thailand, were studied to characterize the gemological and spectroscopic properties using standard gemological instruments to determine their hydrostatic specific gravity, and refractive indices. Internal characteristics were examined with a gemological microscope.

Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra was recorded over an interval of 250–1500 nm using a Hitachi U4001 spectrophotometer, with a slit width of 2 mm and a scan speed of 300 nm/min. Infrared spectra was collected using a Bruker Tensor 27 FTIR spectrometer, with a standard resolution of 4 cm⁻¹, and 120 scans per sample.

Proton-induced X-ray emission (PIXE) was used for elemental analysis on five samples using two MeV protons produced from the 2.5 MV Van de Graaff accelerator at the Department of Physics, Chiang Mai University. The proton beam was collimated with a set of diaphragms that gave a beam spot of 4 mm diameter at the target position. The 13 µm-thick Beryllium window and a Hydrogen detector were used for X-ray detection at an angle of 45° to the beam and counting time for each sample was 400 sec.

Results and Discussion

The specific gravity of blue sapphire samples range from 3.86 to 4.20 (average 3.97) and refractive index are $n_e = 1.762$ – 1.768 and $n_o = 1.770$ – 1.775 respectively. The gemological microscope was used to identify the inclusions and found negative crystals, gas bubbles, fingerprint, rhombohedral parting and mineral inclusions. Some of them show a characteristic fixed six-rayed star-shaped growth zoning or Trapiche and dark blue core.

Spectroscopic methods using UV-VIS-NIR analysis shows prominent peak of Fe³⁺ in the ultraviolet region at 376 nm, as well as in the visible region of Fe³⁺/Fe³⁺ pair at 450 nm (Emmett and Douthit, 1993). The absorption band of Fe²⁺/Ti⁴⁺ Intervalence Charge Transfer (IVCT) between 550 and 750 nm and the increasing absorption of Fe²⁺/Fe³⁺ IVCT towards the near infrared (maximum in the region between approximately 870 to 890 nm) (Emmett and Douthit, 1993) which cause blue colouration are typically found in sapphire from basaltic source (Phlayrahan *et al.*, 2014) (Figure 1). The FTIR spectra of blue sapphire samples show the C/O, C/H and Ti/OH absorption peaks at 2350, 2846, 2915, and 3309 cm⁻¹ (Phlayrahan *et al.*, 2014) due to charge compensation process (Schwarz *et al.*, 1996) in high iron (Fe) content which is typically found in Thai blue sapphire (Saraphanchotwitthaya, 2008) (Figure 2).

Five samples were analyzed for the chemical composition using PIXE. These elements include FeO, TiO₂, Ga₂O₃, Cr₂O₃, and V₂O₃. The detection of each element is

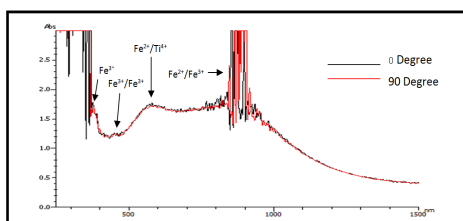


Figure 1. UV-VIS-NIR absorption spectrum pattern of blue sapphire from Den Chai district, Phrae province

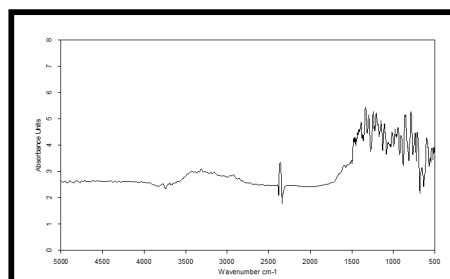
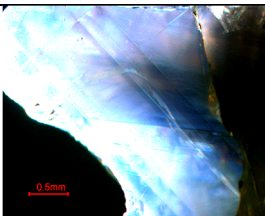
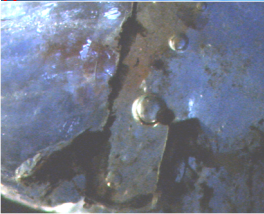
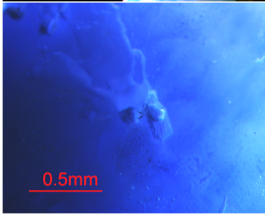
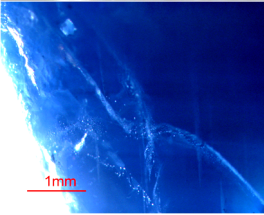
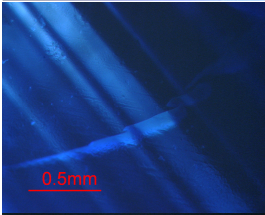
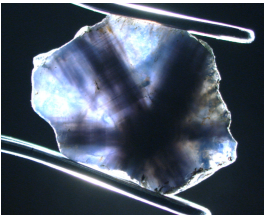
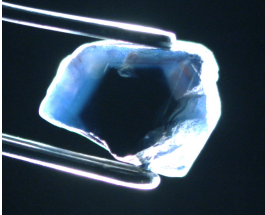


Figure 2. Infrared spectrum pattern of blue sapphire from Den Chai district, Phrae province

Table 1. shows example inclusions found in blue sapphire samples

Inclusions	Pictures	Inclusions	Pictures
Negative crystal		Rhombohedral Parting	
Gas bubble		Mineral inclusions	
Fingerprint		Colour zoning	
Trapiche		Dark blue core	

0.0003, 0.0004, 0.0004, 0.0006, and 0.0006. PIXE analysis reveals high content of FeO in all samples which range from 0.473 wt% to 1.2928 wt% (average 1.057 wt%). The highest

content (1.2928 wt%) belongs to Phr 02 which shows dark blue core. TiO₂ ranges from 0.0446 wt% to 1.4449 wt% (average 0.3898 wt%). The highest TiO₂ content (1.4449 wt%) belongs to

Table 2. shows summary properties of blue sapphire samples examined in this study

Samples	Weight	Specific gravity	Refractive Index	Main Inclusions
Phr 01	3.01	3.86	1.762-1.770	Colour zoning
Phr 02	4.72	3.96	1.762-1.770	Colour zoning,
Phr 03	5.25	3.89	1.768-1.775	fingerprint
Phr 04	2.07	3.97	1.762-1.770	Fracture
Phr 05	2.43	3.97	1.762-1.768	fingerprint
Phr 06	1.84	4.00	1.762-1.770	Colour zoning
Phr 07	1.52	3.98	1.762-1.769	Fingerprint, bubble
Phr 08	1.04	3.93	1.762-1.770	Fingerprint
Phr 09	1.15	4.00	1.764-1.772	Colour zoning
Phr 10	1.72	3.97	1.763-1.771	Fingerprint
Phr 11	1.67	3.86	1.762-1.770	Colour zoning, fingerprint
Phr 12	2.24	3.87	1.762-1.770	Colour zoning
Phr 13	3.90	3.96	1.762-1.770	Fingerprint
Phr 14	1.61	3.92	1.762-1.770	Colour zoning, fingerprint
Phr 15	1.23	3.98	1.767-1.772	Colour zoning, fingerprint
Phr 16	2.38	3.82	1.762-1.770	Fingerprint
Phr 17	3.01	3.98	1.762-1.770	Negative crystal
Phr 18	2.67	3.94	1.762-1.770	Colour zoning, fingerprint
Phr 19	1.75	3.96	1.763-1.771	Rhombohedral parting
Phr 20	2.21	3.93	1.763-1.771	Colour zoning
Phr 21	1.31	3.93	1.762-1.768	Colour zoning
Phr 22	2.22	3.86	1.762-1.768	Colour zoning
Phr 23	1.20	3.88	1.763-1.771	Colour zoning
Phr 24	6.27	3.97	1.768-1.775	Fingerprint
Phr 25	1.53	4.20	1.762-1.770	Colour zoning
Phr 26	2.01	3.96	1.767-1.773	Colour zoning
Phr 27	0.39	4.04	1.763-1.771	Fingerprint
Phr 28	2.07	3.97	1.762-1.768	Fingerprint
Phr 29	2.44	3.94	1.762-1.770	Fingerprint
Phr 30	1.92	3.96	1.768-1.775	Colour zoning

Table 3. shows elemental analysis in some samples using PIXE method

Samples	FeO(wt%)	TiO ₂ (wt%)	Ga ₂ O ₃ (wt%)	Cr ₂ O ₃ (wt%)
Phr 01	0.4760	0.1402	0.0252	0.008
Phr 02	1.2928	0.1028	0	0.01
Phr 03	1.0827	0.0446	0.0114	0
Phr 04	0.4763	1.4449	0	0.077
Phr 05	0.7953	0.2165	0.0359	0

Phr 04 which shows Trapiche. Ga₂O₃, Cr₂O₃, and V₂O₃ contents show no significant in difference. Ga₂O₃ varies from under detection limit to 0.0359 wt%, Cr₂O₃ ranges from under detection limit to 0.077 wt% and V₂O₃ varies from under detection limit to 0.0405 wt%.

Chemical composition analysis using PIXIE also confirmed relatively high FeO and

TiO₂ content with the absorption spectra pattern from UV-VIS-NIR method that shows absorption peaks of Fe²⁺/Fe³⁺ between 870 and 890 nm and Fe²⁺/Ti⁴⁺ between 550 and 750 nm. FTIR result also confirmed with the TiO₂ chemical composition analysis that shows peak of Ti/OH at 3309 cm⁻¹. The rather high Fe content as well as traces of Ti, V, Cr, and Ga can also

confirmed the basaltic origin of these sapphires (Satitkune *et al.*, 2014) (Table 3).

Conclusions

The gemological properties of 30 blue sapphire samples from Den Chai District, Phrae province are similar to blue sapphires from other basaltic origin. Gemological microscope were used and found inclusions in all samples. Typical inclusions are negative crystals, gas bubbles, fingerprint, rhombohedral parting and mineral inclusions. Some of them show a characteristic fixed six-rayed star-shaped growth zoning or Trapiche and dark blue core.

Based on spectroscopic analysis, samples in this study show prominent peaks in the ultraviolet region at 376 nm of Fe^{3+} , as well as in the visible region at 450 nm of $\text{Fe}^{3+}/\text{Fe}^{3+}$ pair. The absorption bands of $\text{Fe}^{2+}/\text{Ti}^{4+}$ IVCT between 550 and 750 nm and increasing absorption of $\text{Fe}^{2+}/\text{Fe}^{3+}$ IVCT towards the near infrared between approximately 870 to 890 nm are related to the absorption peak in mid-infrared range at 3309 cm^{-1} in FTIR due to charge compensation process in high iron (Fe) content which is typically found in Thai blue sapphire (Saraphanchotwittaya, 2008).

Chemical composition analysis reveals relatively high content of FeO and TiO_2 in all samples. The highest FeO content is the dark

blue core sample and the highest TiO_2 content is the Trapiche sample. The rather high Fe content as well as traces of Ti, V, Cr, and Ga can also confirmed the basaltic origin of these sapphires (Satitkune *et al.*, 2014).

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