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EXPERIMENTAL DISSERTATION

CAUSES OF COLOR IN SPINEL FROM MYANMAR

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CAUSES OF COLOR IN SPINEL FROM MYANMAR

Introduction

Spinel is a fascinating and beautiful gem that has been one of the most valued gemstones for a long history. It has long been undervalued even there are many famous large spinels in existence; however it was long believed and has a confusion with another dominant red gemstone to be 'red corundum' or 'Ruby' , for instance those royal jewels from England and Russia in an ancient time known as 'Balas ruby' and so-called 'Black Prince's ruby'. Spinel was not recognized as a separate gem species until the 1800s. (My personal GIA colored stone course material, 2012) Over a period of time, its popularity had suffered as a result of many factors, including its classification as "semi-precious". More recently though, spinel has been making a strong popularity and it is once again on the rise. In the market, some spinel colors are more rare and valuable than others. In general, red spinel is the most desirable and cherished, followed by fine cobalt spinel, then vibrant hot-pink and vivid orange stones. Violet and bluish purple to purple, or lavender stones tend to be less attractive, and less in demand than other rarer colors. Since color is one of the most important factors to grade its quality, it is essential to understand the causes of colors and the treating process that enhance the appearance and result in the increase value.

This experimental report aims to study the causes of color which I was always curious and ask myself where these various spinel colors come from and also the characteristic properties of spinel coming from Myanmar. The experiment is performed by using standard gemological instruments and advanced instruments. This project, I select color to be the variation because its difference hue is the main purpose of this study.

1. Spinel information

Spinel are any of a class of minerals of general formulation ($A^{2+}B_2^{3+}O_4^{2-}$) in the isometric system and lacks pleochroism. The name Spinel is from the Latin word "*spina*" which means spines refer to the stone's needle-like formations. (Houston, 2012) Its characteristic crystal habit is an octahedron, and well-formed crystals are fairly common. Spinel can form flatten twin crystal that look fundamentally different from single octahedron crystals. The spinel used in jewelry is just part of a group of spinel minerals that share the same crystal structure. For normal spinel, the structures are usually cubic close-packed oxides with eight tetrahedral and four octahedral sites per formula unit. The tetrahedral spaces are smaller than the octahedral spaces. B^{3+} ions occupy half the octahedral holes, while A^{2+} ions occupy one-eighth of the tetrahedral holes. Spinel is classified as normal and inverse

spinel, depending on where the more abundant of the cations is housed. If it occurs in the octahedral site, it is classified as normal. If it is equally split between octahedral and tetrahedral sites, it is inverse (Klein, 2012). Mineral spinel MgAl_2O_4 has a normal spinel structure. (See figure 1)

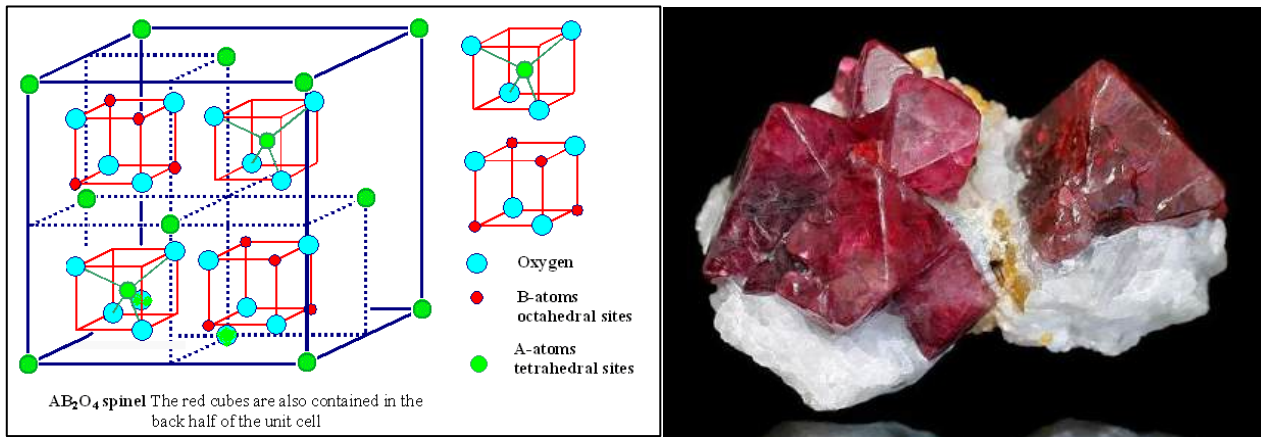


Figure 1 : Schematic of spinel structure (Deer, Howie and Zussman, 1996)
(https://nptel.ac.in/courses/113104005/lecture3/3_9.htm)

1.1 Spinel properties

Physical Properties of Spinel	
Chemical Classification	Oxide
Color	Colorless, pink, red, orange, blue, purple, brown, black
Streak	Colorless , Greyish white
Luster	Vitreous
Diaphaneity	Transparent to translucent
Cleavage	None
Fracture	Irregular/Uneven, Splintery, Conchoidal
Mohs Hardness	7.5 to 8
Specific Gravity	3.5 to 4.1 (Increase with Iron and Zinc content) (Mindat)
Diagnostic Properties	Hardness, octahedral crystals, vitreous luster
Chemical Composition	MgAl_2O_4
Tanacity	Brittle

Table 1: Physical Properties of Spinel

Optical Properties of Spinel	
Crystal System	Isotropic
Refractive index	1.719
Pleochroism	Non-pleochroic

Table 2: Optical properties of Spinel

Polymorphism & Series: Forms 3 series, with magnesiochromite, with gahnite, and with hercynite.

Occurrence: Spinel is a common high temperature mineral in metamorphic rocks and in alumina-rich xenoliths. It occurs, often with forsterite and diopside, in contact metamorphosed limestones, and it is found in a similar association in regionally metamorphosed limestones, where it may occur also with chondrodrite, phlogopite, and calcite. In thermally metamorphosed argillaceous rocks poor in SiO_2 , spinel or pleonaste may form, often with cordierite or orthopyroxene (Deer et al, 1975). Spinel has long been found in the gemstone-bearing gravel of Sri Lanka and in limestones of the Badakshan Province in modern-day Afghanistan and Tajikistan; and of Mogok in Burma. Recently gem quality spinels also found in the marbles of Luc Yen (Vietnam), Mahenge and Matombo (Tanzania), Tsavo (Kenya) and in the gravels of Tunduru (Tanzania) and Ilakaka (Madagascar). Spinel is found as a metamorphic mineral, and also as a primary mineral in rare mafic igneous rocks; in these igneous rocks, the magmas are relatively deficient in alkalis relative to aluminium, and aluminium oxide may form as the mineral corundum or may combine with magnesia to form spinel. This is why spinel and ruby are often found together. The spinel petrogenesis in mafic magmatic rocks is strongly debated, but certainly results from mafic magma interaction with more evolved magma or rock (e.g. gabbro, troctolite)

1.2 Spinel colors

Pure spinel is colorless which contains ideal composition of 28.2% MgO and 71.8% of Al_2O_3 . (Klein, 2002) Transparent, gem quality spinels are almost always contains small amount of Fe, Zn, Mn, Cr, V, Ni, Co, Cu, Ti and Ge (Johnson et al, 1996).



Figure 2: Their colors result from variations in trace element content. Chromium produces red and pink hues, iron produces blue, and a mixture of chromium and iron makes gems purple or violet.

Spinel also offers a wide range of hues from orange to intense “stoplight” red, vibrant pink, and all shades between purple, blue, and violet to bluish green. (See figure 2) Intense reds and pinks are caused by traces of chromium. (See figure 3) Orange and purple stones own their color to a mixture of iron and chromium. Spinel colored only by iron tends to be a violet or grayish violet of low saturation. While those lavender stones can be attractive, they are rarely of fine quality. Quality of fancy spinels depends on the richness of the color (Webster, 1994; Shigley et al, 1990).



Figure 3: In spinel, the higher the chromium content, the stronger the red hue.
(<https://www.gemsociety.org/article/spinel-jewelry-and-gemstone-information/>)

Causes of spinel color (Nassau, 1978)

Causes of spinel color caused by the transition elements that enter during the crystal growth process that varies the spinel color. Fundamentally, Spinel color is created by 3 transition metals: iron, chromium and cobalt. These metal ions replace the colorless magnesium ions in gem Spinel. Iron creates blue and gray colors, and iron is the source of the gray cast that is ubiquitous in Spinel. Cobalt creates only blue color. Red and pink color is created when chromium ions replace the aluminum ions. Combinations of these 3 metals in varying ratios and concentrations produces non-primary colors such as purple and orange. Intervalence charge transfer between ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) contributes green color (D'Ippolito et. al., 2015) The color mechanism can be studied by using spectroscopy instruments and explained by the theory of crystal field theory and/or charge transfer transition. For spinel, causes of color (Fritsch et al, 1987) can be summarized as below;

- red to pink: Cr^{3+} in octahedral coordination (Vogel, 1934: Anderson 1954-1955)
- violet to purple: Cr^{3+} in octahedral coordination and Fe^{2+} in tetrahedral coordination (G. Rossman)

- Cobalt blue: Co^{2+} and Fe^{2+} in tetrahedral coordination (Shigley and Stockton, 1984)
- green: Fe^{2+} in tetrahedral coordination
- orange/yellow: Fe^{3+} and Cr^{3+} in octahedral coordination
- black: complete Fe^{2+} in tetrahedral coordination

1.3 Spinel major deposits and Myanmar localities

Besides historical sources like Sri Lanka and Afghanistan, the Pamir Mountains in the former of Soviet republic of Tajikistan in Central Asia produce large and fine spinel crystals. Other places, like Myanmar's Mogoke region, which is very famous for very fine rubies, also produced equally exceptional fine red and pink spinel, as well as other colors. Some Burmese deposits are known for the finest "hot pink" and red spinel. As well as in other sources such as Vietnam's Luc Yen Valley and Pakistan's Hunza Valley. Spinel and corundum occur together in marble and are found together in nearby alluvial deposits. In some places, spinel is more plentiful than ruby. Moreover, Africa has great potential to produce spinel. Many red spinels are found along with rubies in Tanzania's Morogoro region. Even the Ilakaka area of southern Madagascar is well-known for blue and fancy colored corundum; it also produces a range of different colored spinel, mostly purplish violet to bluish violet with high proportion of violet to grayish violet and lavender. Only a small percentage; perhaps as low as 5% are red, pink and orange. Other significant deposits of spinel have also been found in Cambodia, Thailand, Australia, Brazil, Nepal, Nigeria, Tanzania and the U.S. (bremerjewelry, 2017)



Figure 4: Major commercial sources of spinel is commonly found together with corundum in Myanmar, Sri Lanka, and Vietnam. Additionally, many famous large spinels come from Tajikistan. (Photo by Peter Johnston © GIA) (scanned)

From GIA peer reviewed article by Vincent Pardieu, he concludes the spinel sources from oldest to newest source, they are:

1. Badakhshan: This region is located between Afghanistan and Tajikistan, along the famed Silk Road. It has been a source of spinel since about the 10th century.
2. Myanmar (formerly Burma): Spinel has been found in both the Mogok Valley and the Namya area (See figure 5 and 6)



Figure 5 : Overview of the spinel mining operation at Man Sin, Myanmar. Photo by Vincent Pardieu, © GIA.

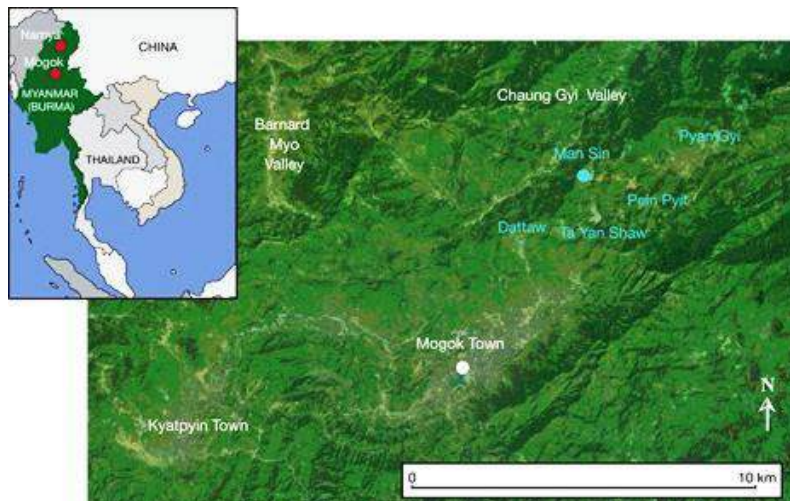


Figure 6: Spinel deposits in Myanmar. © GIA

3. Vietnam: Red and blue spinel, along with ruby, was discovered in the Luc Yen district of northern Vietnam in 1988 (Long, 2013). (figure 7)



Figure 7 : Gemstones mining in the Luc Yen area of Vietnam's Yen Bai province © GIA.
(<http://www.giathai.net/gemstone-mining-luc-yen-vietnam/>)

4. Tanzania: Red spinel was discovered near Mahenge and in the Uluguru Mountains of the Morogoro province in the late 1980s and around Tunduru after 1994.

1.4 Spinel enhancement

As demand has grown and top-quality gems are scarce, it is inevitable and not surprising that attempts are now being made to improve certain colors of spinel. Some treatments are starting to be encountered (Robertson, 2012). Christopher P. Smith (2012) has noticed a general increase in the attempts to improve spinel quality and color, utilizing a variety of treatment practices.

1.4.1 Clarity enhancement

Fissure filling is a common practice to reduce their visibility and improve the apparent clarity. Oils and other materials may be introduced into a fissure, by making the fissure less reflective and reducing its visibility. Detection of clarity enhancement is most readily accomplished with magnification. Iridescence is generally visible along a filled fissure. In addition, areas of higher relief may also be evident where the filling of a fissure was incomplete or the filler has been partially removed.

1.4.2 Heat treatment

Since 2005, the industry started to talk and notice that heating was being used to improve the quality of some spinels from Tanzania. As a result, research was conducted that demonstrated how indeed heating could be used to alter the quality of some spinels

(Saeseaw et.al., 2009). The researchers first concluded that this treatment was not being performed to improve color, since their experiments showed either little to no color modification or a less desirable color resulted from the heating. they later found that the transparency of certain spinels could be significantly improved by heating at temperatures between approximately 950 °C - 1150 °C. The subjected heating temperature is varying from relatively low to very high up to 1700 °C

2. SAMPLING



Figure 8: Spinel samples (group left) were selected to be representatives from pink, red, orange, violet to purple parcel (group right). The stones are cabochon and all of them are oval. They are rather small, approximately 2 to 6 mm in diameter. Table 3 shows the overview samples selected in this study.

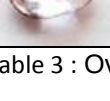
Sample Code	Photo	Color	Weight (cts.)	Dimension (L*W*H) mm.	Color distribution
PD4		dark blue	0.775	5.74 x 5.54 x 2.95	even
PD5		dark purplish blue	0.670	5.35 x 5.39 x 2.81	uneven
PD6		light bluish purple	0.542	5.66 x 5.15 x 2.13	uneven
PD7		purple	0.643	5.23 x 5.02 x 2.85	uneven
PD8		red	0.707	5.08 x 4.52 x 3.23	even
PD9		pink	0.682	5.81 x 5.04 x 2.74	even
PD10		brownish pink	0.583	5.37 x 4.88 x 2.58	uneven
PD11		orange	0.569	5.56 x 5.03 x 2.47	even
PD12		Light pinkish orange	0.561	5.32 x 4.77 x 2.50	uneven
PD13		pinkish purple	0.670	5.42 x 5.37 x 2.64	uneven
PD14		light bluish grey	0.608	5.48 x 4.95 x 2.61	even
PD15		light greyish pink	0.653	5.73 x 4.44 x 3.00	uneven

Table 3 : Overview samples PD4-PD12 selected in this experiment.

The material obtained for this study was given as gift from a Myanmar friend during his visit in Bangkok in 2017. I was assured that the material is untreated and come from Myanmar because he bought the spinel rough and cut them by himself. As a close friend, he has always been honest to me and the internal inclusions are corresponding to the characteristic of spinel from this geographical origin.

3. Experimental methods

To study these colorful spinels, different instruments were used from the classical gemological instruments to more advanced and sophisticated equipment.

3.1 Basic instruments

First, basic gemological instruments were used including hydrostatic weighing balance, refractometer, polariscope, microscope, hand-held diffraction grating spectroscope, and ultra-violet cabinet (LWUV – at 365 nm, and SWUV – at 254 nm; to observe, the samples were placed at approximately 7 centimeters from the bulbs).

3.2 Spectroscopy

3.2.1 UV – Vis – NIR

UV-Vis-NIR spectroscopy has been used to determine the origin of color in the spinel. The spectra were recorded in absorbance on a Perkin Elmer Lambda 1050. (figure 9) Spectral resolution is 2 nm. Photomultiplier tubes (PMT) detector is set with a slit of 1 nm (response 0.20 s and an auto gain) from 350 to 850 nm. Indium-gallium-arsenide (InGaAs) detector is set with a slit of 2 nm (response 0.20 s and a 5 gain) from 860 to 1,800 nm. Spectra were later manually set (Excel) in absorption coefficient to allow comparison between samples.



Figure 9 : UV-Vis-NIR spectrometer at IMN

3.2.2 DFI mid laser+ (UV luminescence spectroscopy plus Raman spectroscopy)

Cr^{3+} luminescence of spinel was examined under 405 nm laser at the excitation at 50 ms and 1 averaging to observe the prominent feature resulting from the disorder rearranges some of the cations in the unit cell caused by heat treatment and synthetic materials with different processes.

3.2.3 FT Raman

Raman spectroscopy has been used to test few samples on a Bruker Alpha-FT raman. The full spectral range of $0 - 1000 \text{ cm}^{-1}$, with 4 cm^{-1} spectral resolution was used and the laser power at 20 mW and 400 scans. It did not give any useful information to this dissertation other than the gem identification and most of the tested samples are poor raman scatterer so I will not emphasize the analysis much on the report. (figure 10)

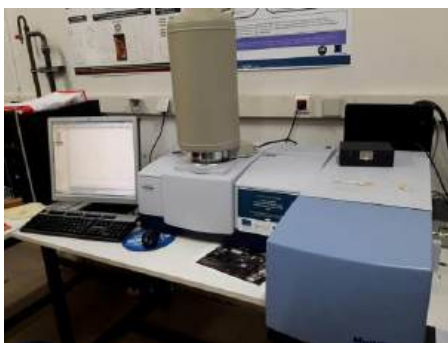


Figure 10 : Raman spectrometer at IMN

3.3 Chemical analysis

3.3.1 Scanning Electron Microscope (SEM)

To know the gemstone causes of color, it is very important to make a chemical analysis of minor and trace elements. This test was performed using the energy dispersive spectroscopy (EDS) of the scanning electron microscope (SEM) of a JEOL JSM-5800 (figure 11). The samples were prepared by metalization process. The EDS function of SEM is actually not the main purpose and not suitable technique to analysis minor and trace elements (Rondeau B., 2017, personal communication).



Figure 11 : scanning electron microscope (SEM) (left) and sample preparation for matallization method (right).

3.3.2 Energy Dispersive X-ray fluorescence (EDXRF)

To obtain more accurate minor and trace element result, I had a chance to test my samples at AIGS Laboratory in Bangkok where I am currently working. The samples were tested using Thermo Fisher (figure 12) with SSDetector and 2 mm qualimeter with spinner. The concentration unit is in oxide weight percent (% mass). Experiments were performed using energy level from 25 kV to 50kV, depending on the observed elements and the selected method (we select different filters for different energy levels)



Figure 12: EDXRF instrument at AIGS Laboratory

4. Results

4.1 Basic gemology

4.1.1 Test summary

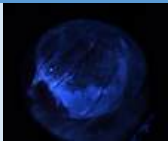
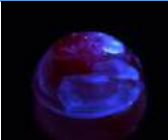
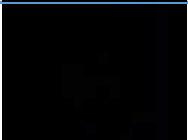
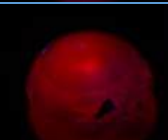
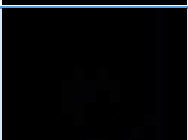
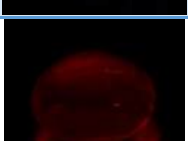
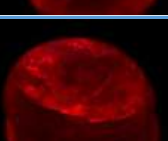
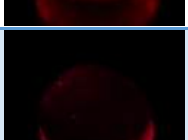
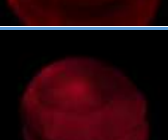
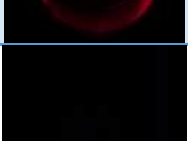
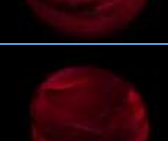
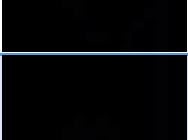
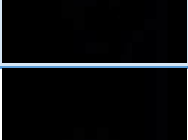
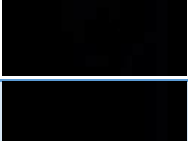
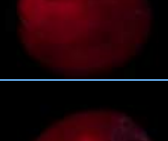
First, basic gemological tests were conducted as shown in table 4. The spot reading of the refractive index (RI) on cabochon samples are not as accurate as the faceted stones. The specific gravity (SG) varies from 3.470-3.738. The test results are consistent with spinel.

Sample	Transparency	Refractive index (SR),(spot reading)	Specific Gravity	UV Fluorescence	
				SWUV	LWUV
PD 4	Transparent	1.71 ± 0.01	3.561	inert	mod-blue
PD 5	Transparent	1.72 ± 0.01	3.577	inert	mod-red/blue
PD 6	Transparent	1.72 ± 0.01	3.738	inert	mod-red
PD 7	Transparent	1.71 ± 0.01	3.674	inert	mod-red
PD 8	Transparent	1.72 ± 0.01	3.583	inert	strong-red
PD 9	Transparent	1.71 ± 0.01	3.647	weak	strong-red
PD 10	Transparent	1.71 ± 0.01	3.470	weak	weak-red
PD 11	Transparent	1.72 ± 0.01	3.671	inert	weak-red
PD 12	Transparent	1.71 ± 0.01	3.567	inert	mod-red
PD 13	Transparent	1.70 ± 0.01	3.591	inert	mod-red
PD 14	Transparent	1.71 ± 0.01	3.589	inert	weak-red

PD 15	Transparent	1.70 ± 0.01	3.579	weak	strong-red
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Table 4: Basic gemological tests of 12 tested samples.

UV reaction to short- wave and long-wave ultraviolet

Sample code	Short Wave Ultraviolet (SWUV) 254 nm excitation			Long Wave Ultraviolet (LWUV) 365 nm excitation		
PD 4						
PD 5						
PD 6						
PD 7						
PD 8						
PD 9						
PD 10						
PD 11						
PD 12						
PD 13						
PD 14						

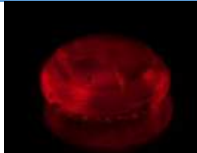
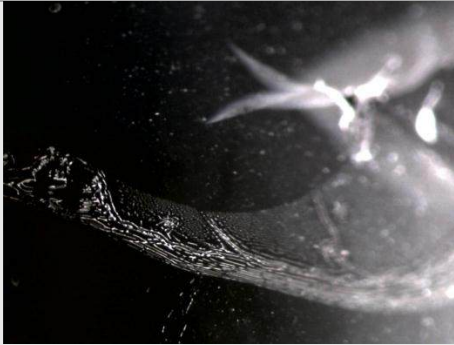
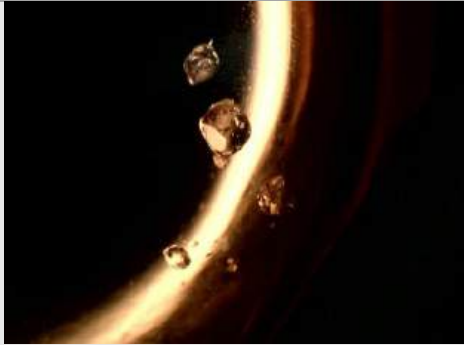
PD 15					
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Table 5: Photos of the tested samples under short and long wave UV reaction

4.1.2 Microscopic observation

Observation through a microscope at 60X to 120X magnification with Leica microscope at AIGS laboratory revealed that the inclusions are the ones typically found in natural spinel from Myanmar. No indication of synthetic inclusion was observed. The inclusions such as fissures crystals, partially healed fractures were found and the photos were taken (figure 13).

Internal Features					
		A			B
		C			D
		E			F

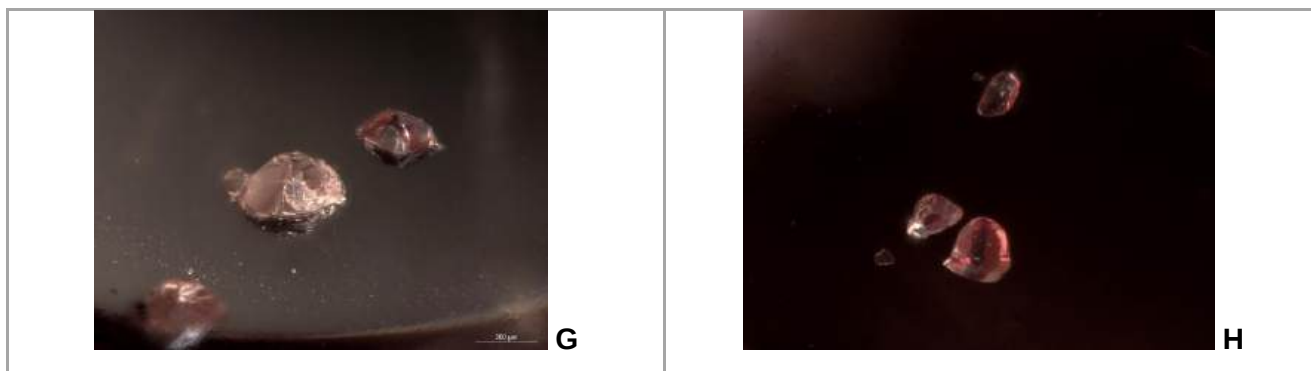


Figure 13: Internal inclusions in the tested samples are found and labeled from A to H.

A) Fissures in most tested samples (no indication of oil-filled). (Gübelin, E.J. and Koivula, J.I. , 2005)

B) A network of coarse negative crystals forms in a fingerprint pattern.

C) A group of irregular shape and various size crystals.

D) An octahedral negative crystal with oriented needles at the corners. (Gübelin, E.J. and Koivula, J.I., 2005)

E) Unaltered partially healed fractures.

F) A cluster of well-formed (might be apatite crystals).

G) Octahedral inclusions in spinel.

H) Euhedral inclusions in spinel display clear etch marks.

4.2 Spectroscopy

4.2.1 UV – Vis – NIR

The absorption curves of the different spinel colors were measured by UV-VIS-NIR spectroscopy. The origin of color is interpreted in terms of Fe^{2+} , Fe^{3+} , V^{3+} , Cr^{3+} (Schmetzer et al. (1986). Red to pink spinel shows distinct broad absorption spectra at 388 and 540 nm and has a shoulder at 415 nm which is the result of Cr^{3+} octahedral coordination (Smith et al, 2008) corresponding to the study of Bunnag and Thanasuthupitak (2003). Purple to blue spinel shows Co^{2+} absorption spectra at 550, 585, and 625 nm and Fe^{2+} absorption spectra at 370, 385, 455, 477 and 555 nm.

Four different types of UV – Vis – NIR spectrum can be identified:

1st type : Sample PD4, PD5 and PD14 share the same feature of Fe^{2+} peaks at ~ 372, 384, 458, 478 and 552 nm. (figure 14) PD6 sample shows similar feature with the unusual peak at 696 nm which may be from high concentration of Cr^{3+} in the sample.

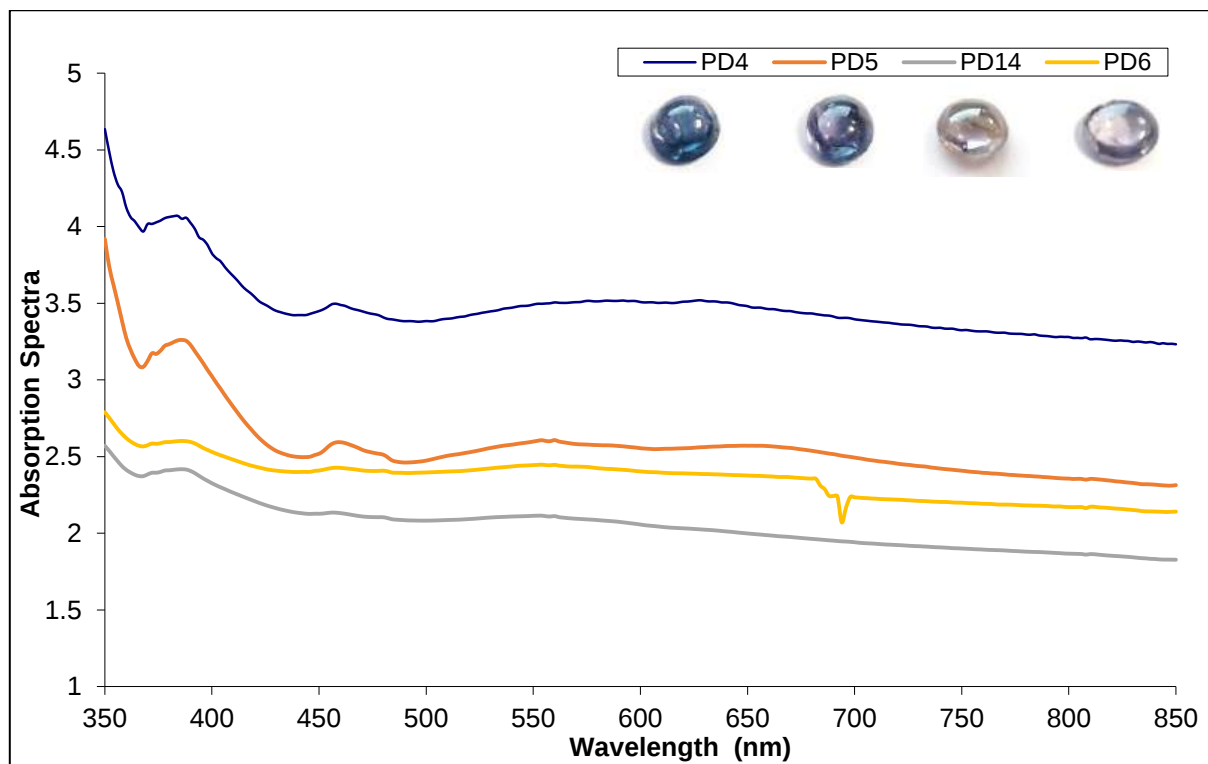


Figure 14 : Samples PD4 – PD5 – PD6 – PD14 which are blue to purplish blue showing the same features

When too many spectra are stacked on the same figure , a representative spectrum of PD5 has been isolated (figure 15).

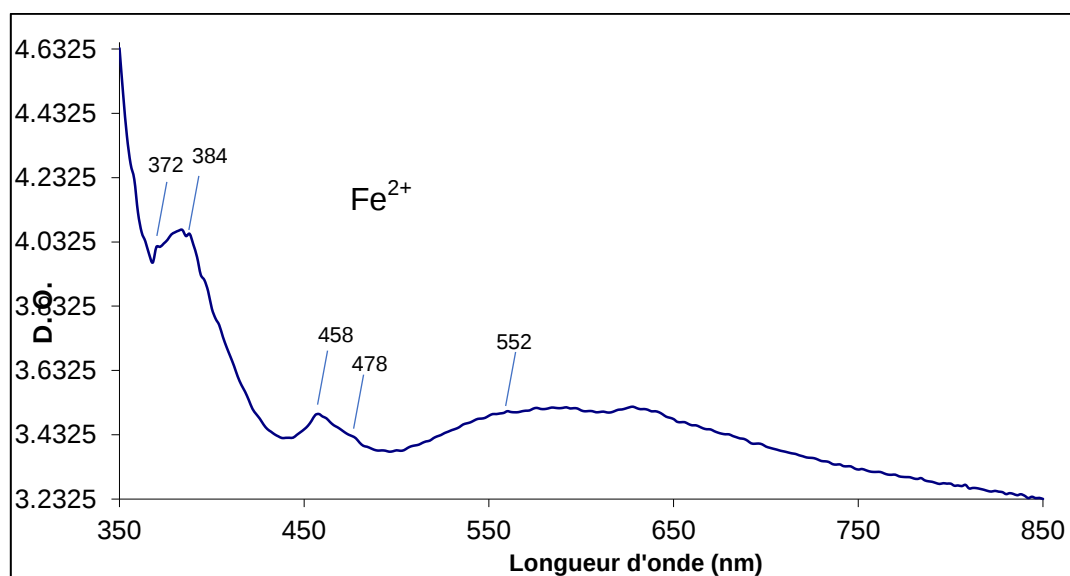


Figure 15: Isolated sample PD5 showing Fe^{2+} absorption spectra

2nd type: PD8, PD9, PD10, PD11 and PD12 show the same feature of Cr³⁺ peaks at ~ 393 and 538 nm. (figure 16)

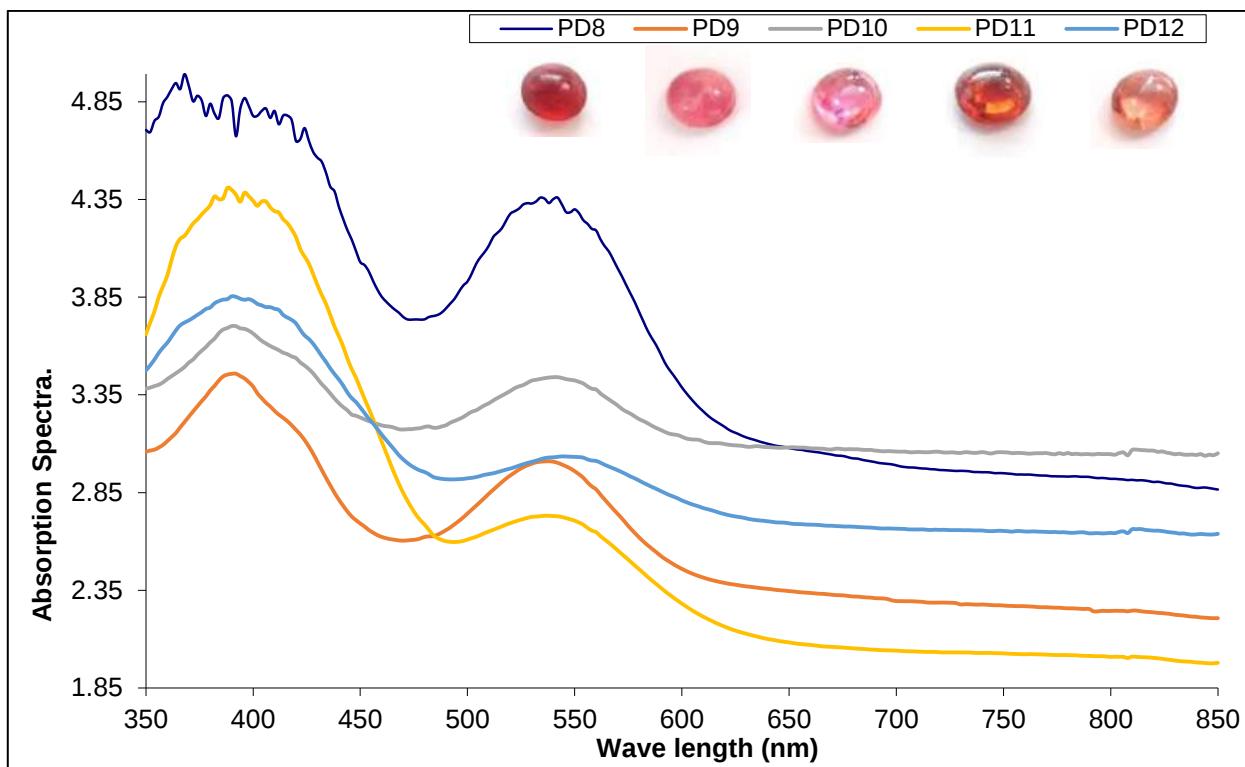


Figure 16 : Samples PD8 – PD9 – PD10 – PD11- showing the same features

A representative spectrum of sample PD8 has been isolated as below (figure 17)

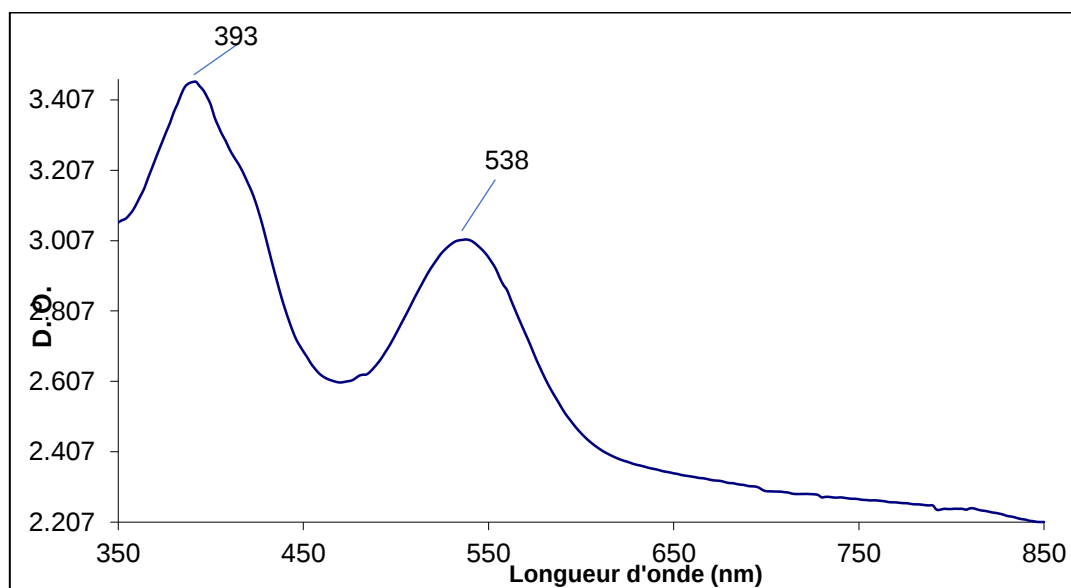


Figure 17: Isolated sample PD8 showing Cr³⁺ absorption spectra

3rd type: Sample PD 13 alone has different feature from the others (figure 18), it shows flattened absorption spectra at the centered ~ 396 and 556 nm peak that usually been found in orange to brown spinel.

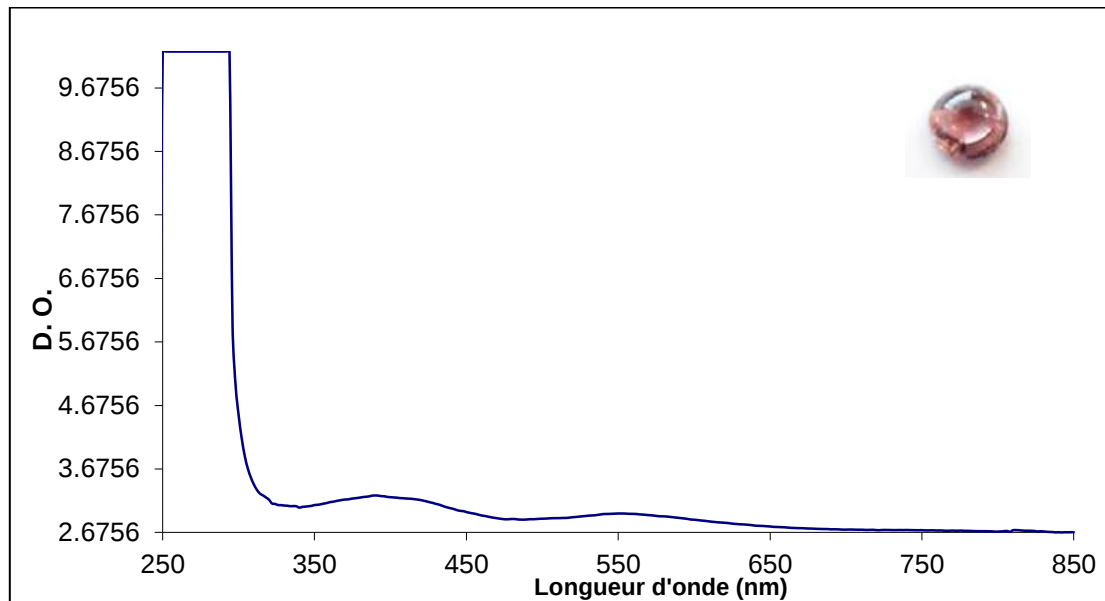


Figure 18: Sample PD13 shows the absorption centered at ~ 396 and 556 nm

Note that sample PD7 analysis is not good and noisy even I have tried to obtain the spectra several times, so I have to honestly admit that I am not able to interpret it. Also sample PD15 gave in unusual absorption which I have to further discuss and will mention later on my oral presentation.

4.2.2 DFI mid laser+

Tested with UV mid laser 405 nm at room temperature, all spectra obtained from 12 spinel samples are corresponding to the study of Saeseaw et al, 2009 and the study by Franck Notari on luminescence of the unheated spinels. After examined its effect on the photoluminescent (PL) emission spectra. The PL spectrum of Cr^{3+} in spinel is complex as it is comprised of a strong zero phonon line near 685 nm as well as vibronic sidebands of that line, and other lines associated with Cr^{3+} pairs. The Full Width of Half Maximum, FWHM ranging from 2.03 - 3.85 nm which is less than the heated samples that exceed 5.82 nm in the study of Saeseaw et al (2009) and those heated and synthetic materials of 6.34 - 11.10 nm collected by Franck Notari in 2017. (figure 20)

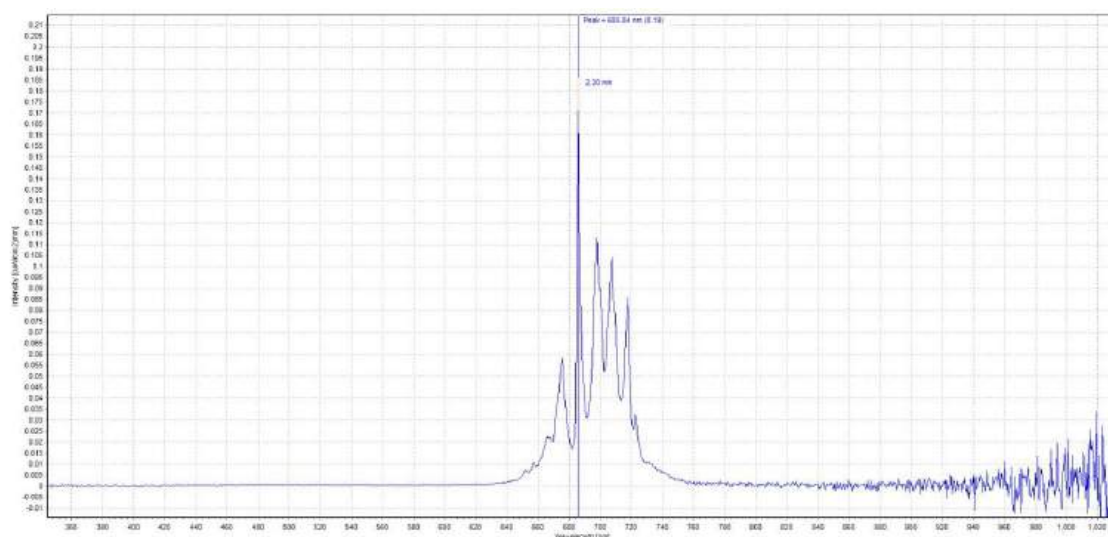


Figure 19 :Well-defined chromium emission features in the photoluminescence spectrum obtained from all 12 samples confirm they are all natural and unheated .

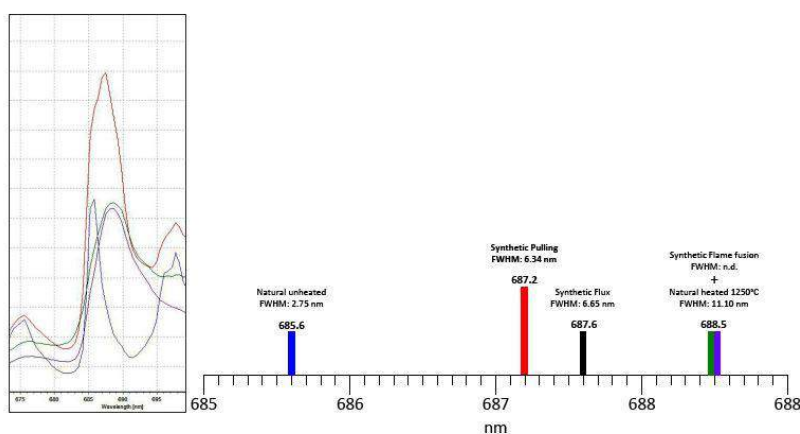


Figure 20 : The main band of Cr^{3+} luminescence positions are measured at the center at the band at half height showing the difference of FWHM of the unheated, heated and synthetic spinel samples. (Notari F, 2017)

FT Raman

Tested with FT raman, PD 4, PD 5 and PD 8 samples show characteristic raman shift for spinel (figure 21). Other samples show poor and noisy signals that cannot be interpreted and considered as not useful information.

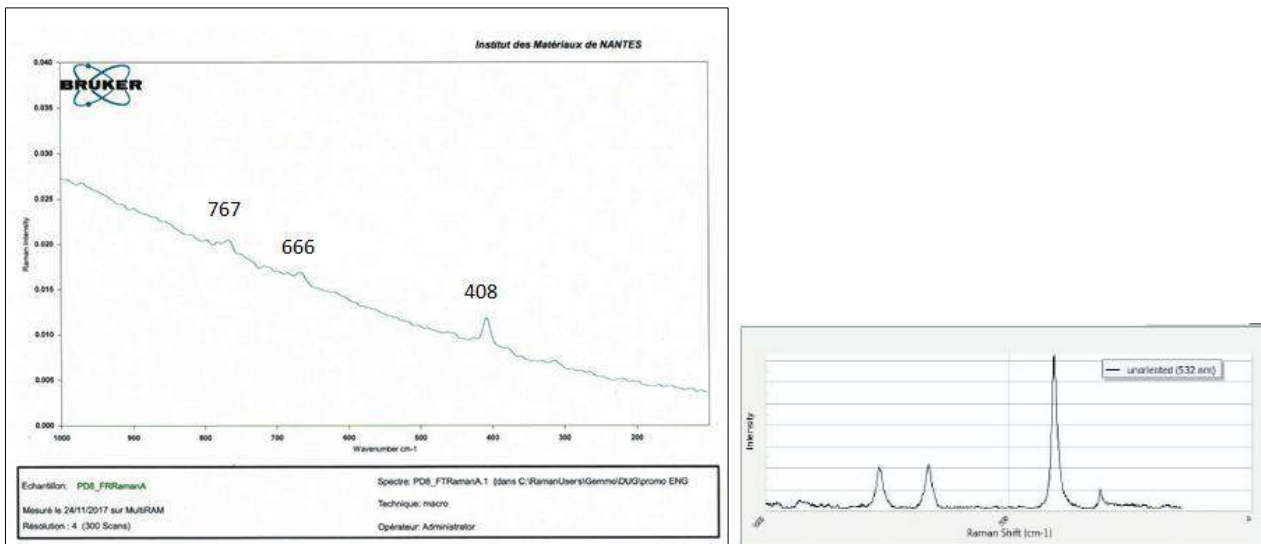


Figure 21: PD 8 sample shows raman shift at 408 , 666 and 767 cm-1 (left) which corresponds to the raman spectra from myanmese spinel of RRUFF ID: R050184 (right). (<http://rruff.info/Spinel/R050184>)

4.3 Chemistry

4.3.1 SEM

PD 4 sample photo taken from scanning electron microscope (SEM) shows the uneven surface of the cabochon and poor polished sample after the metallization (figure 22). Fortunately, thanks to the sample preparation by Nicolus, SEM technician that the electronic charges did not interrupt the testing.

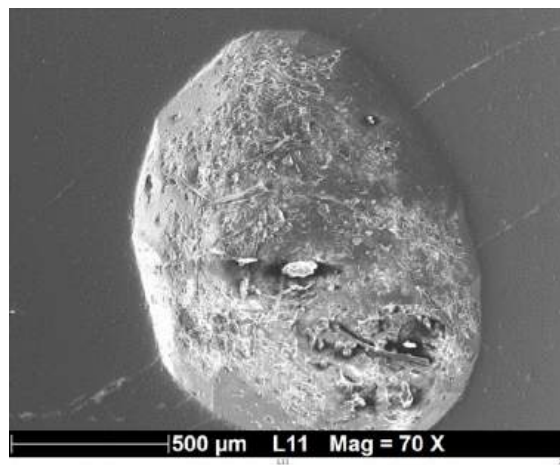


Figure 22: SEM photo of sample PD4 (secondary electrons)

For SEM chemical analysis report obtain from 6 samples which are PD4, PD6, PD7, PD9, PD10 and PD11. Two different types of spectra were collected ;

1st type of spectra obtained from PD4, PD6, PD7, PD10 and PD11 show the element peak of Mg, Al, and O which only indicates the structural spinel composition.(figure 23) As mentioned above, this technique is not suitable for this dissertation.

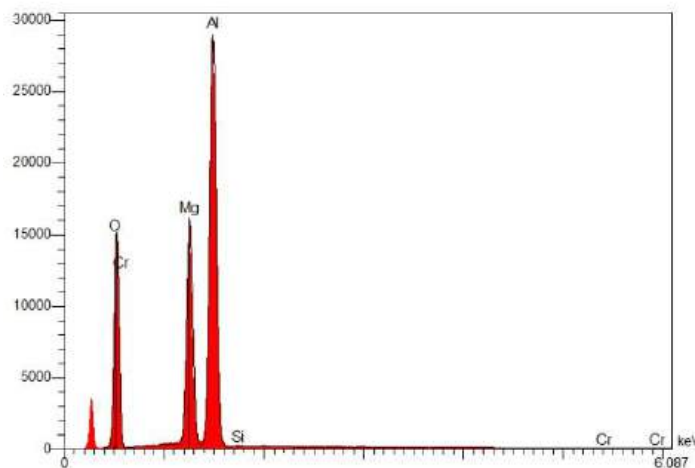


Figure 23 : SEM chemical spectra obtained from PD4, PD6, PD7, PD10 and PD11

2nd type of spectra was collected from one out of six tested samples which is PD 9. The result is quite surprising since Cr peak which is the minor element is present in this pink sample (figure 24) with its main composition, while Cr peak is absent in PD10 which is more intense red.

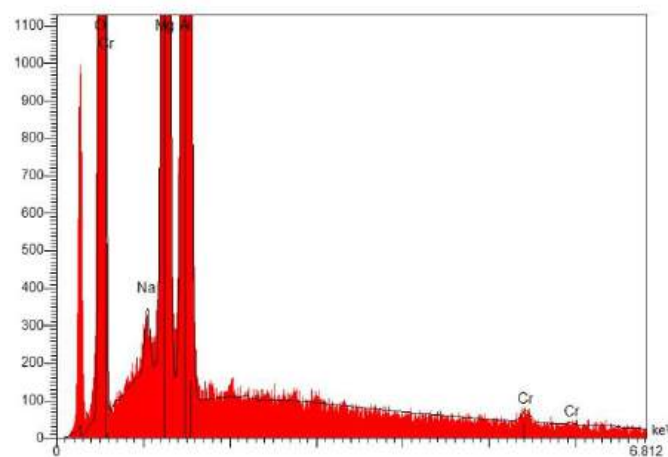


Figure 24 : SEM chemical spectra show Cr peak was obtained from PD 9 sample.

The chemistry results provided by SEM with EDS function are summarized in table 6. Though trace/minor element peaks are absent, the concentrations of V, Cr, Fe are

calculated in A% as below. Surprisingly, Na is present in few samples and Co is absent in all tested samples from this analysis.

Sample code	Concentration (A%)								
	O	Na	Mg	Al	Si	V	Cr	Fe	Total
PD 4	49.06	ND	16.43	34.20	ND	ND	ND	0.31	100
PD 6	46.95	0.18	16.83	35.80	ND	ND	0.04	0.20	100
PD 7	54.64	ND	15.47	29.75	ND	ND	ND	0.14	100
PD 9	52.97	0.42	15.54	30.84	ND	ND	0.19	0.04	100
PD 10	49.18	ND	16.54	34.08	0.15	ND	0.05	ND	100
PD 11	48.68	ND	16.98	34.07	ND	0.21	ND	0.05	100

Table 6 : Data given in atomic % and ND stands for not detected.

The chemistry analysis later provided by EDXRF and summarized in table 7.

Sample number	Concentration (mass %)									
	MgO	Al ₂ O ₃	TiO ₂	V ₂ O ₅	Cr ₂ O ₃	Fe ₂ O ₃	CoO	Ni ₂ O ₃	ZnO	Ga ₂ O ₃
PD 4	29.67	66.97	0.0452	0.0130	0.0036	2.576	ND	0.0073	0.6400	0.0783
PD 5	31.46	65.95	0.0366	0.0204	0.00597	2.297	ND	0.00346	0.1370	0.0850
PD 6	31.93	66.88	0.0366	0.0187	0.00576	1.0098	ND	0.00226	0.0736	0.0401
PD 7	31.80	67.08	0.1158	0.0469	0.00803	0.7855	ND	0.00094	0.1409	0.0291
PD 8	32.02	66.21	0.1619	0.6047	0.8738	0.0747	0.00025	0.00117	0.0455	0.00919
PD 9	31.60	66.73	0.0581	0.0565	0.5922	0.1124	0.00058	0.00916	0.7423	0.0894
PD 10	31.80	67.21	0.0245	0.1010	0.3263	0.1390	0.00121	0.00266	0.2733	0.1229
PD 11	31.76	67.05	0.0254	0.8954	0.0350	0.0657	ND	0.00241	0.1306	0.0329
PD 12	31.91	67.45	0.0091	0.4702	0.0102	0.0367	0.00024	0.00209	0.0847	0.0314
PD 13	32.03	67.07	0.0252	0.2359	0.0184	0.3655	0.00130	0.00283	0.2067	0.0461
PD 14	31.49	66.93	0.0206	0.1290	0.0092	1.1137	0.0002	0.01370	0.1791	0.1198
PD 15	31.90	67.48	0.00570	0.0711	0.01875	0.1233	0.00070	0.00228	0.3203	0.0837

Table 7: Data given in mass%. MgO : magnesium oxide, Al₂O₃: aluminum oxide, Fe₂O₃: iron oxide, Cr₂O₃: chromium oxide, TiO₂: titanium oxide, CoO : cobalt oxide, Ga₂O₃: gallium oxide, V₂O₅: vanadium oxide, Ni₂O₃: nickel oxide, ZnO: zinc oxide and ND: not detected.

5. Discussion

5.1 Colors of the Spinel

In this study, the colours of sapphires can be gathered in four categories: orange, purple, pink to red, and blue. For future study, we need to study more spinel colors with different tone and shade.

5.2 Chemical analysis

Composition of the studied samples show that they represent spinel end member, which contain the principle components: Al_2O_3 (65.95-67.48 wt%) and MgO (29.67-31.93 wt%) in normal proportions (71.8 wt% Al_2O_3 and 28.2 wt% MgO). Depending on the color of individual samples, their trace element contents are in range of 0.0036 - 0.8738 wt% Cr_2O_3 and 0.0367- 2.576 wt% Fe_2O_3 . The influence of the specific trace elements can be proved by studying the absorption spectra. Since I used to be Dr.Dietmar Schwarz's assistant and we together had collected the data and made the spinel correlation diagram which could be helpful for the geographical origin report. I do not discuss in this report but put in annex.

5.3 Absorption spectra

For UV-Vis spectroscopy, the study were gathered and collected from many researchers as below;

Bunnag and Thanasuthupitak (2003) studied spinel samples from Mogok, Myanmar and found the Cr^{3+} absorption red spinel at 388, 415 and 540 nm. While greenish blue and purple spinel show the absorption of Fe^{2+} (tetrahedral coordination) at 371, 383, 457, 559 and 659 nm, and the absorption of $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge transfer at 912-925 nm.

Peretti and Gunther (2003) studied spinel samples from Namya, Myanmar and found that Purple to green spinel shows the absorption spectra at 630-650, 550-565, 460, 378 and 373 nm. Brown to orange-red spinel shows the absorption spectra at 550 nm, and pink to red spinel shows the absorption spectra at 538 and 391 nm.

Smith et al (2008) studied spinel samples from Vietnam and found that red to pink spinel shows distinct broad absorption spectra at 388 and 540 nm and has a shoulder at 415 nm which is the result of Cr^{3+} octahedral coordination corresponding to the study of Bunnag and Thanasuthupitak (2003). Purple to blue spinel shows Co^{2+} absorption spectra at 550, 585, and 625 nm and Fe^{2+} absorption spectra at 370, 385, 455, 477 and 555 nm.

Sriprasert et al (2009) studied spinel samples from Myanmar and found that heated red to purplish red spinel show the Cr^{3+} absorption spectra at 390 and 545 nm, and Fe^{2+} absorption spectra at 372 nm

Saeseaw et al (2009) studied spinel samples from Tanzania, Tajikistan, Myanmar and Srilanka and found that red and pink spinel heated at 800 °C will change the absorption range from 536-539 nm to 544-547 nm.

From those studied, it can be concluded that spinel from different geographical origins show the same absorption spectra due to the same transition elements that give its color and that enables spinel from different deposits to the similar colors. (Budsabakorn, 2013)

5.4 Other chemical analysis technique: Proton Induced X-ray Emission, PIXE

In the study of Srisataporn B. (2013), she used PIXE technique to get the chemical analysis and her myanmese spinel show the spectra of main composition of Mg and Al, and also trace/minor elements including Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn and Ga. (see figure 25). From the spectra, it was obtained by the high energy of proton particles excite the orbital electron of each element (most are in K-shell), and release the energy in a form of electromagnetic waves in X-ray region. From the study, the chemical analysis result is related and corresponding to the sample colors.

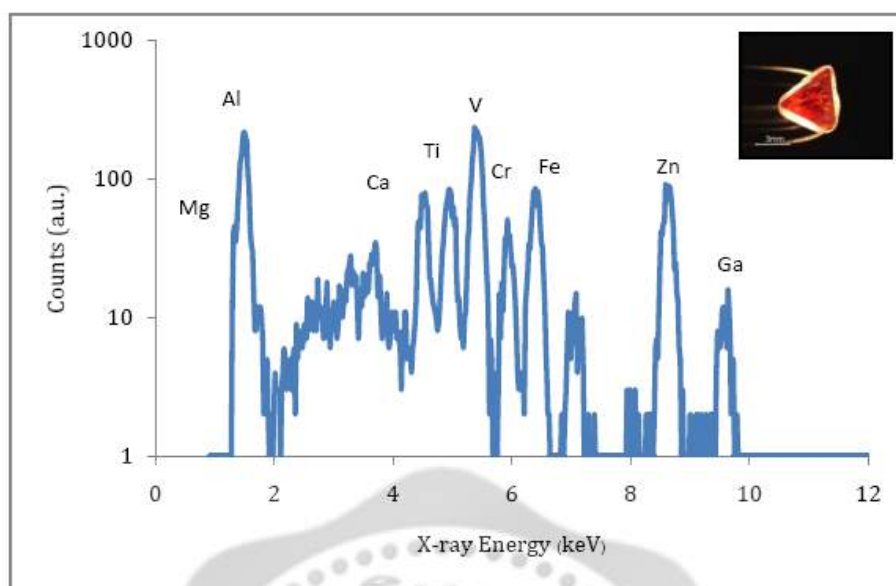


Figure 25: Spectrum obtained from PIXE technique of orange red spinel from Myanmar Srisataporn B. (2013)

Conclusion

The aim of this experimental dissertation was to study gemological/chemical characteristic and causes of fancy color spinels from Myanmar by using basic gemological and spectroscopy techniques and also to observe the features and physical properties that may be considered as an indication of the material from this geographical origin. The analyses demonstrate the combination effect of chromium, iron and cobalt on the color and also the concentration of minor/trace element that influence its hue and intensity. I have to admit that I had better do the experiment with faceted samples than the cabochon with poor polish so it will be better for spectroscopy analysis and microscopic examination. With bigger samples, it will be better when performed EDS test with Thermo Fisher and the result would be more accurate and more certain. Advanced testing of Raman is not relevant in this study, also I did not obtain good spectra from the tested samples and also EDS technique on SEM testing, it is not suitable to analyse trace/minor element concentration which is the important cause of color in spinel. For further study, more samples and color variety should be selected and analysed, to document more data and could be possible to find more correlation between the spinel from this geographical origin.

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