CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter consists of two main parts which are the identification of corundum deposit and the modification of corundum optical properties. Hundreds of natural corundum-including blue sapphires and dull white sapphires from Sri Lanka, rubies from Bo rai in Thailand and from Mogok in Myanmar, blue-green sapphires from Bang Kha Cha in Thailand, dark-blue sapphires from Pailin in Cambodia, yellow sapphires from Montana, the USA, pink sapphires from Madagascar, and light-blue green sapphires, dark-blue green sapphires, green blue sapphire, blue sapphires, white sapphires, pink sapphires, pale yellow sapphires, blue green Africa sapphires which are unknown deposit – were selected for this investigation.

4.1 Fingerprint of deposit by PIXE analysis

Corundum consists of aluminium as the matrix element in the Al_2O_3 form. Trace elements are found as impurity such as Si, K, Ca, Ti, V, Cr, Fe, Zn, Ga, etc. which their concentrations vary with corundum type and deposit. According to the experimental description in the previous chapter, the mean concentrations of the main trace elements are shown in Table 4.1 which has large standard deviation because of a large variety of samples.

As seen in Figure 4.1, PIXE spectra of rubies show obviously that the dominant trace element is chromium because it is the main cause of red color in corundum. By the way, an iron is the major trace element in the bluish sapphires because the blue color comes from the intervalence charge transfer (IVCT) process which co-activate between an iron and titanium. In case of Ti-rich, these sapphires would appear in the light-blue tone such as the blue sapphire from Sri Lanka. On the other hand, sapphires which contain an enormous of iron would appear in the dark-blue tone. Additionally, the ratio of Fe/Ti refers to the bluish tone in corundum but may be avoiding the +3 charge state of an iron in the calculation. If there is sufficient of +3 charge state of iron presence in corundum, the yellowish tone can show up instead. Since the green color is occurred due to the mixing of blue and yellow color, the iron in blue-green sapphire will appear in both +3 and +2 charge state. For pink sapphires, chromium is also found in the gemstone, however, its concentration is lower than a ruby.

As shown in Table 4.1 for the well-known origin's corundum, blue sapphires and dull white sapphires from Sri Lanka contain the highest concentration of Ti (> 370 ppm) but the lowest of Fe (< 4,100 ppm). As explained in Chapter 2, this indicates that both sapphires are from metamorphic deposits. According to Atichart *et al.* (2010), it seems that they are of Awissawella origin. On the other hand, other sapphires in this investigation contain higher concentrations of Fe (> 4,500 ppm) but lower of Ti concentrations than those from Sri Lanka. Yellow sapphires from Montana have the highest abundance of iron and chromium compared to other sapphires. It is interesting to note the large difference in Fe and Ti between blue sapphires from Sri Lanka and Cambodia. This confirms that the difference of sapphire origins tends to be correlated with the different concentrations of trace elements. The standard deviations of trace elements are quite large due to the very wide range of data above the terms of limit of detection, which agrees very well with the findings of Calligaro *et al*. (1999).

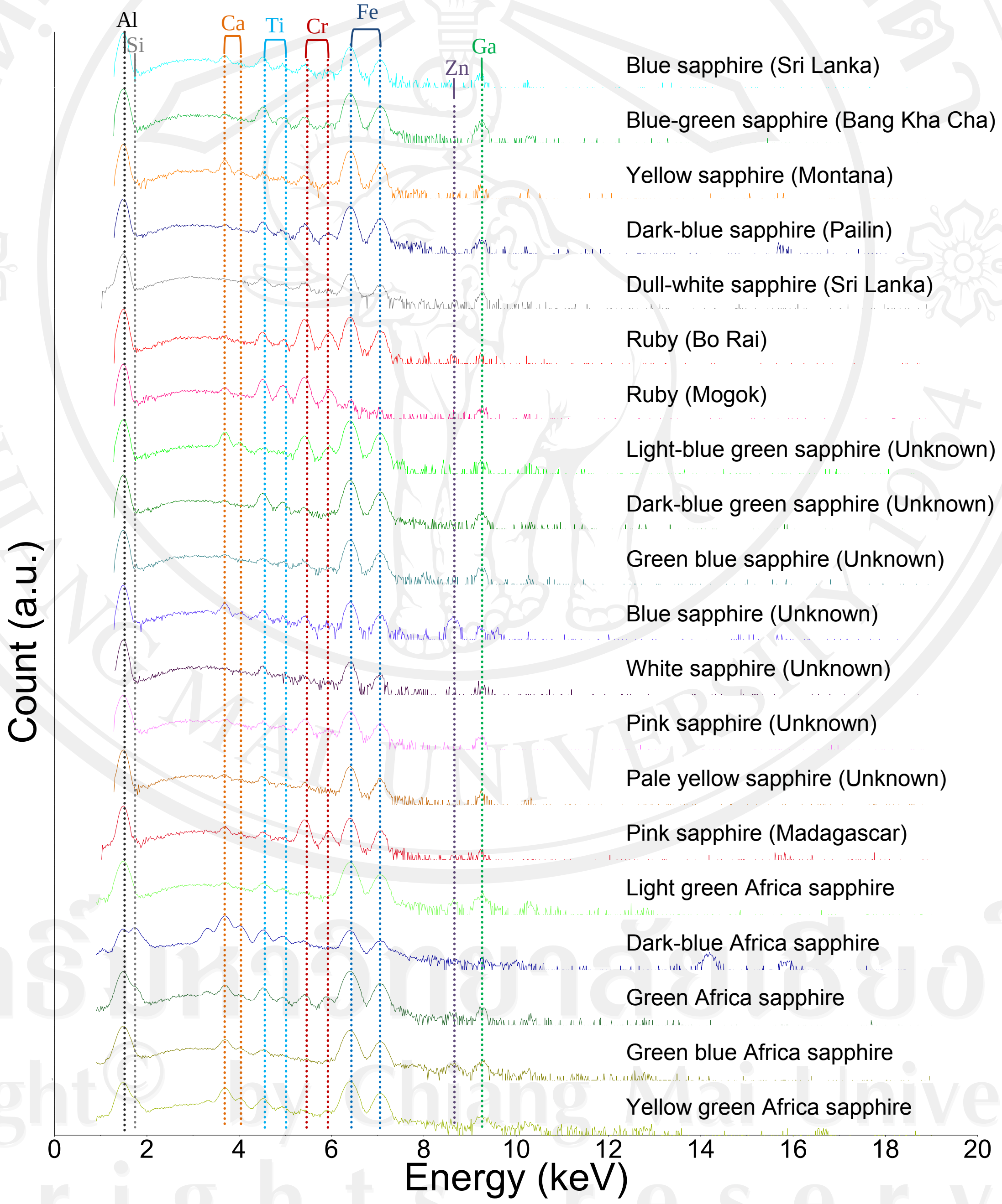


Figure 4.1. PIXE spectra of all corundum investigated in this study.

Table 4.1. The concentrations of Ti, V, Cr, Fe and Ga in each type of corundum, in parts per million (ppm) by weight as measured by PIXE technique.

Type of corundum	Trace elements concentrations (ppm)									
	Ti		V		Cr		Fe		Ga	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
(1)	372.30	306.00	11.43	7.23	78.00	96.18	4119.30	8311.42	50.22	14.01
(2)	134.20	110.55	17.63	10.99	159.50	178.25	6859.70	3758.95	154.00	69.60
(3)	210.20	164.68	22.00	23.87	312.66	208.09	11287.60	9330.31	63.07	35.97
(4)	220.60	223.86	11.50	12.28	89.50	64.15	4629.00	2654.23	97.80	87.80
(5)	449.26	533.21	17.53	15.89	28.95	21.84	1230.11	1051.23	69.11	44.54
(6)	145.80	69.98	22.22	10.54	2219.90	935.27	4510.00	885.67	30.25	15.90
(7)	828.00	595.09	182.50	59.31	2711.60	1348.90	56.50	45.73	43.20	9.17
(8)	60.90	9.79	11.70	10.06	196.00	231.73	6455.80	2080.62	41.90	10.90
(9)	229.20	160.25	8.40	7.54	32.40	12.44	5276.00	1242.41	95.60	22.11
(10)	98.40	32.86	10.00	9.92	24.00	17.39	3550.20	363.73	100.80	21.53
(11)	226.33	134.03	12.56	12.97	81.67	74.18	897.11	433.40	71.00	41.26
(12)	516.00	420.53	10.20	7.07	25.00	12.45	898.30	418.77	59.60	17.46
(13)	327.67	209.41	41.92	33.69	392.50	378.09	5885.67	9645.28	51.17	21.76
(14)	116.33	85.35	10.33	17.90	58.33	35.57	1339.00	380.05	28.33	14.98
(15)	60.64	19.81	3.09	3.42	3184.73	1622.85	1850.27	841.95	28.64	16.75
(16)	352.83	429.87	20.33	13.84	123.50	149.04	6958.67	2555.82	86.17	67.02
(17)	1623.25	786.17	128.00	46.07	294.50	113.67	3935.75	724.57	50.50	26.84
(18)	354.86	254.36	9.71	13.20	341.71	193.33	10914.57	3908.09	159.86	90.87
(19)	76.67	21.39	10.00	4.58	11.00	15.72	8163.00	1773.87	130.33	58.62
(20)	518.00	161.22	5.50	7.78	229.00	264.46	9191.50	4076.47	95.50	19.09

NOTE:

(1) refers to blue sapphire from Sri Lanka.

(2) refers to blue green sapphire from Bang Kha Cha, Thailand.

(3) refers to dark-blue sapphire from Pailin, Thailand.

(4) refers to yellow sapphire from Montana, the USA.

(5) refers to dull white sapphire from Sri Lanka.

(6) refers to ruby from Bo rai, Thailand.

(7) refers to ruby from Mogok, Myanmar.

(8) refers to light-blue green sapphire (Unknown).

(9) refers to dark-blue green sapphire (Unknown).

(10) refers to green blue sapphire (Unknown).

(11) refers to blue sapphire (Unknown).

(12) refers to white sapphire (Unknown).

(13) refers to pink sapphire (Unknown).

(14) refers to pale yellow sapphire (Unknown).

(15) refers to pink sapphire from Madagascar.

(16) refers to light-green sapphire from Africa.

(17) refers to dark-blue sapphire from Africa.

(18) refers to green sapphire from Africa.

(19) refers to green blue sapphire from Africa.

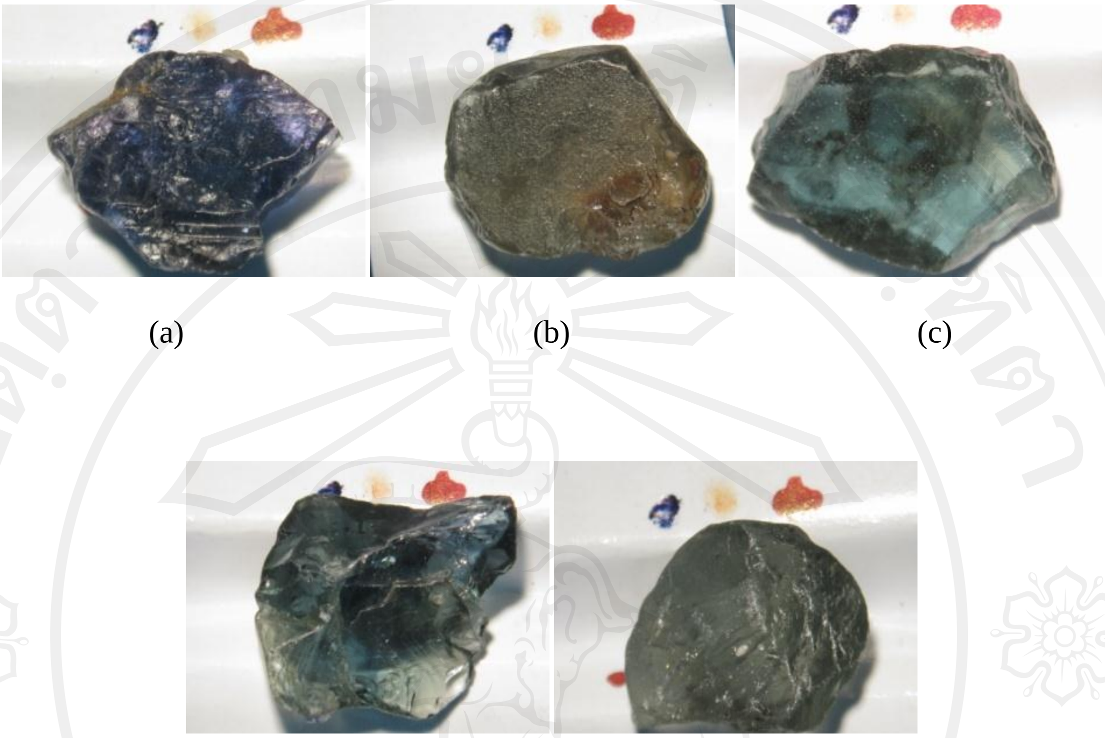
(20) refers to yellow green sapphire from Africa.

* Mean = mean value concentration; Std = standard deviation

The Africa sapphires, No. (16) – (20) as shown in Table 4.1 and can be seen in Figure. 4.2, were cut from the same original piece which is the blue green sapphire. It is worth to mention that the Fe^{2+}/Ti^{4+} IVCT process is the main source of the blue color of sapphire, therefore, these samples are a good source for identifying the relation between the ratio of Fe/Ti concentration and the gemologist color grading. The color can be graded to five tones by naked-eye, including dark-blue, yellow green, light-green, green, and green blue tones. The ratio of Fe/Ti of each of them is calculated as shown in Table 4.2.

Table 4.2. The color tone of Africa sapphire and the ratio of Fe/Ti concentrations.

Tone of Africa sapphire	Ratio of Fe/Ti concentration
Dark-blue	3.21
Yellow green	19.93
Light-green	34.69
Green	54.83
Green blue	99.19



(a) (b) (c)

(d) (e)

Figure 4.2. The five sapphires which were cut at five different color zone of a bigger piece of African sapphire: (a) from dark-blue zone, (b) from yellow green zone, (c) from light-green zone, (d) from green zone, and (e) from green blue zone.

4.2 Fingerprint of deposit by IL analysis

Figure 4.3 shows the IL spectra of all the investigated corundum. The results agree well with the previous report (Kamwanna, 2010), indicating that ion beam luminescence is a very sensitive method for detecting Cr^{3+} inclusion in an alumina matrix. The measurements show that an emission peak is clearly seen at a wavelength of ~692 nm. By ligand field theory (Nassau, 2001), this peak is the splitting of energy in a d-orbital of Cr^{3+} due to six surrounding O^{2-} ions. The peak is an electron transition from ^2E (first excited state) to $^4A_2$ (ground state) with emission of ~1.79 eV associate to the red color region. Additionally, the luminescence of Cr^{3+} at 692 nm is increasing, depending on the Cr^{3+} concentration in corundum, i.e. from dark-blue sapphire, blue sapphire, blue green sapphire, yellow sapphire, and ruby. Near the main peak, the spectra show dwarf peaks at 657.5 nm and 667.5 nm generated from electron transition from $^2T_1$ (second excited state) to $^4A_2$. There are also two lines at 702.6 nm and 704.6 nm, so-called n-line, which are an effect of paired Cr^{3+} (Powell, 1967). Finally, the side band at 711.7 nm is caused by molecular vibration (Rothamel et al., 1983). Note that the spectra of dark-blue and blue green sapphires have additional peaks centered at 330, 480 and 540 nm. These peaks belong to the F^+-center (Moroño et al., 1997), F_2 center (Mukhurov *et al.*, 2010) and F_3 center (Abdukadyrova, 1997), respectively. This implies that the iron in these sapphires is very sensitive to irradiation process while another has the highly crystallization structure and not luminescence. Although, the IL result cannot predict the deposit, but the database is valuable for Cr^{3+} luminescence investigation that correlate with the concentration of iron and chromium in the same type of corundum.

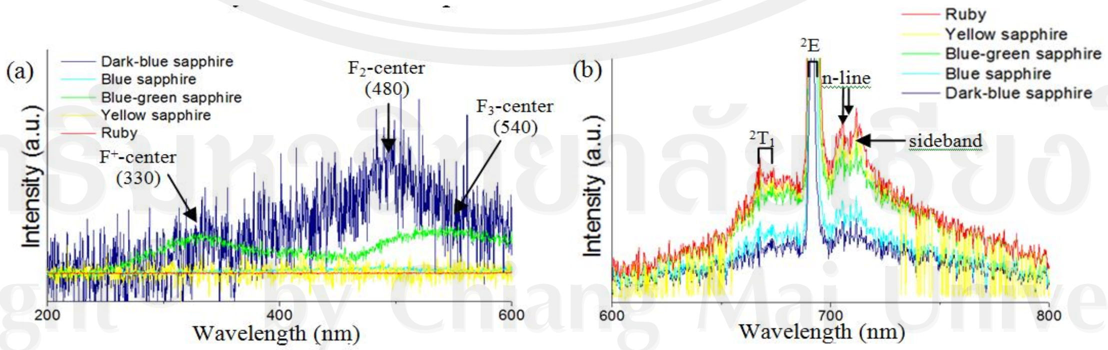


Figure 4.3. IL spectra of corundum in regions 200–600 nm (a) and 600–800 nm (b).

4.3 UV-Vis-NIR spectroscopy analysis

The color is generated by the certain wavelengths of light reflected by the crystal lattice while others absorbed. Those wavelengths of light which are reflected are perceived by the viewer to possess the property of color. All of investigated corundum, therefore, is analyzed by the UV-Vis-NIR spectroscopy in the range of 250 – 800 nm and the results show in Figure 4.4. The absorption spectra show two peaks at 405 nm and 554 nm only for ruby, corundum contain very high content of Cr. These peaks occur due to the substitution of Cr^{3+} in Al_2O_3 matrix, from ground state $^4A_2$ to the $^4T_1$ and $^4T_2$, respectively (McClure, 1962). However, the peak at 692 nm which remain investigated in the absorption spectra is very low compared to the others. It can be explained that all absorption between the splitting energy level can occur. By the way, the absorption peaks also appear at 388 nm of Fe^{3+}, and at 377 nm of Fe^{3+}/Fe^{3+}-pair charge transfer which related to the yellowish tone. Alternatively, these peaks also relate to brownish tint in a blue sapphire. Furthermore, the peak at 450 nm of Fe^{3+}/Fe^{3+} valence charge transfer (Milos *et al.*, 2008) is the main peak of the pale yellowish sapphire which describes to the color tone of greenish sapphire in mixing of blue and yellow color. The last one is the broad band centered at 560 nm which is the Fe^{2+}/Ti^{4+} intervalence charge transfer (IVCT) process that interpret the intense blue in the sapphire and the violet tint in the ruby. Note that the blue sapphire in this work is transparent so the based-line of absorption spectra is very low compared with the rest. In other words, the saturation in this sapphire is low which is similar to the yellow sapphire. Therefore, the based-line of the absorption spectra can refer to the transparent of corundum.

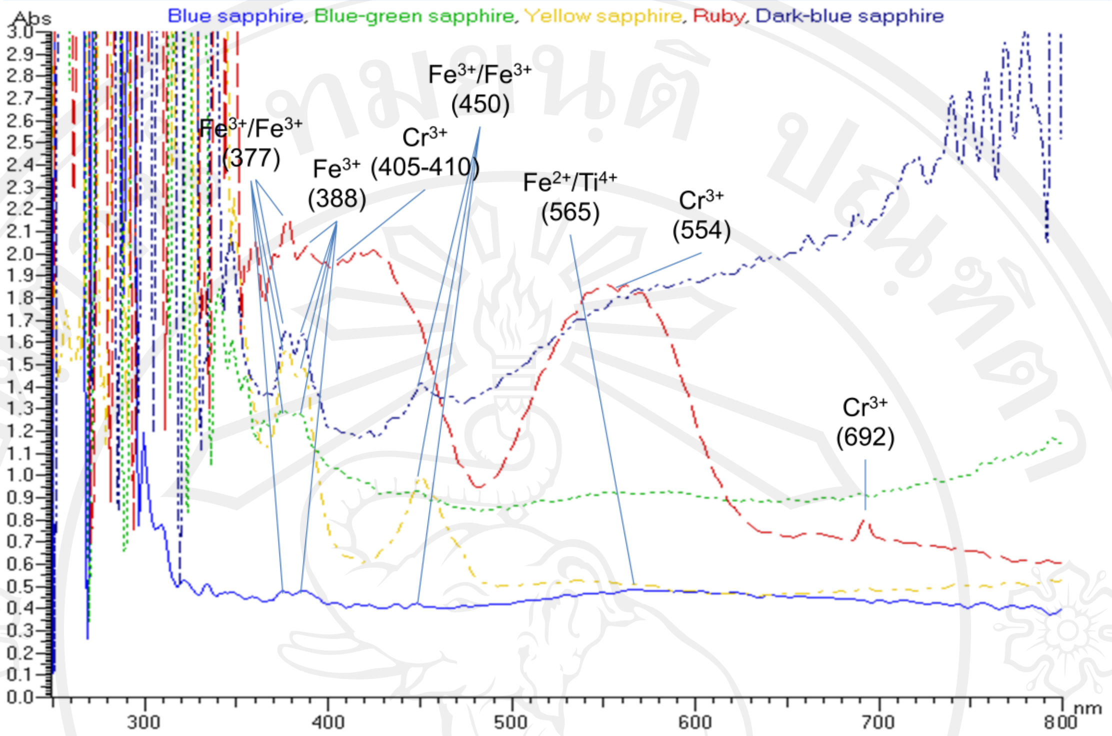


Figure 4.4. UV-Vis-NIR spectra of blue sapphire from Sri Lanka (light blue curve), ruby from Bo rai (red curve), blue-green sapphire from Bang Kha Cha (green curve), dark-blue sapphire from Pailin (navy blue curve), and yellow sapphire from Montana (yellow curve).

Compare to IL results, UV-Vis-NIR spectra also show the absorption peak at 692. On the contrary, other peaks observed by UV-Vis-NIR of Cr^{3+} are not observed in the IL spectra since the transition of Cr^{3+} from $^4T_1$ and $^4T_2$ to $^4A_2$ are forbidden by the selection rules. Furthermore, the absorption spectrum of Fe is observed by UV-Vis-NIR spectroscopy, but cannot be observed by the IL analysis because of the forbidden by the selection rules, too.

4.4 Corundum's deposit investigation

The several plots of elements or ratio of elements are selected for deposit analysis. The data is extracted from the PIXE results. Figure 4.5 shows the relation between the ratio of Cr/Ga and Fe/Ti concentrations. It is clearly seen that the points from different types of corundum located at different areas. It should be noted that the points with Fe/Ti ratio lower than 10 is belong to basaltic deposits and those above 10 is belong to metamorphic deposits. In this manner, the A-line in Figure 4.5 acts likely as a boundary between the two deposits. For example, Bo rai rubies (6), which have Fe/Ti > 10, are from basaltic deposits. It is also remarkable to note that the data points belong to metamorphic deposits are clustered according to their origin. Therefore, the unknown deposits sapphire can be characterized by this relation to whose blue sapphire (11) and white sapphire (12) are metamorphic deposit. In addition, dark-blue Africa sapphire (17) also occurs in the metamorphic condition, which difference from another type of Africa sapphire. These indicate that this dark-blue sapphire has been transformed from its original form. On the other hand, other unknown deposit's corundum are the basaltic deposit type, including light-blue green sapphire (8), dark-blue green sapphire (9), green blue sapphire (10), pink sapphire from Madagascar (15), light green Africa sapphire (16), green Africa sapphire (18), green blue Africa sapphire (19), and yellow green Africa sapphire (20). However, the pale yellow sapphire (14) and pink sapphire (15) cannot be identified by using this relation.

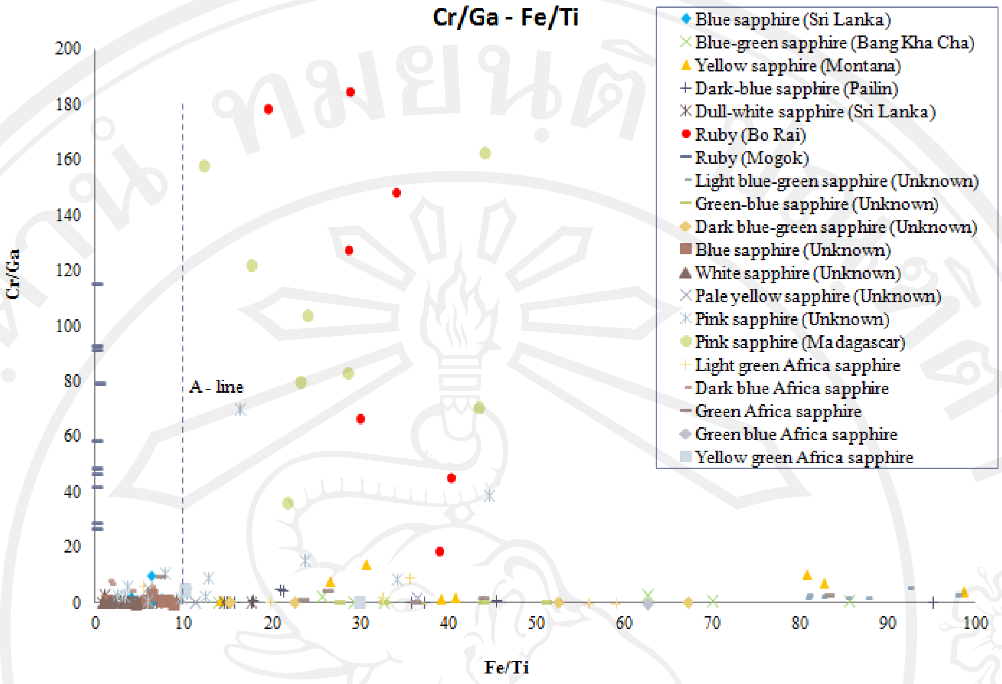
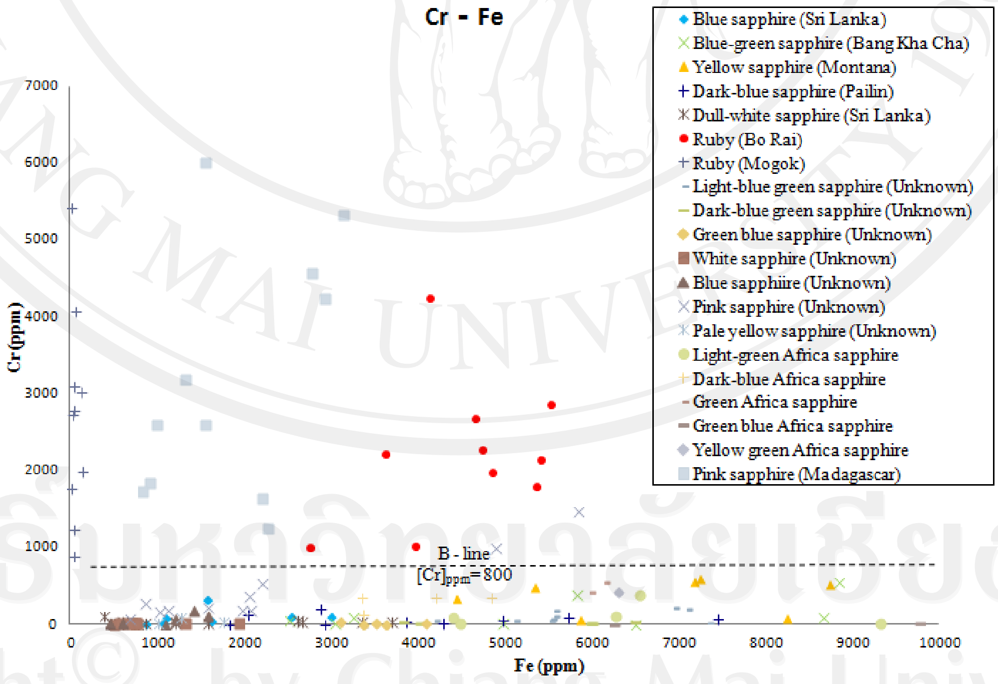
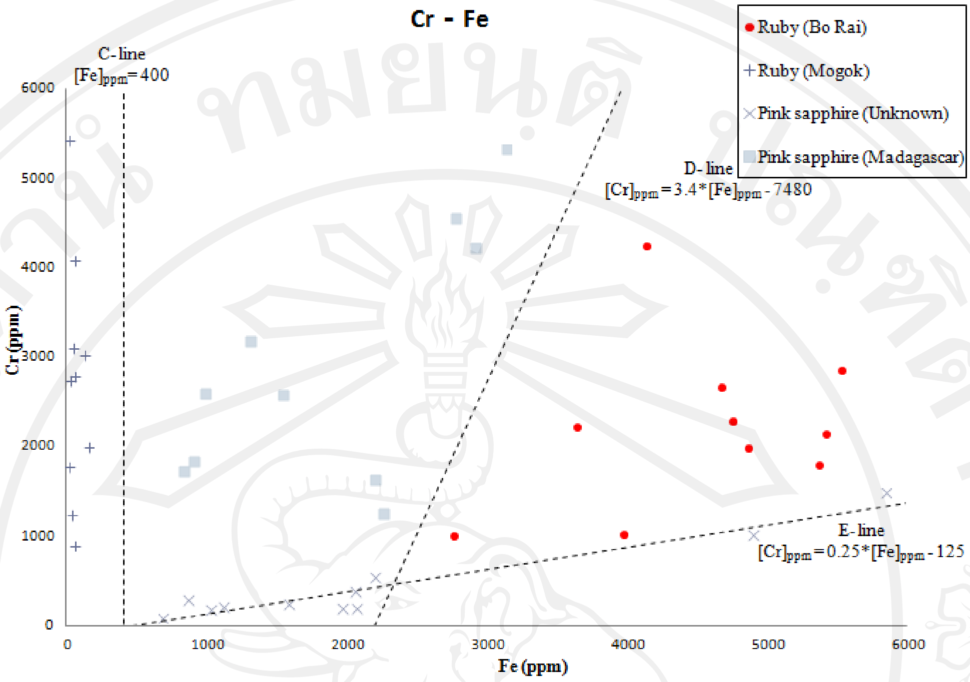


Figure 4.5. The relation between the ratio of Cr/Ga and Fe/Ti concentrations.



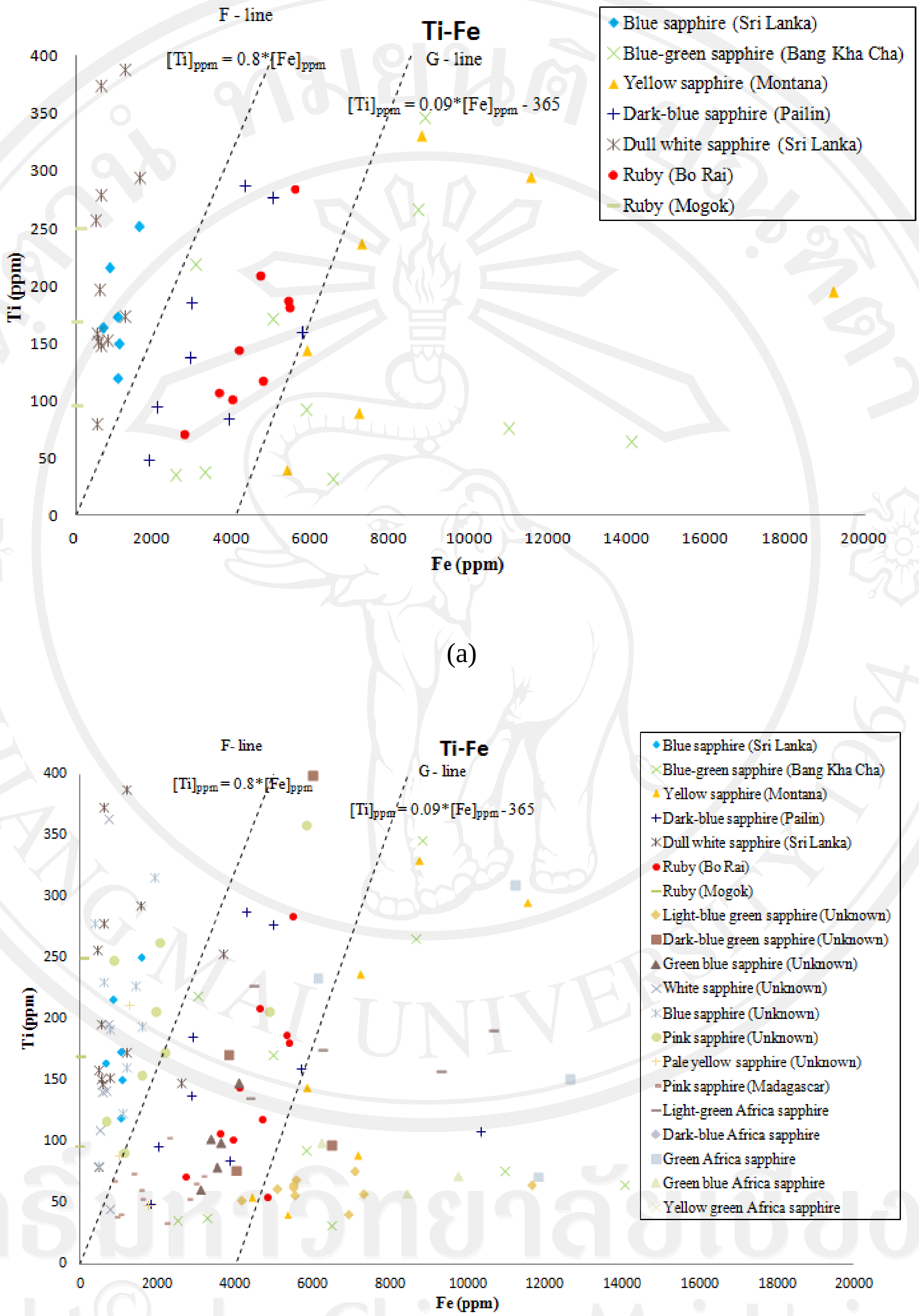
(a)



(b)

Figure 4.6. The relation between the Cr and Fe concentrations

Figure 4.6 (a) and Figure 4.6 (b) are the relation between the Cr and Fe concentration. Certainly the red tone corundum is distinguished from the non-red tone corundum by the B-line in Figure 4.6 (a). In Figure 4.6 (b), the pink sapphires from Madagascar (15) lie between the C-line and D-line, in other words, between Mogok (7) and Bo rai origin. Besides, these sapphires contain high Cr concentration which should be called ruby. It is worth pointing that the data belonging to pink sapphires from unknown deposit is settled along the E-line (the corresponding equation is shown in Figure 4.6 (b)). All of segregation confirms that Cr is the main cause of the red color in both ruby and pink sapphire – which has the different of red tone in each origin depending on the Cr concentration.



(a)

(b)

Figure 4.7. The relation between the Ti and Fe concentrations.

Figure 4.7 (a) and Figure 4.7 (b) show the relation between the Ti and Fe concentration. It can be seen that data points belong to blue sapphires (1) and dull white sapphires (5) of Sri Lanka lie close together, and can be separated by the F-line, the corresponding equation is also included in Figure 4.7 (a). These sapphires contain low iron and high titanium content, and thus deemed to be a metamorphic deposit. Conversely, the others, containing high iron and low titanium, can be classified as a basaltic deposit. The G-line serves as a dividing line for separating Montana origin (4) (on the right) from Pailin (3) and Bo rai origins (on the left). In other words, corundum of Montana origin is rich in iron, whereas those of Bo rai and Pailin origins are the opposite. Unfortunately, data belong to Bang Kha Cha sapphires (2) are spread over the basaltic area, so it is not possible to separate them from the other basaltic deposits by this relation.

As shown in Figure 4.8, the data points for Bang Kha Cha and Pailin origins show a moderate degree of clustering on specific areas of the graph. Pailin data tend to be separated from those representing Bang Kha Cha origin by the H-line (the corresponding equation is shown in Figure 4.8). This implies that corundum of Pailin origin contain less gallium than those from Bang Kha Cha. Furthermore, this straight line also distinguish the sapphires from Bang Kha Cha and Bo rai origins. Since Bang Kha Cha sapphire contains more Ga than Bo rai, the data belong to Bang Kha Cha lies above the H-line, while that of the latter lies below. Hence, the H-line appears to be a good separation line for domestic Thai origin. Noteworthy, samples from Bo rai of Thailand and Pailin of Cambodia are indistinguishable due to the similarity of geological deposits.

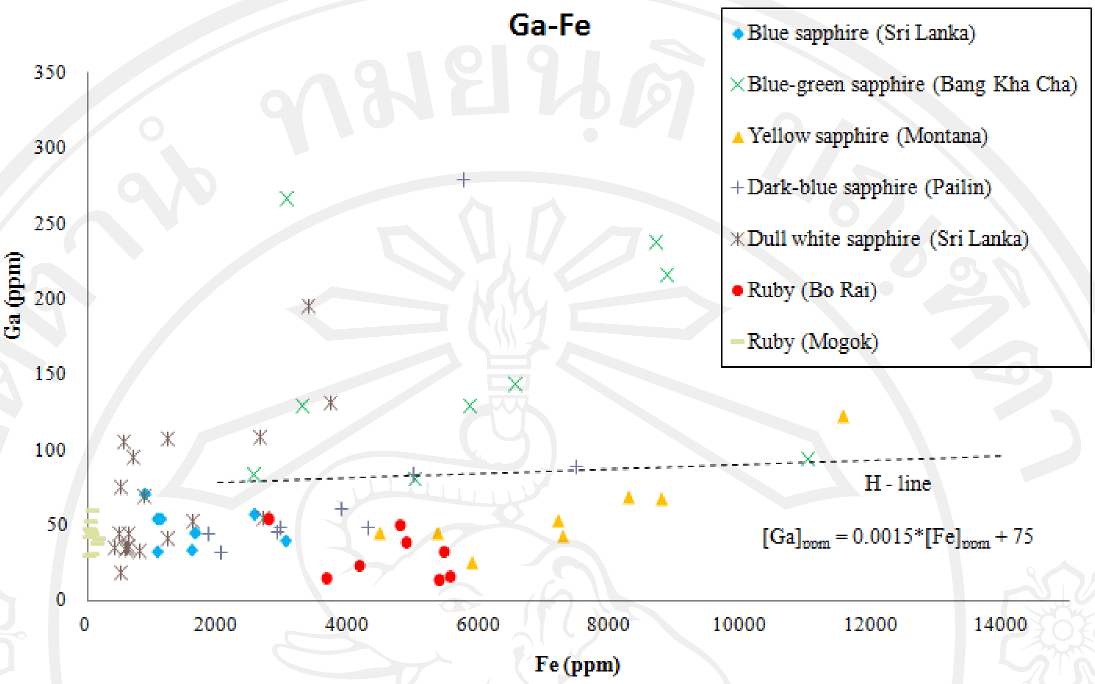


Figure 4.8. The relation between the Ga and Fe concentrations.

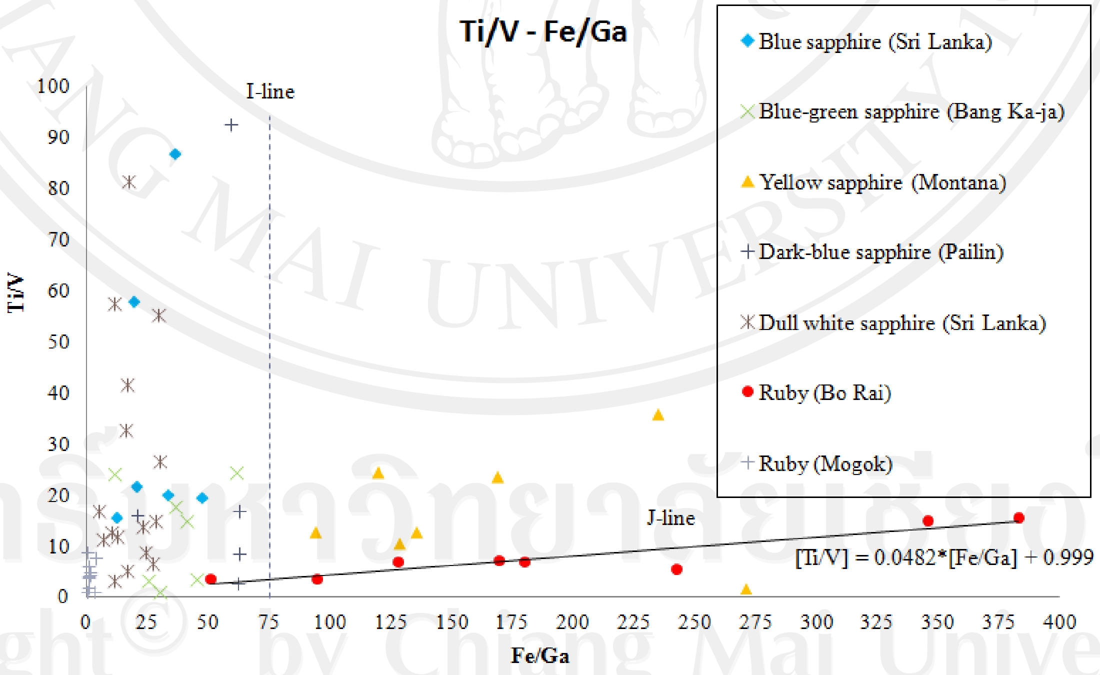


Figure 4.9. The relation between the ratio of Ti/V and Fe/Ga concentrations.

Figure 4.9 shows the relationship between the ratio of Ti/V and Fe/Ga concentrations. This relation clearly demonstrates the separation of corundum of different origins, except for Sri Lanka sapphires and Bang Kha Cha sapphires where the data points are slightly grouped together in the same area. As explained above in Figure 4.6, the relative concentrations of Ti and Fe, cannot be used to separate Bang Kha Cha from Montana origins. However, these can be separated by the I-line at Fe/Ga = 75, as shown in Figure 4.9. Furthermore, the data belong to Bo rai rubies is settled along the J-line (as seen at the equation in Figure 4.9). These points are also clearly separated from those of Montana sapphires.

4.5 Ion beam modification

In this section, corundum were modified by ion implantation process and the results were investigated by comparing with the image, PIXE analysis, and UV-Vis-NIR spectroscopy as shown in Figures 4.10 – 4.26 and Tables 4.3 – 4.12, The irradiation conditions also are illustrated for energy (keV) and period of irradiation time (hr:min:sec).

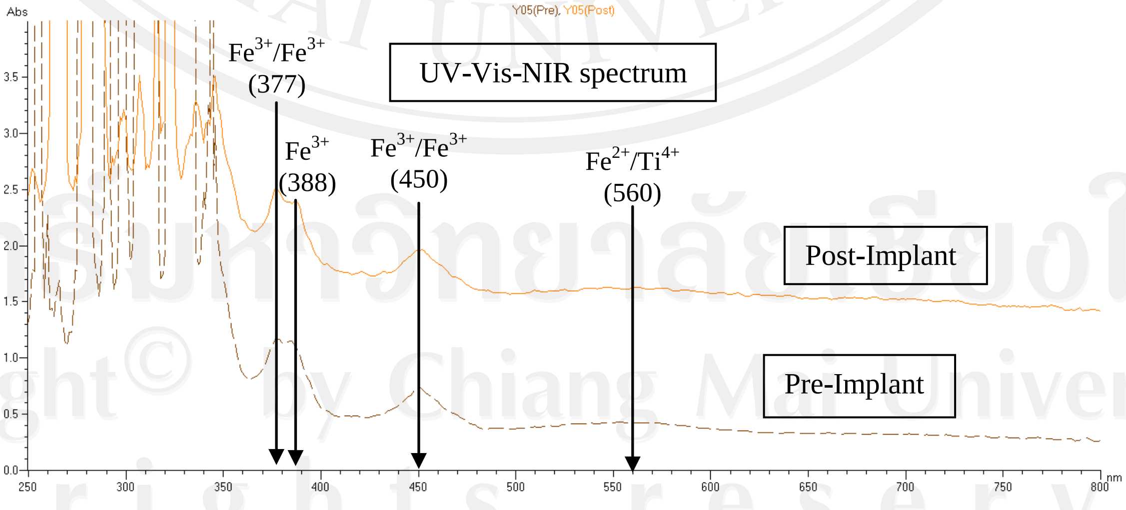
Before ion implantation, virgin samples were characterized by ion beam analysis. Additionally, all of the absorption spectra of corundum were investigated by the UV-Vis-NIR spectroscopy method which illustrating in the following results. After treatment, the observation found several alterations in corundum, mainly by an optical microscope recording. The preliminary result found that the charge state of easily alter transition element can be compensated by the deformation of the crystal structure where as the energetic ions dissipate their kinetic energy along the C-axis of corundum which is a less dense direction (Guan *et al.*, 2006). Note that the fingerprint data as explained earlier are important for the explanation of the modified samples after ion beam treatment. The results can be summarized as followings:

4.5.1 Nitrogen ion implantation

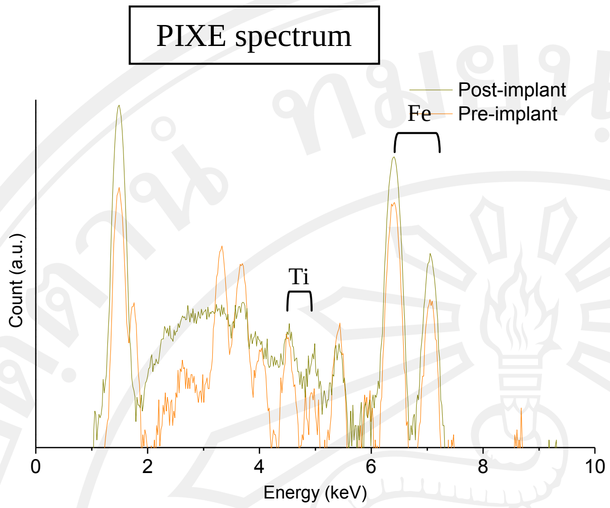
A variety of rubies and sapphires were treated by a range of 80 to 100 keV N_2^+ beam. Since N_2 gas is the main content in air, the environment in the chamber become N_2-rich or in other words is the discrimination of oxygen. For heat treatment, this condition was called “reducing” because, by this treatment, an electron is reduced from the oxygen in the Al_2O_3 molecule. Figures 4.10 (a) – (e) show the comparison of before and after treatment of yellow sapphire from Montana, the U.S.A. The irradiation was repeated three times with total fluence of 4×10^{18} ions/cm^2. The appearance changed from yellow color to green-blue color for Fe^{3+} – the cause of yellow color – altered to a Fe^{2+} (Emmeth *et al.*, 2003). As a result of reducing atmosphere, nitrogen ion dramatically affix the valence electron of iron by charge compensation. The appearance and trace element concentration alteration is confirmed by the conventional technique and ion beam technique, respectively. The absorption UV-Vis-NIR spectroscopy show a pair of Fe^{3+}/ Fe^{3+} peak centered at 450 nm dramatically decreases after modification in agreement with Emmeth and Douthit (1993). This is the evidence of the greenish reducing appearance in sapphire. Furthermore, as shown in Table 4.3, the PIXE spectra show that the amount of ratio of Fe/Ti which refer to the bluish color increasing (from 26.54 to 89). Since, valence electron of iron change charge state from +3 to +2, consequently releasing oxygen out of the compound, the relative concentration of iron to overall will drop off. If any photon absorbed by Fe^{2+}, its valence electron can transfer to Ti^{4+} along with Fe^{2+}/Ti^{4+} IVCT process. These phenomena increase blue color, which mix to the original yellow producing finally greenish tone (Kitbutrawat, 2006). The relation plot between Fe/Ti and Cr/Ga shows the alteration of trace element concentration that the ratio of Fe/Ti increase when compared to the before modification samples. Other interesting effect is the decreasing of inclusions which makes the sample more clear and vivid in appearance. According to the UV-Vis-NIR spectroscopy, the higher baseline spectrum means that the corundum's tone is darker than the lower baseline.

(a)

(b)



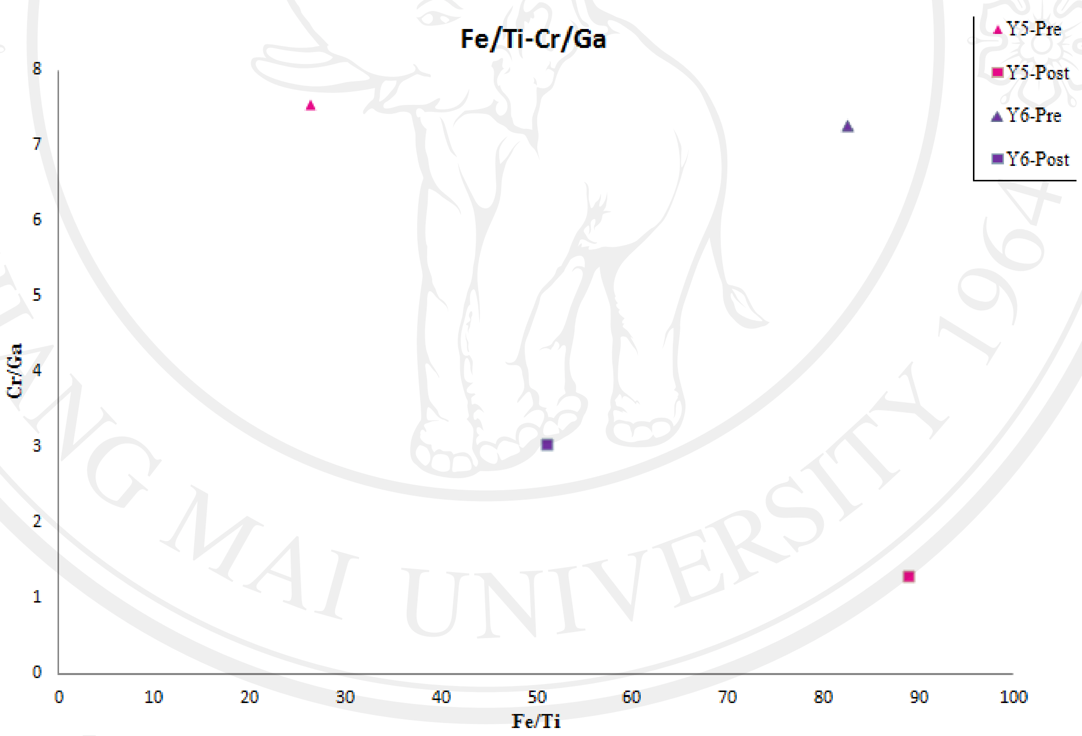
(c)



(d)

Table 4.3. The Fe/Ti concentration ratios of pre- and post- implantation of Y5.

	Pre-implantation	Post-implantation
Fe/Ti	26.54	89



(e)

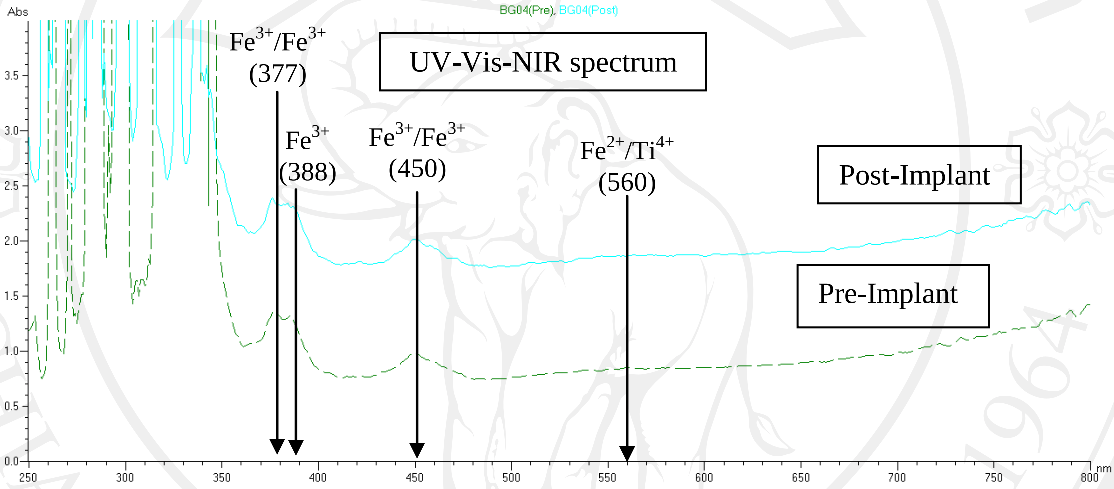
Irradiation conditions:
1st Energy 100 keV, Time 2:05:47
2nd Energy 100 keV, Time 1:38:24
3rd Energy 70 keV, Time 2:19:59

Figure 4.10. The changing from yellow to green-blue color of yellow sapphire (Y5) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the Ti and Fe concentrations of the before and after implantation (e).

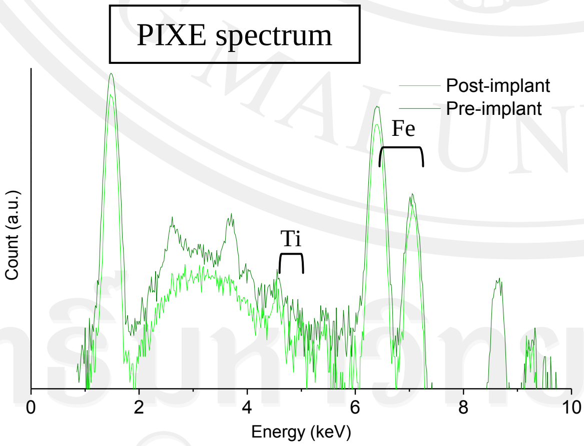
In this way, Figure 4.11 reveal the decreasing of vivid blue-green sapphire (Bang Kha Cha, Thailand) to be lighten green when be treated by 4.8×10^{17} ions/cm^2 for 80 minutes. According to green color produced by the combination of yellow and blue color, the yellow color, production by Fe^{3+}, is decreased – as described above – the single Fe^{3+} peak centered at 388 nm is decreased together with the very small absorption in blue region centered at 560 nm as shown in Figure 4.11 (c). As shown in Table 4.4, the ratio of Fe/Ti concentrations approaches to about 100 which nearly the value of yellow sapphire (Y5). Besides, the relation plot between Cr/Ga and Fe/Ti shows the alteration of trace element concentration compared to pre-treatment sample that the ratio of Fe/Ti is decreased. Alternatively, there is lighter and brilliant observation in greenish color by the clarity effect instead of bluish tone. Furthermore, this explanation is strongly supported by the modification of the dark-blue sapphire from Cambodia and the blue sapphire from Sri Lanka as shown in Figure 4.12. The blue sapphire (B7) from Sri Lanka is raised to deep blue and darker tone. In addition, Ti^{4+} in blue sapphire is still enough to interact with Fe^{2+} in IVCT process and the excess Fe^{2+} is altered to be the Fe^{3+} which is confirmed by the more Fe^{3+} absorption at 328 nm of the UV-Vis-NIR spectroscopy.

(a)

(b)



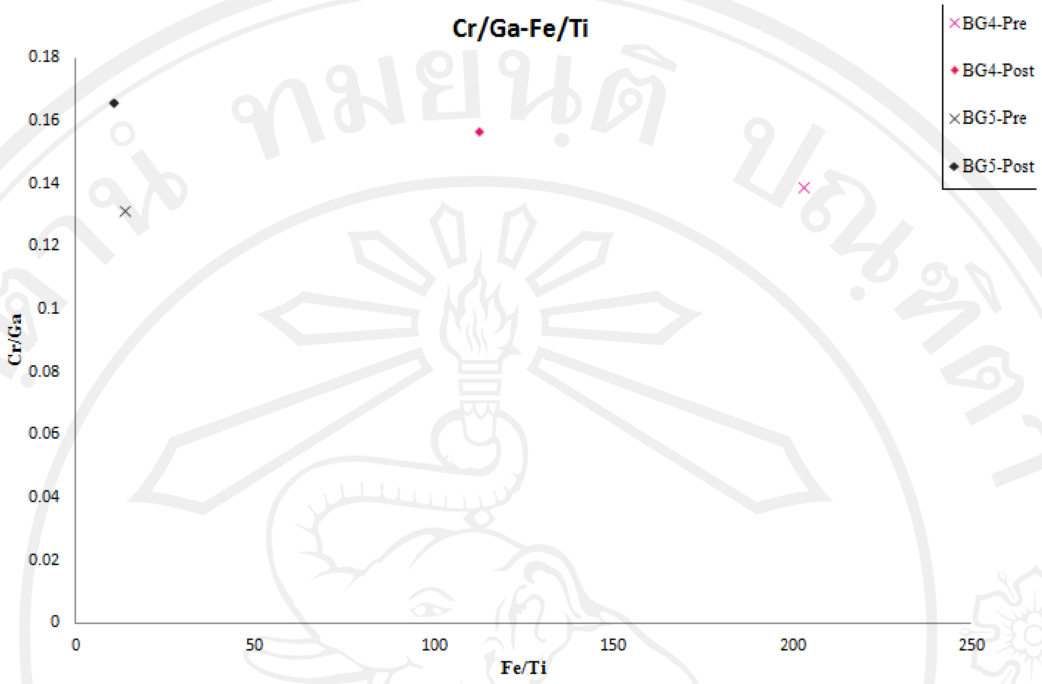
(c)



(d)

Table 4.4. The Fe/Ti concentration ratios of pre- and post- implantation of BG4.

	Pre-implantation	Post-implantation
Fe/Ti	203.12	112.65



(e)

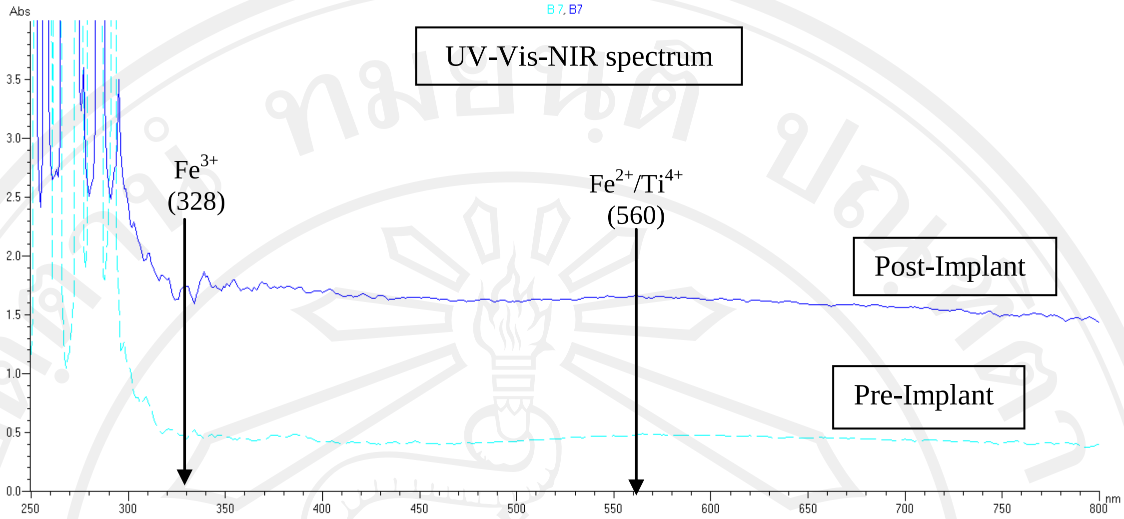
Irradiation conditions: 1st Energy 100 keV, Time 2:05:47

2nd Energy 100 keV, Time 1:38:24

3rd Energy 70 keV, Time 2:19:59

Figure 4.11. The brighter green tone of blue-green sapphire (BG4) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

(a) (b)



(c)

Irradiation conditions: 1st Energy 100 keV, Time 2:05:47

2nd Energy 100 keV, Time 1:38:24

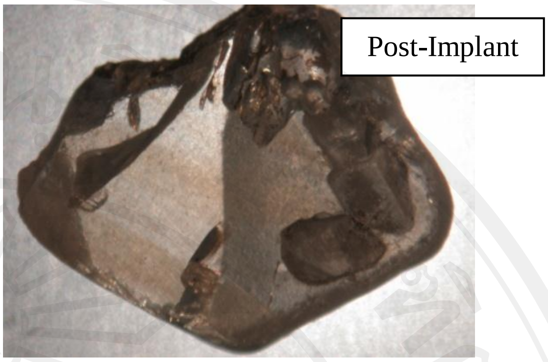
3rd Energy 70 keV, Time 2:19:59

Figure 4.12. The deep blue saturation of blue sapphire (B7) (a) – (b), and UV-Vis-NIR spectrum of the before and after implantation (c).

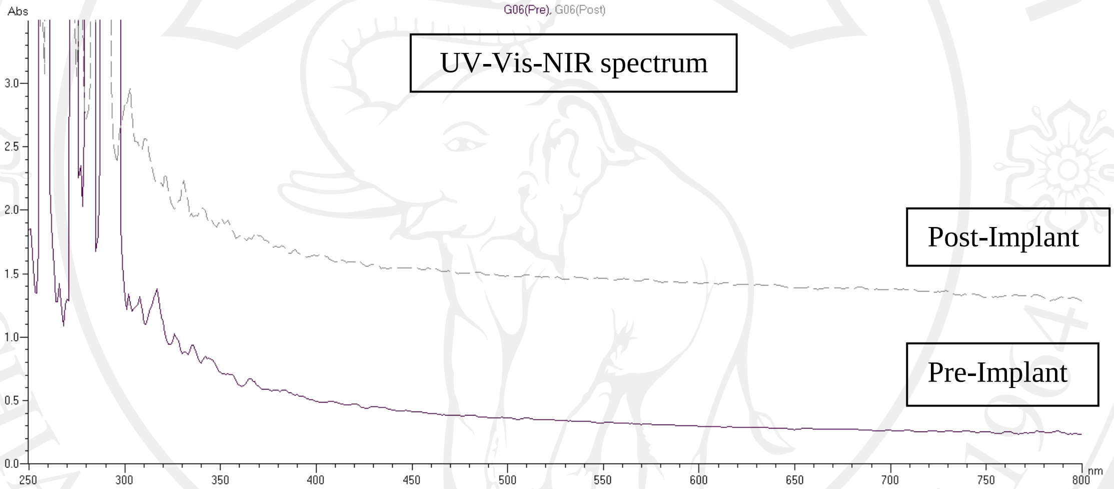
The last investigation is the dull white sapphire (Geuda) from Sri Lanka. Although the color is unchanged but the clarity and vivid appearance are increased as shown in Figure 4.13. The cause of clarity enhancement in this case is explained in the next subtopic. The relation plot between Cr/Ga and Fe/Ti shows the more Ti contents implies to the more colorless in the matter. By the way, the red ruby from Bo rai (Thailand) which original appearance was deep red and slightly opaque does not show any alteration in this type of treatment. As is well known that Cr^{3+} has interaction with oxygen, the energetic ion is not capable to disturb or replace to the localize chromium position (Nassau, 1978).


Pre-Implant

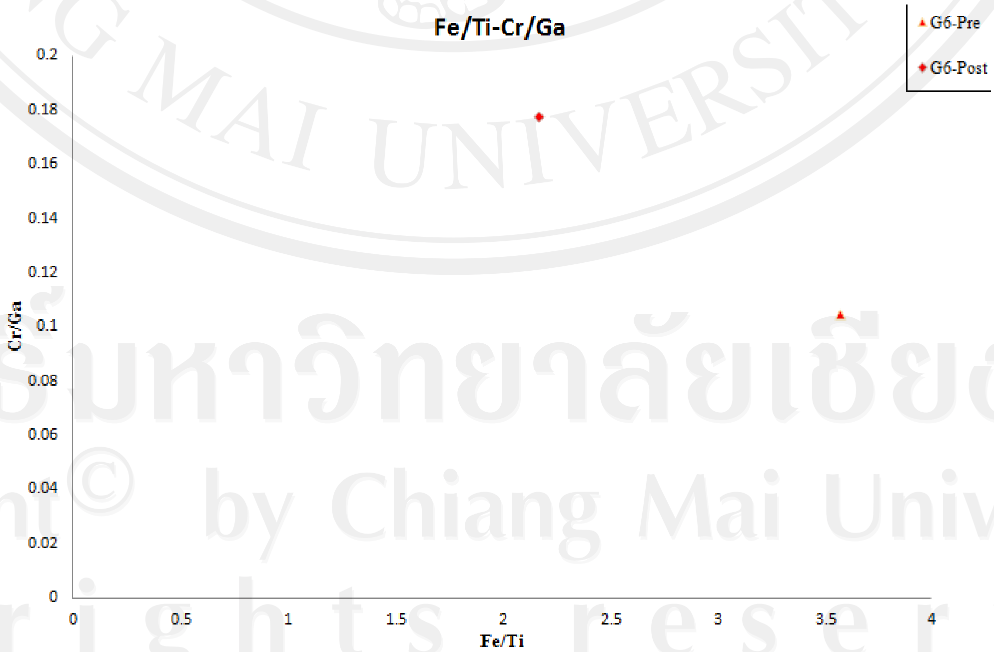
(a)


Post-Implant

(b)


Abs
G06(Pre), G06(Post)
UV-Vis-NIR spectrum
Post-Implant
Pre-Implant
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
300
350
400
450
500
550
600
650
700
750
800
nm

(c)


Fe/Ti-Cr/Ga
G6-Pre
G6-Post
Cr/Ga
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Fe/Ti
0
0.5
1
1.5
2
2.5
3
3.5
4

(d)

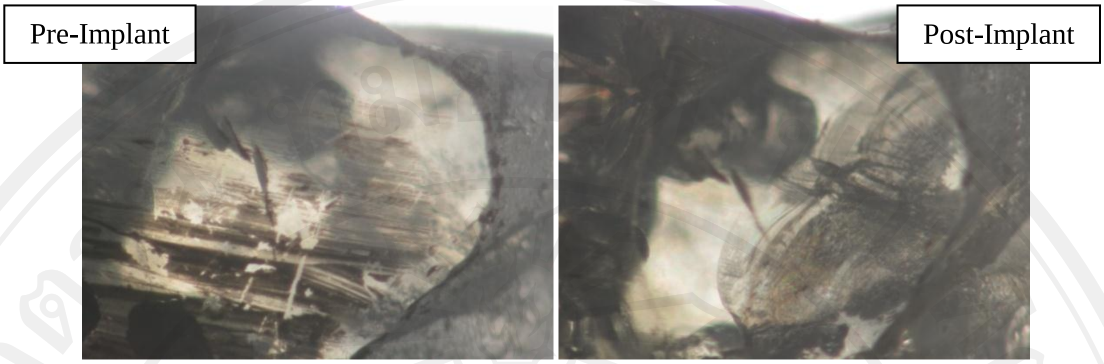
Irradiation condition: Energy 70 keV, Time 2:19:59

Figure 4.13. The clarity enhancement of dull white sapphire (G6) (a) – (b), UV-Vis-NIR spectrum (c), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (d).

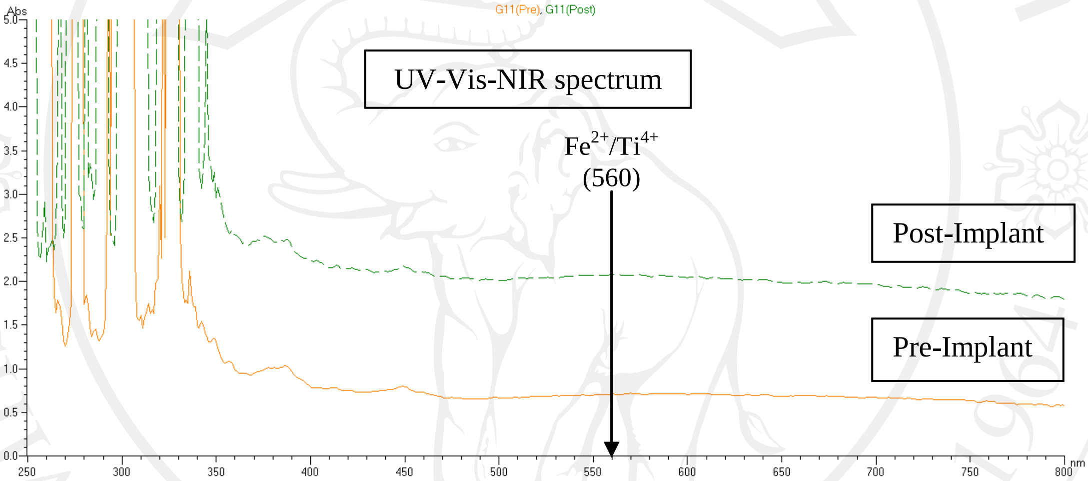
4.5.2 Argon ion implantation

Another ion type in the reducing condition which was used for this investigation is Argon positive ion (Ar^+). Both N_2^+ and Ar^+ ions have high capability to capture the electron because their valence electron configurations have also partially space. However, it is interesting to know the different effect to corundum between these two ion species.

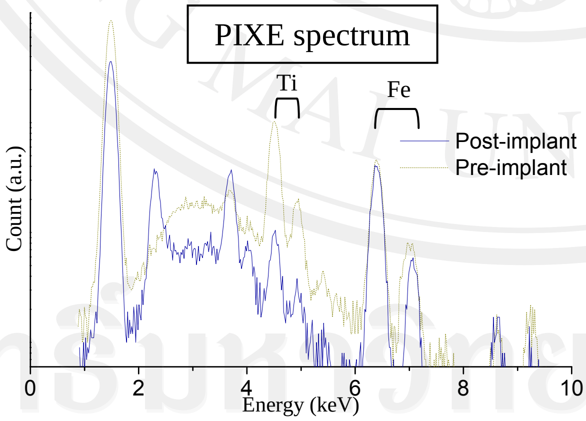
The huge change in clarity of sapphire by Ar^+ treatment is achieved. As seen in Figure 4.14, the needle inclusions in dull white sapphire are eliminated. The baseline of UV-Vis-NIR spectra after modification is over that of before modification. It means that this sapphire become darker tone after treatment. The PIXE analysis proves that the concentration of Ti which exist in Rutile is eliminated since the ratio of Fe/Ti concentration increasing as shown in Table 4.5. Additionally, the relation between Cr/Ga and Fe/Ti shows the decrease of Fe/Ti ratio according to the reducing of Ti in the sapphire. This implies that Ti in the Rutile needle-structure dissolve thoroughly in the gemstone associate with Fe^{2+} increasing to produce intense blue color by Fe^{2+}/Ti^{4+} IVCT process. The presence of Fe^{2+}/Ti^{4+} process is confirmed by the slightly absorption peak centered at 560 nm compared with the baseline by UV-Vis-NIR spectroscopy.



(a) (b)



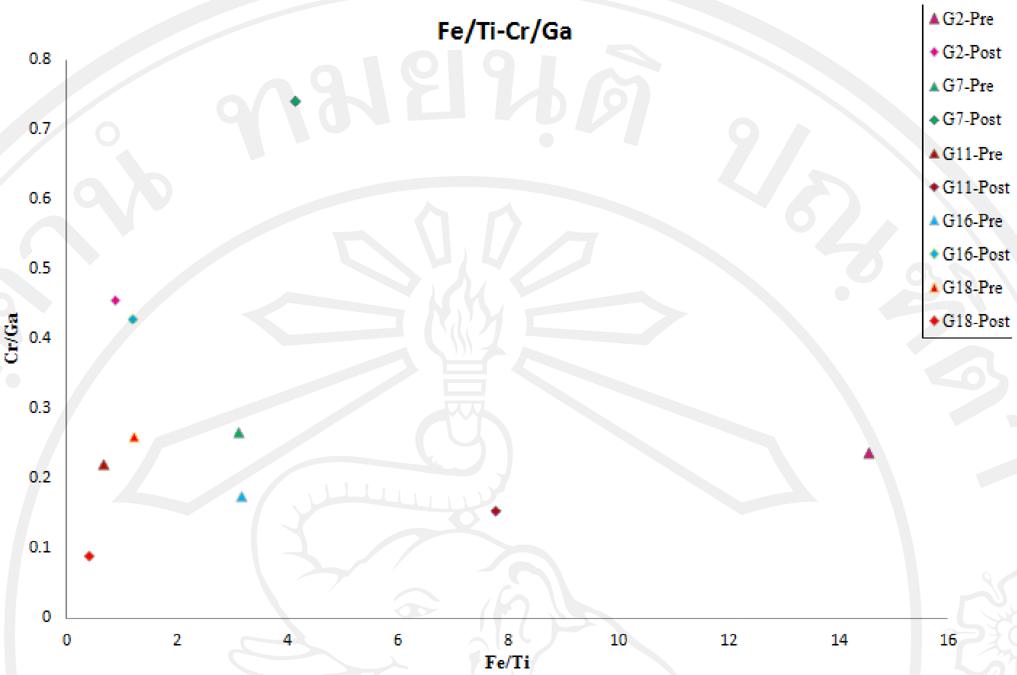
(c)



(d)

Table 4.5. The Fe/Ti concentration ratios of pre- and post- implantation of G11.

	Pre-implantation	Post-implantation
Fe/Ti	0.69	7.78

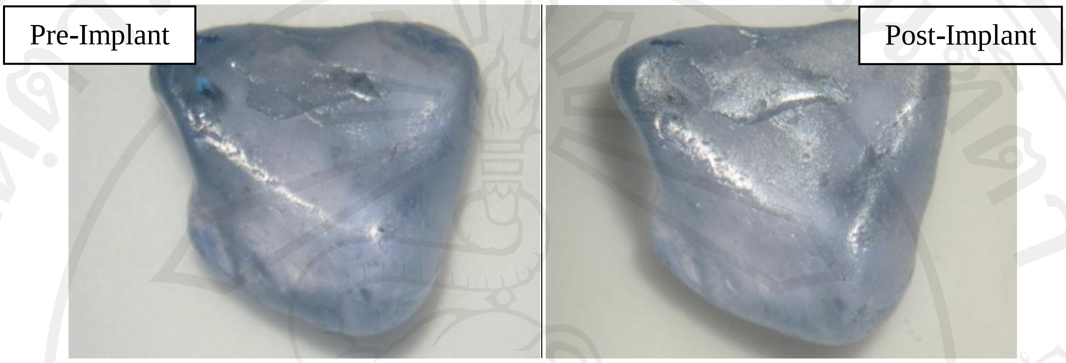


(e)

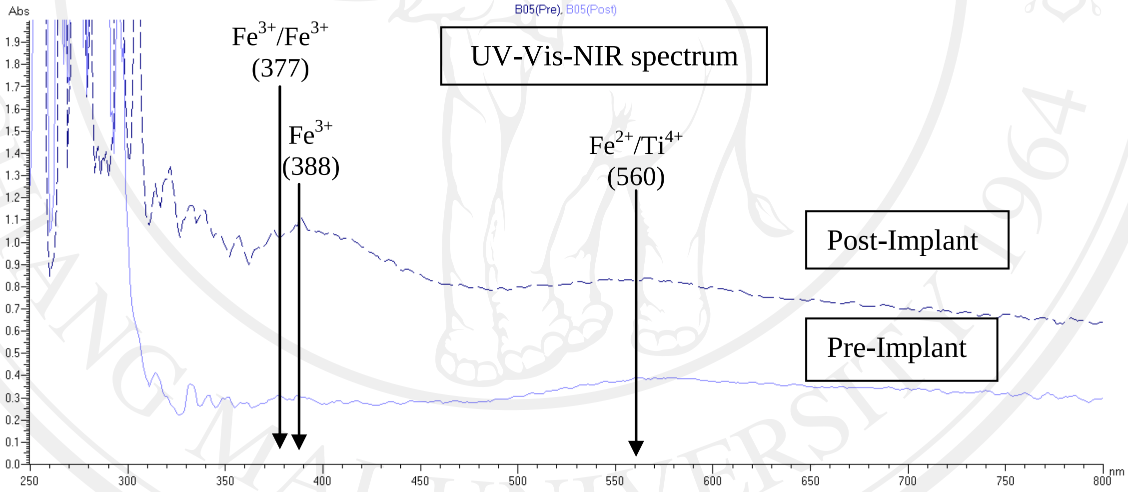
Irradiation condition: Energy 50 keV, Time 0:46:44

Figure 4.14. The clarity enhancement of dull white sapphire (G11) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

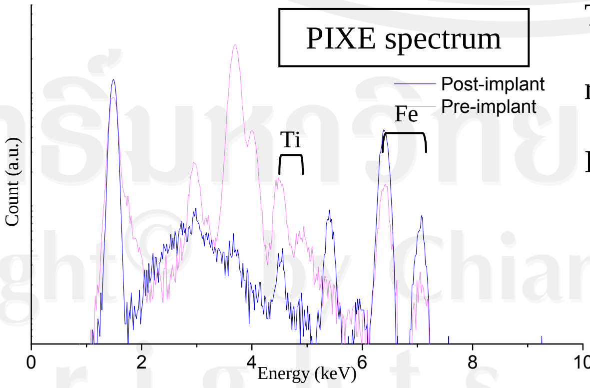
Another result, as shown in Figures 4.15 – 4.16, demonstrate that sapphire become colorless when bombarded with Ar^+, verify that Ar^+ can expel the chromophoric element. Nevertheless, the UV-Vis-NIR analysis shows that the saturation color remains increase for before and after implantation. Each of absorption peaks is more dominantly compared with the baseline. By PIXE analysis, the ratio of Fe/Ti concentration increases according to the dissolving of excess Ti by ion beam producing the deep blue color as shown in Tables 4.6 and 4.7. Accordingly, the relation between Cr/Ga and Fe/Ti shows the increasing ratio of Fe/Ti which means the blue color is enhanced but the presence is hidden by the discoloration effect.



(a) (b)



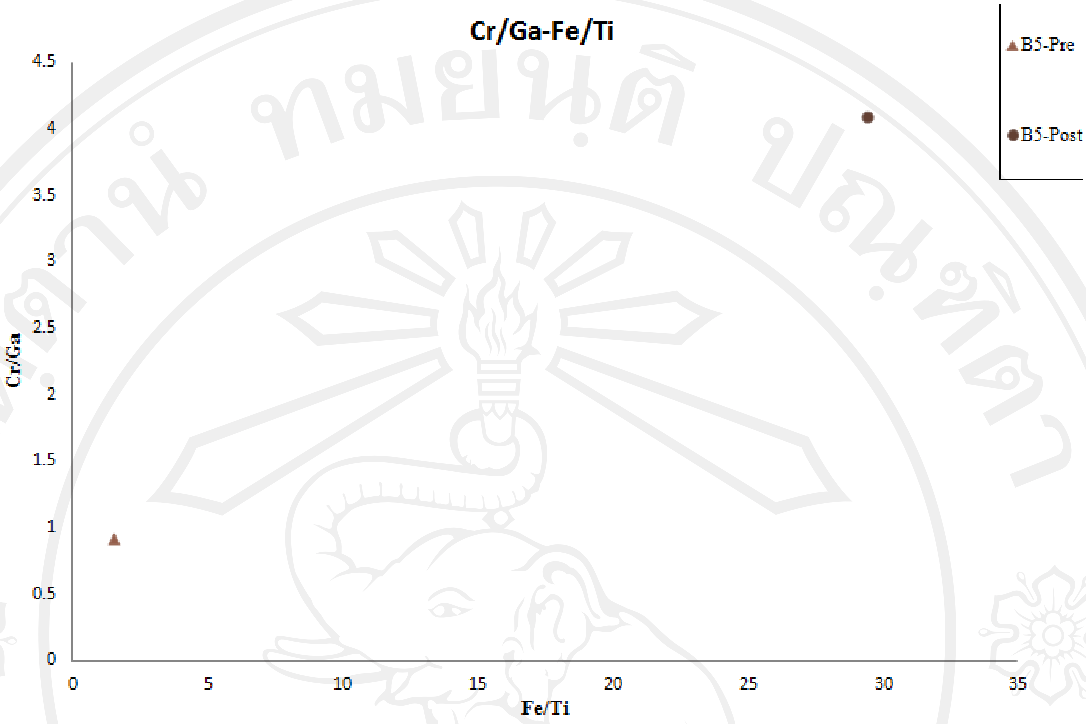
(c)



(d)

Table 4.6. The Fe/Ti concentration ratios of pre- and post- implantation of B5.

	Pre-implantation	Post-implantation
Fe/Ti	1.56	29.42



(e)

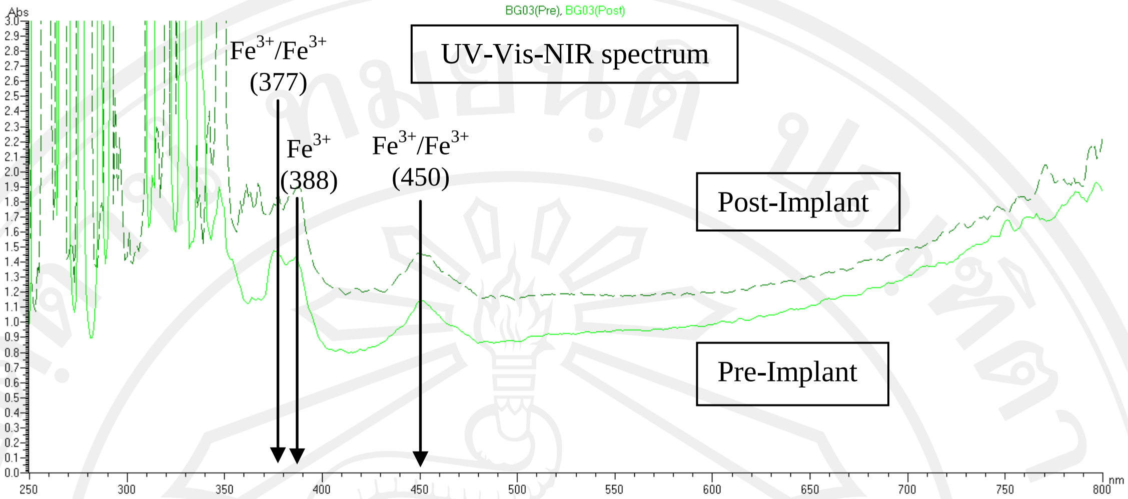
Irradiation condition: 1st Energy 100 keV, Time 1:57:38

2nd Energy 50 keV, Time 0:46:44

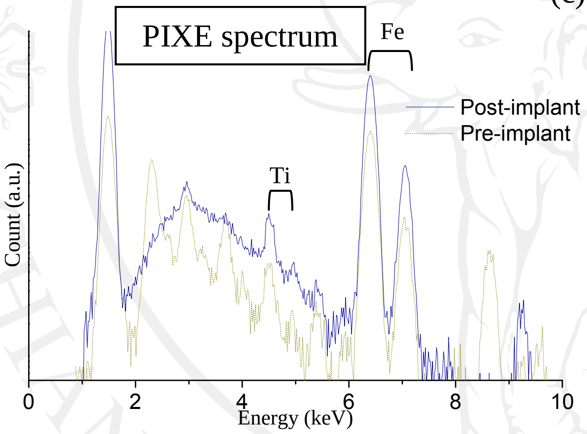
3rd Energy 70 keV, Time 3:05:30

Figure 4.15. The discoloration of blue sapphire (B5) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

(a) (b)



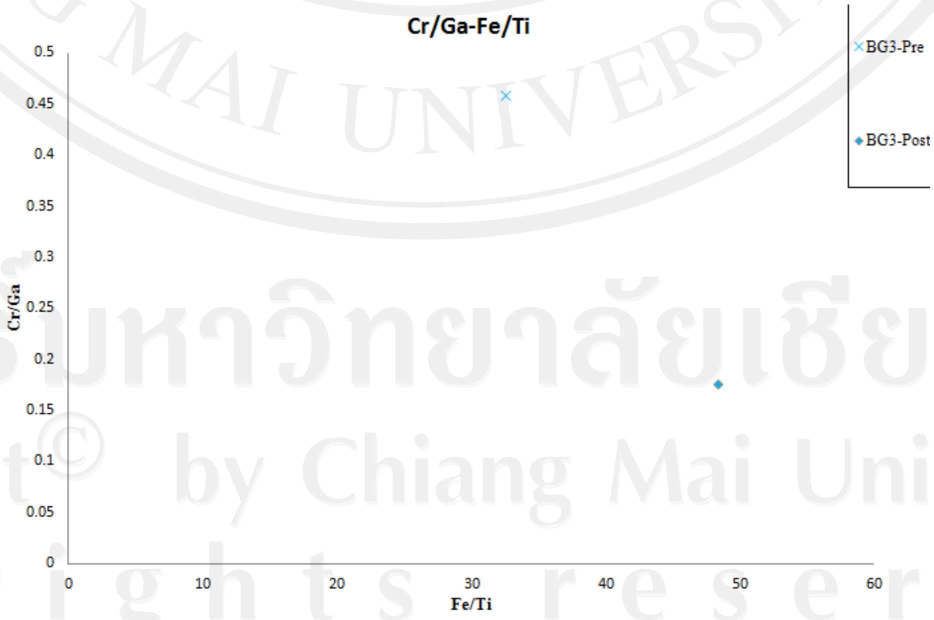
(c)



(d)

Table 4.7. The Fe/Ti concentration ratios of pre- and post- implantation of BG3.

	Pre-implantation	Post-implantation
Fe/Ti	32.54	48.32



(e)

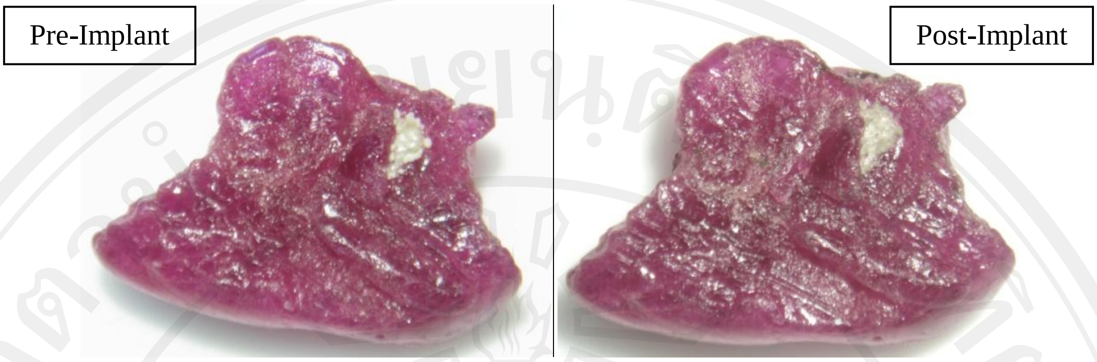
Irradiation condition: 1st Energy 100 keV, Time 1:57:38

2nd Energy 50 keV, Time 0:46:44

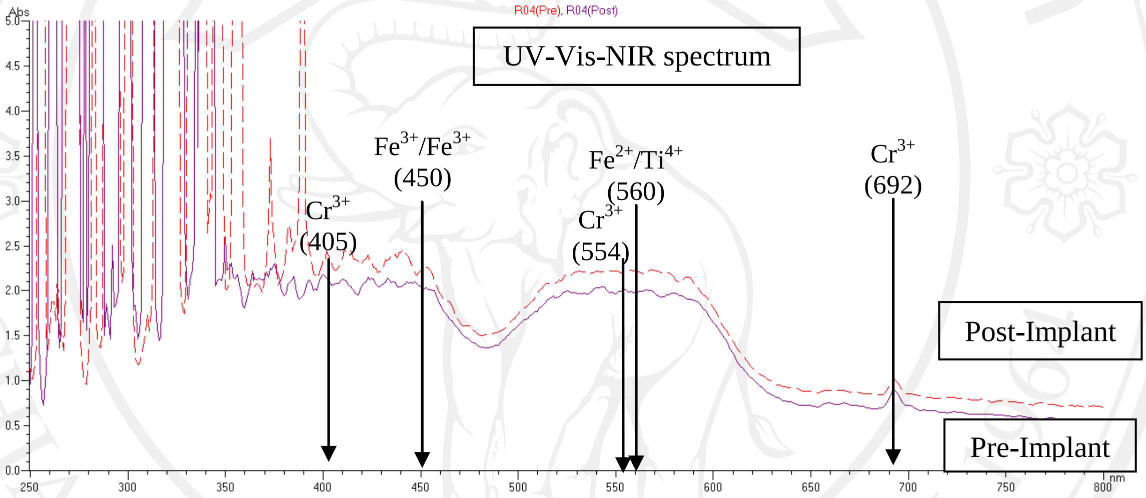
3rd Energy 70 keV, Time 3:05:30

Figure 4.16. The discoloration of blue-green sapphire (BG3) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

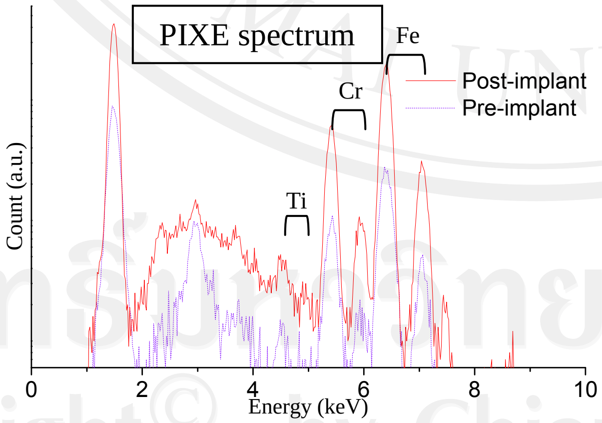
On the other hand, the ruby from Bo rai turn to more violet tint after Ar^+ implantation by a range of 50 to 100 keV as shown in Figure 4.17. The violet is the color between red and blue where as red color is occurred by the presence of Cr^{3+} and blue color is occurred by the Fe^{2+}/Ti^{4+} IVCT process. The violet appearance in this case is occurred by the presence of excess Fe in the ruby. According to the fact that Fe can emerge into either +2 or +3 charge state, the Fe^{2+} could couple with the Ti^{4+} and present ultimately the blue color. The evidence is that the absorption peak of Fe^{2+}/Ti^{4+} centered at 560 nm for post-implantation is higher than the pre-implantation and Fe^{3+} peaks faintly raised. In other words, the Fe^{3+} prefers to change the charge state to Fe^{2+} to corporate with Ti^{4+} giving blue color. Furthermore, the Cr^{3+} peaks are not difference between pre and post implantation which means the Cr_2O_3 is barely alter to the new phase. According to the fact that Cr^{3+} is the main cause of red color and the ratio of Cr/Ga decreases, so the red color is reduced. As shown in Table 4.8, the ratio of Fe/Ti increasing means that the blue color is enhance in ruby. These results conform to the relation plot between Fe/Ti and Cr/Ga that the ratio of Fe/Ti increasing. Eventually, the red tone which is mixing with the violet tint, thus, appears in the ruby.



(a) (b)



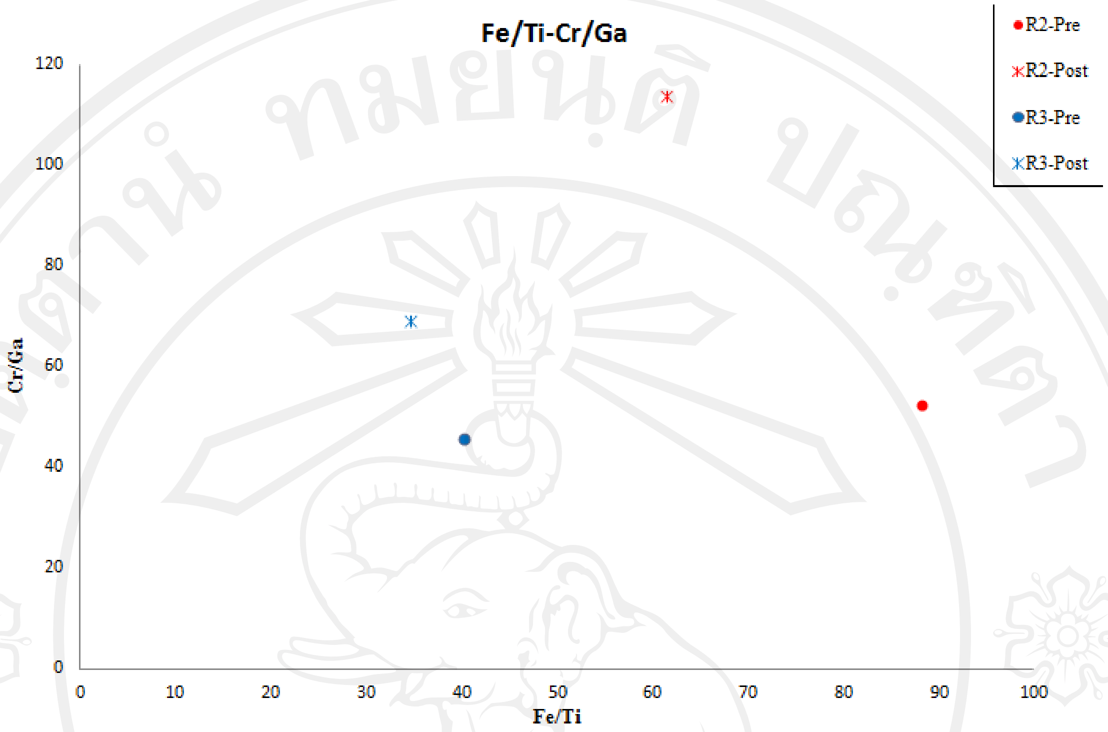
(c)



(d)

Table 4.8. The Fe/Ti and Fe/Cr concentration ratios of pre- and post-implantation of R4.

	Pre-implantation	Post-implantation
Fe/Ti	32.54	48.32
Fe/Cr	3.90	1.92



(e)

Irradiation condition: 1st Energy 100 keV, Time 1:57:38

2nd Energy 50 keV, Time 0:46:44

3rd Energy 70 keV, Time 3:05:30

Figure 4.17. The more violet tint of ruby (R4) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

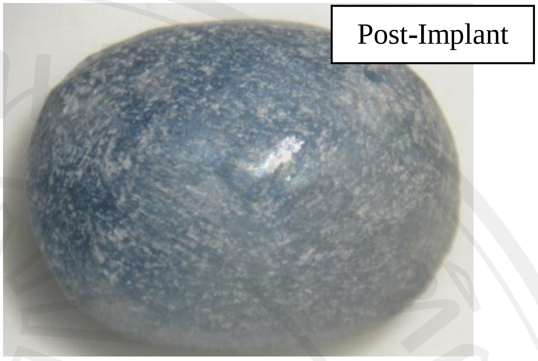
N_2^+ can also induce the environment around the modified corundum to the reducing condition as same as in the lacking of oxygen gas in the furnace of the conventional heat treatment. The ion beam modification can enhance the color of corundum since the exchange charge process occurs in the shallow surface. Although, the incident ion cannot penetrate deeper than the ion range (about 1 µm), but, the color of the whole piece is altered because the incident ion could induce the surrounding atoms to rearrange their position.

By the way, the enormous kinetic energy of the incident ion can transfer to the localize atom which can diffuse to another lattice point. The clarity is also enhanced by the kinetic energy transfer from the energetic ion to the loosely bound apart of the bulk during bombardment. The energetic ion can push off the loosely bound non-chromophoric element or inclusion deeper into the gemstone. Accompanied with more massive than N_2^+, the momentum of Ar^+ is twice larger than N_2^+ means that the more interaction probability. As a result, this implies that the opportunity to modify the clarity in corundum by ion implantation increase dramatically by using higher momentum (depending on energy and mass) projectile. The localized element could also be removed, subsequently, let the intensely external light can transmit to the matter. On the other word, Ar^+ has greater the sputtering yield than N_2^+, therefore, the treated corundum by Ar^+ emerge more clarity effect than treated by N_2^+. In addition, ion bombardment provides them the smoother surface by sputtering the rough surface and fill out the crack, fracture or cavity on the surface region (Townsend *et al.*, 1994).

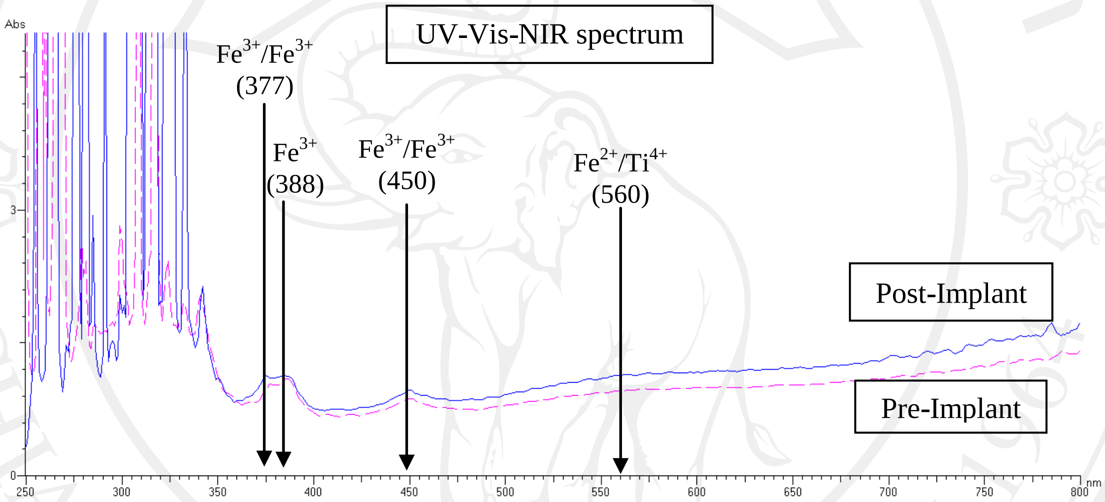
4.5.3 Oxygen ion implantation

The negative ion source in the tandem accelerator is used for oxygen bombardment. For the 23 keV oxygen-ion implantations, there are various interesting results which can be summarized as follows.

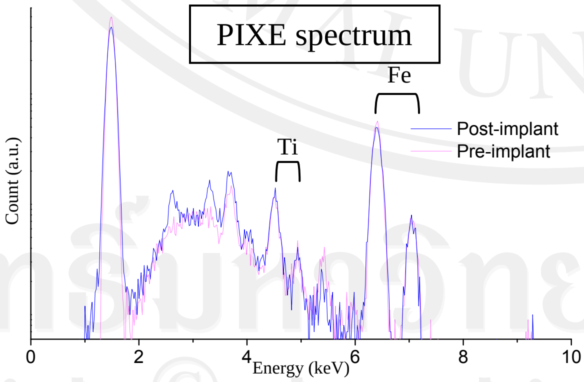
(a)



(b)



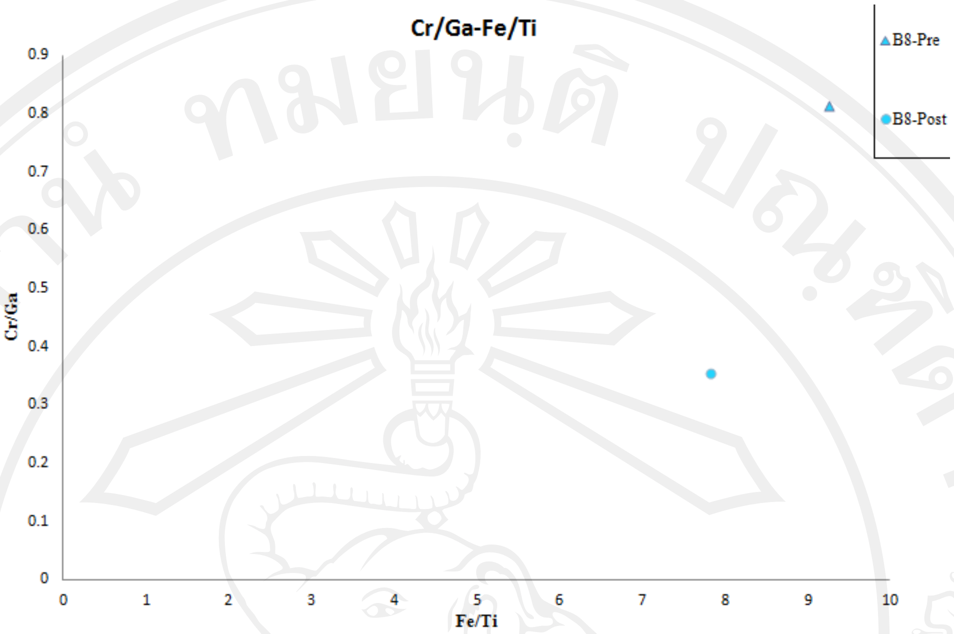
(c)



(d)

Table 4.9. The Fe/Ti concentration ratios of pre- and post- implantation of B8.

	Pre-implantation	Post-implantation
Fe/Ti	9.26	7.83



(e)

Irradiation condition: Energy 23 keV, Time 1:20:00

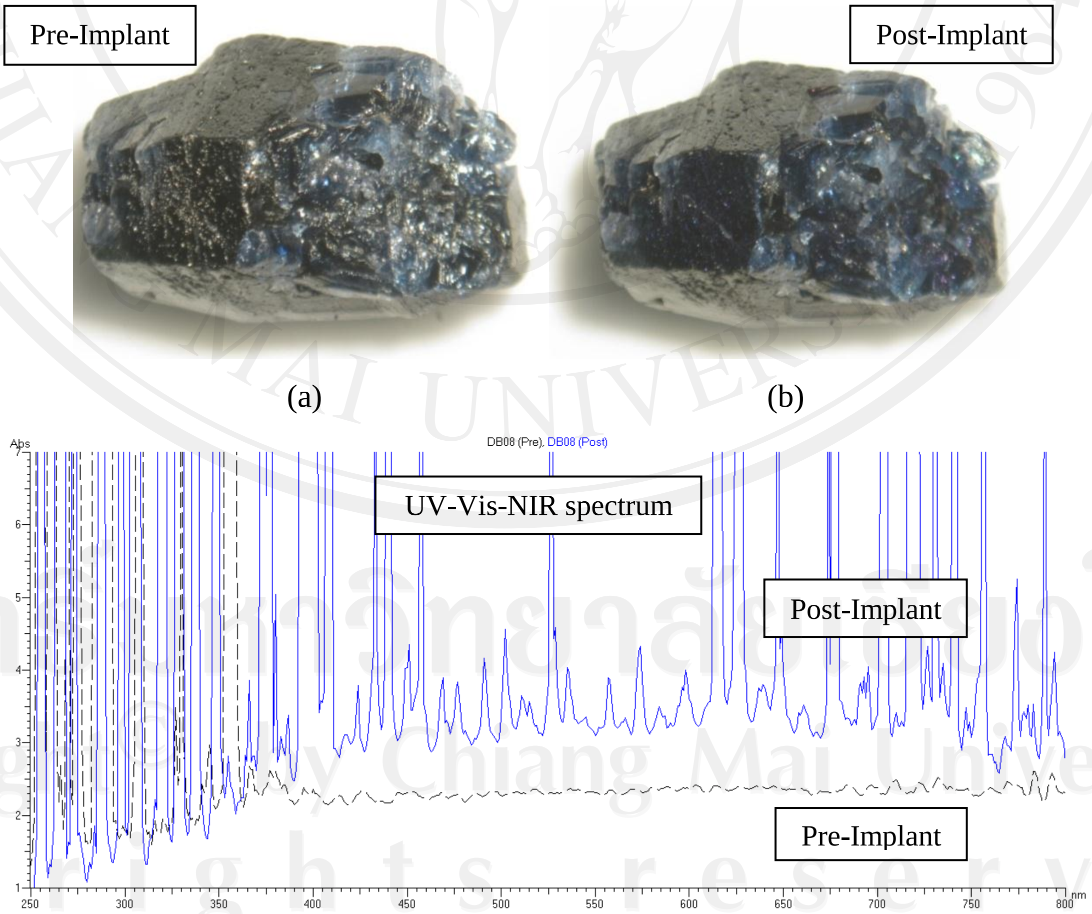
Figure 4.18. The less brownish tint of blue sapphire (B8) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation plot between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

Figure 4.18 shows the comparison of blue sapphire from Sri Lanka for the before and after treatment to ion fluence of 4.8×10^{17} ions/cm^2 for 80 minutes. The brownish tint and pale blue tone appearance becomes brighter blue and less brownish tint since the Fe^{3+} related to the yellow color. The UV-Vis-NIR spectroscopy illustrates that the blue absorption region increase after modification which indicate the deep blue tone in the sapphire. However, the relation between Cr/Ga and Fe/Ti also shows the diminishing ratio of Fe/Ti. As seen in Table 4.9, the PIXE analysis shows that the Fe/Ti changes from 9.26 to 7.83 implying that both Fe^{2+} and Fe^{3+} is reduced and the brownish tint is eliminated.

(a) (b)

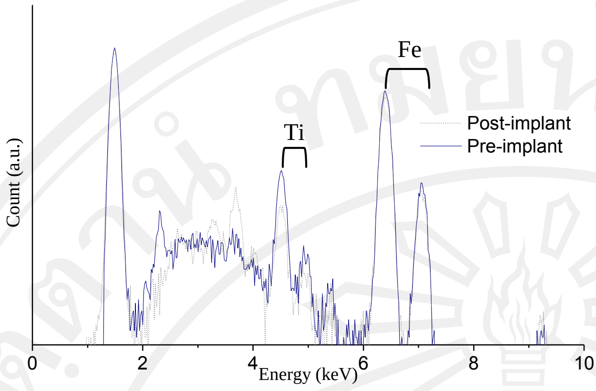
Irradiation condition: Energy 23 keV, Time 1:57:00

Figure 4.19. The reduction of green color in blue green sapphire (BG8) (a) – (b) of the before and after implantation.



(a) (b)

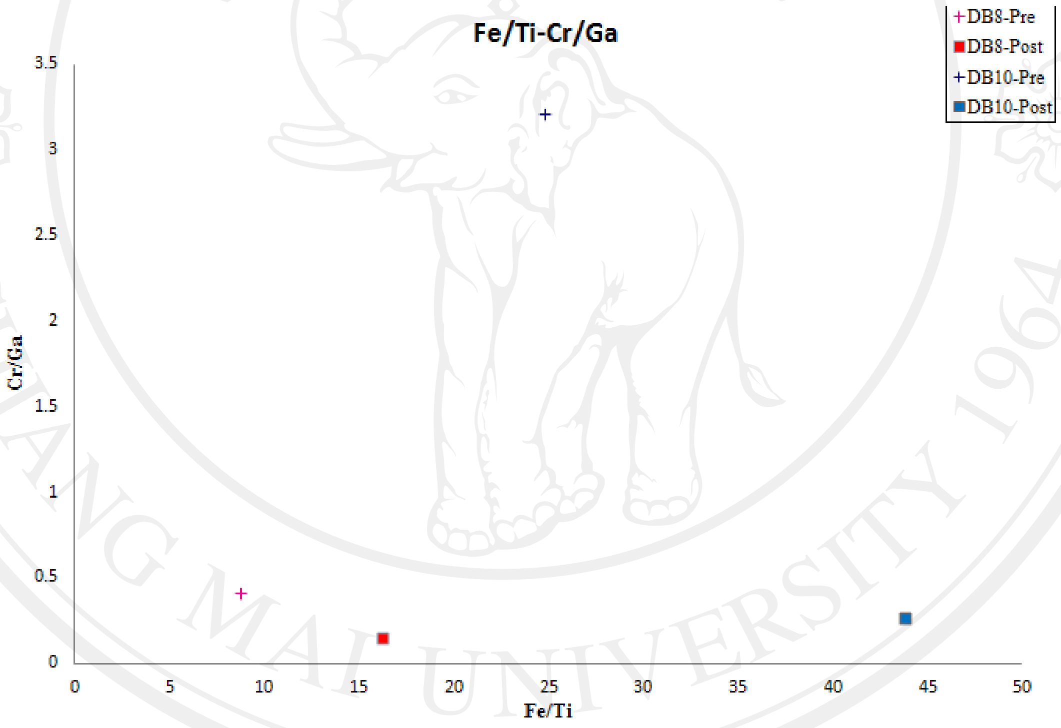
(c)



(d)

Table 4.10. The Fe/Ti concentration ratios of pre- and post- implantation of DB8.

	Pre-implantation	Post-implantation
Fe/Ti	8.82	16.26



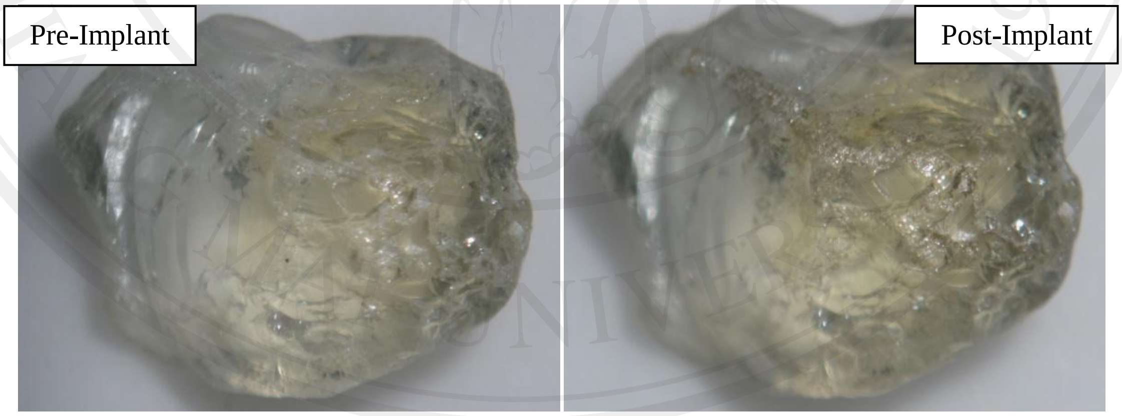
(e)

Irradiation condition: Energy 23 keV, Time 1:22:00

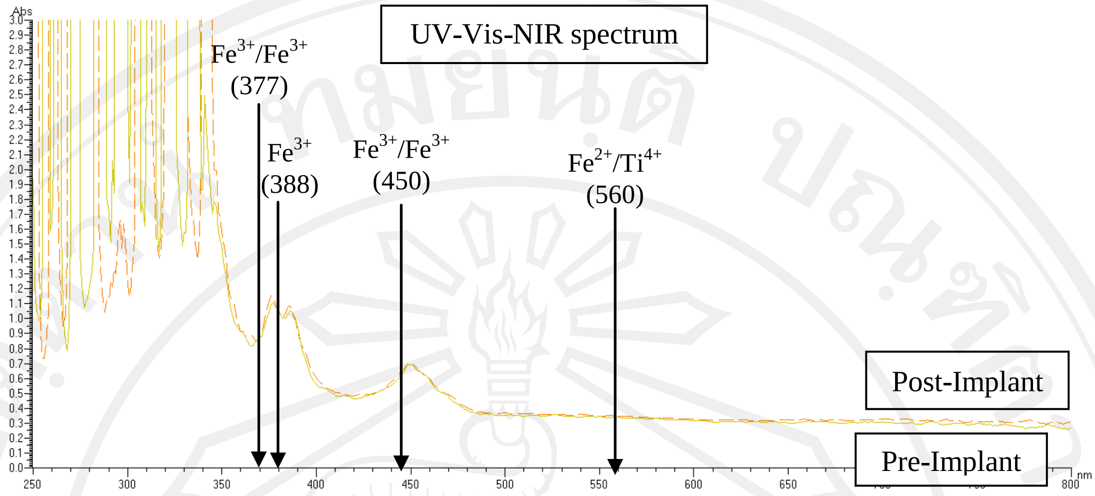
Figure 4.20. The lightener bluish tone of dark-blue sapphire (DB8) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

Figure 4.19 shows the reduction of green color in blue-green sapphire (Bang Kha Cha) to be a more slightly yellowish tone when treated by 4.8×10^{17} ions/cm^2 for 80 minutes. It is worth to mention that green color is the combination of yellow color and blue color which caused by Fe^{3+} and Fe^{2+}/Ti^{4+} IVCT process, respectively. In this case, corundum in the oxidizing state which has as much as Fe^{3+} can create more yellowish tone and appear the yellow green sapphire ultimately. Besides, this determination associates with Figure 4.20, which shows the comparison of dark-blue sapphire from Cambodia for before and after treatment. The sapphire changes to lighter blue which increases in value of the market. Although the UV-Vis-NIR spectroscopy for post-implantation is interfered by the low transparency of the sample, it also implies that the chromophoric elements in the sapphire are compressed till the light cannot go through the gemstone. Nevertheless, the ratio of Fe/Ti concentration, as shown in Table 4.10, increase, but an amount of Fe is somewhat constant while the Ti is reduced to half of the former. The explanation is that the most of Ti is on the surface and sputtered while being bombardment with ion. However, the relation between the ratio of Cr/Ga and Fe/Ti shows the different trend to the blue sapphire from Sri Lanka. The ratio of Fe/Ti increases while the ratio of Cr/Ga decreases mean that the sapphire has more bluish tone. The explanation is that the dark-blue sapphire consists of many Fe which is more opportunity for bonding with the incident ion – oxygen – than the Ti. Thus, an amount of Fe/Ti increases dramatically with another chromophoric element. Perhaps, the blue color is produced in the lighter blue feature because the ratio of Cr/Ga reduces which indicates the less of chromophoric elements in the sapphire.

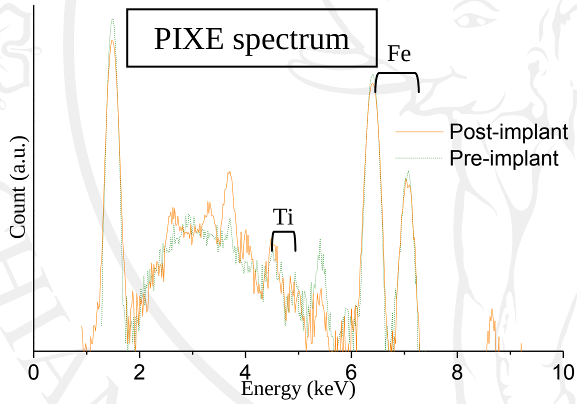
Furthermore, the yellow sapphire (Y9) with color zone has more vivid appearance after implanted by the negative oxygen ion. The vivid yellow hue is generated by the Fe^{2+} changed to Fe^{3+} as seen in the increasing of Fe^{3+} absorption peak of UV-Vis-NIR spectroscopy. Blue color is reduced and yellow is increased from Fe oxidizing alteration. In Table 4.11, the PIXE result illustrates the decrease of Fe/Ti ratio to about one-half. The saturation of yellow color is also confirmed by the plot between Cr/Ga and Fe/Ti relation which shows the increase of Ti compared with Fe. The Fe^{2+}/Ti^{4+} reducing implies that the hidden blue color which cannot observe by the naked-eye has been removed. Therefore, the remaining yellow color has more vivid appearance than the original color. This enhancement, as shown in Figure 4.21, confirms that an excess Fe^{2+} alter to Fe^{3+} charge state.



(a) (b)



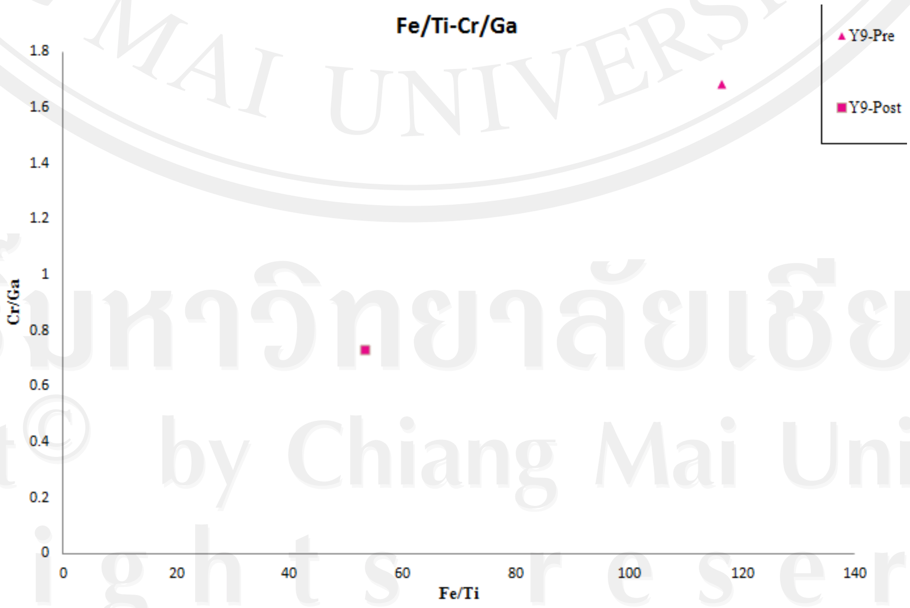
(c)



(d)

Table 4.11. The Fe/Ti concentration ratios of pre- and post- implantation of Y9.

	Pre-implantation	Post-implantation
Fe/Ti	116.52	53.50

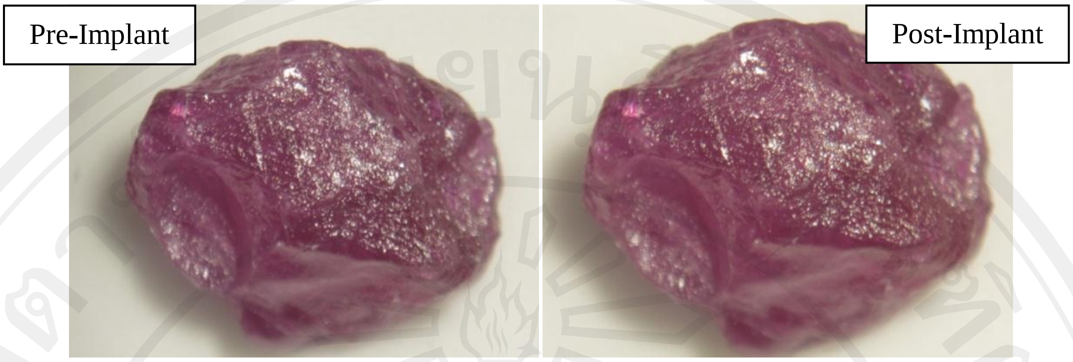


(e)

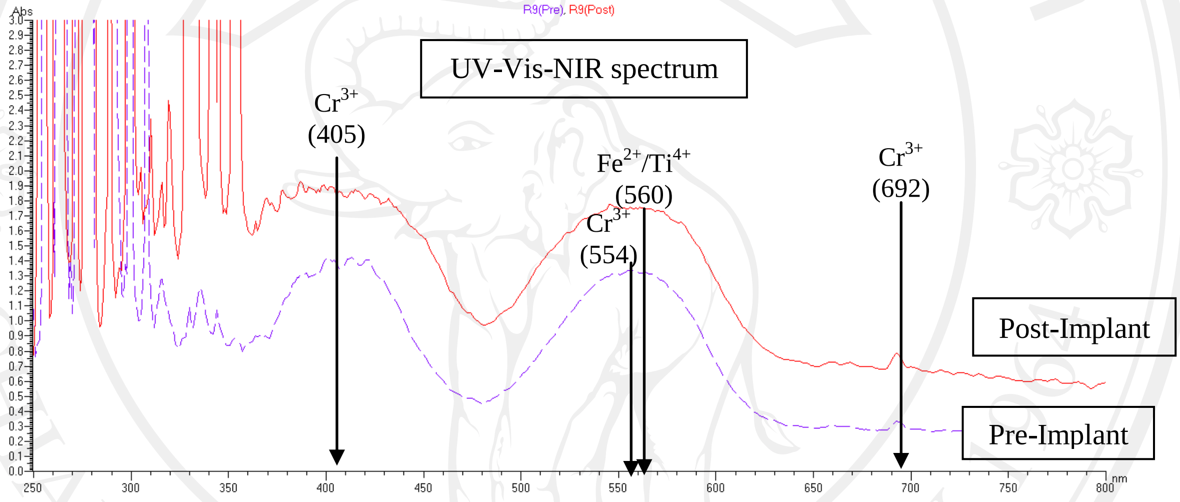
Irradiation condition: Energy 23 keV, Time 1:57:00

Figure 4.21. The more vivid of yellowish zone of yellow sapphire (Y9) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

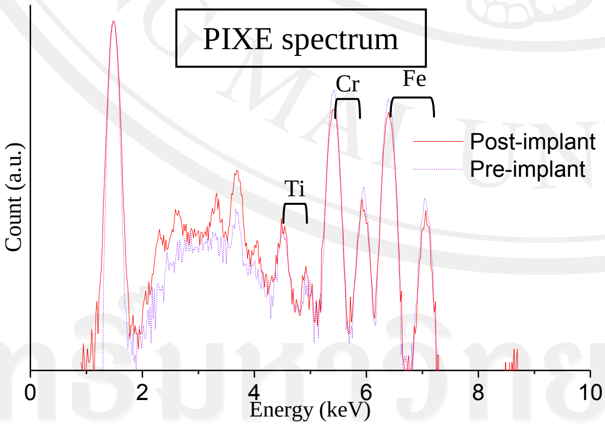
For the Cr^{3+}-dominant concentration corundum, i.e. ruby and pink sapphire, they are enhanced in reddish saturation and become more vivid in appearance as shown in Figure 4.22. The explanation for this modification is that the pale violet tint is reduced by the oxidizing of Fe^{2+} to be Fe^{3+} state. As mentioned earlier that the Ti concentration is slightly low, thus Fe^{2+} have not enough pair for producing the strong blue color while the Fe^{3+} still produce yellowish tone so that the reddish tone is more development. Consequently, the reddish tone appearance is verified by the clear absorption peaks of Cr^{3+} in UV-Vis-NIR spectroscopy. In addition, the PIXE result show the reduction of the ratio of Fe/Ti which means the violet tint is reduced, but does not show any significant alteration of the amount of Cr compared with Fe as seen in Table 4.12. Furthermore, the relation between Cr/Ga and Fe/Ti shows the increasing of Ti compared with Fe. This implies that the dark-tone of the iron is decreased. The reddish's corundum tone modification also occurs in pink sapphires, as shown in Figures 4.23 – 4.24, which has been enhanced in red tone and reducing of the violet tint, respectively. Additionally, the dull white sapphire which is initially colorless is replaced by the pale pink as shown in Figure 4.25.



(a) (b)



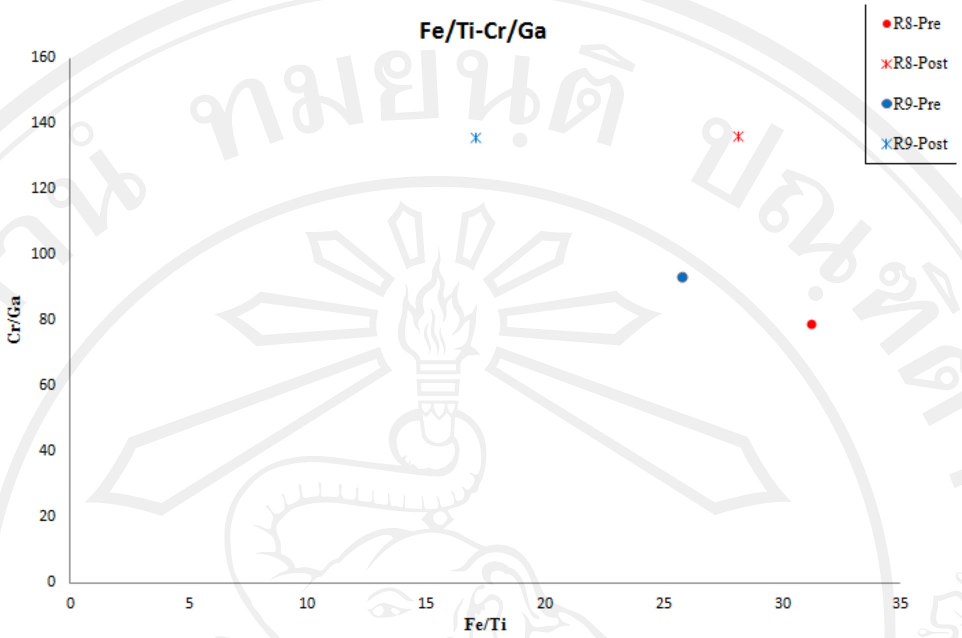
(c)



(d)

Table 4.12. The Fe/Ti and Fe/Cr concentration ratios of pre- and post-implantation of R9.

	Pre-implantation	Post-implantation
Fe/Ti	25.79	17.08
Fe/Cr	1.20	1.24



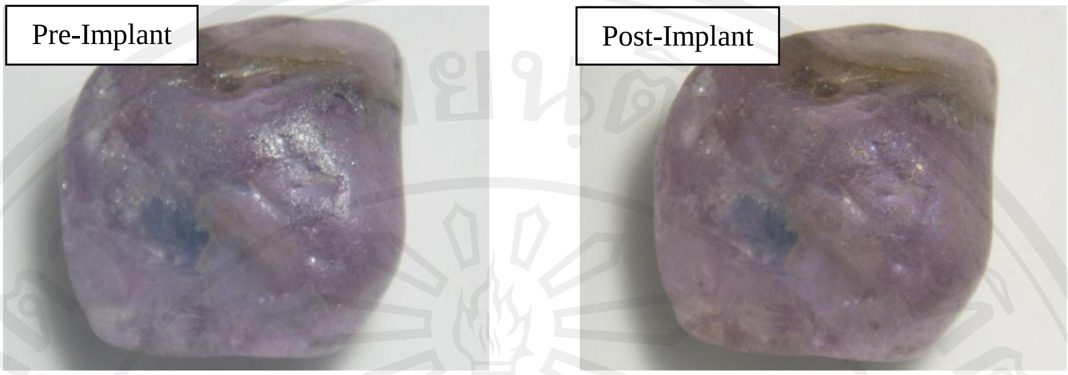
(e)

Irradiation condition: Energy 23 keV, Time 1:30:00

Figure 4.22. The implanted effect for ruby (R9) (a) – (b), UV-Vis-NIR spectrum (c), PIXE spectrum (d), and the relation between the ratio of Cr/Ga and Fe/Ti concentrations of the before and after implantation (e).

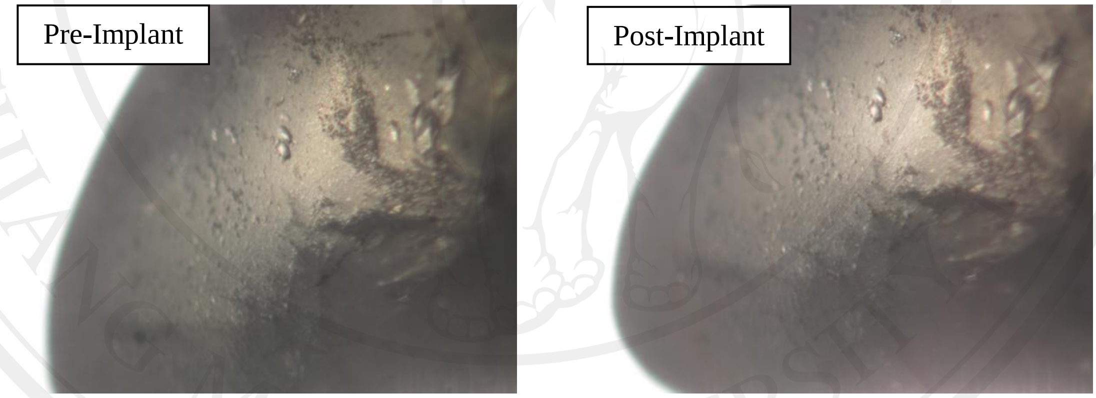
(a) (b)

Figure 4.23. The pink sapphire (Moz7) before implantation (a) has more reddish tone after implantation (b).



(a) (b)

Figure 4.24. The pink sapphire (PS12) before implantation (a) has less violet tint after implantation (b).



(a) (b)

Figure 4.25. The dull white sapphire (G13) before implantation (a) has paler pink tint after implantation (b).

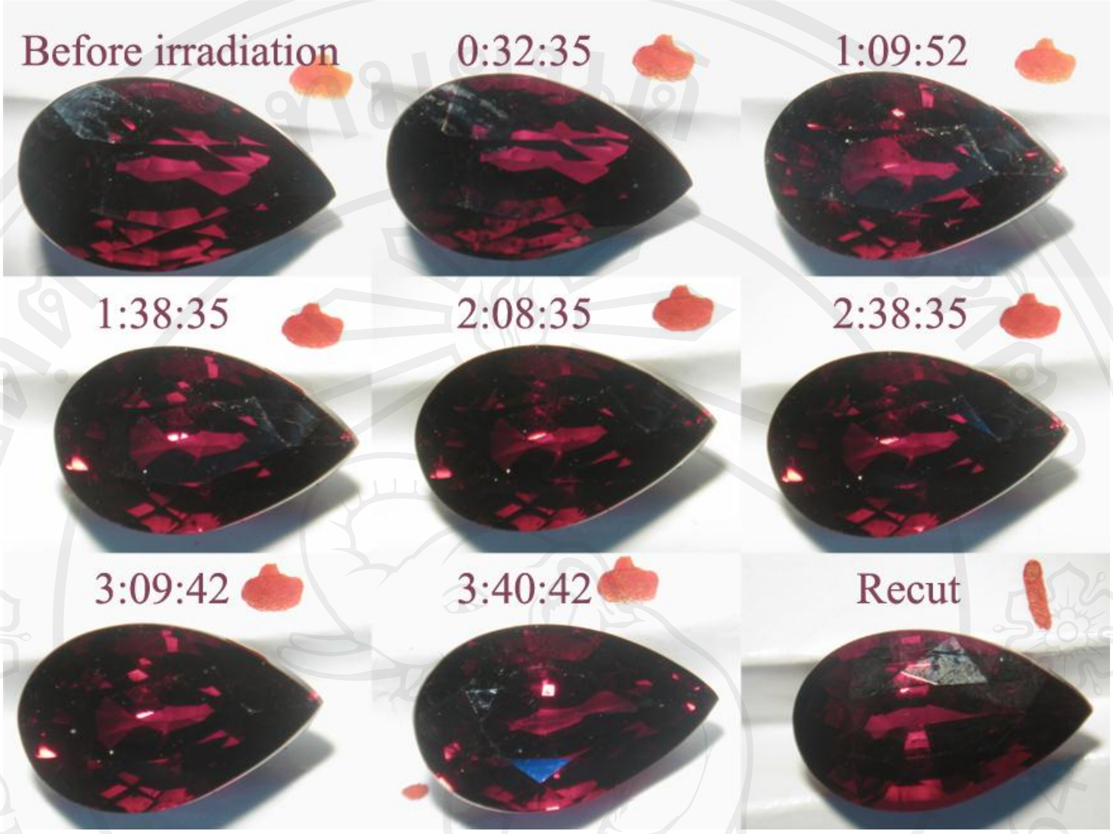


Figure 4.26. The change in appearance of the faceted ruby after being consecutively irradiated, with 23 keV O^- ions beam, at different period of time in hr:min:sec.

Note that: The red points are also intended for using as a color monitoring for each different photo taking.

These treatment conditions resemble to the oxidizing condition in the traditional heat treatment. Although, using the O^- which has enormous electron affinity (Clark, 2000) in the general atmosphere, an enormous kinetic energy of ion is enough to attract the electron of divalent states, element charge state equals to +2, from the positive transition ion in the matter. The remarkable result is shown in Figure 4.26 which is the sequence of irradiation for faceted ruby. These are the sequence alteration during ion beam bombardment. However, the alteration is hardly seen since the sample being coated by some of oxide compound, i.e. the dark zone in the figures. Later, this ruby was re-cut for eliminating the oxide compound as shown in the last figure. At this stage the light can pass through the bottom of the gemstones and it become more transparent.

The oxygen ion implantation is almost similar to the oxidizing condition in the furnace of the heat treatment. This can be explained that the oxygen partial pressure is the main factor to alter the charge state inside the matter. As much as free ion of Fe and Ti could capture the negative oxygen ion. The oxidizing condition can dissolve more individual Rutile (TiO_2) to the matrix which affects more interaction with Fe^{2+} inside the matter (Emmeth and Douthit, 1993). Hence, the Fe^{2+}/Ti^{4+} in IVCT process settle the blue color appearance, the formation in the octahedral structure which d-shell valence electron wavefunctions of them are superposition. If any photon transmits along the C-axis to the Fe^{2+}, its valence electron can transfer to Ti^{4+} along with Fe^{2+}/Ti^{4+} IVCT process. Note that the reducing of blue color in the ruby means to reduce the violet tint appearance and leads to the higher price in the jewelry market. For sapphire if it contains too much Fe and Ti such as dark-blue sapphire, the dark tone can be reduced by capturing with the oxygen ion.