CHAPTER V

CHEMICAL COMPOSITION

5.1 Introduction

Chemically, corundum contains two aluminum atoms and three oxygen atoms that lead to average of 52.91% aluminum and 47.08% oxygen by weight. Corundum is colorless when it is in pure form. In nature, colorless corundums are however very rare. Corundums often contain certain coloring elements; known as chromophores, such as chromium, titanium, iron, vanadium and probably magnesium, even with very small amount; consequently colors are produced. In addition, non-coloring elements, such as Ga, Si, Na, Ca, may also be found as trace compositions in corundum.

Corundum is an allochromatic mineral, owing its color to one or more chromophoric transition metal elements that can absorb some visible light, causing distortion and producing electromagnetic energies. Some of these chromophoric elements may be present in corundum as impurities, replacing some aluminium atoms. The chromophoric ions may be present in the corundum lattices in various valences and configuration as single or multiple ions of the same element, and/or in combination with other ions from other elements, often in multi-valence state, and where mixed valences occur, a great variety of colors are produced.

Study of trace composition in Songea corundums are separated into two methods. Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF) technique is initially applied to analyze semi-qualitatively trace elements in all samples of five color varieties. These data are used to compare statistically among them and to investigate causes of color in relation with UV-VIS-NIR spectroscopy. Moreover, they are used to discuss on their characteristic in the next chapter. However, the EDXRF method is limited to analytical accuracy therefore, Laser Ablasion-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) was also used to analyze quantitatively trace elements in Songea corundums. However, operation cost of this method is extremely high, only some samples were selected for this analysis. These quantitative analyses can be used to explain the cause of color and potential for heat treatment.

5.2 Energy Dispersive X-Ray Fluorescence

Chemical elements in these corundums were firstly analyzed for Fe, Ti, Cr, Ga and V contents by using an EDXRF Spectrometer, model OXFORD, ED2000 at the Gem and Jewelry Institute of Thailand (GIT) (Figure 5.1). Among fifty two samples, thirty seven samples have homogeneous colors that can represent all five color varieties; their analytical results are summarized in Table 5.1. The other samples contain color patches or zones which their results are presented in Appendix B

Figure 5.1 Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF) at GIT was used to analyze trace composition in Songea corundums.

Table 5.1 Ranges, averages and standard deviations of EDXRF analyses yielded from 37 samples representing all five color varieties.

Oxide (wt.%)	Red variety (12 samples)	Purple variety (8 samples)	Blue variety (4 samples)	Yellow variety (10 samples)	Colorless (3 samples)
Fe_2O_3 range	1.04-1.69	1.01-1.91	1.13-2.06	1.03-4.39	1.21-2.26
Mean±S.D.	1.33±0.19	1.32±0.28	1.43±0.43	1.58±0.99	1.56±0.60
Cr_2O_3 range	0.05-0.54	<0.14	<0.03	<0.05	<0.07
Mean±S.D.	0.21±0.15	0.04±0.04	0.02±0.01	0.01±0.02	0.04±0.03
Ga_2O_3 range	<0.01	0.01-0.02	0.01-0.02	0.01-0.02	0.01-0.017
Mean±S.D.	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01
TiO_2 range	0.03-1.37	0.01-0.23	0.02-0.16	0.02-1.09	0.04-0.24
Mean±S.D.	0.18±0.38	0.09±0.08	0.08±0.06	0.18±0.33	0.14±0.10
V_2O_5 range	<0.04	<0.02	<0.01	<0.03	<0.01
Mean±S.D.	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01	0.01±0.01

5.3 Result

As expected the red variety contains generally high contents chromium (Cr_2O_3 0.05-0.54 wt.%, av. 0.21 wt.%) and iron (Fe_2O_3 1.04-1.69 wt.%, av. 1.33 wt.%). Titanium (TiO_2 0.03-1.37 wt.%, av. 0.18 wt.%), vanadium (V_2O_5 <0.04 wt.%, av. 0.01 wt.%) and gallium (Ga_2O_3 <0.01 wt.%, av. 0.01 wt.%) are found in minor to trace amounts.

The purple variety contains lower chromium (Cr_2O_3 <0.14 wt.%, av. 0.04 wt.%) as those of the red variety but approximately the same iron content (Fe_2O_3 1.01-1.91 wt.%, av. 1.32 wt.%). Contents of other elements are roughly the same as those of the other varieties; gallium (Ga_2O_3 <0.02 wt.%, av. 0.01 wt.%), titanium (TiO_2 0.01-0.23 wt.%, av. 0.09 wt.%) and vanadium (V_2O_5 <0.02 wt.%, av. 0.01 wt.%).

The blue variety appears to have high iron contents (Fe_2O_3 1.13-2.06 wt.%, av. 1.43 wt.%) while the contents of chromium (Cr_2O_3 <0.03 wt.%, av. 0.02 wt.%), gallium (Ga_2O_3 <0.02 wt.%, av. 0.01 wt.%), titanium (TiO_2 0.02-0.16 wt.%, av. 0.08 wt.%) and vanadium (V_2O_5 <0.01 wt.%, av. 0.01 wt.%) are low.

The yellow variety contains very high iron content (Fe_2O_3 1.03-4.39 wt.%, av. 1.58 wt.%). Contents of the other element are moderate to low; chromium (Cr_2O_3 <0.05 wt.%, av. 0.01 wt.%), gallium (Ga_2O_3 <0.02 wt.%, av. 0.01 wt.%), vanadium (V_2O_5 <0.03 wt.%, av. 0.01 wt.%) and titanium (TiO_2 0.02-1.09 wt.%, av. 0.18 wt.%; some samples show values up to 1.09 wt.%).

The colorless variety also have rather high iron contents (Fe_2O_3 1.21-2.26 wt.%, av. 1.56 wt.%) while contents of other elements are very low; chromium (Cr_2O_3 <0.07 wt.%, av. 0.04 wt.%), titanium (TiO_2 0.04-0.24 wt.%, av. 0.14 wt.%), gallium (Ga_2O_3 <0.02 wt.%, av. 0.01 wt.%) and vanadium (V_2O_5 <0.01 wt.%, av. 0.01 wt.%).

Average analyses and their standard deviation (S.D.) of each variety are graphically shown in Figure 5.2. In general there are rather high in Fe_2O_3 contents and low in Ga_2O_3, V_2O_5 contents. As expected, the highest Cr_2O_3 content are recorded from the red variety while those of the violet variety are somewhat lower. The highest TiO_2 contents are found in the red and yellow varieties. Unexpectedly, the blue variety does not yield TiO_2 values as high as those of the red and yellow varieties, even purple and colorless stones still have average TiO_2 higher than those in blue samples. However, analytical errors are clearly large as shown by the error bars in Figure 5.2; therefore EDXRF analyses should not be conclusive evidences.

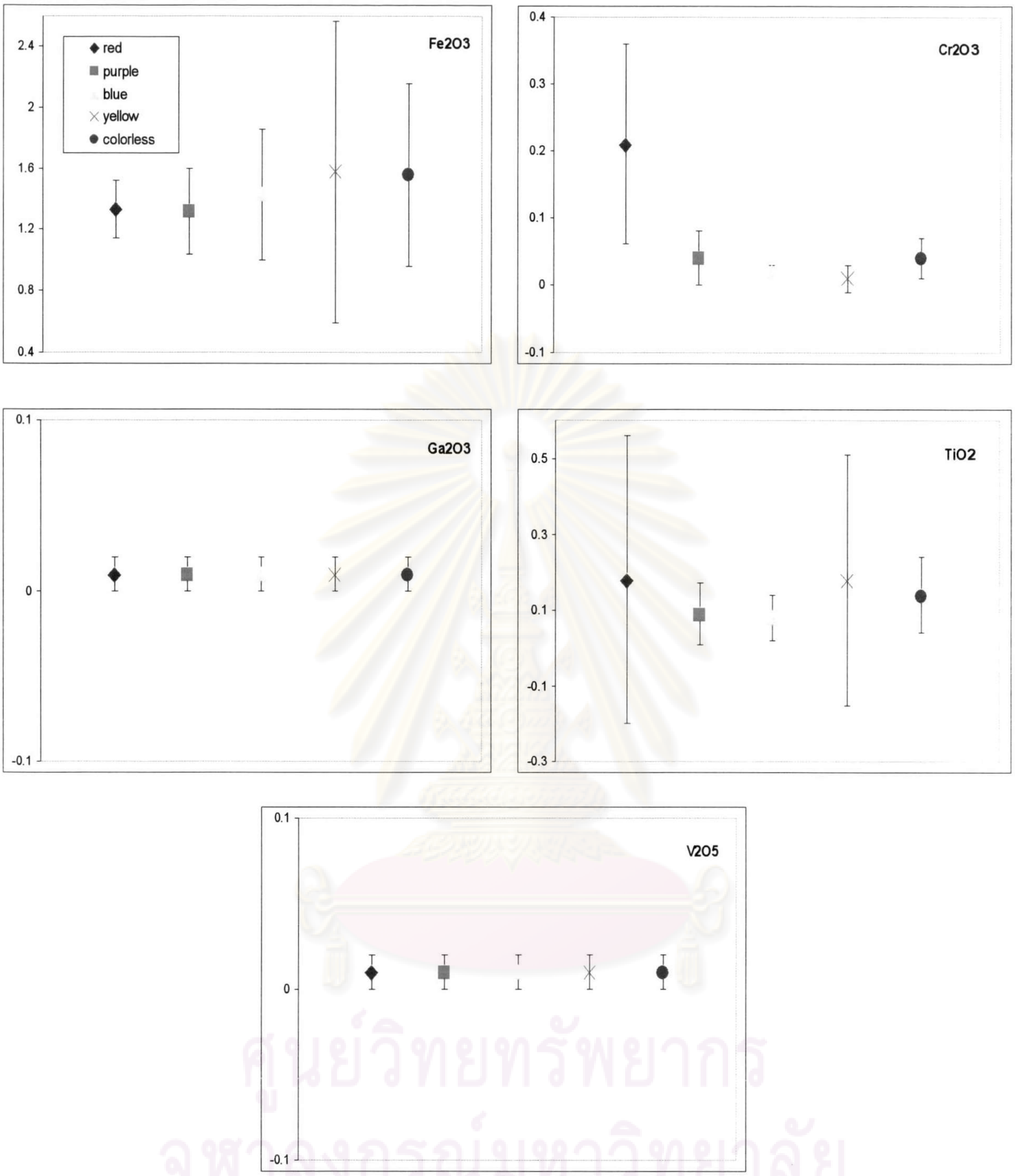


Figure 5.2 Average of trace elements revealed as symbols obtained by EDXRF and their standard deviations in form of lines.

5.4 Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer

Seven samples from Songea were selected for trace analysis using Laser Ablasion-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) at Macquarie University, Australia (Figure 5.3). These samples are unfortunately were selected from only 3 color varieties; i.e. red, purple, and yellow varieties. Besides some samples are bi-colors. Samples were polished until they have smooth surfaces for good analytical condition. The samples were put in resin block and held with glue tape, and then they were put in the vacuum chamber attached with microscope and TV monitor. When the analysis started, a laser beam was drilling into the sample and leaving a small hole about 100 μm on the surface representing the analyzed point (Figure 5.4). At least three analytical points were selected and analyzed for each sample having homogeneous color. More analytical points were done to cover all color zones (or patch) in some samples (see Figure 5.4)

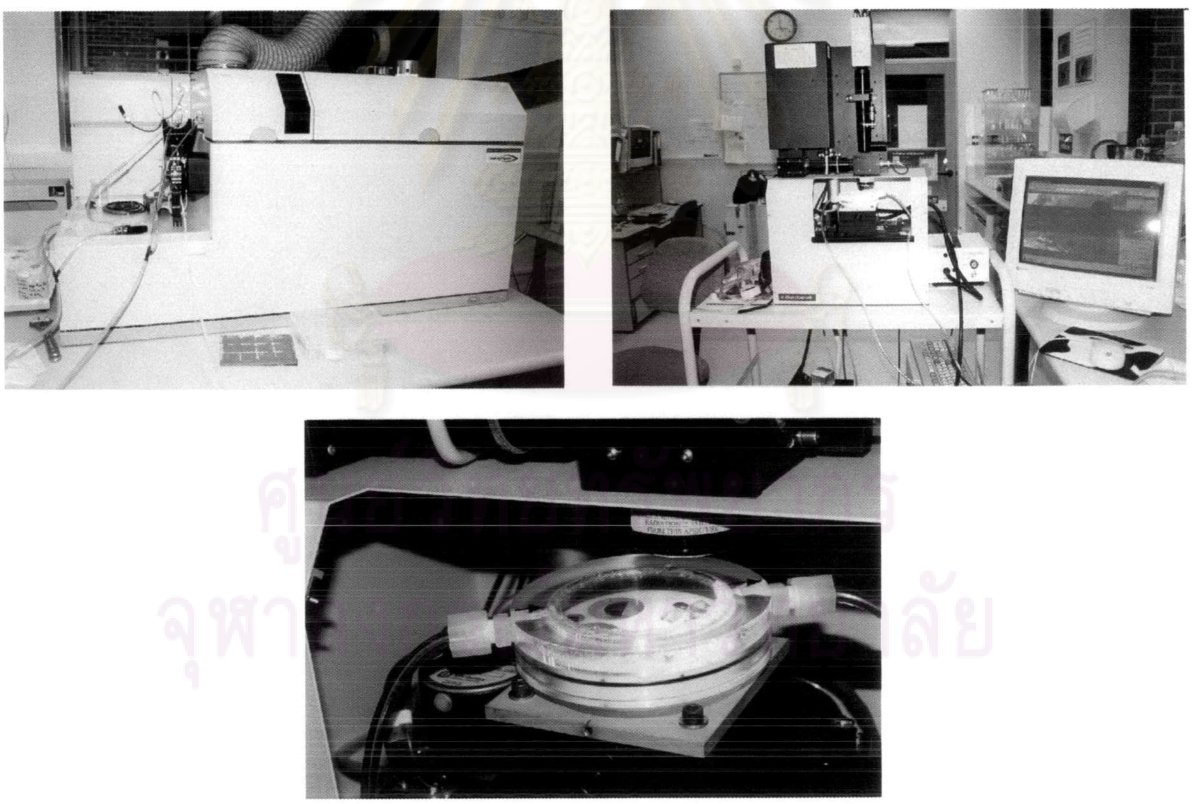
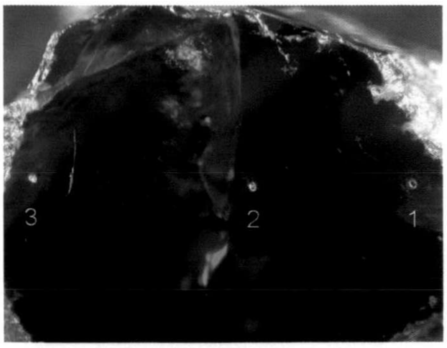
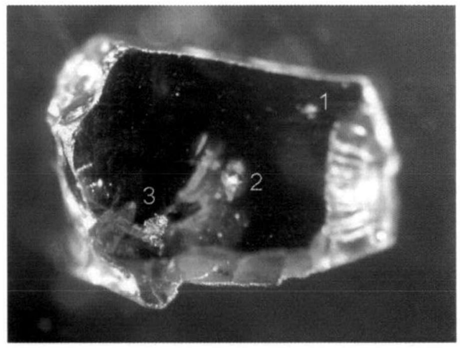


Figure 5.3 Laser Ablasion-Inductively Couple Plasma Mass Spectrometer (LA-ICPMS) at Macquarie University, Australia was assumed to their major and minor trace compositions.

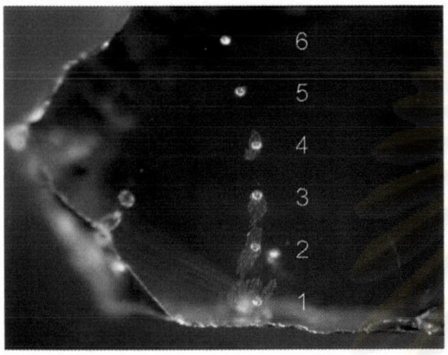


Sample sga5 of red variety

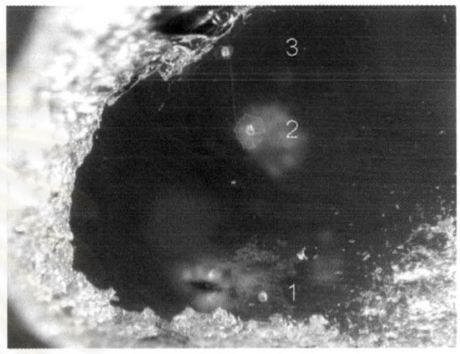
(color code R7/3)



Sample sga4 with bi-colors of pink and near colorless (color code O4/3, oY2/3)

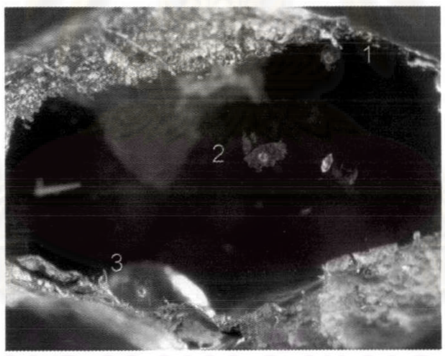


Sample sgd99 shows bi-colors of purplish red rim and purplish blue core (color code P6/4, bP3/1)



Sample sga7 of purple variety

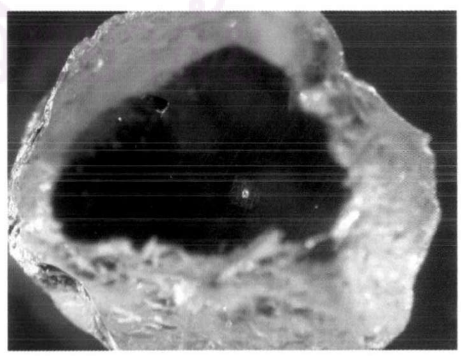
(color code vl.P3/1)



Sample sga15 of purple variety

(color code PR/RP2/1)

Sample sga18 of yellow variety (color code YG/GY2/1)



Sample sga11 of yellow variety

(color code vl.oY2/3)

Figure 5.4 Laser drill holes in 7 samples of Songea corundum analyzed using LA-ICP-MS.

Table 5.2 Atomic mole ppm of trace compositions of Songea corundum calculated from raw analyses obtained by LA-ICP-MS, shown in Appendix C.

Sample / Cations	sga5			sga4			sga18			sga11		
	rim1 red	core2 red	rim3 red	rim1 orange yellow	core2 reddish orange	rim3 reddish orange	rim1 yellowish green	core2 yellowish green	rim3 yellowish green	rim1 orange yellow	core2 orange yellow	rim3 orange yellow
(Atom Mole ppm)												
Li7	2.30	3.67	2.77	2.13	3.21	3.00	2.72	2.86	2.04	2.86	2.42	2.16
Be9	1.61	1.73	1.86	1.21	1.39	1.64	1.31	1.87	1.19	1.10	1.55	1.69
Na23	13.45	21.86	16.66	18.84	26.38	18.20	16.19	25.79	12.07	16.72	22.67	13.12
Mg24	23.03	28.94	29.02	18.66	16.51	20.55	17.96	29.70	17.65	14.26	12.74	20.25
Al27	396260.51	396454.47	396386.16	397484.62	397256.26	397221.17	397899.13	397920.44	397749.37	397603.08	397569.24	397567.55
Ti47	24.32	30.52	30.23	16.79	17.41	19.23	18.07	26.63	16.68	10.28	9.65	12.71
V51	29.47	27.81	28.66	9.52	10.57	11.42	3.90	3.06	4.67	3.84	3.64	4.11
Cr53	1089.01	981.13	1003.04	204.23	494.30	493.02	0.46	0.46	2.48	94.16	100.00	87.95
Mn55	0.05	0.08	0.06	0.05	0.07	0.07	0.06	0.07	0.05	0.06	0.08	0.06
Fe57	2538.69	2432.40	2483.76	2227.54	2157.33	2195.08	2023.37	1971.94	2176.90	2235.98	2260.57	2272.59
Ni60	1.25	1.10	1.31	0.11	0.15	0.18	0.06	0.12	0.08	0.13	0.12	0.06
Zn66	0.36	0.26	0.34	0.08	0.09	0.05	0.29	0.44	0.14	0.79	0.52	0.86
Ga71	15.90	15.99	16.07	16.19	16.26	16.34	16.45	16.53	16.61	16.68	16.76	16.84
Sn188	0.03	0.04	0.05	0.03	0.05	0.04	0.04	0.07	0.06	0.05	0.03	0.05
Total (Atom Mole%)	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Cr%	95.83	94.29	94.42	85.21	93.58	92.53	1.25	0.82	6.73	79.33	81.70	72.75
Ti %	2.14	2.93	2.85	7.01	3.30	3.61	49.53	46.90	45.31	8.66	7.89	10.51
Mg%	2.03	2.78	2.73	7.78	3.12	3.86	49.22	52.29	47.96	12.01	10.41	16.75

Table 5.2 (Continue).

Sample / Cations	sga15			sga7			sgd99					
	rim1	core2	rim3	rim1	core2	rim3	rim1	core2	core3	core4	core5	rim6
	purple red	purple red	purple red	purple	purple	purple	blue purple	blue purple	blue purple	purple	purple	purple
(Atom Mole ppm)												
Li7	1.99	2.57	1.81	2.05	2.95	2.05	2.07	2.45	1.90	2.01	1.84	2.10
Be9	1.53	1.96	1.19	1.40	1.69	1.33	1.15	1.46	1.15	1.28	1.21	1.82
Na23	69.30	16.31	11.13	20.56	24.24	19.35	11.66	14.63	15.86	17.96	11.91	20.56
Mg24	16.60	17.68	16.38	18.91	17.65	20.77	14.16	18.78	20.80	17.91	20.36	19.17
Al27	397693.10	397748.11	397775.27	397961.39	398034.92	397834.70	397675.10	397390.20	397251.92	397064.44	396928.55	396493.42
Ti47	15.74	17.01	16.83	17.14	16.02	17.86	14.65	19.97	19.45	17.88	18.06	17.86
V51	4.28	4.18	4.16	4.22	4.15	4.34	16.88	18.89	16.13	15.21	14.66	14.95
Cr53	84.86	86.50	87.35	72.49	66.38	72.72	114.41	128.82	218.37	329.89	503.40	966.34
Mn55	0.05	0.06	0.04	0.05	0.06	0.05	0.04	0.05	0.04	0.04	0.04	0.05
Fe57	2095.32	2088.40	2068.38	1884.19	1814.28	2009.17	2132.03	2386.90	2436.35	2515.40	2481.85	2445.49
Ni60	0.09	0.07	0.10	0.06	0.10	0.07	0.29	0.24	0.32	0.21	0.23	0.28
Zn66	0.14	0.09	0.21	0.31	0.23	0.20	0.08	0.13	0.13	0.09	0.14	0.16
Ga71	16.93	17.01	17.09	17.18	17.27	17.34	17.41	17.48	17.56	17.63	17.70	17.76
Sn188	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.02	0.04	0.03	0.04	0.05
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Cr%	72.40	71.38	72.45	66.79	66.35	65.31	79.88	76.88	84.44	90.21	92.91	96.31
Ti %	13.43	14.03	13.96	15.80	16.01	16.04	10.23	11.92	7.52	4.89	3.33	1.78
Mg%	14.16	14.59	13.58	17.42	17.64	18.65	9.89	11.21	8.04	4.90	3.76	1.91

5.5 Result

Table 5.2 presents trace analyses in atom mole ppm of each analytical point in all seven samples. Color appearances at those analytical points are also specified in the table. Statistically, the results of all analyses are quite similar in the same color of each sample. As expected from the analytical results Cr contents are rather high in the red variety but lower in the violet variety (as well as orange samples) and almost none in the yellow varieties (Table 5.2). The analytical results also confirm that Songea corundums usually contain high Fe content, whereas Ga and V contents are very low. However, Ga contents seem to be more consistant in most color varieties analyzed, while V contents are moderately different in different color varieties. Vanadium appears to have higher concentrations in the red sample and somewhat lower in the purple stones. Finally, in contrast to those analyzed by EDXRF, the Ti contents seem to be rather consistent in most color varieties analyzed.

Because of the extremely high Fe contents in all color varieties of Songea corundum as compared with those of the other trace elements, then if the Fe, Mg and Ti contents of all the data points were selected to plot in a ternary diagram as previously used by Haeger (2001). As the result, the calculated Fe component would make up nearly 100% and all of data points would fall very close to the Fe corner in the ternary diagram which makes it difficult to visualize. In this study, however, the other crucial colorating elements, i.e. Cr, Mg and Ti, were selected for plotting in the ternary diagram instead of Fe (Figure 5.5) because the Cr contents show large variation from high in the red variety to very low in the yellow variety.

As shown in Figure 5.5, based on the color appearance, nine symbols were consequently set for different stones and colors. Most plots fall closely to and perhaps within line of 1:1 ratio of Ti:Mg. However, high Cr contents are mostly present in the shades of red, orange and purple (e.g. sga4, sga5 and sgd99). Yellow shades contain low Cr (sga18) to moderately high Cr content (sga4 and sga11). The significant sample sgd99 that have two color zones (bluish purple blue and purple), show obviously different plots of both color zones. The purple zone clearly contains higher Cr content than that of the bluish purple zone.

It should be noted further that Mg:Ti atomic ratio of 1:1 is likely expected to turn colorless or pink when stone is heated at high temperature either under reducing or oxidizing environment (Haeger, 2001). Results of heating experiment will be reported in the last chapter.

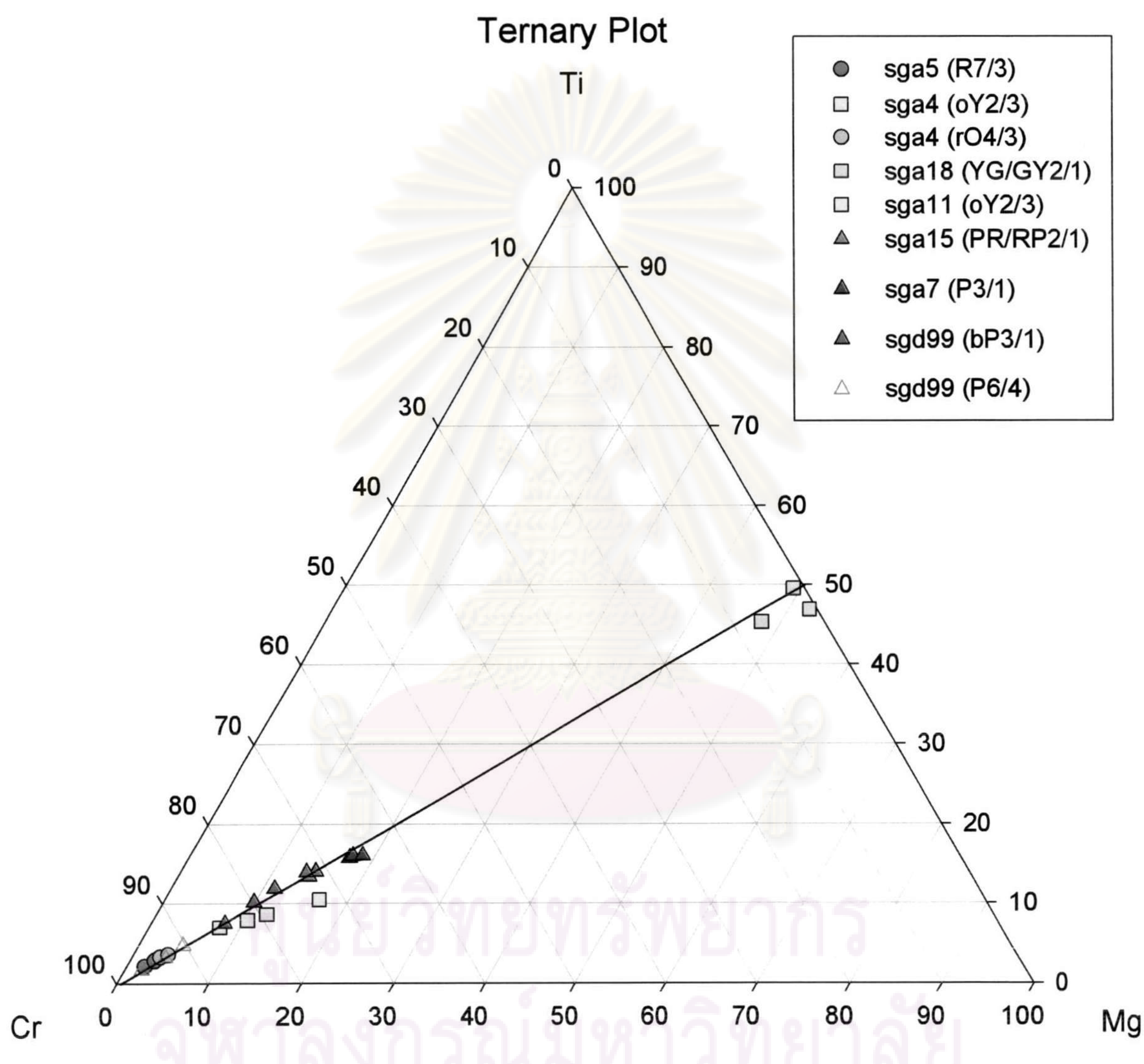


Figure 5.5 Cr-Ti-Mg ternary diagram of Songea corundums; that are plotted based on trace analyses in different colors.