CHAPTER VII

DISCUSSION AND CONCLUSIONS

7.1 Cause of Color after Heat Treatment

Fritsch et al. (1987) studied the origin of color in gem materials, five basic mechanisms have been identified: dispersed metal ions, charge-transfer phenomena, color centers, band theory and physical optics. Dispersed ions are single atoms and thus the smallest possible cause of color. Charge-transfer phenomena and the creation of color centers both require small groups of atoms. A much larger cluster of atoms is involved in band theory. Lastly, physical structures of considerable dimension compared to the size of the atom are responsible for colors explained by physical optics. Blue color in sapphire samples are caused by intervalence charge transfers between metal ions of different chemical elements (e.g., Fe and Ti). The heat treatment of near colorless sapphires (known as geuda) produces blue color because natural inclusions of rutile and spinel in the corundum can be dissolved at high temperatures. Fe and Ti from the inclusions are therefore released while random diffusion initiates and may bring pairs of Fe^{2+} and Ti^{4+} ions close to each other, in which Fe^{2+}/Ti^{4+} IVCT occurs and yields the blue coloration (Harder et al., 1986 cited in Fritsch et al., 1987) and/or Fe^{2+}/Fe^{3+} charge transfer (Ferguson et al., 1971, 1972 cited in Häger, 2001) is taken place in first or second nearest neighbour position.

Schmetzer et al. (1990) reported natural blue sapphires can be subdivided into two basic types, depending on presence or absence of the Fe^{2+}/Fe^{3+} charge-transfer. However, colors of both heat-treated and unheat treated blue sapphires are caused significantly by the Fe^{2+}/Ti^{4+} IVCT. Heat treatment of milky white sapphires (so-called geuda) produces absorption spectra with dominant Fe^{2+}/Ti^{4+} absorption bands but without any Fe^{2+}/Fe^{3+} intervalence transfer absorption. The absence of Fe^{3+} absorption bands in heat treated samples, which were spectroscopically found to be present in unheated samples, was explainable using conversion of trivalent iron to bivalent iron in connection with the dissolution of rutile particles after the scheme:

$$TiO_2 + (Al^{3+}, Fe^{3+})_2O_3 \longrightarrow (Al^{3+}, Ti^{4+}, Fe^{2+})_2O_3$$

rutile corundum (colorless) corundum (blue)

According to this scheme, in samples in which titanium contents exceed iron contents, no residual Fe^{3+} absorption bands are expected to be present after extended heat treatment.

Cornelius et al. (1991) described the mechanism proposed to induce or intensify a blue color. One mechanism proposed is the reduction of Fe^{3+} to Fe^{2+}, the latter of which is then available for a charge-transfer-produced blue color:

$$Fe^{2+} + Ti^{4+} \longrightarrow Fe^{3+} + Ti^{3+}$$

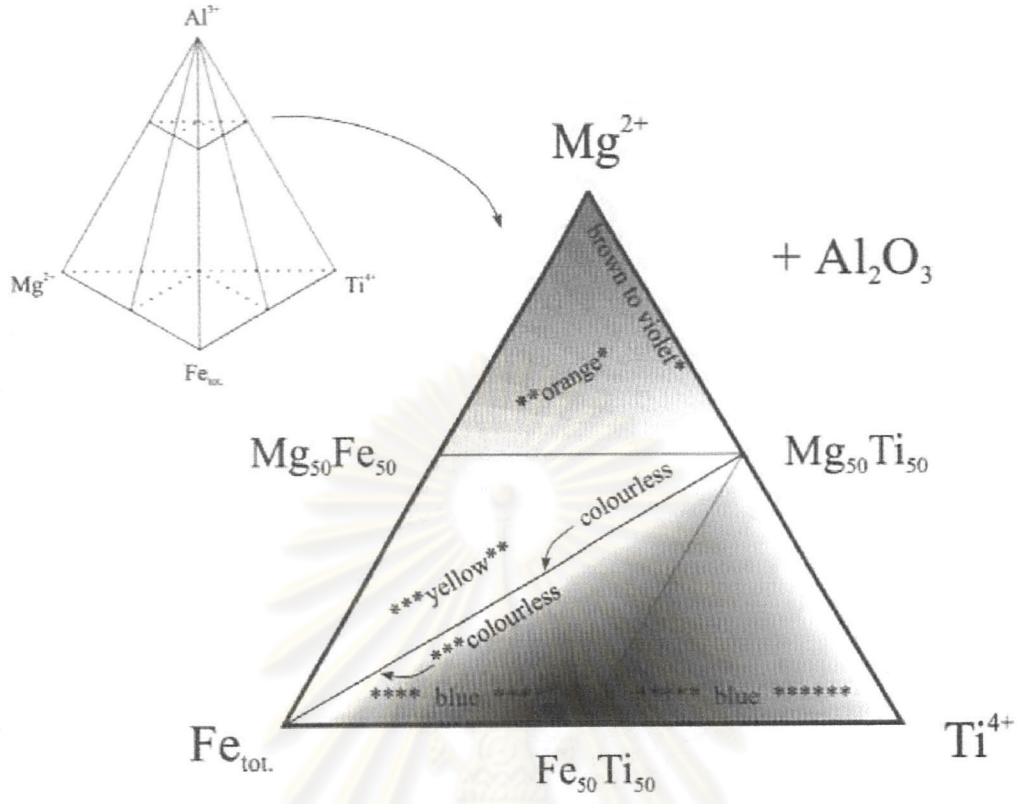
The research experiment into the spectral absorption features of "Geuda" rough before and after heating has led to it being theorized that heat treatment causes formation of a $(FeTi)^{6+}$ biparticle with significant reduction in Ti^{4+} and less of a reduction in Fe^{3+}. Another mechanism proposed is the taking of titanium from inclusions into solid solution, making it available as a chromophore.

Emmett et al. (1993), reported that $Fe^{3+} + Ti^{3+}$ would become $Fe^{2+} + Ti^{4+}$ during growth at any reasonable temperature to created blue color. Other sapphire impurities such as magnesium (Mg^{2+}) are also electron acceptors (Mohapatra et al, 1977 cited in Emmett et al.,1993), which replaces aluminium (Al^{3+}) in the sapphire lattice, there is a point defect at the site which has insufficient charge known as color centers, heat treated sapphire under highly oxidizing conditions, a hole is created in the lattice which has an effective electrical charge of +1 and yellow color was presented.

Nassau (1994) suggested that combination of iron plus titanium oxides in corundum can produce a wide range of color, varying from colorless via yellow and green to blue-green, blue and blue-black. The color produced by specific amounts of these impurities is not fixed, but it depends on many factors, including maximum temperature reached and conditions during heating.

Häger (2001) summarized coloration models of corundums that have been treated at high temperatures in oxidizing and reducing atmospheres. Natural sapphires from different localities were experimented at 1850 °C with oxidizing environments and at 1750 °C with reducing environments. Experimental results of natural stones and some evidences proven by doped synthetic corundums lead to conclusion that colors yielded from high temperature treatment are strongly based on interaction between Mg, Fe and Ti. These trace elements may form colorless $MgTiO_3$ clusters (known as Geikielith clusters) and/or color effective $FeTiO_3$ clusters. Häger suggested that trace components of Mg, Fe and Ti would form firstly $MgTiO_3$ clusters before the excess Ti will combine with Fe as $FeTiO_3$ clusters. The $FeTiO_3$ clusters are related to Fe^{2+}/Ti^{4+} IVCT absorption bands near 580 and 735 nm in UV-VIS-NIR spectra. The remaining Ti contents after formations of $MgTiO_3$ and $FeTiO_3$ clusters may precipitate as TiO_2 (rutile crystals). On the contrary if there is an excess of Mg after forming $MgTiO_3$ clusters, the excess Mg may stabilize color centers causing stable yellow. Consequently, graphical models of sapphires heat treated at high temperatures under either oxidizing or reducing atmosphere have been proposed by Häger (2001).

The model which illustrates the reaction of sapphire during heat treated at 1850 °C in oxidation atmospheres shown in Figure 7.1. The small tetrahedral graph (Figure 7.1, left) shows the system of Al-Fe_{tot}-Ti-Mg. The large triangular (Figure 7.1, right) is a section through the tetrahedron. In the triangle Mg_{100}-$Mg_{50}Ti_{50}$-$Mg_{50}Fe_{50}$ the Mg-content exceeds the Fe+Ti-content. The colors vary from the brownish violet line Mg_{100}-$Mg_{50}Ti_{50}$ to pure yellow at the corner $Mg_{50}Fe_{50}$. In the triangle $Mg_{50}Fe_{50}$-$Mg_{50}Ti_{50}$-$Fe_{tot.100}$ all samples are yellow colored by yellow stable defect centers. The color of the sapphires represented in this small triangle decreases from the corer $Mg_{50}Fe_{50}$ to the line $Mg_{50}Ti_{50}$-$Fe_{tot.100}$. Sapphires represented in the small triangle $Fe_{50}Ti_{50}$-$Mg_{50}Ti_{50}$-$Fe_{tot.100}$ are all transparent blue. The blue hue increases from the colorless line $Mg_{50}Ti_{50}$-Fe_{100} to the corner $Fe_{50}Ti_{50}$. In the triangle in the lower right $Fe_{50}Ti_{50}$-$Mg_{50}Ti_{50}$-Ti_{100} all samples are blue to colorless and showing precipitation of TiO_2, if the solubility limit of Ti without charge compensation is reached.



* color center due to Mg

** color center due to Mg and Fe

*** yellow due to Fe^{3+}

**** Fe^{2+}/Fe^{3+} charge transfer green due to Fe^{3+}

***** Fe^{2+}/Ti^{4+} - charge transfer

****** precipitation of TiO_2

Figure 7.1 Model of sapphires heat-treated at 1850 °C in oxidising atmospheres proposed by Häger (2001).

The model of sapphire heat treated at 1750 °C in reducing atmospheres, as shown in Figure 7.2, is somehow different from heat treating model under oxidizing environments. For example, all yellow shades including orange and brown that appear in the oxidizing model along appropriate locations between Fe, Mg and $Mg_{50}Ti_{50}$ corners are obviously absent in the reducing model. These areas are consequently colorless zone in Figure 7.2. The endpoint $Fe_{50}Ti_{50}$ of the $Mg_{50}Ti_{50}$ - $Fe_{50}Ti_{50}$ line moves towards to Ti_{100} depending on the power of reducing atmosphere and the duration of heat treatment. This likely implies that deeper blue color resulted from reducing heat treatment may be related to more Ti content depending on the degree of reducing atmosphere.

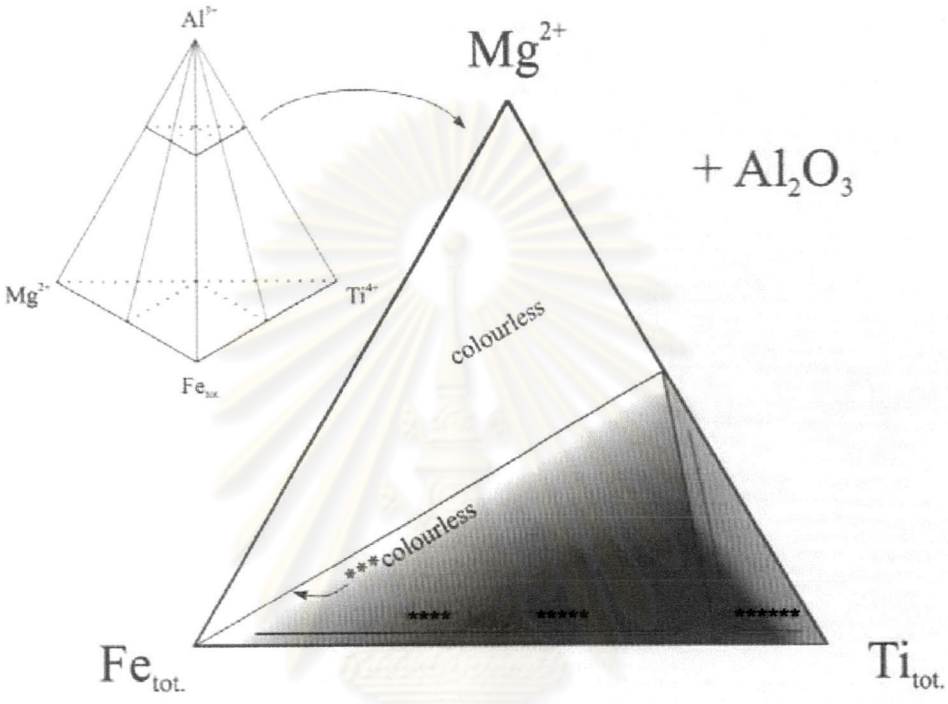
EPMA analyses of all sapphire samples heated at 1650 °C were recalculated based on 3 oxygen atoms into atomic cations and are listed in Table IV.2, Appendix IV. Atomic proportions between Mg, Ti and Fe were subsequently normalized into 100% and plotted in triangular diagram of heat treating model in reducing atmospheres proposed by Häger (2001). All analyses of individual sapphire groups are plotted in Figure 7.3 in which the analyses of each color zone are not considered in this diagram. Moreover, the same set of data are also plotted in the form of major different color zones (e.g. colorless, light blue and blue) in Figure 7.4. This is intended to verify the relationship of effect of trace compositions, particularly Mg, Fe and Ti and the color appearances of the stones. Therefore, consideration of this effect in overall sapphire groups would be firstly carried out before moving on to specific aspect. As reported in chapter 5, sapphire samples have been changed in colors during step heating experiment. In general, most sapphire samples were lost their blue color shades after heating at 1000 °C and 1200 °C. Some stones have been developed blue components again when temperatures were risen to 1400 °C and 1650 °C, while, some sapphires have lost their blue shades permanently.

Based on characteristics mentioned above, some sapphire samples of 6 original color groups (e.g. dark blue, medium blue, very light blue, milky very light blue, dark violet and medium violet) were consequently selected for quantitative analysis using EPMA as reported in the previous chapter. Fe-Mg-Ti Plots in Figure 7.3 is quite

clearly to recognize colors of stones after high temperature treatment. Medium blue sample (IMB 1) and milky very light blue sample (MVLB 6) are a couple of good examples represent chemical compositions of sapphires yielded colorless after high temperature heat experiment (Figure 7.5). Both samples are plotted very close to $Mg_{50}Ti_{50}$ compositional line (see Figure 7.3) that would be colorless as suggested by Hä ger (2001), which colors yielded from high temperature treatment are strongly based on interaction between Mg, Fe and Ti. These trace elements may only form colorless $MgTiO_3$ clusters. There was no excess Ti to form color effective $FeTiO_3$ clusters. Sample DV 1 of dark violet sapphire group is another sample that its blue shade was lightened after heating (Figure 7.6). Its Mg : Ti ratio is also about 1 : 1, however it is plotted in the Fe – rich conner (Figure 7.3). In combination with Cr composition, this stone is therefore changed from dark violet to purple. The best sample for sapphire yielded dark blue after high temperature heat may be represented by sample MVLB 3 of milky very light blue group. This sample has been changed obviously from very light blue to dark blue (Figure 7.7). Chemically, Fe – Mg – Ti proportion of this sample is in area between $Mg_{50}Ti_{50}$ and Ti with lower Fe, in which dark blue color would be appeared in the model of heat treatment in reducing atmosphere (Häger, 2001) (see also Figure 7.2). In conclusion, color appearances after high temperature heat treatment are strongly effected by trace elements, particularly Fe, Mg and Ti.

All the data are re-plotted in Figure 7.3 by which their color appearances are regrouped into only three main colors (i.e., colorless, light blue and blue after 1000 ^{o}C heating). Therefore three sets of symbols are assigned for those three colors and presented in Figure 7.4. It clearly shows that three different colors are compatible to model of Häger (2001). Analytical points with colorless are plotted along or closely to $Mg_{50}Ti_{50}$ line, whereas light blue appearances move into higher Ti area. For blue zones, all analytical points contain higher Ti content than those of the former zones. The analyses from two different color zones in a very light blue sample (IVLB 2) (Figure 7.8) are clearly present different trace composition that are plotted far away from each other (Figure 7.4). Colorless (IVLB 2-2) zone is plotted on the $Mg_{50}Ti_{50}$ line, whereas the blue zone (IVLB 2-1) is plotted in blue area of Häger's model. This evidence strongly

supports Fe – Mg – Ti interaction model for sapphire coloration resulted from high temperature treatment.



*** yellow due to Fe^{3+} **** Fe^{2+}/Fe^{3+} charge transfer green due to Fe^{3+}

***** Fe^{2+}/Ti^{4+} - charge transfer ****** precipitation of TiO_2

Figure 7.2 Model of sapphires heat-treated at 1750 °C in reducing atmospheres proposed by Häger (2001).

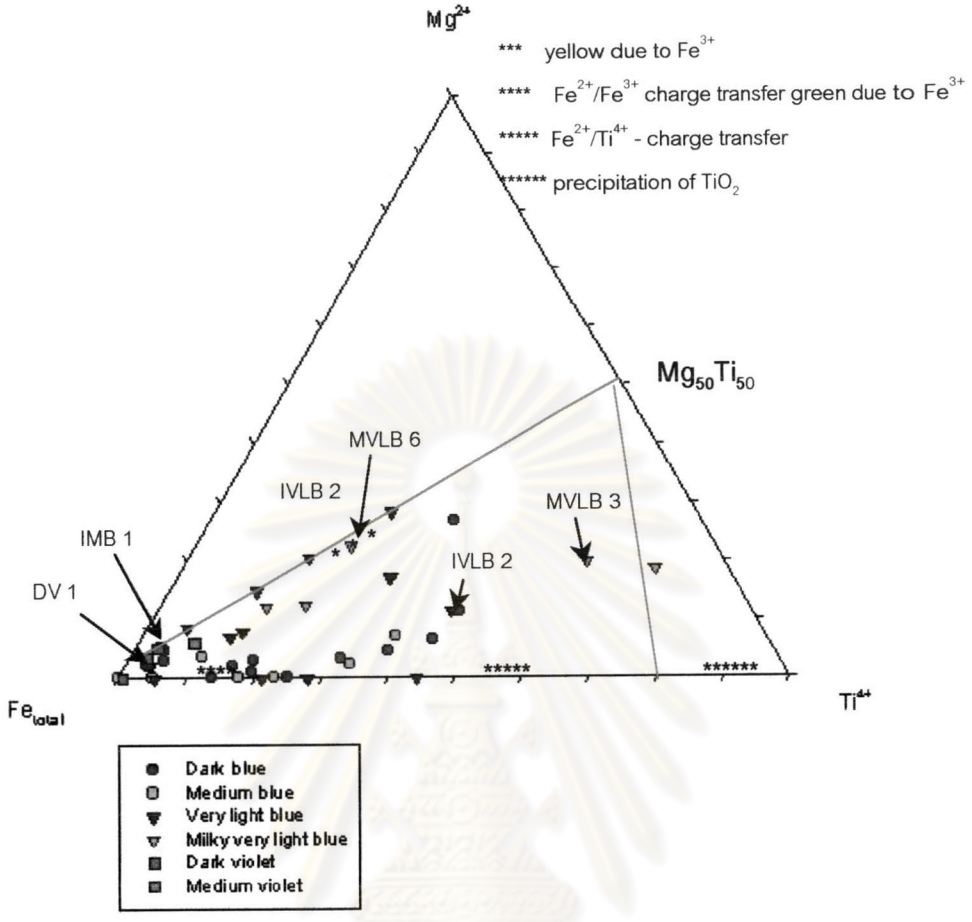


Figure 7.3 Triangular diagram showing atomic proportions between Mg, Fe and Ti of 24 sapphire samples selected from 6 color groups. The analyses were performed using EPMA after step-heating up to 1650 °C under reducing atmosphere.

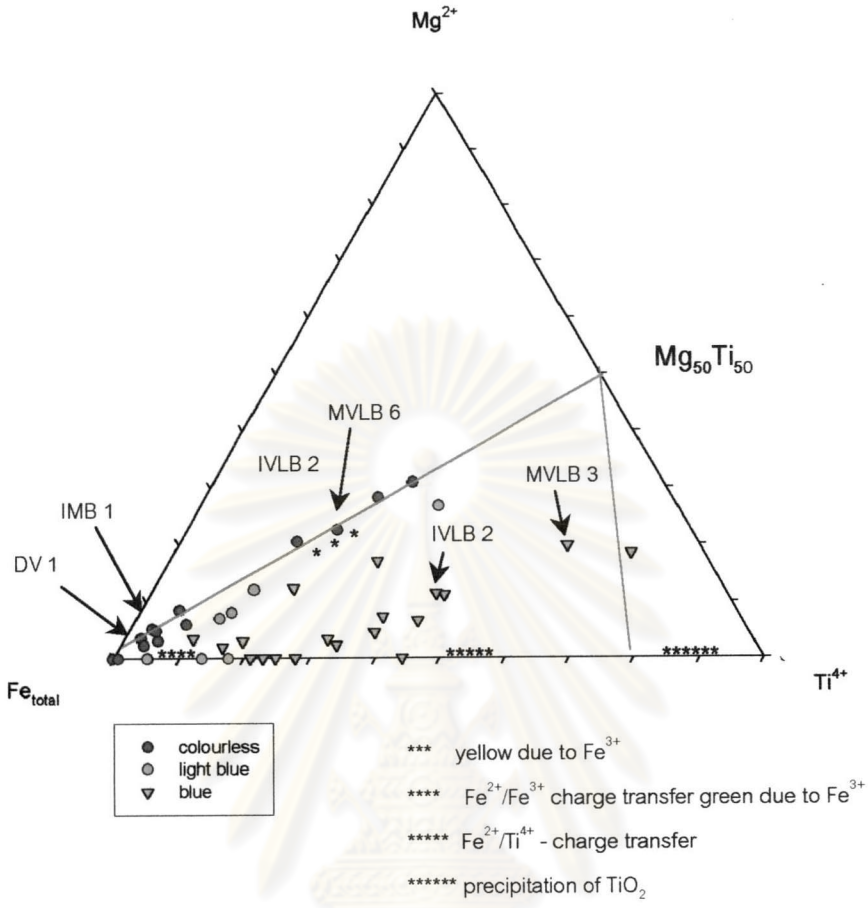
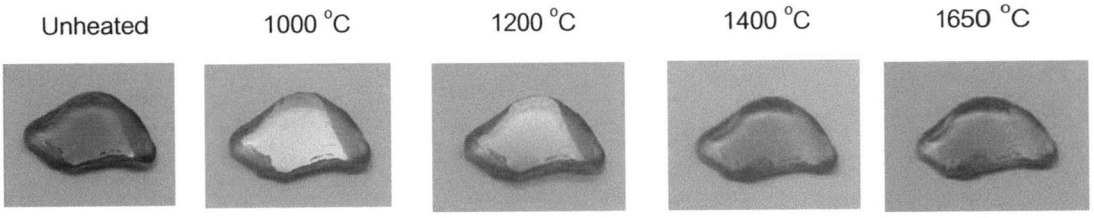
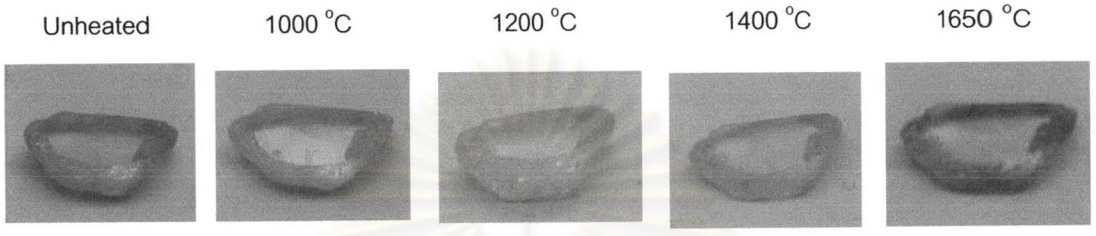


Figure 7.4 Mg – Fe - Ti plots of the same analytical data set as used in Figure 7.3. All analyses are grouped into 3 different colors according to their appearances in stones.

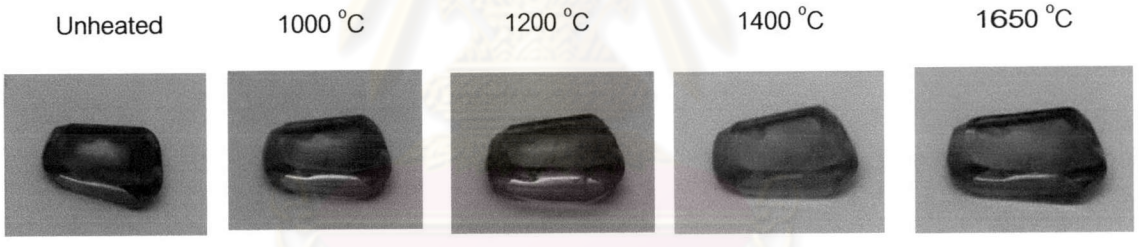


IMB 1



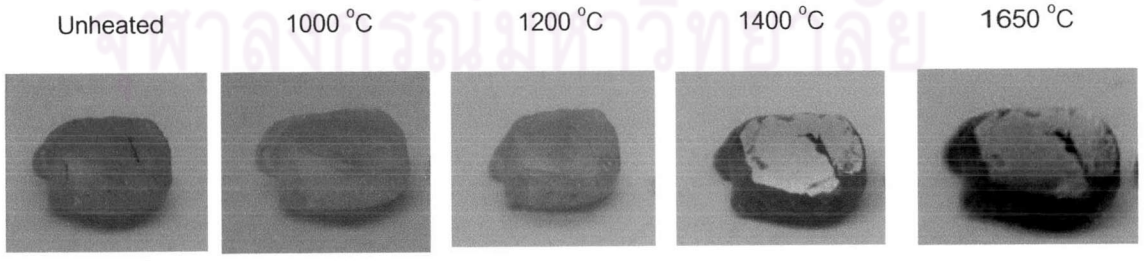
MVLB 6

Figure 7.5 A couple of sapphire samples from medium blue sapphire (IMB 1) and milky very light blue sapphire (MVLB 6) that appear colorless after step heating.



DV 1

Figure 7.6 Dark violet sapphire sample (DV 1) has partially lost its blue shade and turned purple after step heating.



MVLB 3

Figure 7.7 Milky, very light blue sapphire (MVLB 3) has become dark blue after step heating.

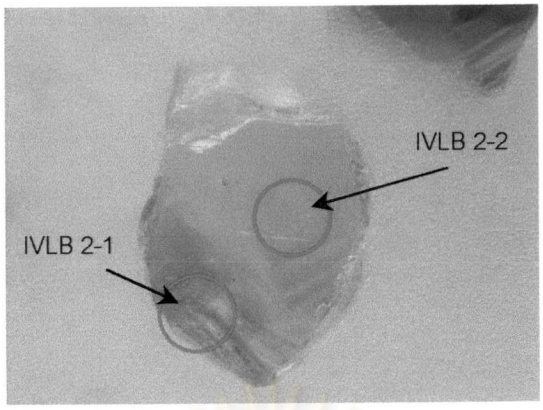


Figure 7.8 Very light blue sapphire (IVLB 2) shows blue (IVLB 2-1) and colorless (IVLB 2-2) zones after heating at 1650 °C in reducing atmosphere. Both zones were analyzed using EPMA and their Mg – Ti – Fe proportions are plotted in Figures 7.3 and 7.4.

7.2 Potential Heat Treatment

Due to experimental results, blue shades were removed after heat-treated at 1000 °C and 1200 °C in reducing atmosphere. Sapphire samples with color change effect were lost their phenomena after heated at 1000 °C and this effect has never appeared during the high temperature treatment. Therefore, heat treatment of sapphires in reducing atmospheres should be operated at temperatures higher than 1400 °C, otherwise blue shade may be lightened and the values will be certainly reduced.

Lightening of blue components after heat sapphire in reducing environments within temperature range of 1000 °C – 1200 °C has never been reported before. The cause of this remarkable event is still in doubt. A possible cause is suggested for this study. Heating chamber might still contain oxygen gas that was enough to cause oxidizing environment. Nitrogen gas fed into the chamber was used to neutralize oxidizing atmosphere; nitrogen, itself, is not a reducing gas. Therefore atmospheric pressure in the chamber, when it is heated at 1000 °C – 1200 °C, may not be high enough to push oxygen away; consequently, the chamber is not purely cleaned up. Loss of color change effect from heat treatment is also not unraveled, because real cause of this

effect has not been reported up to now. However, sapphires possessing color change effect should not be subject to heat treatment, based on results from this study.

Some very light blue samples were improved their color after heated at 1400 °C and 1650 °C. Most milky, very light blue sapphires with cloudy appearance were obviously intensified blue color after heated at 1400 °C and dark blue color appeared at 1650 °C. It seems likely that these two groups of sapphire from Ilakaka – Sakaraha deposits are the most potential stones to be heat treated at high temperatures (higher than 1400 °C) in reducing atmospheres, The other groups most be treated with great care, otherwise their values will be lost.

7.3 Conclusions

1. Ilakaka-Sakaraha gem fields occur as secondary deposits in alluvial plain and river terrace. The sapphires and associated minerals (e.g. zircon, spinel, garnet, topaz and chrysoberyl) have been recovered from those deposits. The Ilakaka-Sakaraha sapphire samples were classified into 7 groups, based on their color shades, as dark blue, medium blue, very light blue, milky very light blue, dark violet, medium violet and light violet. Some sapphires show color- change effect, particularly in dark blue, dark violet and medium violet groups.

2. The most common mineral inclusions in sapphire samples are zircons which usually occur as single crystal or cluster with or without tension discs. Other mineral inclusions are apatite, calcite and rutile (formed as crystal or needle). Internal features are frequently presented by healed fractures or fingerprints and white dust or minute particles. Apatite and zircon inclusions were slightly decomposed into whitish with extended of tension disc after step-heating at 1400 °C which can be used as indication of thermal enhancement in sapphire sample. Rutile needles appeared to have been altered at high temperatures especially at 1400 °C and 1650 °C.

3. Heating conditions were operated at 4 steps of maximum temperatures (e.g.1000 °C, 1200 °C, 1400 °C and 1650 °C) for a period of 3 hours soaking under reducing atmospheres. The blue coloration was generally intensified

when heating at 1400 °C to 1650 °C, especially milky, very light blue group. The color–change effect in all sapphire samples disappear after experiment at 1000 °C and it could not be developed during high temperature treatment. This caution would be concerned strongly for heat treated stones with natural color – change effect. Moreover, heat treating stones at temperatures lower than 1400 °C may lighten blue component and it would not be developed unless trace composition is proper.

4. The UV-VIS-NIR spectra show the absorption peaks at 385 – 388 nm (Fe^{3+}), 449 – 450 nm (Fe^{3+}/Fe^{3+}) and 588, 704 nm due to the Fe^{2+}/Ti^{4+} IVCT. The color-change sapphires show the absorption peak caused by Cr^{3+} at 410 – 4112, 553 – 560 and 692 – 693 nm. The height of absorption peak of Fe^{2+}/Ti^{4+} IVCT is related to the intensity of blue coloration.

5. Based on EDXRF and EPMA analyses, dark blue and milky very light blue sapphires show higher titanium contents than the others. Most milky very light blue sapphires appear to be dark blue after step heat treatment. Color-change effect group show chromium concentration that is higher than those of other sapphire groups. All sapphire types show fairly uniform vanadium and gallium concentrations.

6. Causes of color in treated sapphire samples at 1650 °C can be mostly explained by heat treatment model under reducing atmospheres suggested by Häger (2001).