CHAPTER 5

CONCLUSIONS

5.1 Deposit characterization

PIXE and IL analysis are the interesting method for non-destructive analysis of gemstones. Both techniques require very short accumulation time. They have several advantages over the other methods. For example, EDS induces strong bremsstrahlung radiation because the electron as an incident ion is lighter than the proton so that electron is severely decelerated by the coulomb field in the atomic region more than proton. Hence, the deceleration generates dramatically the X-ray background. The electrical conductivity surface coating is necessary for EDS while not necessary for PIXE. Additionally, the proton has longer projected range and less lateral spreading than electron. For XRF, this technique need the radiation shield of X-ray source compared with PIXE. By the way, the IL technique can directly detect the luminescence of transition elements in a matter which can support the data of photoluminescence (PL) measurement. The luminescence in the latter technique is produced by the resonance radiations which has the emission photon energy equate to absorption photon energy. However, the emission photon energy in the IL technique is generated by the incident energetic proton while the PL technique requires the photon as an exciting source. Both of them are important techniques for observing crystalline quality and its purity in the matter.

PIXE is an appropriate technique for detecting trace elements in quantities of a few ppm. The preliminary results correlate the trace element concentration with the color appearance, deposit type, and origins. These correlations need to consider interrelations between trace elements, for example the relation between the ratio of Cr/Ga and Fe/Ti concentration can distinguish the corundum's deposit from basaltic and metamorphic process. Furthermore, the unknown deposits corundum can be used this relation to identify their deposit types. Using this technique, the basaltic deposits (Thailand, Cambodia and the USA) have high Fe and low Ti, while metamorphic deposits (Sri Lanka) have low Fe and high Ti. Basaltic deposits required plots of the relation between the ratio of element concentrations to be able to distinguish their origins. Another interesting point is the plot between the concentration of Cr and Fe is able to identify several of red color corundum (ruby). It is interesting that Bo rai of Thailand and Pailin of Cambodia cannot be distinguished due to similarity of geological landform. However one can separate Bang Kha Cha sapphires from Bo rai, by their high concentration of Ga, even though both of them are from Thailand. Additionally, Montana deposit shows high abundance of iron and chromium in comparison with other corundum of basaltic deposit.

Despite IL analysis cannot indicate the corundum deposit, the technique is clearly very sensitive for detecting the emission of Cr^{3+} which substitutes Al^{3+} in the corundum matrix. The luminescence intensity of Cr^{3+} peak dramatically changes with the Cr concentration. The observation can likewise compare the red tone appearance. Nevertheless, the Fe^{3+} luminescence cannot be detected by this technique because of the forbidden of the selection rules. In comparison with IL, UV-Vis-NIR spectroscopy is less sensitive for detection of Cr^{3+}**.** Anyhow, a conventional technique such as UV-

Vis-NIR spectroscopy is still necessary to detect other contributions from Fe^{3+}, Fe^{3+}/Fe^{3+} and Fe^{2+}/Fe^{3+} valence charge transfer which produce yellow color or Fe^{2+}/Ti^{4+} which is the cause of the blue color. The color center luminescence can declare the crystallization in the matter. In other words, the more defect material would reflect the more intense from the vacancy luminescence.

5.2 Ion beam enhancement

The alteration of treated corundum could be justified by various methods such as gemologist color grading and UV-Vis-NIR spectroscopy. This work has proposed the new method which is the relation plot between the ratio of Cr/Ga and Fe/Ti concentration from PIXE analysis in order to identify the modification in fulfilling other techniques. Ion implantation is a powerful for improving low cost corundum. The energetic ions effectively interact with the localized impurity of the stone and will not harm to the sample if suitable ion energy and irradiation time are chosen. The other significant factor is the charge state alteration, reduction or oxidation state, which controlled by the oxygen partial concentration in the surroundings. The conclusion on the effects of ion implantation to corundum is the following:

- Effects of N_2^+ ions implantation
  - Intensify blue
  - Eliminate yellow tint in greenish tone
  - Enhance the clarity in dull sapphire
- Effects of Ar^+ ions implantation
  - Be colorless or paler tone

- Effects of O^- ions implantation
  - Affects the reddish tone in corundum
  - Enhance the vivid yellow color
  - Lightening the dark tone of blue sapphire

The reducing condition is very useful for blue color intensification in blue sapphire or alters the greenish tone from yellow tone. In addition, as much as Fe^{2+} is concern, it has more opportunity to incorporate with Ti^{4+} for creating blue color. However, some useless modifications are found such as ruby has increase violet tint. The latter condition, oxidizing, affects the ruby and reddish tone sapphire by reducing violet tint and increasing reddish tone. In addition, the vivid yellow can be enhanced by oxidizing of iron (Fe^{3+}) enriched. One can apply this method to lightening the dark tone of blue sapphire for market value adding. In all cases the energetic ion can transfer its kinetic energy to reduce the impurity, corundum become transparent and the clarity is increased. All of these alterations can be observed by ion beam analysis technique accompanied with the conventional gemological technique such as UV-Vis-NIR spectroscopy.

These enhancement methods are an alternative technique for a trader to provide a wide range of corundum modification. The worth of modified corundum could be increased depending on the treatment condition. The ion implantation has an advantage/limitation with another conventional method such as heat treatment or radiation by the following:

- Advantage of ion implantation
  - Can alter the color tone in corundum

- Be safe for customer (Temperature , Radiation)
- Using the shorter operation time
- Durable modification
- None of contamination (Clean)
- Accurate selection for modification

- Limitation
  - High cost and high technology

5.3 Suggestions for further study

The investigated corundum should be in the form of table cutting for conventional analysis. For safety, the silicate and calcite elimination process should use 37% hydrochloric instead of 48% hydrofluoric. The trace element analysis needs more than ten samples for fingerprints characterization. Furthermore, the set up of detectors for PIXE and IL techniques should be fixed at the same position in order to maintain the same analysis parameters. Avoid attaching corundum on the sample holder by epoxy, because it can create stain on the surface. The chosen sample for modification should not contain the silicate or calcite inside corundum in order to prevent the fracture while performing ion beam irradiation. In this case, the sample holder lay on vertical direction is difficult for the sample attachment. Hence, using the ion implanter with the vertical ion beam direction should have more advantages. Although, the relation ratio plotting of the trace element concentration can distinguish and track the alteration of corundum, the selective point for investigation should be at the same position which require for the very precise ion beam position control.