CHAPTER 1

INTRODUCTION

1.1 Introduction

Ion beam technology, in terms of ion implantation, has capability and applications usage in a surface modification method especially for the doping in semiconductor and surface hardening in the metals. In addition, the advantages of this process of fast and precisely controlling, a non-destructive analysis can be utilized. For ion beam analysis (IBA), which includes particle-induced X-ray emission (PIXE), Rutherford backscattering spectrometry (RBS), ionoluminescence (IL) and nuclear reaction analysis (NRA), etc, they are simple and very sensitive analytical technique that can be used to identify and quantify trace elements (Kamwanna et al., 2010). In recent year, these processes have implications in the modeling of major and trace element migration, evaluating mineral phases for geochronology, investigating of gases in extraterrestrial environments, and waste in geological repositories. In nature, mineral alteration and diffusion processes occur gradually over a long timescale, under conditions of variable pressure, temperature and chemistry. The details history of geologic materials is generally difficult to determine under laboratory methods since natural materials have variable compositions and uncertain occurrence histories. In contrast, ion beam has potential for precisely characterization these elements in sample by tight binding electron emission. Also ionoluminescence (IL) offers a highly sensitive method for measuring optically active impurities and defects in samples (University of Leipzig, 2010). IL is especially sensitive for a luminescence detection of small amounts of rare earths in natural gemstone.

In this research we focus on the using of ion beam techniques to analyze and modify corundum with emphasis on optical property of corundum, accompanied with extract the physical information after modification. The most frequently used IBA techniques in this work are particle-induced X-ray emission (PIXE) and ionoluminescence (IL), together with UV-Vis-NIR spectroscopy analysis technique for comparison.

1.2 Corundum

Corundum is a crystalline form of aluminium oxide (Al_2O_3) in a hexagonal structure which is naturally clear or has no color, but can show some colors when incorporate with chemical types, structure and quantity of elements. Strength of corundum as jewelry is only lower than a diamond leading to a good property of high resistance to abrasive and corrosion quite similar to the high level value gems. In 2011, the gem's industry in Thailand was the 4th amongst Thailand's top ten exports as shown in Table 1.1. The value and quality of gemstone depend on the "4C" indices which are color, clarity, carat weight and cutting. Natural corundum is the rarest and the most valuable for color gemstone and the marketing is growing while the sources of excellent qualities materials tend to be insufficient. Gems traders, therefore, try various methods to improve corundum's characteristic such as saturated color and transparency. However, treating gems by some techniques especially the heat treatment, which is a thermionic radiation process below corundum's melting point would affects corundum properties directly via volumetric expansion (Themelis, 1992). Since these high temperature treatments cause the transformation of crystalline to be unnatural, crack, cleavage, fracture, undesired oxide such as silicate or calcite (Srisupawatana, 2011). Hence, a new standard and reliable technique for improving their properties is required for the condition of thermal stability (Intarasiri, 2010).

The visual appearance and characteristics of corundum is determined by many variables including: brilliance, color, fire (light dispersion), and luster. A variety colors of corundum are depend on trace element present, for red color is called as ruby, and another color is called as sapphire. For a sapphire to be pink there must have small amount of chromium inside, and for that pink color to turn more saturated and red, a larger amount of chromium must be present. Blue and yellow sapphires are

Table 1.1. Top ten of Thai exports in 2011 (Ministry of commerce, 2012).

Ranking	**Exports**	**Values (million Bath)**
1	Computer accessories and parts	513,709.4
2	Car accessories and parts	511,483.7
3	Rubber	397,079.8
4	Gems and jewelry	371,239.3
5	Refined fuels	279,413.9
6	Plastics in primary forms	265,312.7
7	Rubber products	252,969.8
8	Petrochemical products	250,046.8
9	Electrical circuits	238,173.4
10	Rice	196,117.0

included with iron as trace element in different electrical charge state, where orange or the more popular padparadscha sapphire needs both iron and chromium. Note that the green sapphire is the mixing of the blue color and yellow color. Apparently, purple sapphire is comprised of a small amount of vanadium while a larger amount of vanadium in the structure could cause the creation of another color sapphire (Themelis, 1992).

1.3 Modification of corundum by ion implantation

Color and optical property enhancement of corundum by ion implantation can be a new trend of the modification method. The enhancement is based on thermal spike that cause the point defect and phase transformation in corundum (Townsend et al., 2004). For examples, sapphires that were implanted by a 200 keV Ar^+ beam at room temperature could produce the color center (Aoki et al., 1996). In addition, synthetic rubies and sapphires that were implanted by 120 keV N-ions had included with point defects in which are those sites with missing oxygen (Chaiwong et al., 2005). They also stated that during implantation ion beam current should not exceed tens of microampere for avoiding thermal heat at the sample. After implantation, annealing or cooling process is contributed the retaining of point defects. Aoki et al. (1996) reported that, after ion implantation, synthetics sapphire has shown the luminescence spectra centered at 330 nm and 411 nm. These spectra referred to the F^+-center and F-center, respectively. They found that high fluence implantation leads to the decrement of luminescence intensity implied that more defect is produced. For high fluence effects, the blistering can occur that leads to the decrement of the corundum refractive index, and gaseous production (Chaiwong et al., 2005). Nevertheless, the high fluence enhancement was reported by Intarasiri et al. (2009). The high fluence (2x10^{18} ions/cm^2) and ion current (100 μA) of a 120 keV oxygen implantation had reduced blue color in rubies by reducing Fe^{2+}. Moreover, oxygen ion induced the brilliance of yellowish tone in yellow sapphires by included of Fe_2O_3. They also reported that N-ion implantation could eliminate green color in blue sapphire. By the way, Dalal et al. (1988) stated that an optical absorption band depend on the direction of implantation with respect to crystal axis. The studies showed that heavier ions produce more F-center than F^+-center and C-axis parallel cutting generated wider absorption band than C-axis perpendicular cutting. Additionally, low temperature (77 K) can retain more defects than high temperature (300 K).

1.4 PIXE for corundum analysis

PIXE technique is a very well-known, powerful, non-alteration and non-destructive analytical technique which is suitable for trace elements quantification (Kamwanna, 2008). Whenever an energetic proton hits corundum, its kinetic energy can transfer to an inner shell electron, in other words, proton frees these electrons from atoms. Consequently, an outer shell electron jumps down to replace the vacancy controlled by the selection rule and release precise excess energy in the form of "characteristic X-rays" which labeled by Prof. Kai Siegbahn. Alternatively, PIXE is a popular technique for trace element analysis. In the literatures, proton as excitation projectile was generated by accelerator at several values such as 1.9 MeV (Calligaro et al., 1999), 3 MeV (Osipowicz et al., 1995), and 2 MeV (Tang et al., 1988).

Different proton energy contributed the dissimilar differential cross section implied difference in probability for X-ray emission count rate. All investigations stated in the same way that the recording of PIXE spectra was generally limited by a X-ray background of bremsstrahlung effect which typically occurs during radiation of a thick insulating sample. Gemstones must be prepared carefully, without any contamination and outgassing materials, before analysis. Osipowicz et al. (1995), described the preparation method for a ruby. Samples were mounted in resin, ground and polished, in order to eliminate inclusion close to the surface. The specimens were also cleaned with acetone in an ultrasonic bath. To prevent charging up of the non-conducting samples, those authors coated the samples with 20 Å of Au but in our case, the electron gun as an electron source is used to neutralize the total charge in samples during measurement. The samples were supported by super epoxy glue that was free from interfering impurities. Generally the literatures showed that the detector was commonly lithium-drifted silicon or Si(Li) detector, but acquisition condition was set up depend on the cross section of characteristic X-ray. For example, Calligaro et al. (1999), acquired PIXE spectra for a few minutes with a beam current about 1 nA; Osipowicz, et al. (1995), acquired spectra with a 200 – 400 pA beam current by Si(Li) detector-positioned at angle of 135^o relative to beam direction; Tang et al. (1988), used Si(Li) detector at an angle of 90^o to the beam and recorded the spectra for about 150 seconds for each of samples. All of these set up acquisition systems are similar to Chiang Mai university system in which Si(Li) detector is placed at 120^o to the beam directions. The above investigations showed that the measurement can be performed by using a beam current of only about hundreds of picoampere to a few of nanoampere. It would save the samples from radiation damage. However, it is necessary to acquire spectra until it overwhelm statistic error. Eventually, spectra were analyzed by GUPIX software allowing for a quantitative analysis of PIXE spectra.

There are many investigations on trace element analysis of corundum. Calligaro et al. (1999) have found that the trace element content varied depending on the local geological surrounding, leading to high standard deviations in mean of trace elements content which is similar to Sun et al. (2001). Their investigations stimulate our decision for using ion beam techniques to classify deposits sites of corundum in Thai market. Rubies from Mong Hsu were studied by Osipowicz et al. (1995), their results have been compared with reference reported by Tang et al. (1989) and Hlaing (1993) in order to confirm the accuracy of the data. The results showed the high Fe concentrations in Thai rubies. On the contrary, the presence of V in Burmese rubies was much higher concentrations than Thai rubies. On the other hand, Cu was not detectable in any of Thai rubies (Osipowicz et al., 1995). Both results were useful as a "fingerprints" pattern. Thus, ruby in Thai market of our research should have similar concentration to these studies. It can confirm our study such as having a few ppm of Cu. Sun et al. (2001), also investigated the sapphires from many deposits sites locations in Myanmar (Burma). They found that magmatic deposit sites were found to contain very high concentrations of Ti, Fe, and Ga. These results agree well with what was observed by Sutherland, et al. (1998) in their research in Australia and Cambodia. On the other hand, sapphires of metamorphic deposit sites were observed to have low concentrations of Ti and Fe. Moreover, V, Cr and Ga concentrations in these deposit sites were also high compared to magmatic deposit sites. The method used by the authors is benefit for identifying the geological region of corundum origins in

Myanmar. Therefore, our study of trace element concentration of corundum in Thai market could be able to compare with the above-mentioned database. Lastly, Tang et al. (1988), exhibited the approach to distinguish color or inclusion between Burmese and Thai ruby. The program AXIL (analysis of X-ray spectra by iterative least-squares fitting, version 04) was used to determined the integrated counts of the X-ray peaks (Tang et al., 1989). Commonly, Thai rubies had higher Fe contents than Burmese rubies. They also compared with the ratio of Fe K_{α} intensity per Cr K_{α} intensity which illustrated below 0.3 for Burmese origin, but greater than 0.7 for Thai origin. For their research, they have demonstrated the way for qualitative analysis of corundum deposit sites by compared ratio of two elements. Consequently, characteristics X-ray spectrum was investigated following above relation. An advantage of PIXE technique was also discussed briefly.

1.5 Ionoluminescence (IL) for corundum analysis

IL is a highly sensitive method for measuring optically active impurities and defects in a sample. Not only energetic protons have potential to release the tightly bound electron, but the energetic protons can also stimulate sharing valence electrons in each atoms of molecule. These electrons are excited and emit photon in range of visible light. As mechanism of IL occurs in molecular frontier, via distortion of molecular energy state, it is really complicate to explain or extract data related to the optical properties. Description of IL requires knowledge on luminescence mechanism of the whole molecular systems of investigated samples. However, both PIXE and IL were accustomed for research related to the origins, physical qualities and trace elements quantities of gemstones (Kamwanna, 2008; Sanchez et al., 1997).

There are description of the IL spectra that two bands, consist of F^+ center at 330 nm (3.76 eV) and F center at 414 nm (3.0 eV), are directly related to point defects in Al_2O_3 (Kamwanna et al., 2010). Similarly, Calvo del Castillo et al. (2007), used IL technique to determine luminescence process of rubies and sapphires. They found that sapphires also have intrinsic defects at 316 and 417 nm, (F^+ and F^- oxygen vacancy color centers), respectively. Additionally, the sharp peak of rubies centered at 694 nm, attributed to impurity Cr^{3+} called R-line that contained two main lines – R_1 at 692.9 nm and R_2 at 694.3 nm – which correspond to a transition from the first excited state (^2E) to the ground state ($^4A_2$) of Cr^{3+} in Al_2O_3. Next, we investigate luminescence of corundum and checked the data with the above-mentioned research. Due to the lack of a relation between PIXE and IL information of corundum, we will try to fill this vacancy. Furthermore, there are three effects on the ruby R-line spectrum. Due to lower Cr concentrations in sapphire, the line widths of sapphire are narrower than ruby. Next, the peak positions shift to higher energy caused by electric-dipole transitions.

1.6 Objective of this work

This work is concentrated on two main parts; i.e., ion beam analysis and ion beam treatment. On one hand, the former is aim for characterizing of corundum by using nondestructive character of ion beam techniques. These results can be utilized for documenting fingerprints of corundum. Furthermore, such characterizations contribute to the understanding of relationship between naked-eye observation and intrinsic properties, e.g., trace element concentrations, luminescence mechanism, derivation of defects, original fingerprint, etc. Understanding these properties, especially trace element concentrations and luminescence mechanism, are crucial for setting up the treatment conditions. Hence, particle-induced X-ray emission (PIXE) and ionoluminescence (IL) would be applied as the standard techniques for analyzing trace element concentrations and luminescence property, respectively. This information is useful in selecting corundum for the treatment. On the other hand, the latter is applying basic principles of ion implantation for enhancing the optical properties of corundum. The method appears to be a new and a sustainable for improving gemstones properties. The study on ion implantation technique would be focused on the effects of ion energy, ion type, and ion fluences on a variety of corundum. This study will report on every detectable modification in corundum either positive or negative effects.