CHAPTER I

INTRODUCTION

1.1 General Statement

Thailand is a significant center of the world gem and jewelry market. Many gem industries (e.g. jewellery design and production) have been supported by the government, because the country has earned high exporting value of these products (Figure 1.1). Unfortunately, gemstone deposits generally have been found in a few areas in Thailand; in addition, corundum (both ruby and sapphire) is the only significant type of gem material found in the country. The other gemstones (e.g. zircon, pyroxene, spinel and garnet) are accessory minerals in corundum deposits. Diamond has been reported to occur in several localities in the southern part of Thailand. However, these occurrences are not economically important. Even corundum reserves are rapidly declining within last few decades. Consequently, gemstone imports have been a key strategy and tended to increase every year (see Figure 1.1). Although varieties of gemstone are supplied to the industries, corundums are still the highest demand for gem materials in the country.

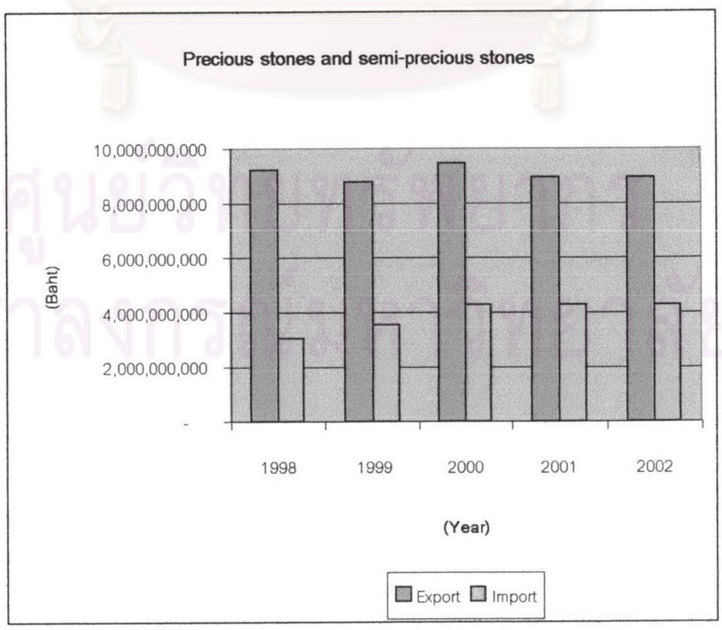

Figure 1.1 Export and import values of precious and semi-precious stones in Thailand (GIT, 2003)

Rubies and sapphires from all over the world to have been imported to Thailand for enhancing, cutting and setting for jewellery before exporting to the world market. Gemstone heat treatments in Thailand have started and developed by local people who have earned their personal experiences in which their processes and techniques have not been disclosed to the public. Moreover, these techniques are generally discovered by trial and error; scientific methods have not much been concerned to improve the techniques.

Gemstone enhancement was initially happened in Greece and Rome before the Christian Era (Nassau, 1994). Heat treatment of ruby and sapphire is one of the most common techniques which is still in used today to enhance their qualities such as color, clarity and phenomena. These enhancements appear to have been permanent and heat-treated corundums are acceptable in the world market. Because natural, non-heat-treated, rubies and sapphires with good color and clarity are very rare. The rarity makes them more expensive; therefore, heat treatments are required to improve qualities of the stones before trading to the market.

The most important factors for the heat treatments of corundum suggested by Nassau (1994) are composed of highest temperature reach, soaking time at highest temperature, heating rate, cooling rate, chemical nature of heating atmosphere and atmospheric pressure.

Chemically, corundum consists of a ratio of two aluminium atoms per three oxygen atoms or aluminium oxide (Al_2O_3) crystallizing in the hexagonal system. Pure corundum is naturally colorless, which is very rare. Corundum is an allochromatic mineral; however, colors of corundum can be produced, when they contain some trace elements. The different colors or varieties of corundum are usually caused by trace amounts of chromatic element and perhaps crystal defects. Corundums can be separated, based on their colors, into two main varieties; ruby and sapphire. Rubies have red shade in which their colors are significantly caused by chromium (Cr^{3+}) in crystal structure. Term of sapphire means other colors except red shade; thus sapphires may have blue, yellow, green, pink, orange, violet and other mixed colors. Master colors of sapphire varieties are actually yellow and blue. Iron (Fe^{2+}) and titanium (Ti^{4+}) typically cause blue color, whereas yellow may be caused by iron (Fe^{3+}) or color centers (crystal defects). Colors of the other varieties are combinations between red, blue and yellow that may be results of various mixtures and ratios of elements as mentioned above.

Perera et al. (1991) reported heat treatment of Sri Lanka sapphires that are light blue or colorless with dark blue patches on outer surface which known as "ottu" were operated at 1800 °C – 1850 °C for 1 hour under reducing condition. After experiment, three types of results were described. First results showed clear blue stones. The second showed clear stones but did not attain a satisfactory color (very pale blue to colorless stones). Over 50% of the results belong to the third group, which showed non-transparent white coating stones. EPMA analysis was using to study the cause of color after heated. The first and second groups showed low Fe and Ti (0.03 – 0.15%) concentration. On the contrary, non-transparent white coating stones presented medium Fe (0.15 – 0.3%) and high Ti (above 0.3%).

Themelis (1992) developed blue color in milky, silky, white, colorless, semi-translucent to semi-transparent sapphires from Sri Lanka by heat-treated at over 1650 °C in a reducing atmosphere for 1 to 2 hours.

Emmett et al. (1993) reported that Fe^{3+} + Ti^{3+} would become Fe^{2+} + Ti^{4+} (iron would gain one electron while titanium would loose one) during growth at any reasonable temperature to create blue color. Heat treated sapphire samples at 1650 °C in reducing atmosphere that contains some hydrogen. The wide ranges of blue color were present. The good blue stones require a high titanium concentration.

Pemadasa et al (1994) reported heat treatment of poor quality corundum which known as gueda sapphires under reducing conditions. Slightly bluish or milky stones must be heat treated at 1850 °C for 30 minutes, in order to convert this samples to blue sapphires. The appropriate heat treatment temperature of translucent samples with brownish impurities is 1859 °C for 1 hour. Colorless or slightly bluish sapphires included by very finely scattered impurities were converted into blue sapphires by heat treatment for 10 hours at 1750 °C.

Hughes (1997) reported the heat treatment process to develop blue color by heat to between 1600 $^{\circ}$C – 1900 $^{\circ}$C in a reducing atmosphere.

Kyi et al. (1998) reported the heat treatment of geuda-like (milky or contain abundant silk) sapphires from Mogok under reducing atmospheres for 2 hours, step heating temperatures from 1200 $^{\circ}$C, 1300 $^{\circ}$C, 1400 $^{\circ}$C, 1500 $^{\circ}$C, 1600 $^{\circ}$C and 1700 $^{\circ}$C. After heated at 1200 $^{\circ}$C the milky sapphires turned to transparent or translucent colorless stones with the exception of a very light blue milky sapphires with zonal structure which turned white. Repetition of the experiment to 1300 $^{\circ}$C and 1400 $^{\circ}$C caused no further dramatic changes in the sapphires. At the temperature of 1500 $^{\circ}$C, the heating period was much longer than for the treatments described above, some milky sapphires change to medium blue. The light blue milky sapphire which had turned to white at 1200 $^{\circ}$C also changed to blue at 1500 $^{\circ}$C. When the temperature was raised to 1600 $^{\circ}$C and the heating period further extended, the color dramatically changed from medium blue to a beautiful blue. When the temperature was increased to 1700 $^{\circ}$C and the period of heating increased over that used at 1600 $^{\circ}$C, the beautiful blue sapphire turned to medium blue.

Read (1999) heat treated geuda sapphires (milky-colored translucent sapphires) in timeed steps through 1200 $^{\circ}$C to about 1700 $^{\circ}$C in an oxygen free atmosphere, a process which may take up to 30 hours, the titanium dissolves in the alumina and produces a transparent blue stone.

Somboon (2000) studied the internal characteristics of sapphire samples from Ilakaka-Sakaraha, Madagascar by heat-treated at 1000 $^{\circ}$C and 1650 $^{\circ}$C for 3 hours. The most of internal features of sapphire samples after heated at 1000 $^{\circ}$C for 3 hours were still unchanged only a few characteristics can be observed at this temperature. When the samples were re-heated up to 1650 $^{\circ}$C for 3 hours many internal characteristics change can be observed. The blue color was developed at 1650 $^{\circ}$C.

Pattamalai (2002) studied heat treatment of some corundum from Madagascar. Most pink, purple and medium violet sapphires were selected for the research, consequently some changes in color and internal characteristics were reported after heat treatment at various temperatures (e.g. 800 °C, 1,000 °C, 1,200 °C, 1,400 °C and 1,650 °C) under oxidizing atmosphere for one hour soaking.

Red or pink colors (caused by Cr^{3+}) in those samples are combined with bluish shades (usually resulted by intervalence charge transfer between Fe^{2+} and Ti^{4+}) and consequently yield purplish overcast colors. Hence, deduction of Fe^{2+}/Ti^{4+} IVCT would get rid of bluish shades and then reddish shades will be purified. In this case, oxidizing atmosphere is then selected for heating. On the other hand, heat treating under reducing atmosphere could develop and intensify blue color in sapphires. This is because pairs of Fe^{2+} and Ti^{4+} would possibly be increased during the treatment. Reaction of both phenomena can be explained as equation below (Nassau, 1994).

$$Fe^{3+} + Ti^{3+} \underset{\text{oxidizing}}{\overset{\text{reducing}}{\rightleftharpoons}} Fe^{2+} + Ti^{4+}$$

1.2 Objectives

The main objective of this research is to study the physical properties and to observe internal characteristics of some blue sapphires from Ilakaka-Sakaraha that could be improved their colors and qualities during heat treatment. The method is to compare their characteristics such as color, absorption spectra and internal characteristics between preheat stones and heated stones at various temperatures. The aims of this study are to illustrate and understand the changes of these characteristics, which will be used as crucial criteria for laboratory certification to declare the heat-treated sapphire. Moreover, knowledge for the effective heat treatment method for the Ilakaka-Sakaraha sapphires should be gained from this study.

1.3 Methodology

The methods of study are summarized as flowchart in Figure 1.2 that contains several steps of investigation. Literature survey of the previous works related to this study was the first step. Natural sapphire samples and heat treatment procedure were consequently acquired and planed. Preparation before thermal enhancement was the next crucial step that was dealt with sapphire samples under the study. Samples were devided into 7 groups based on their color shade in comparison with GIA gem set color chart. Subsequently, physical and optical properties (e.g. refractive index (RI), birefringence, specific gravity (SG) and luminescence under long wave (LW, 365 nm) ultraviolet and short wave (SW, 254 nm) ultraviolet) were determined using refractometer, electronic balance and ultraviolet lamp, respectively.

In addition, measurement of the absorption spectra of most samples before heat treatment were carried out using Fourier Transform Infra-Red spectrophotometer (FTIR) and UV-VIS-NIR spectrophotometer. This procedure covers whole range of infrared, visible light and ultraviolet, and may help to understand nature of samples and causes of their colors. Semi-quantitative analyses of the major element (Al_2O_3) and some trace elements (e.g. Fe_2O_3, TiO_2, Cr_2O_3, V_2O_3 and Ga_2O_3) were carried out using Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF). Internal characteristics, especially inclusions, were carefully investigated under microscope before taking photos and further identification of Laser Raman Spectroscope. All equipment and instruments mentioned above are based at the Gem and Jewelry Institute of Thailand (GIT).

Step heating treatment was subsequently experimented at various highest temperatures (i.e. 1,000°C, 1,200°C, 1,400 °C and 1,650 °C) under oxygen free condition (purched with pure N_2 gas). Three hours soaking time at each highest temperature was set consistently during this study. Electric furnace, mode! HT 1800 Plus VAC Bottom Loader based at Department of Geology, Chulalongkorn University was engaged for this experiment. Then internal characteristics, luminescence and absorption spectra were observed and measured again after each step of heating. Subsequently, comparison between unheated characteristics and heated characteristics of each highest temperature were made. The heated samples were quantitatively analyzed for some trace elements (e.g. Fe_2O_3, TiO_2, Cr_2O_3, V_2O_3, Ga_2O_3, SiO_2, MnO and MgO). The measurement was done using Electron Probe Micro-Analyzer (EPMA) at Center of Gemstone Research, University of Mainz, Germany. Consequently, interpertation of collected data, discussion, conclusion and thesis writing were carried out.

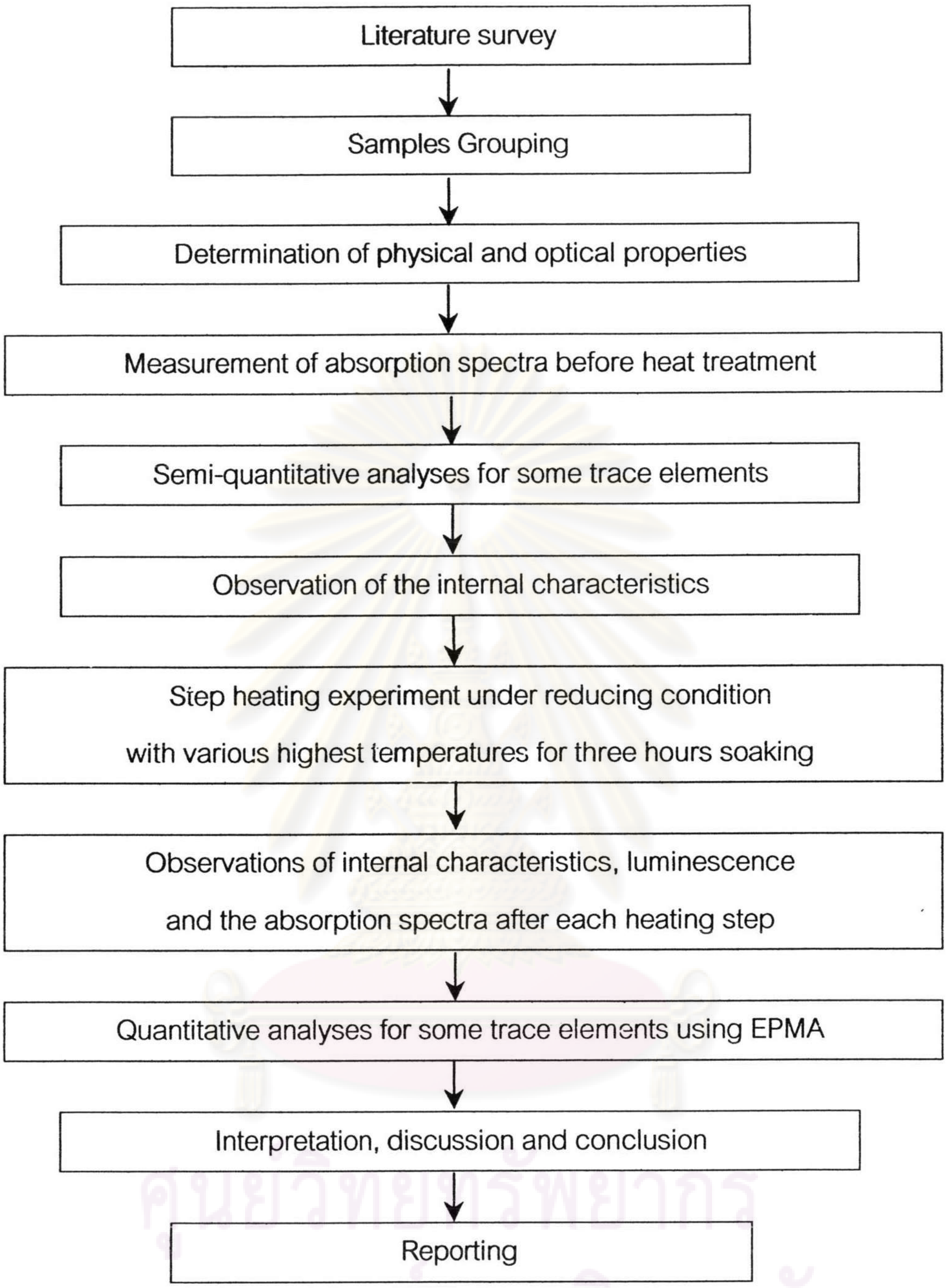

Figure 1.2 Flowchart showing method of study.