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YELLOW COLORATION IN HEAT-TREATED NATURAL SAPPHIRES

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การศึกษาสาเหตุของการเกิดสีเหลืองในพลอยบุษราคัมธรรมชาติที่ผ่านการเผา สามารถทำได้โดยการทดลองเผาตัวอย่างพลอยบุษราคัม ที่มีกำเนิดสัมพันธ์กับกระบวนการหินแปร และพลอยบุษราคัมที่มีกำเนิดสัมพันธ์กับหินบะซอลต์ ตัวอย่างพลอยที่มีกำเนิดสัมพันธ์กับกระบวนการหินแปรที่นำมาศึกษาในครั้งนี้ได้แก่ พลอยบุษราคัมเผาแล้วด้วยวิธีปรกติจำนวน 5 ตัวอย่าง จากประเทศศรีลังกา เมื่อนำพลอยดังกล่าวมาเผาถอยสีในสภาวะการเผาแบบขาดออกซิเจน ที่อุณหภูมิ1650°C เป็นเวลา 5 ชั่วโมงแล้ว พบว่าสีของตัวอย่างเปลี่ยนจากสีเหลืองทองเป็นใสไม่มีสี และเมื่อตรวจสอบการเปลี่ยนแปลงของสีดังกล่าวกับสเปกตรัมการดูดกลืนแสงในช่วงคลื่นยูวีถึงช่วงคลื่นตามองเห็น ทราบว่าสีเหลืองที่ได้จากการเผาก่อนการทดลองนั้น เกิดจากกระบวนการศูนย์กลางสี ส่วนผลวิเคราะห์องค์ประกอบทางเคมีของธาตุร่องรอยหลังเผาด้วยเครื่องมือ LA-ICP-MS บ่งบอกว่ามีปริมาณธาตุเหล็กเป็นองค์ประกอบค่อนข้างต่ำ และ Mg > Ti ในตัวอย่างดังกล่าว ทำให้ทราบว่ากระบวนการศูนย์กลางสีที่เกิดขึ้น มีสาเหตุมาจากการที่ Mg ที่มากพอเข้าไปทำให้เกิดศูนย์กลางสีที่เสถียร หรือที่เรียกว่าศูนย์กลางสีที่ตรึงโดยแมกนีเซียม

พลอยบุษราคัม ที่มีกำเนิดสัมพันธ์กับหินบะซอลต์ที่นำมาศึกษาในครั้งนี้ได้แก่ พลอยบุษราคัมสดจากแหล่งบางกระจะ จังหวัดจันทบุรี ประเทศไทย ตัวอย่างพลอยดังกล่าวสามารถแบ่งตามลักษณะสีออกได้เป็น 2 กลุ่มย่อย โดย ตัวอย่างกลุ่มย่อยแรกมีโทนสีเหลืองแกมเขียวและเขียวแกมเหลือง พบว่ามีปริมาณธาตุเหล็กเป็นองค์ประกอบค่อนข้างสูงและ Ti > Mg ส่วนตัวอย่างกลุ่มย่อยสองเป็นพลอยบุษราคัมสีเหลืองอ่อน 2 ตัวอย่าง พบว่ามีปริมาณธาตุเหล็กเป็นองค์ประกอบค่อนข้างสูงและ Mg > Ti ตัวอย่างดังกล่าวทั้งสองกลุ่มย่อยได้ทำการเผาที่อุณหภูมิสูงในสภาวะออกซิเจนพอเพียง พบว่าผลที่ได้แตกต่างกันอย่างเห็นได้ชัดเจน โดยกลุ่มย่อยแรกที่มีปริมาณ Ti >Mg ไม่เห็นการเปลี่ยนแปลงของสีเหลืองแกมเขียวและเขียวแกมเหลืองเลย ส่วนกลุ่มย่อยสองที่ปริมาณ Mg > Ti มีการเปลี่ยนสีจากสีเหลืองอ่อนเป็นสีเหลืองทองหรือสีเหลืองน้ำตาล (สีเหลืองแม่โขง)หลังเผาอย่างเด่นชัด จากการทดลองทำให้สรุปได้ว่ากลุ่มย่อยแรกที่มีปริมาณ Ti >Mg ธาตุทั้งสองมีการรวมตัวเกิดเป็นกลุ่มของ $MgTiO_3$ ในพลอยซึ่งไม่มีสี ทำให้มีธาตุแมกนีเซียมเหลือไม่พอที่จะเข้าไปทำให้เกิดศูนย์กลางสีที่เสถียร ดังนั้นสีอมเหลืองที่พบในพลอยกลุ่มย่อยแรกมีสาเหตุมาจาก spin forbidden transition of Fe^{3+} เพียงอย่างเดียว ส่วนกลุ่มย่อยสองที่ปริมาณ Mg > Ti ธาตุแมกนีเซียมที่เหลือสามารถทำให้เกิดศูนย์กลางสีเหลืองที่เสถียรได้จากการเผา

ภาควิชา..............................ธรณีวิทยา.....................ลายมือชื่อนิสิต..
สาขาวิชา............................ธรณีวิทยา.....................ลายมือชื่ออาจารย์ที่ปรึกษา...
ปีการศึกษา.........................2549..............................

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The cause of colour change in yellow sapphires can be explained through the process of heat treatment experiments performed on differing sets of samples from both 'metamorphic' and 'basaltic' origins. In this study 'metamorphic' yellow sapphires were five simply heat-treated stones obtained from Sri Lanka. These sapphires were re-heated in a reduced atmosphere at 1650°C for 5 hours. After the treatment the samples changed from their strong yellows to colourless. The residue spectra observed from this experiment showed that the colour change could be identified as that of a "colour centre pattern". Trace element analysis by LA-ICP-MS showed that these samples had low Fe and Mg > Ti in content. We can deduce from this that the colour change in metamorhic samples occur through the stabilized assistance of Mg in the "colour centres" process or the so-called 'Mg-trapped hole colour centres'.

The basaltic origin samples from Bang Kacha area, Chanthaburi Province were grouped into two sets based on the colour variety. The first group (seven untreated stones) were found to be high Fe and Ti > Mg of greenish yellow to yellowish green variety, with the other set (two untreated stones) being high Fe and Mg > Ti of yellow variety. Both sets of samples were heated in an oxidized atmosphere at high temperatures. We discovered differing results from the two sets after heat treatment. The set with the higher content of Ti to Mg showed little to no change in colour. The set with Mg > Ti showed a significant colour change to strong brownish yellow. What we can deduce from this experiment is that the set with Ti > Mg had little to no change in colour because the Ti and Mg combine to form $MgTiO_3$ and no Mg was left to assist any colour centre process. The yellow hues in this set of samples were likely to have been from the spin forbidden transition of Fe^{3+} that can occur in 'basaltic' sapphires. The set with high Mg assisted the stabilization of the yellow colour centres and allowed significant colour change to take place in the sapphires.

Department……...……Geology……………Student's signature……………………………

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CHAPTER I

INTRODUCTION

1.1 Preamble

In the last several decades, it has become generally well accepted that Thailand is the major producer of rubies and sapphires. Approximately 80% of rubies and sapphires trading in the world have been exported from Thailand. The reason for this stems from the fact that Thailand is not only the worlds most important centre for ruby and sapphire heat-treatment but also as one of the fine craftsmanship centres for gemstone cutting, jewellery design and manufacturing. As the indigenous raw materials are almost exhausted Thai traders need to import rough stones from many countries such as Tanzania, Madagascar and Sri Lanka. The majority of the rough stones are normally inferior in quality and require treatment to enhance their colour and clarity, then are cut and subsequently exported or set in a piece of jewellery before being exported into the international market. Gemstone heat treatment is a practice that Thai gem traders have been using for more than 50 years. The practice is widely known and can be considered acceptable and sometimes unacceptable in gem industry depending on the method of heat treatment being used. The complex heating processes or techniques have been mostly discovered through trial and error and the practical experience of the person involved. As such the techniques remain closely guarded secrets amongst the individuals involved in the practice.

In order to understand the role of trace elements which cause colour in Al_2O_3 structure during the heat treatment processes we need to know the basic knowledge on the cause of colour in corundum. Fortunately enough, today we understand the mechanisms and causes of colour in corundum better than in the past (Hughes, 1997; Nassau, 1994; Themelis, 1992). Pure corundum (Al_2O_3) is colourless, but colour does occur when the element Al in the Al_2O_3 structure is being replaced by another specific type of trace element. These trace elements are called chromophoric elements and are mostly transition elements. Coloured gemstones formed in this way are called allochromatic gems. For example, ruby is the red variety of corundum in which its red colour is caused by Cr replacing the Al in Al_2O_3 lattice.

In the case of yellow sapphires, there are two types of stable yellow coloration found naturally. The first group of stable yellow sapphires owns their colour from spin forbidden transition of Fe^{3+} (Lehman and Harder, 1970; Krebs and Maisch, 1971; Ferguson and Fielding, 1971, 1972; Nassau and Valente, 1987). However, the probability of this transition occurring naturally is very low, and this mechanism requires approximately 1% weight Fe^{3+} to create an intense yellow colour. Sapphires of this group generally contain rather high Fe content and mainly originate from basaltic-type occurrences such as from Thailand, Australia and North Madagascar or from the metamorphic occurrence in Umba, Tanzania (Lomthong, 2004). The typical absorption spectrum of the high Fe sapphire shows pronounced absorption peaks at 450, 388 and 377 nm due to Fe^{3+} (Figure 1.1).

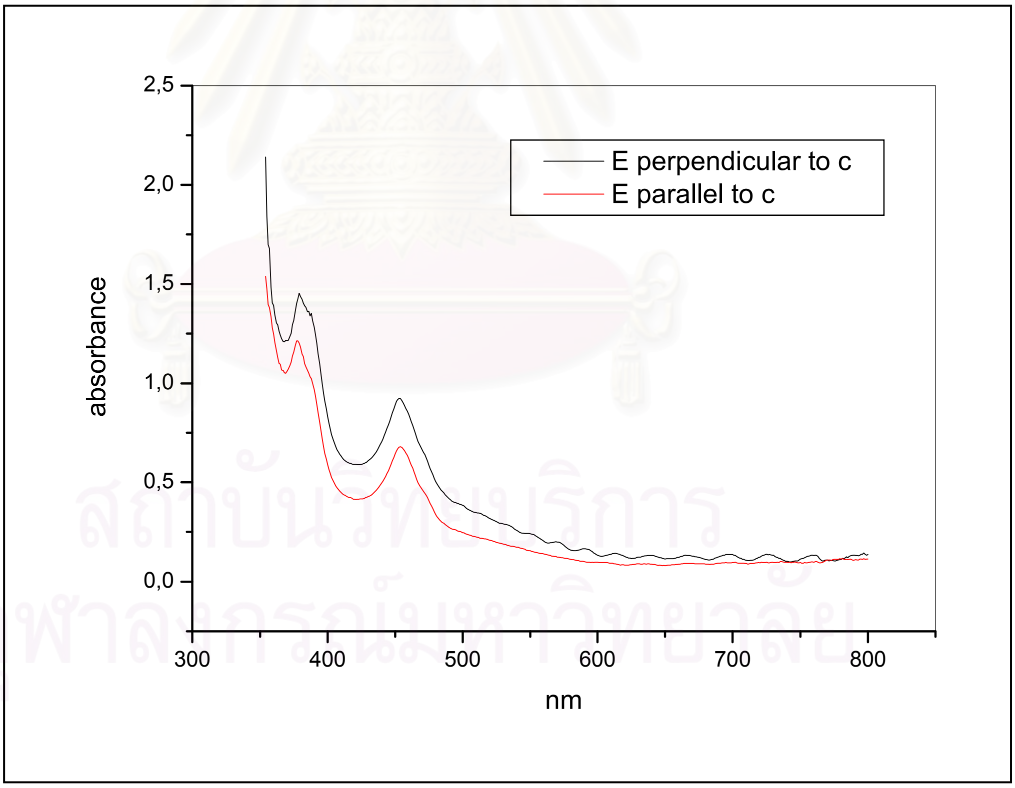


Figure 1.1 Spectra of an un-treated yellow sapphire from Thailand (Khao Phloi Wean, Chanthaburi) with E perpendicular to c-axis (o-ray, black) and E parallel to c-axis (e-ray, red). The colour is due mainly to Fe^{3+} forbidden transition.

The second group of stable yellow sapphires are coloured by processes known as defect centres or colour centres. This group contains rather low iron content and generally originates from metamorphic-type occurrences such as from Sri Lanka. The typical absorption spectrum of the low Fe sapphire shows continuous increase absorption toward the UV part of the spectrum with a small shoulder at 460 nm (Figure 1.2). Hence, yellow coloration of these two groups of sapphires can be differentiated by their typical UV-Vis absorption spectra.

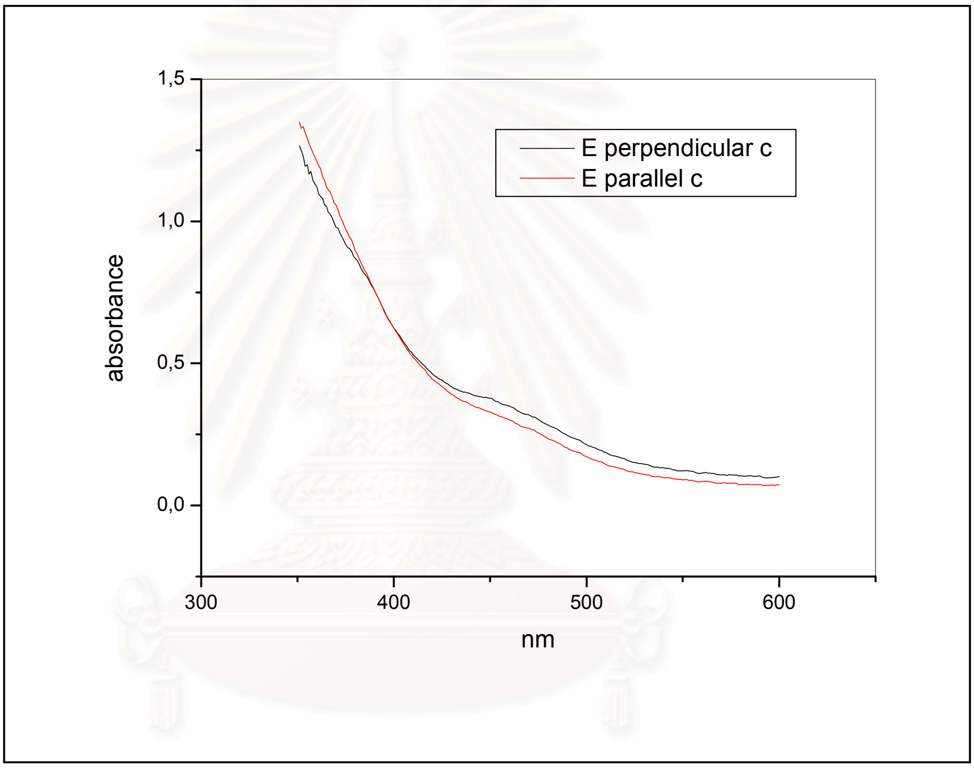


Figure 1.2 UV-Vis-spectra of a heat-treated natural yellow sapphire from Sri Lanka with E perpendicular to c-axis (o-ray, black) and E parallel to c-axis (e-ray, red). The colour is due to stable defect centres.

It is generally known that the ‘simply’ oxidation heating (heating in an oxidised furnace condition without introduction of chemical element such as beryllium from an external source) is capable of turning some very light yellow sapphires, colourless sapphires and colourless sapphires with a yellow patch, from Sri Lanka, Madagascar and Chanthaburi, Thailand into rich, intense and stable yellow sapphires. This heating process is well-known and has been generally accepted in the gem industry for many years. The role of trace elements in causing colour in those heat-treated sapphires is not so clear, however, especially in heat-treated yellow sapphire from the high Fe (or basaltic-type) sapphires such as from Chanthaburi, Thailand whether the yellow coloration is due to spin forbidden transition of Fe^{3+} alone or with the combination of stable colour centres. It is therefore the author’s motive to study the yellow coloration in naturally occurring sapphires from metamorphic occurrences such as from Sri Lanka or Madagascar and from basaltic origins such as from Thailand or Australia or Northern Madagascar by applying scientific approach.

1.2 The purpose of study

The purpose of this study is to understand the causes of colour in heat-treated yellow sapphires from metamorphic and basaltic occurrences before and after treatment.

1.3 The scope of work

The scope of this research is to study the gemmological properties, UV-Vis absorption spectroscopy and chemical compositions of samples, before and after heat treatment in both oxidised and reduced atmospheres. The author intends to compare the colour of the samples, UV-Vis absorption spectroscopy prior to and after heat manipulation and to establish which kind of process (i.e., spin forbidden transition of Fe^{3+} or by stable colour centres or both) occurred in those samples under specific experimental conditions. This study also aims to show the relationship between yellow coloration in heat-treated natural sapphires with the amount of the trace elements found in those sapphires, measured by Laser Ablation Inductively-coupled-Plasma Mass Spectrometry (LA-ICP-MS).

CHAPTER II

METHODOLOGY

2.1 Sample

The yellow sapphire samples used in this study were divided into 3 groups based on their iron contents, occurrences and colour varieties. The first group is the low iron yellow sapphires or the so-called 'metamorphic-type' sapphires. This group comprises five simply heat-treated yellow stones from Sri Lanka which are known to originate from metamorphic source. The second group is the high iron sapphires of greenish yellow to yellowish green variety; this group comprises seven untreated stones of mixed green-yellow variety of the so-called 'basaltic-type' sapphires from the Bang Kracha area of Changwat Chanthaburi in the eastern Thailand. The third group is the high iron sapphires of yellow variety; this group comprises two untreated yellow stones of the 'basaltic-type' sapphires from the Bang Kracha area of Changwat Chanthaburi.

2.2 Method of study

The method of study can be summarized as a flowchart in Figure 2.1. A review of the previous works related to this study is referred to Chapter III. All the rough samples were located the c-axis by using a polariscope then cut and polished perpendicular to the C- axis. All polished samples were weighed, photographed, and the basic physical and optical properties were measured initially to confirm that they were essentially the sapphire samples. The basic properties include refractive indices (RI) using a refractometer, specific gravity (SG) using an electronic balance, colour under daylight lamp and fluorescence under long wave ultraviolet light (LWUV, 365 nm) and short wave ultraviolet light (SWUV, 254 nm). After these properties were recorded, the UV-Vis-NIR spectrum of each sample was measured by a Hiitachi UV-Vis-NIR Spectrophotometer (Model U-4001). As the basic of molecular structure and chromorphoric element contained in the structure, spectroscopic methods are applied to investigate yellow sapphires and cause of their colours. The absorption spectra over UV-Vis-NIR range were observed before and after heating. The semi-quantitative analysis of major and trace element concentrations (Al_2O_3, total Fe_2O_3, TiO_2, Cr_2O_3, V_2O_3 and Ga_2O_3) were carried out using an Oxford Energy Dispersive X-Ray Fluorescence Spectrometer, model ED 2000 at the Gem and Jewelry Institute of Thailand (Public Organization) or GIT. Trace element contents were reported as weight % oxides (e.g. Fe_2O_3, TiO_2, Cr_2O_3, V_2O_3 and Ga_2O_3). Each sample was analysed at the centre of both polished surfaces.

The sapphire samples from each group were then placed into an alumina crucible for heating under each pre-determined condition. The first group, the low iron (metamorphic-type) yellow sapphires, was heat-treated under pure N_2 atmosphere (reducing condition) at $1650^{O}C$ for 5 hours soaking time whereas the second group, the high iron (basaltic-type) sapphires of greenish yellow to yellowish green variety, was heated under pure O_2 atmosphere (oxidizing condition) at $1650^{O}C$ for 24 hours soaking time in a Linn electrical furnace, model HT 1800 Plus VAC Bottom Loader at the Department of Geology, Faculty of Science, Chulalongkorn University. The third group, the high iron (basaltic-type) yellow sapphires, was reportedly heat-treated at high temperature under an oxidizing condition in an electric furnace at the Department of Mineral Resources. After the heating experiments the samples were photographed, subjected to a fading test and the UV-Vis-NIR spectrum of each sample was recorded again at the same position and condition. The samples were then analysed for trace element concentrations (i.e., Be, Mg, Ti, Cr, V, Fe and Ga) using a Laser Ablation Inductively-coupled-Plasma Mass Spectrometry (LA-ICP-MS) at the Macquarie University, Sydney, Australia. A five-points-profile analysis was performed across the polished surface of each sample by this technique.

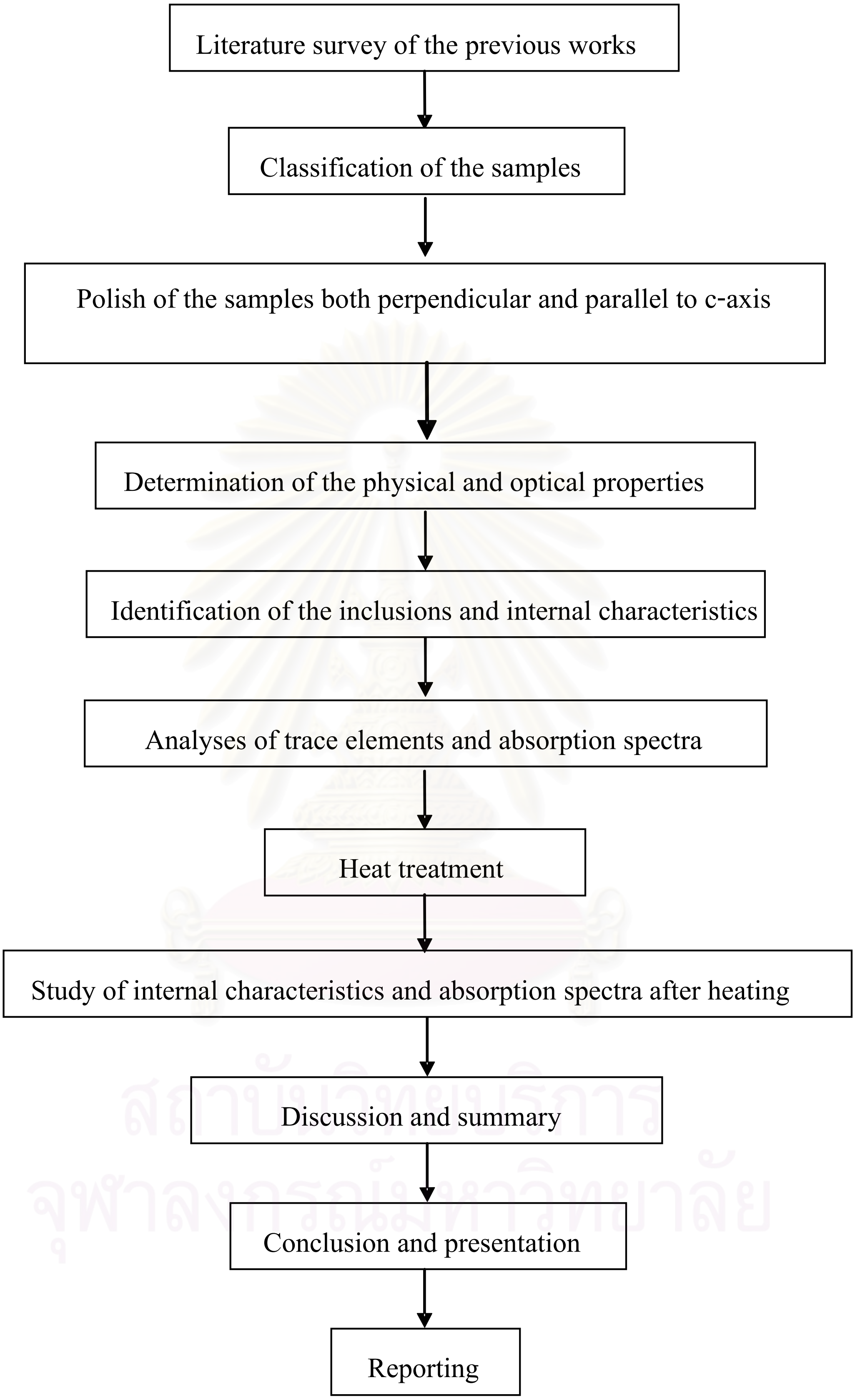


Figure 2.1 Flowchart showing method of study

2.3 Additional details of the equipment being used in this study

2.3.1 Energy Dispersive X-ray Fluorescence spectrometer

The Oxford energy dispersive X-ray fluorescence (EDXRF) spectrometer, model ED 2000 based at the GIT was mainly used for this study. The EDXRF analysis is a nondestructive analytical method; therefore, it has been conventionally used to investigate chemical compositions of gemstones in most gemological laboratories all over the world. The technique is an application on energy emission of electrons in atoms. These electrons are excited by X-ray and then they move to the higher energy level in their own atoms or may be ejected away from their atoms. Consequently, electrons in the higher energy level will replace the lost electron; this process must emit energy in particular range. Each element has different atomic weight that leads to dissimilar energy level. Therefore, those different energies can be utilized for determination of chemical constituent of material.

The X-ray source used in the machine was silver (Ag) X-ray tube, while standardless calibration was applied for all analysis. EDXRF analyses with standardless calibration were most likely yielded semi-quantitative result. Moreover, all trace elements and major Al contents measured from this technique are automatically recalculated to make up total values as 100%; therefore concentrations of trace elements analysed from this technique are normalized values and can be used as a rough estimated values only.

Figure 2.2 Oxford energy dispersive X-ray fluorescence spectrometer, model ED 2000, based at the GIT

2.3.2 High temperature furnace

The furnace used in this experiment is the Linn electrical furnace model HT 1800 Plus VAC Bottom Loader based at the Department of Geology, Faculty of Science, Chulalongkorn University. The furnace consists of a heating chamber attached with bottom-side sample loader. U-shaped rods of molybdenum disilicide ($MoSi_2$) are used as heating element. A pair of heating rods is hung on the top of the chamber. Heating steps and soaking temperatures are automatically controlled using preset programs. The atmospheric condition in the chamber can be controlled by feeding gas such as pure O_2, air, pure N_2 throughout the heating and cooling processes.

Figure 2.3 Linn electrical furnace model HT 1800 Plus VAC Bottom Loader based at the Department of Geology, Faculty of Science, Chulalongkorn University.

Successive segments (e.g. heat-up, soaking and cool-down) were set in every heating process. Heat-up segment was started from room temperature to maximum temperature. The rate of the temperature increment was controlled at about 4°C/minute.

2.3.3 UV-VIS-NIR Spectrophotometer

The absorption spectra in UV-Vis-NIR region of all studied samples were measured using the Hitachi UV-Vis-NIR spectrometer, model U-4001 (Figure 2.4) based at the GIT. The UV-Vis-NIR Spectrophotometer contains a light source which is monochromatic light generating wavelengths over the range of ultraviolet (UV), visible light (Vis) and near infrared (NIR). Absorption spectra are detected with the photocell and then signal is transferred to display on the monitor. This instrument has double beams. A beam of light is switched between a reference path and a sample path, which are re-combined at the detector, which thus compares the two beams. The signal from the reference path is subtracted from that of the sample path to give a spectrum of the sample. UV-Vis-NIR Spectroscopy gives the information about the absorption spectra in this range, which in turn may related to electron transition of the trace elements or other structural defects in yellow sapphires.

The oriented sample was fixed in the middle of the black plate with 2.5 mm diameter slit and placed into the cell holder. Each sample was measured perpendicular to c-axis for ordinary ray (o-ray) by using polarizing filter. The absorption spectra of the yellow sapphire samples were examined between 250 to 1500 nanometer (nm) with spectral resolution 2 nm.

Figure 2.4 Hiitachi UV-Vis-NIR Spectrophotometer (Model U-4001) based at the GIT

2.3.4 Laser Ablation Inductively-Coupled-Plasma Mass Spectrometry

The LA-ICP-MS unit at the Macquarie University in Sydney, Australia was used for the detailed analysis of trace elements in this study (Figure 2.5). The detailed descriptions of LA-ICP-MS instrumentation, analytical and calibration procedures are similar to those given by Norman et al. (1996). The UV laser ablation microprobe (a New Wave Research 266 nm Nd:YAG) is coupled to an Agilent 7500 ICP-MS. All analyses were done with a pulse rate of 5 Hz and beam energy of approximately 0.5 mJ per pulse, producing a spatial resolution of 30-50 μm in diameter on the samples. Quantitative results of isotopes for nine trace elements (Be9, Na23, Mg24, Ti47, V51, Cr53, Mn55, Fe57 and Ga71) were obtained through calibration of relative element sensitivities using the NIST-610 multielement glass standard and pure Al_2O_3 internal standards. The BCR2G basaltic glass standard was also used as an external standard. The contents are reported as μg/g or ppm by weight. The detection limits vary from analysis to analysis and are typically less than 1 ppm for Be, V and Ga; less than 4 ppm for Mg, Ti and Mn; less than 13 ppm for Cr; less than 40 ppm for Na and less than 80 ppm for Fe.

Figure 2.5 Laser Ablation Inductively-Coupled-Plasma Mass Spectrometry (LA-ICP-MS) at the Macquarie University in Sydney, Australia

CHAPTER III

REVIEW OF PREVIOUS WORKS

Colour is an important factor in beauty and is one of the main attributes of gemstone characteristics. Colour can greatly influence our enjoyment and our understanding of gems. Experience in the observation of colour is crucial in gem identification. Each gemstone has its particular molecular structure and may contain different chromophoric elements which can absorb light differently. So absorption or transmission spectra of a gemstone can be used to understand some of its molecular structure and the colour causing mechanism in that variety of gemstone.

3.1 Yellow Sapphire

Corundum is an oxide, meaning a naturally occurring mineral compound in which oxygen in combined with one or more metals. As with hematite, to which it related, the ratio metal to oxygen in yellow sapphire is X_2O_3. The yellow sapphire is an important variety of corundum; chemically corundum consists of crystallized alumina, e.g. aluminum oxide (Al_2O_3). All the other elements present are impurities. When the corundum is pure, colourless sapphire results; the colour of yellow sapphire is due to the traces of iron (Fe) and the colour centre.

3.2 Causes of colour in yellow sapphire

Nassau (1978 and 1994) formulated two sets of theories to explain the cause of coloration in yellow sapphires and these can be understood as follows:

Crystal field theory formalism is one method by which sapphires attain their colour and can be separated into two types. The first type is caused by transition metals and the other is defect centre or colour centre. In the case of transition metal compounds the colour is produced from unpaired electrons. Normally, there are no unpaired electrons when all electron shells are completely full or empty in transition elements such as Fe^{2+}, Cr^{6+} or Cu^{+} which create a colourless corundum. However corundum regularly contains transition elements that do not have complete outer shells such as Fe^{3+} ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$,

$3d^3$). In this example the three unpaired electrons in the 3d shell create an electrical field about the central transition metal ion. This is known as the “crystal field”, which can interact with visible light so as to produce absorption and colour in yellow sapphire.

The other crystal field theory formalism known as “colour centre” is caused by defects in the crystal structure that absorb light. Unpaired electrons can be located on non-transitional elements which create a crystal defect by being deficient in an ion. This deficiency creates a hole colour centre where the missing electron should be and this hole partially absorbs the light to produce colour in sapphires. In the case of yellow sapphires, the colour centre is represented by the presence of Mg^{2+} impurity substituting for the Al^{3+} ions.

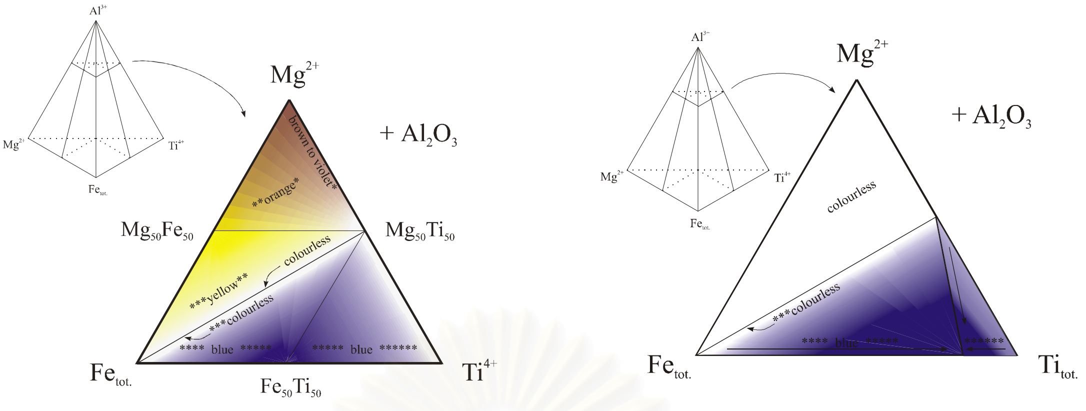
For Nassau’s second theory which he called “the molecular orbital formalism” or “charge transfer” he found that visible light instigated electron transfers between the ions. In some materials, electrons are able to move from one type of ion to another and back again by absorbing light of a particular energy level. This is a transfer of an electrical charge in the form of a negatively-charged electron (e-) from one ion to another. Charge transfer can also occur between ions of the same metal. Iron is a good example of this, as it is a common element found in the yellow sapphire. For example the transition of Fe^{3+}- Fe^{2+} charge transfer.

Häger (1996, 2001) further expanded on Nassau’s theories to explain the causes of colour in natural yellow sapphires. He envisaged that the causes of colour of natural yellow sapphires can be divided into two groups. The first group owes its colour to a spin forbidden transition of Fe^{3+} (Lehmann and Harder, 1970; Krebs and Maisch, 1971; Ferguson and Fielding, 1971, 1972; Nassau and Valente, 1987). However, he emphasized that the probability of this transition is very low, and therefore, approximately 1 weight % Fe^{3+} is needed to create an intense yellow with this mechanism. Sapphires of this group generally contain rather high iron content and originate mainly from the basaltic-type occurrences such as from Thailand, Australia and North Madagascar, or from the metamorphic occurrence in Umba, Tanzania (Lomthong, 2004). Typical spectra resulting from this kind of mechanism are shown in Figure 1.1.

The second group is coloured by the so-called colour centres whose UV-Vis-spectra are characterized by an increase of absorption in the UV-part of the spectrum (Figure 1.2). Sapphires of this group contain rather high iron content and originate mainly from metamorphic-type occurrence such as from Sri Lanka. The spectrum E (the electric vector of light) parallel to *c*-axis (e-ray) is very similar to the spectrum E perpendicular to *c*-axis (o-ray), and such sapphires therefore show weak pleochroism. On the basis of the stability of the colour or defect centres, it is possible to differentiate this group into two sub-groups. The first sub-group contains natural sapphires whose colour is due to irradiation (Lehmann and Harder, 1970; Nikolskaya *et al*., 1978; Nassau and Valente, 1987). The colour centres of this group are not stable to light and heat. The defect centres of the second sub-group are stable to UV light and to heat up to about 500^{o} or 600^{o}C. It is not possible to differentiate between these two sub-groups on the basis of UV-Vis-spectroscopy, and the best method of distinguishing them is to use the fading test (Nassau and Valente, 1987). The defect centres of the second sub-group are stable with respect to light and heat in an oxidizing atmosphere, therefore it can also be called ‘stable colour centres’ or ‘trapped hole colour centres’.

The role of trace elements in causing stable yellow colour centres and blue colour in sapphire are further reviewed briefly here. Based on several quantitative experiments it has been shown that in addition to the classical trace elements like Fe and Ti which influence the colour of blue sapphire, Mg is also important. The role or interaction of Mg, Ti and Fe in creating stable yellow colour centres or blue colours is well understood and can be depicted in Figure 3.1 (Häger, 1992, 1993, 1996, 2001; Emmett and Douthit, 1993). The divalent Mg and tetravalent Ti form colourless $MgTiO_3$ (geikielite) clusters, and after formation of these clusters, any excess Mg could combine with Fe in an oxidizing atmosphere to produce colour-active defect centres or stable (or trapped hole) yellow colour centres. However, in corundum with rather low Fe content such as Mg-doped synthetic stones, stable (or trapped hole) brown or brownish violet colour centres, rather than yellow, are produced (Wang *et al*., 1983; Häger, 1996, 2001). As such the Mg seems to act as a stabilizer of the defect centre. On the other hand, if there is an excess of Ti after the calculation of $MgTiO_3$, the excess Ti in combination with

Fe could form colour-active $FeTiO_3$ clusters under both reducing and oxidizing conditions. These clusters create Fe^{2+}/Ti^{4+} inter-valence charge transfer absorption bands near 578 and 735 nm which are responsible for the blue coloration of sapphire (Townsend, 1968; Ferguson and Fielding, 1972; Häger, 1992, 1996, 2001; Emmett and Douthit, 1993). If Ti-content exceeds the sum of Mg + Fe, the excess of Ti will precipitate during heat treatment at 1850°C in an oxidizing atmosphere. As shown in Figure 3.1, the most important line of the large triangular in Figure 3.1A is the connecting line between the Fe corner and the Mg50-Ti50 point where the Mg to Ti ratio is always 1:1; there, the samples neither show any kind of colour centres nor an Fe^{2+}/Ti^{4+} charge transfer band. Above this line are stable yellow colour centres such as found in natural sapphires from Sri Lanka. In the Mg corner are stable defect centres. Below the line, where Ti:Mg ratio is more than 1:1, are the Fe^{2+}/Ti^{4+} charge transfer bands. If the titanium content exceeds the sum of Mg + Fe a titanium-containing phase can precipitate. If the sapphires are treated in reducing conditions, the colour centres are destroyed completely and any titanium precipitates are dissolved (Figure 3.1B). The amount of additionally dissolved precipitates depends on the kinds of the reducing gases used.



(A) (B)

*	colour centre due to Mg	**	colour centre 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 3.1 Model representing the interaction of trace elements in the system Al-Mg-Fe-Ti (tetrahedron). Out of this tetrahedron a slice is cut. This slice represents sapphires with total trace element content in the ppm region. The resulting diagram is a triangle. Sapphires of this composition were heat treated at 1850°C in an oxidizing atmosphere(A) and at 1750°C in a reducing atmosphere (B), Häger (1996, 2001).

Pisutha-Arnond *et al*. (2004) presented studies on UV-Vis-spectroscopy and trace-element chemistry of irradiated and Be-treated synthetic and natural colourless sapphires, yellow and orangey yellow Be-treated natural sapphires and some Be-treated natural blue sapphires, and established that the majority of Be-treated sapphires showed indications of Be diffusion into the corundum lattice from an external source. The chemical analyses obtained by LA-ICP-MS consistently showed that there were excess contents of (Be+Mg) over Ti in all of the yellow sapphires which were coloured by stable defect centres. The oxidation and reduction heating experiments also showed that oxidizing conditions were an important factor in the formation of stable colour centres. They therefore believed that after combining Mg and Be with any Ti present to form colourless $MgTiO_3$ and/or $BeTiO_3$ clusters, any excess of (Be+Mg), in combination with iron and the heat treatment in an oxidizing atmosphere can produce stable yellow colour centres in yellow Be-treated natural sapphires. They also assumed the divalent Be could have the same effect in the corundum structure as Mg. However, Mg and many other trace elements are usually present in natural corundum and the direct relationship of Be and Fe in any natural sapphire treated with Be can not be evaluated with certainty. Hence in order to prove such an assumption Pisutha-Arnond *et al*. (2006) carried out additional Be-diffusion experiments with pure synthetic and Fe-doped synthetic sapphires without the influence of Mg and other trace elements. In addition, they also carried out more LA-ICP-MS analyses on natural blue sapphires both untreated and treated with Be to test the assumption of similarity of Be and Mg. The results have confirmed that with the diffusion of Be, the stable brown colour centres can be activated in synthetic sapphires without iron while the stable yellow colour centres can create with the presence of iron in Al_2O_3 structure. Hence the divalent Be acts essentially in the same way as that of Mg, i.e. as a stabilizer of colour centres.

CHAPTER IV

LOW IRON (METAMORPHIC-TYPE) YELLOW SAPPHIRES

4.1 Basic properties

The first group, the low iron yellow sapphires or the so-called 'metamorphic-type' sapphires selected for this study, is five simply heat-treated yellow sapphires from Sri Lanka that were obtained from a reliable source. The basic properties of those sapphires are summarized in Table 4.1 and their chemical compositions analysed by EDXRF are listed in Table 4.2. As shown in Table 4.2 most samples contain rather low Fe_2O_3 contents (0.1 to 1.2 wt%). It should be noted that at present time it is rather difficult to obtain a simply heated yellow sapphire from the market place because most yellow sapphires available in the market are Be-treated stones.

Table 4.1 Basic properties of five simply heat-treated yellow sapphires from Sri Lanka, RI = refractive indices, SG = specific gravity, SW UV = short wave ultraviolet, LW UV = long wave ultraviolet.

Sample no.	Weight (ct)	RI		Colour	SG	Luminescence		Picture
		Min	Max			SW UV	LW UV	
PC1 (Sri Lanka)	0.486	1.761	1.769	Yellow	3.950	inert	inert	
PC2 (Sri Lanka)	0.723	1.761	1.769	Yellow	3.940	Moderate orange	Weak orange	
PC3 (Sri Lanka)	0.773	1.760	1.769	Yellow	3.964	inert	inert	
PC4 (Sri Lanka)	0.491	1.760	1.768	Yellow	4.025	Weak orange	Very weak orange	
PC5 (Sri Lanka)	0.744	1.760	1.769	Yellow	3.951	inert	inert	

Table 4.2 Trace element contents (wt %) of five simply heat-treated yellow sapphires from Sri Lanka, obtained from EDXRF.

Sample no.	Al_2O_3	Cr_2O_3	Fe_2O_3	TiO_2	V_2O_3	Ga_2O_3
PC1	99.7664	0.0076	0.1052	0.1132	0.0000	0.0075
PC2	99.8296	0.0000	0.0968	0.0611	0.0066	0.0058
PC3	99.7930	0.0128	0.1360	0.0431	0.0000	0.0152
PC4	99.7511	0.0000	0.0868	0.1398	0.0166	0.0056
PC5	99.7962	0.0026	0.1661	0.0135	0.0016	0.0200

4.2 Heating experiment

All five samples of heat-treated yellow sapphires from Sri Lanka were re-heated again at 1,650 °C in reducing condition (N_2 atmosphere) for 5 hours. The colour of all samples did change from strong yellow before experiment into colourless after heating in the reducing condition (Figures 4.1-4.5).

Figure 4.1 A heat-treated sapphire (PC1) shows strong yellow before experiment (left) and becomes colourless (right) after re-heating at 1,650 °C in N_2 atmosphere for 5 hours

Figure 4.2 A heat-treated sapphire (PC2) shows strong yellow before experiment (left) and becomes colourless (right) after reheating at 1,650°C in N_2 atmosphere for 5 hours

Figure 4.3 A heat-treated sapphire (PC3) shows strong yellow before experiment (left) and becomes colourless (right) after reheating at 1,650 ºC in N_2 atmosphere for 5 hours

Figure 4.4 A heat-treated sapphire (PC4) shows strong yellow before experiment (left) and becomes colourless (right) after reheating at 1,650 ºC in N_2 atmosphere for 5 hours

Figure 4.5 A heat-treated sapphire (PC5) shows medium yellow before experiment (left) and becomes colourless (right) after reheating at 1,650 ºC in N_2 atmosphere for 5 hours

4.3 UV-Vis absorption spectra

The UV-Vis absorption spectra of those five sapphires were recorded both before and again after the heating experiment at exactly the same position and condition. As expected (Figures 4.6 to 4.10), the UV-Vis spectra of those five samples before experiment show a continuous increase in absorption towards shorter wavelengths with a shoulder at around 460 nm. This spectral pattern is generally known to be caused by stable defect centres typical of Sri Lankan yellow sapphire. As also anticipated, the spectra of all five (colourless) samples measured after reducing experiment show no absorption. As such the residue spectra (obtained by subtraction of spectra measured before the experiment from that measured after the experiment at the same position) show the absorption of colour centre pattern.

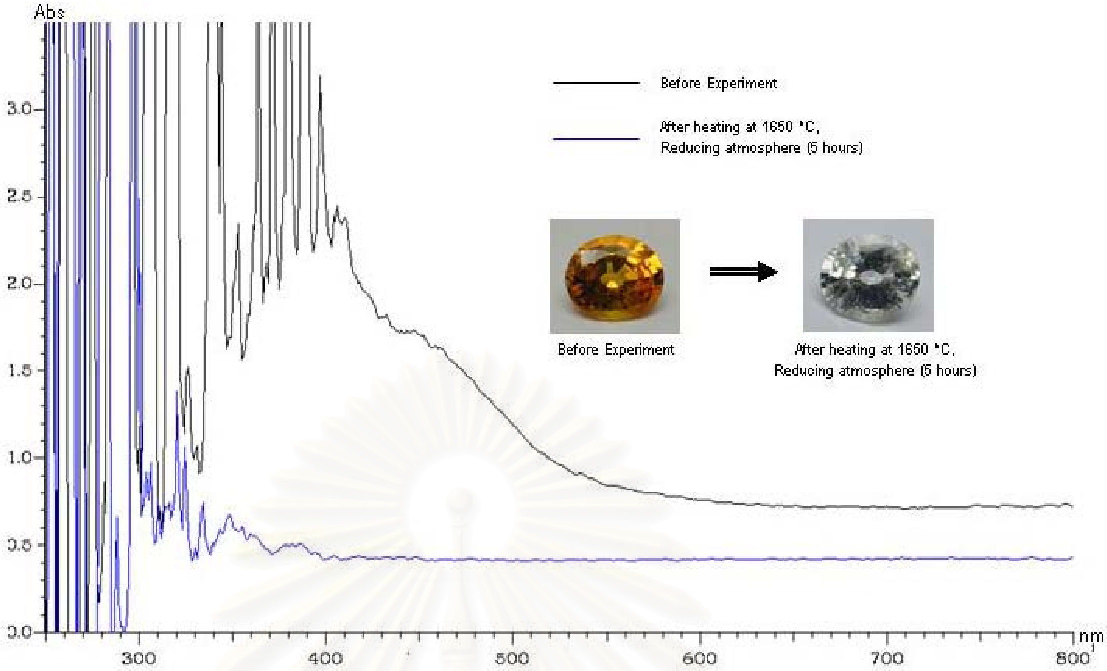


Figure 4.6 UV-Vis spectra (o-rays) of the sample PC1 measured before and after heating experiment at 1,650ºC in N_2 atmosphere for 5 hours.

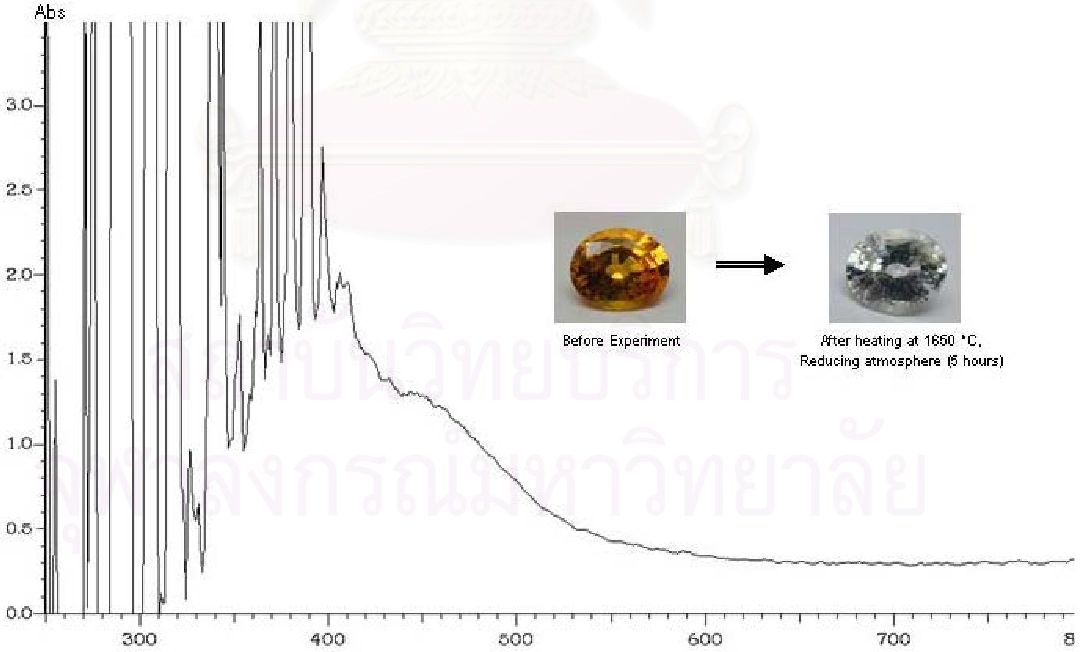


Figure 4.7 Residue spectrum of the sample PC1 obtained by subtracting the spectrum recorded before from the one after the experiment shown in Figure 4.6.

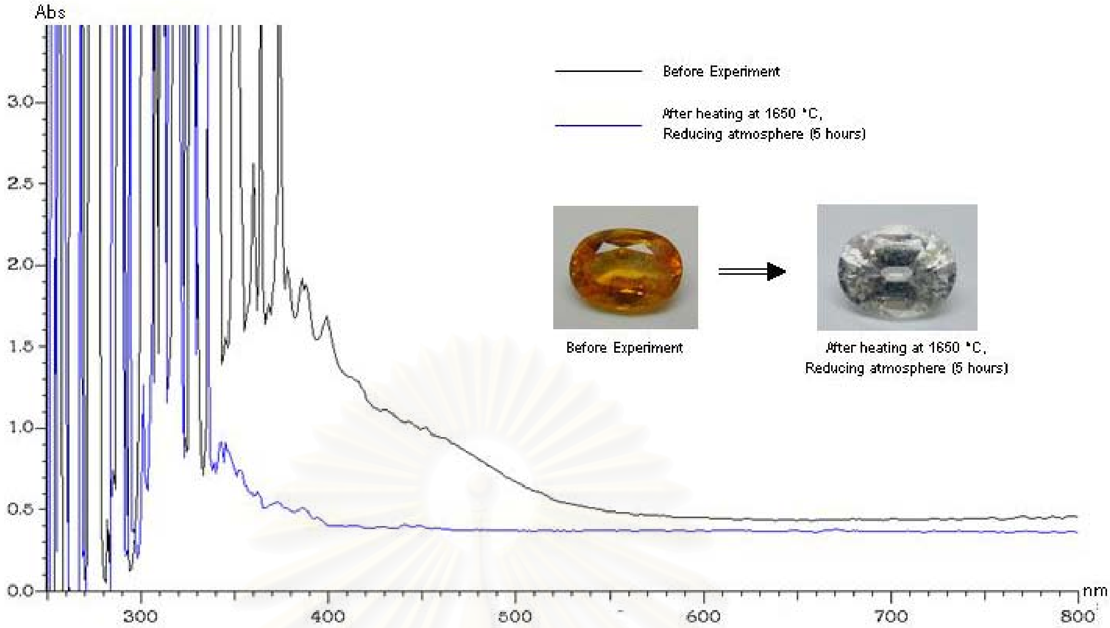


Figure 4.8 UV-Vis spectra (o-rays) of the sample PC2 measured before and after heating experiment at 1,650°C in N_2 atmosphere for 5 hours.

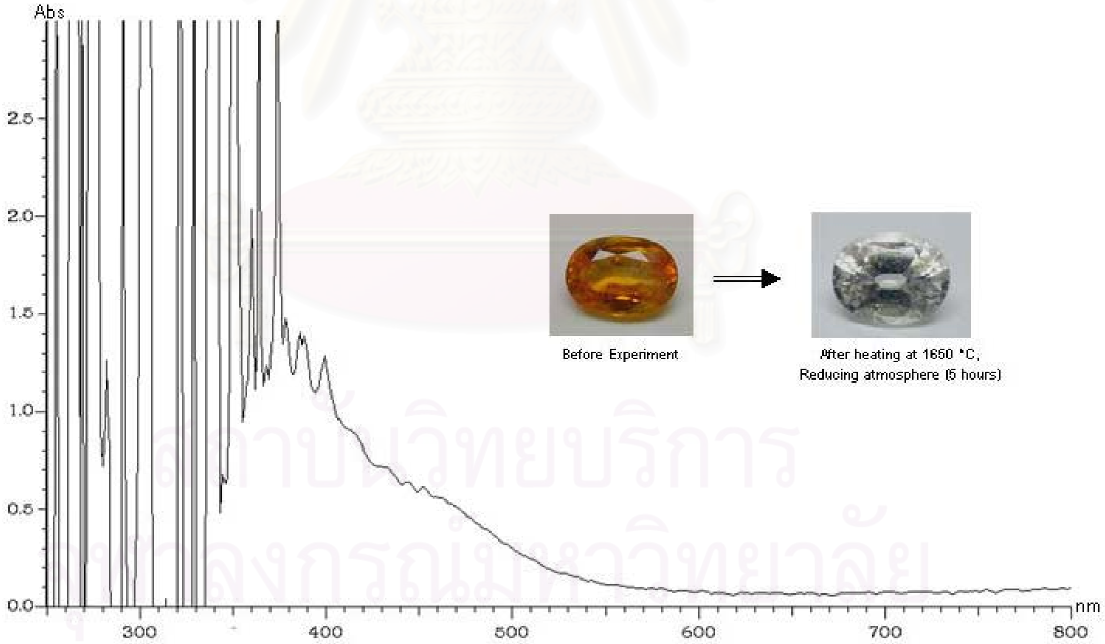


Figure 4.9 Residue spectrum of the sample PC2 obtained by subtracting the spectrum recorded before from the one after the experiment shown in Figure 4.8.

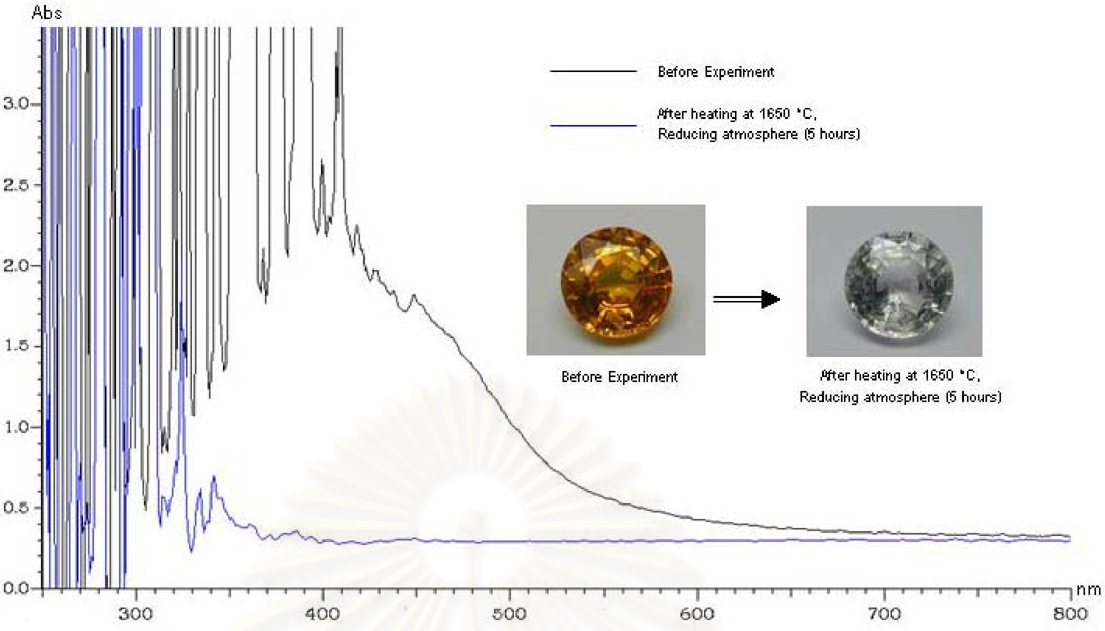


Figure 4.10 UV-Vis spectra (o-rays) of the sample PC3 measured before and after heating experiment at 1,650ºC in N_2 atmosphere for 5 hours.

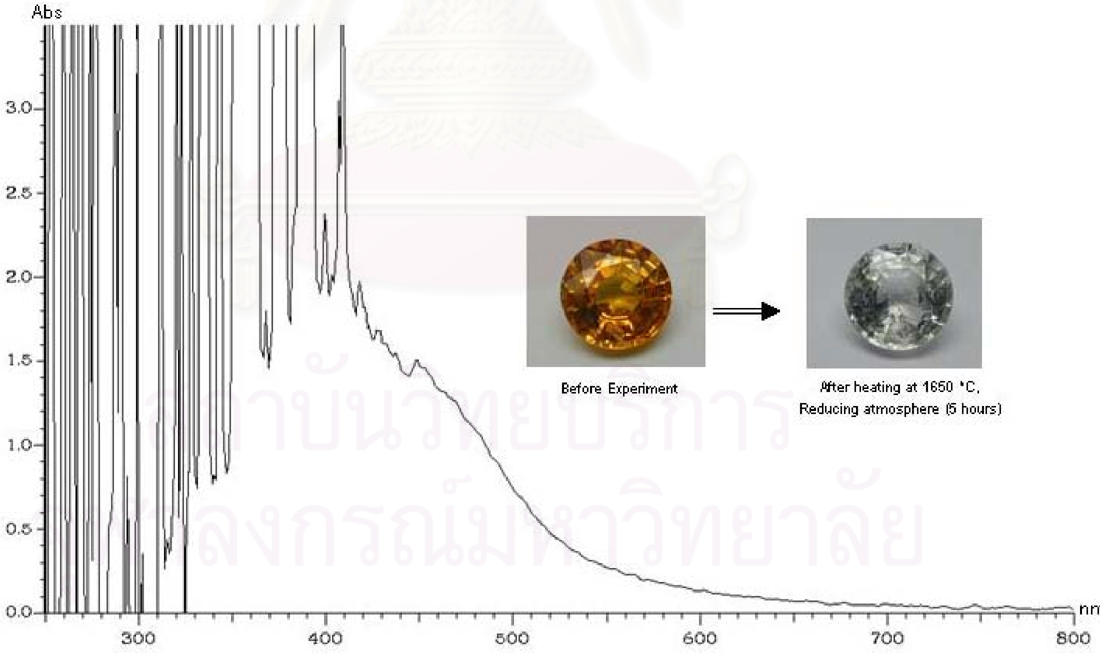


Figure 4.11 Residue spectrum of the sample PC3 obtained by subtracting the spectrum recorded before from the one after the experiment shown in Figure 4.10.

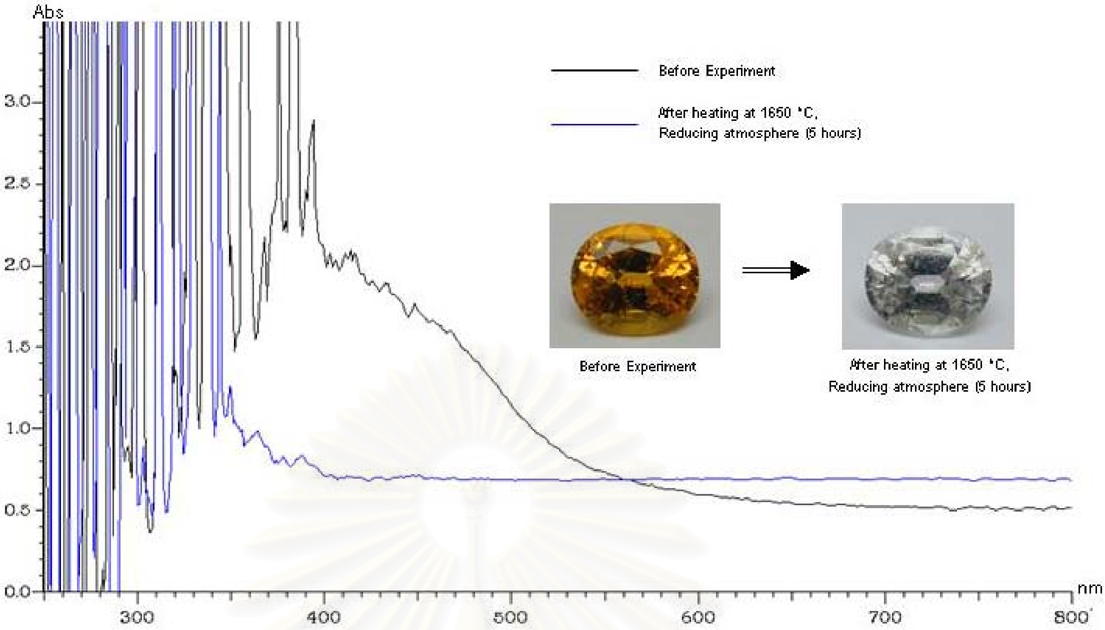


Figure 4.12 UV-Vis spectra (o-rays) of the sample PC4 measured before and after heating experiment at 1,650ºC in N_2 atmosphere for 5 hours.

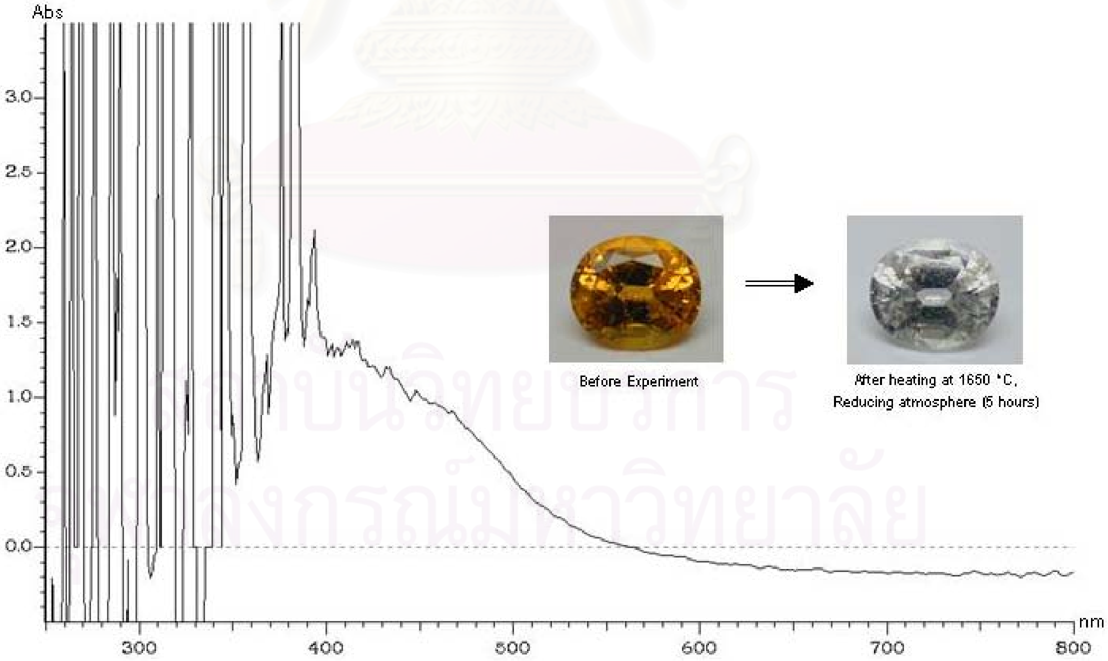


Figure 4.13 Residue spectrum of the sample PC4 obtained by subtracting the spectrum recorded before from the one after the experiment shown in Figure 4.12.

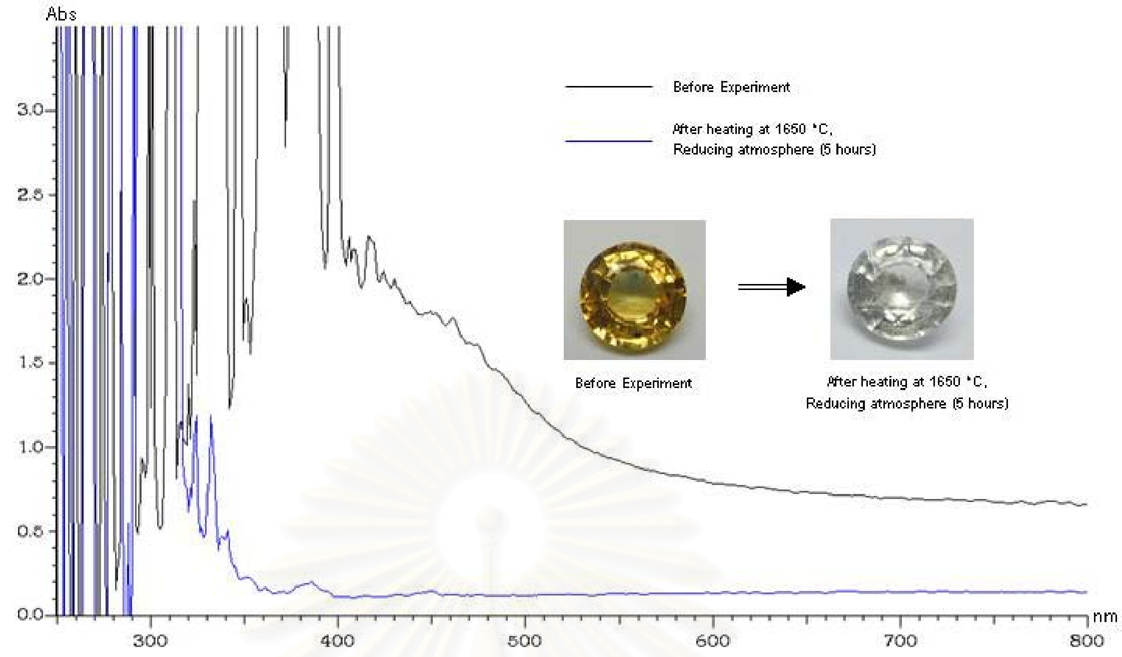


Figure 4.14 UV-Vis spectra (o-rays) of the sample PC5 measured before and after heating experiment at 1,650ºC in N_2 atmosphere for 5 hours.

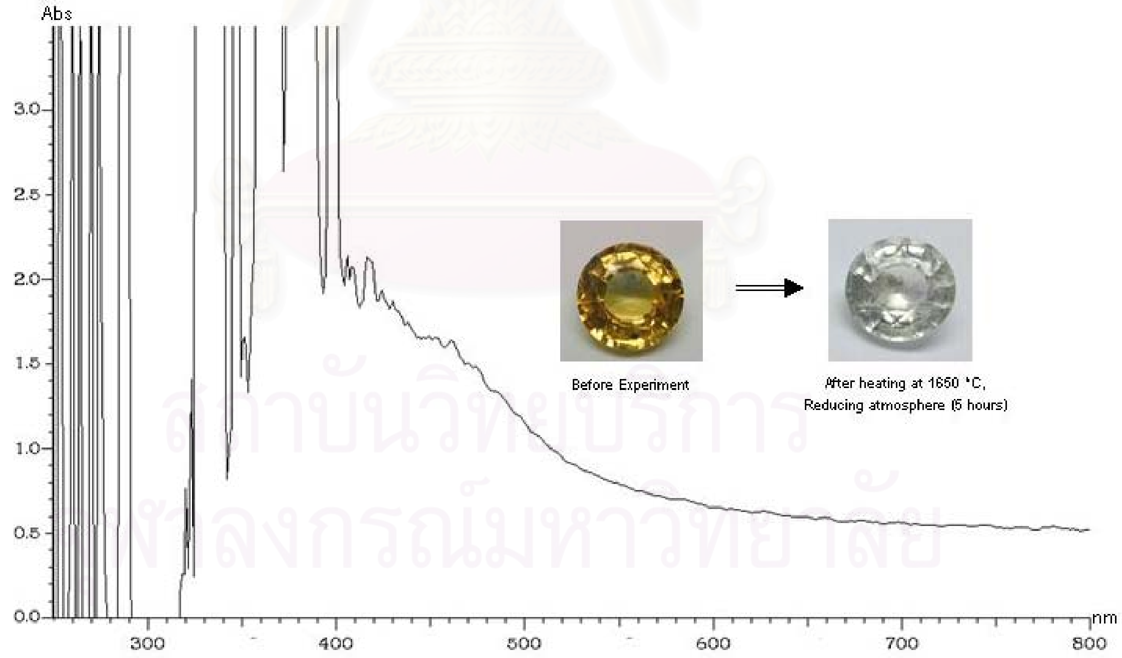


Figure 4.15 Residue spectrum of the sample PC5 obtained by subtracting the spectrum recorded before from the one after the experiment shown in Figure 4.14.

4.4 LA-ICP-MS Analyses

All the sapphires were measured for the important trace element concentration at five points across the table facets by LA-ICP-MS technique to monitor the role of those elements in causing colour in those sapphires (Figures 4.16-4.25 and Tables 4.3-4.7). In order to compare the trace element contents from LA-ICP-MS analyses and understand their interaction, all cations are calculated as atom mole ppm (or abbreviated as amp) and normalized to 40 atoms of cations, which corresponds to 60 atoms of oxygen in Al_2O_3 structure (Table 4.3-4.7). As shown in those figures and tables, all the samples show rather low Fe contents (∼85 – 350 atom mole ppm) and large excess of Mg over Ti (> ∼20 atom mole ppm) in almost all spots analysed except only a few points are almost equal.

Figure 4.16 Close-up view of the sample PC1 showing the locations of the five point analyses from left to right by LA-ICP-MS.

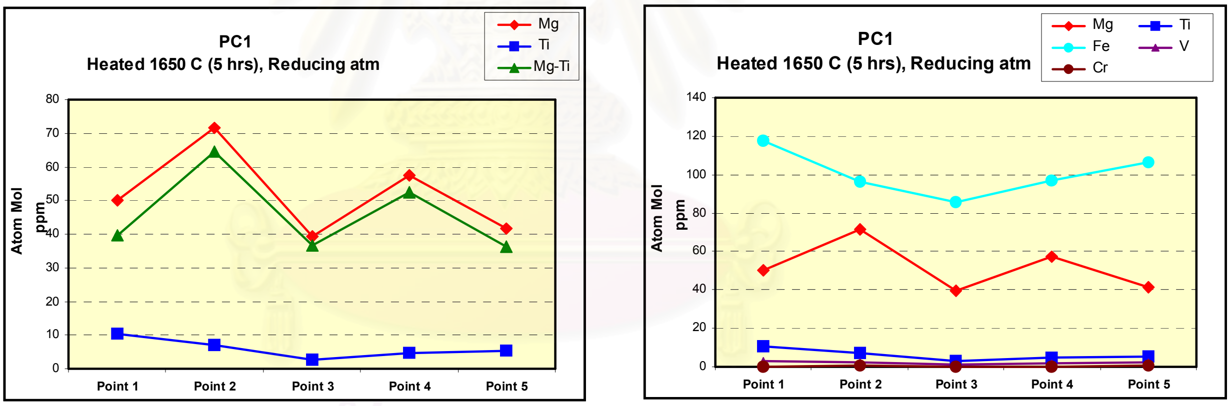


Figure 4.17 Plots of trace element contents at the points where the analyses were taken on the sample PC1 shown in Figure 4.16. The analyses show rather low Fe contents and large excess contents of Mg over Ti in all the points analysed.

Table 4.3 Trace element contents of the yellow sapphires from Sri Lanka: PC1, obtained by LA-ICP-MS

PC1	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.22	<0.17	<0.17	<0.11	0.09
Na	3.45	10.67	1.96	<0.85	0.77
Mg	59.73	85.44	47.04	68.41	49.62
Al	529250.44	529250.44	529250.38	529250.44	529250.44
Ti	24.58	16.87	6.40	11.41	12.65
V	7.58	5.26	3.69	4.71	5.91
Cr	0.00	0.90	0.74	0.52	0.91
Mn	0.00	0.00	0.00	0.10	0.00
Fe	322.89	263.72	234.05	264.83	291.81
Ga	37.66	40.52	35.73	37.37	37.19
Total %	52.97	52.97	52.96	52.96	52.96
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.21
Na	3.06	9.46	1.74	0.00	0.68
Mg	50.09	71.65	39.45	57.37	41.61
Al	399804.52	399801.18	399858.45	399828.07	399832.02
Ti	10.46	7.18	2.72	4.86	5.38
V	3.03	2.10	1.48	1.88	2.36
Cr	0.00	0.35	0.29	0.20	0.36
Mn	0.00	0.00	0.00	0.04	0.00
Fe	117.83	96.24	85.42	96.65	106.50
Ga	11.01	11.85	10.45	10.92	10.87
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	39.63	64.47	36.73	52.51	36.23
Mg%	28.08	40.93	30.92	36.11	27.11
Ti %	5.86	4.10	2.13	3.06	3.50
Fe%	66.06	54.97	66.95	60.83	69.29

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

Figure 4.18 Close-up view of the sample PC2 showing the locations of the five point analyses from left to right by LA-ICP-MS.

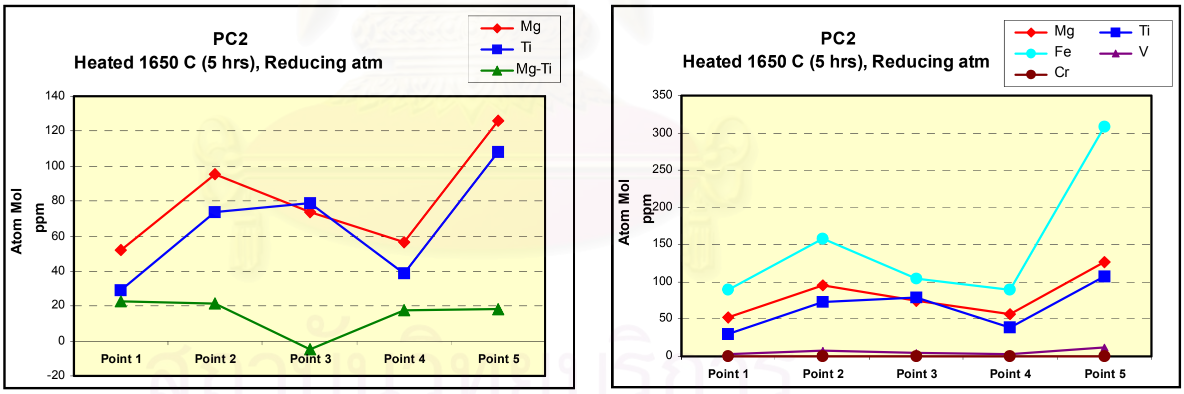


Figure 4.19 Plots of trace element contents at the points where the analyses were taken on the sample PC2 shown in Figure 4.18. The analyses show rather low Fe contents and large excess contents of Mg over Ti in almost all the points analysed except point 3 which is slightly deficient.

Table 4.4 Trace element contents of the yellow sapphires from Sri Lanka: PC2, obtained by LA-ICP-MS

PC 2	Point 1	Point 2	Point 3	Point 4	Point 5
Cations (ppm by weight)					
Be	<0.12	<0.14	3.06	<0.13	0.19
Na	<0.89	1.10	<0.12	<0.97	<1.09
Mg	62.09	113.52	88.26	67.06	150.56
Al	529250.44	529250.44	529250.38	529250.44	529250.44
Ti	68.82	173.06	185.46	91.01	253.81
V	7.93	17.22	9.49	8.29	28.23
Cr	0.00	0.00	0.00	0.48	0.00
Mn	0.00	0.00	0.00	0.00	0.00
Fe	243.81	433.39	284.58	245.44	847.01
Ga	22.40	27.43	24.61	23.35	33.48
Total %	52.97	53.00	52.98	52.97	53.06
Cations (Atom Mole ppm)					
Be	0.00	0.00	6.92	0.00	0.44
Na	0.00	0.97	0.00	0.00	0.00
Mg	52.07	95.16	74.00	56.23	126.14
Al	399819.95	399657.26	399725.37	399805.14	399435.66
Ti	29.28	73.61	78.90	38.72	107.89
V	3.17	6.89	3.80	3.32	11.28
Cr	0.00	0.00	0.00	0.19	0.00
Mn	0.00	0.00	0.00	0.00	0.00
Fe	88.98	158.10	103.83	89.57	308.81
Ga	6.55	8.02	7.19	6.83	9.78
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	22.78	21.55	-4.90	17.51	18.24
Mg%	30.57	29.11	28.82	30.47	23.24
Ti %	17.19	22.52	29.93	20.99	19.86
Fe%	52.24	48.37	39.38	48.54	56.84

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

Figure 4.20 Close-up view of the sample PC3 showing the locations of the five point analyses from left to right by LA-ICP-MS.

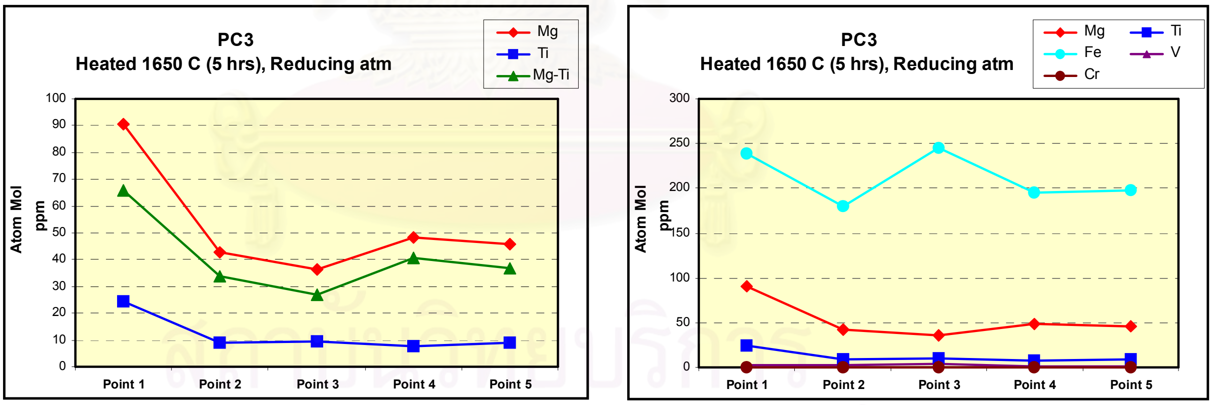


Figure 4.21 Plots of trace element contents at the points where the analyses were taken on the sample PC3 shown in Figure 4.20. The analyses show rather low Fe contents and large excess contents of Mg over Ti in all the points analysed.

Table 4.5 Trace element contents of the yellow sapphires from Sri Lanka: PC3, obtained by LA-ICP-MS

PC3	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.10	<0.13	<0.12	<0.15	<0.10
Na	<0.82	<1.03	<0.94	<1.09	<0.80
Mg	107.88	50.83	43.31	57.47	54.53
Al	529250.44	529250.44	529250.38	529250.44	529250.44
Ti	57.74	21.15	22.54	17.72	21.15
V	7.21	5.37	9.21	4.56	4.35
Cr	0.42	0.00	0.00	0.00	0.47
Mn	0.00	0.00	0.00	0.00	0.00
Fe	653.02	492.58	672.47	534.63	541.57
Ga	22.40	27.43	24.61	23.35	33.48
Total %	53.01	52.98	53.00	52.99	52.99
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00
Mg	90.43	42.62	36.31	48.18	45.72
Al	399637.22	399758.48	399697.89	399740.56	399735.97
Ti	24.56	9.00	9.59	7.54	9.00
V	2.88	2.15	3.68	1.82	1.74
Cr	0.16	0.00	0.00	0.00	0.18
Mn	0.00	0.00	0.00	0.00	0.00
Fe	238.20	179.73	245.34	195.07	197.60
Ga	82.99	72.04	79.02	75.07	72.06
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	65.87	33.62	26.72	40.65	36.72
Mg%	25.60	18.42	12.47	19.21	18.12
Ti %	6.95	3.89	3.29	3.01	3.57
Fe%	67.44	77.69	84.24	77.78	78.31

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

Figure 4.22 Close-up view of the sample PC4 showing the locations of the five point analyses from left to right by LA-ICP-MS.

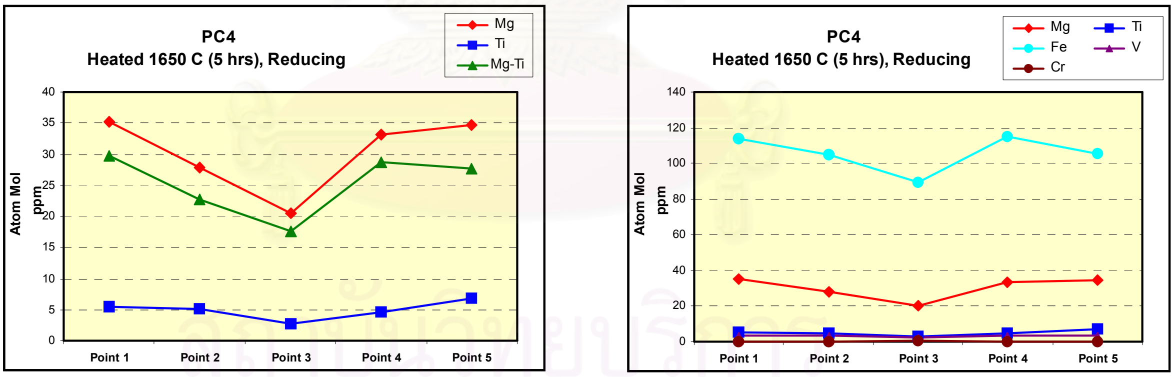


Figure 4.23 Plots of trace element contents at the points where the analyses were taken on the sample PC 4 shown in Figure 4.22. The analyses show rather low Fe contents and large excess contents of Mg over Ti in all the points analysed.

Table 4.6 Trace element contents of the yellow sapphires from Sri Lanka: PC4, obtained by LA-ICP-MS

PC4	Point 1	Point 2	Point 3	Point 4	Point 5
Cations (ppm by weight)					
Be	0.206	<0.12	<0.15	<0.12	0.13
Na	9.47	<0.85	<1.03	<0.84	<0.95
Mg	42.07	33.24	24.37	39.60	41.35
Al	529250.44	529250.44	529250.38	529250.44	529250.44
Ti	12.93	11.89	6.55	10.69	16.24
V	9.38	8.35	6.50	9.45	9.01
Cr	0.00	0.72	1.02	0.57	0.58
Mn	0.00	0.00	0.00	0.00	0.00
Fe	311.96	287.49	244.16	315.38	289.54
Ga	30.18	28.80	26.15	30.66	30.01
Total %	52.97	52.96	52.96	52.97	52.96
Cations (Atom Mole ppm)					
Be	0.47	0.00	0.00	0.00	0.30
Na	0.00	0.00	0.00	0.00	0.00
Mg	35.28	27.88	20.44	33.21	34.68
Al	399832.32	399850.10	399877.01	399834.17	399839.83
Ti	5.50	5.06	2.79	4.55	6.91
V	3.75	3.34	2.60	3.78	3.61
Cr	0.00	0.28	0.40	0.22	0.23
Mn	0.00	0.00	0.00	0.00	0.00
Fe	113.85	104.92	89.12	115.10	105.67
Ga	8.82	8.42	7.65	8.96	8.77
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**29.78**	**22.82**	**17.65**	**28.66**	**27.77**
Mg%	**22.82**	**20.22**	**18.19**	**21.73**	**23.55**
Ti %	**3.55**	**3.67**	**2.48**	**2.98**	**4.68**
Fe%	**73.41**	**76.11**	**79.33**	**75.30**	**71.61**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

Figure 4.24 Close-up view of the sample PC5 showing the locations of the five point analyses from left to right by LA-ICP-MS.

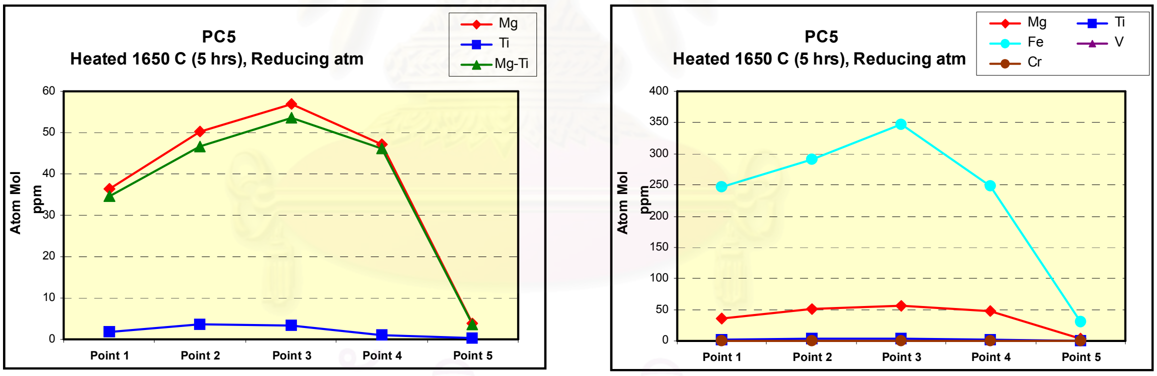


Figure4.25 Plots of trace element contents at the points where the analyses were taken on the sample PC5 shown in Figure 4.24. The analyses show rather low Fe contents and large excess contents of Mg over Ti in almost all the points analysed except point 5 which is only slight excess.

Table 4.7 Trace element contents of the yellow sapphires from Sri Lanka: PC5, obtained by LA-ICP-MS

PC5	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	0.131	<0.14	<0.27	<0.15	0.02
Na	<0.70	<0.93	<1.61	<1.10	<0.08
Mg	43.46	60.01	67.84	56.35	4.65
Al	529250.44	529250.44	529250.38	529250.44	529250.44
Ti	4.51	8.45	7.94	2.47	0.52
V	1.13	1.50	1.66	1.04	0.16
Cr	0.42	0.00	0.00	0.00	0.47
Mn	0.00	0.00	0.00	0.00	0.00
Fe	678.05	796.16	952.39	680.06	81.65
Ga	93.47	98.71	114.79	94.20	10.48
Total %	53.01	53.02	53.04	53.01	52.93
Cations (Atom Mole ppm)					
Be	0.30	0.00	0.00	0.00	0.30
Na	0.00	0.00	0.00	0.00	0.00
Mg	36.43	50.30	56.85	47.24	3.90
Al	399686.06	399626.25	399558.24	399675.68	399962.46
Ti	1.92	3.59	3.38	1.05	0.22
V	0.45	0.60	0.66	0.42	0.06
Cr	0.16	0.00	0.00	0.00	0.18
Mn	0.00	0.00	0.00	0.00	0.00
Fe	247.37	290.41	347.34	248.09	29.81
Ga	27.32	28.84	33.54	27.53	3.06
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**34.51**	**46.71**	**53.48**	**46.19**	**3.68**
Mg%	**12.75**	**14.61**	**13.95**	**15.94**	**11.50**
Ti %	**0.67**	**1.04**	**0.83**	**0.35**	**0.65**
Fe%	**86.49**	**84.35**	**85.22**	**83.71**	**87.09**

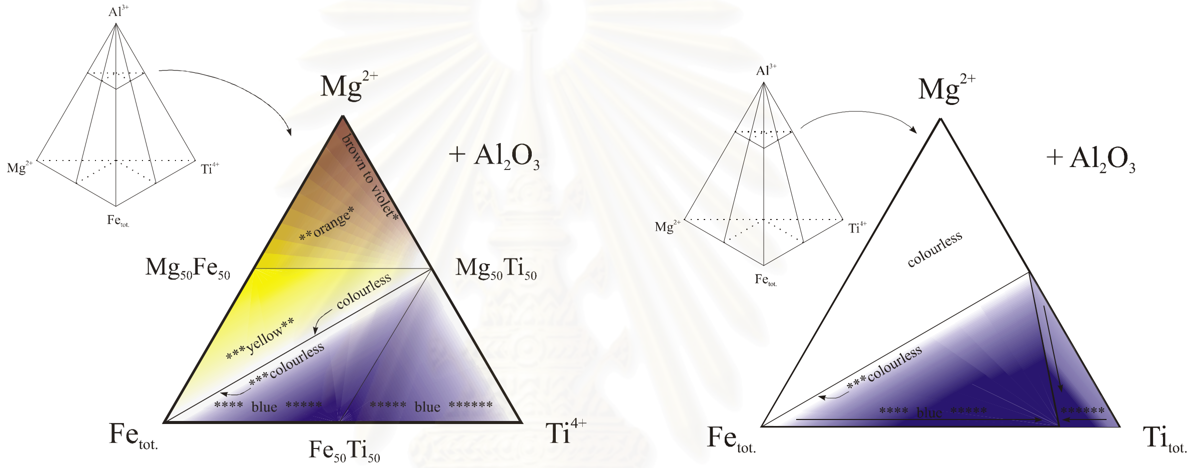
< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

4.5 Discussions

These five simply heat-treated yellow stones from Sri Lanka are the low iron sapphires or the so-called ‘metamorphic-type’. In the heating experiment, the colour did change from very strong yellow in the as-received state into colourless after re-heating at 1,650 ºC in N_2 atmosphere for 5 hours. The UV-Vis spectra recorded in the as-received state show a continuous increase of the absorption to the UV-part of spectrum and a distinct shoulder at approximately 460 nm while the spectra taken after the re-heating appear almost flat without any absorption. As such, the residue spectra (obtained by subtraction of spectrum measured after an experiment from that of the before an experiment of each individual sample) show the increase of the absorption toward the shorter wave length with a shoulder at approximately 460 nm. This is the typical absorption spectrum of “colour centres”.

The LA-ICP-MS analyses of the five-point profiles across the table facets of the sapphires from this group shows large excess of Mg over Ti (Mg-Ti >∼25 atom mole ppm) in almost all spots analysed except only a few points are almost equal. There is a point at the position 3 of the sample PC2 shows only a few atom mole ppm of Ti higher than Mg (approximately 5 atom mole ppm). At this point the Ti might be related to the inclusions of white minute particles and very slightly blue zone appeared in this sample. The Fe contents in these samples are relatively low (∼85 – 350 atom mole ppm) which are typical for the ‘metamorphic’ sapphires.

Hence, based on this experiment, the author believe that Mg^{2+} act in a way as the stabilizer of colour centres when the samples were heated in an oxidizing atmosphere or the so-called “ Mg-trapped hole colour centres” and it can easily be eliminated by reduction heating (e.g. Kvapil *et al*., 1972, 1973; Andreev *et al*., 1976; Wang *et al*., 1983; Emmett and Douthit, 1993; Hager, 1996; 2001Emmett *et al*., 2003; Pisutha-Arnond *et al*.,2004). But the yellow coloration cannot be produced by only Mg-related colour centres (or Mg-trapped hole colour centres) in the pure Al_2O_3 system alone. It has been shown in the previous studies (Häger; 1996, 2001) that yellow coloration can be produced from the combination of Mg-related colour centres with Fe which is usually available in natural sapphires (Figure 4.26). Therefore as the trace element data of the first group are plotted in triangular diagram in Figure 4.27, almost all the points fall within the yellow area of the diagram in Figure 4.26A and are above the 1:1 line in Mg-Ti cross plot (Figure 4.28). Hence, the yellow coloration of low Fe-type (or metamorphic-type) sapphires created during the heating process is caused by defect centres which are stabilized by Mg in the Al_2O_3 structure or the so-called 'stable colour centres or Mg-trapped hole colour centres'.



(A) (B)

*	colour centre due to Mg	**	colour centre 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 4.26 Model representing the interaction of trace elements in the system Al-Mg-Fe-Ti (tetrahedron). Out of this tetrahedron a slice is cut. This slice represents sapphires with total trace element content in the ppm region. The resulting diagram is a triangle. Sapphires of this composition were heat treated at 1850°C in an oxidizing atmosphere(A) and at 1750°C in a reducing atmosphere (B), Häger (1996, 2001).

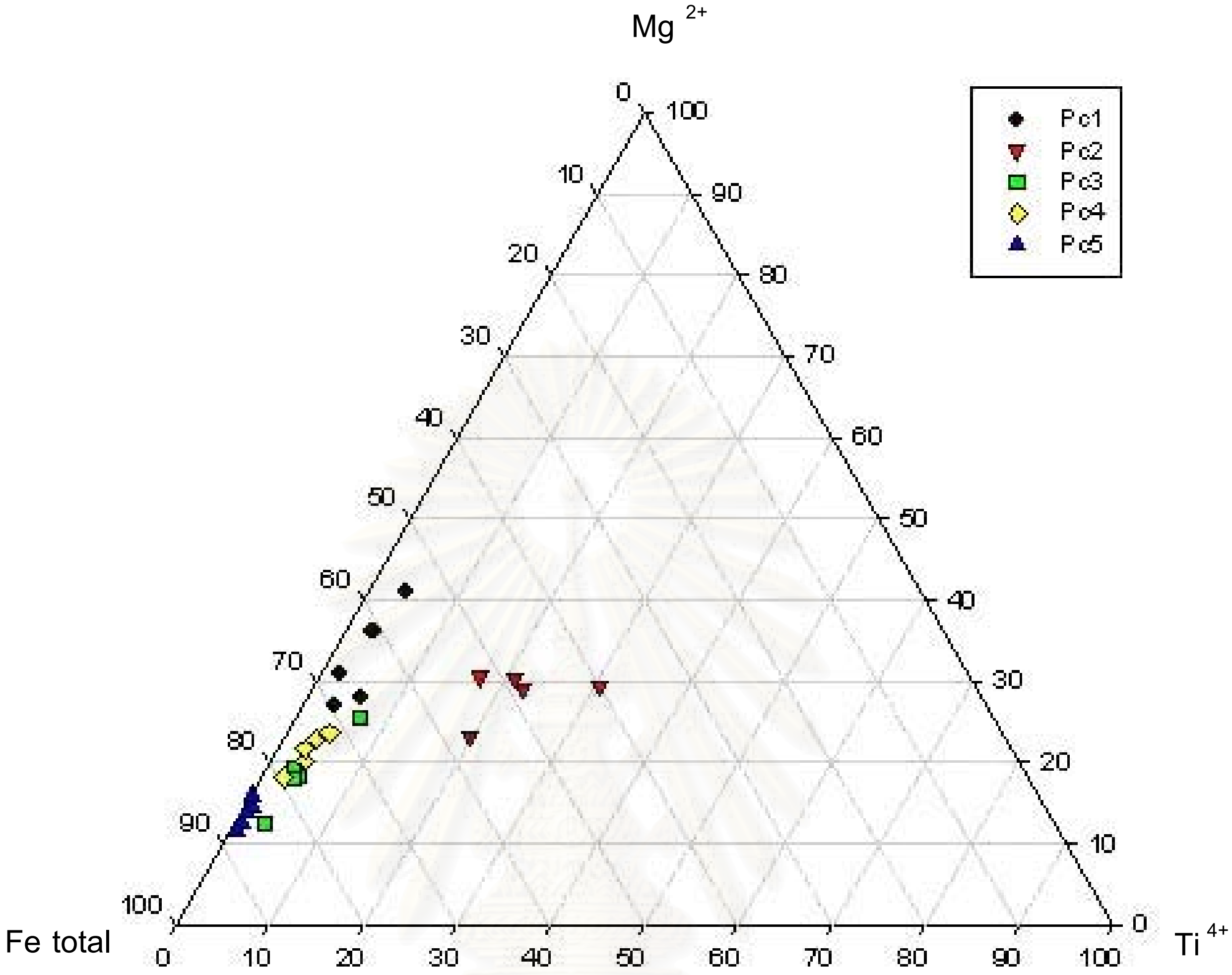


Figure 4.27 Triangular plot of all Group 1 (PC1-5) data points of the low iron (metamorphic-type) yellow sapphires from Sri Lanka

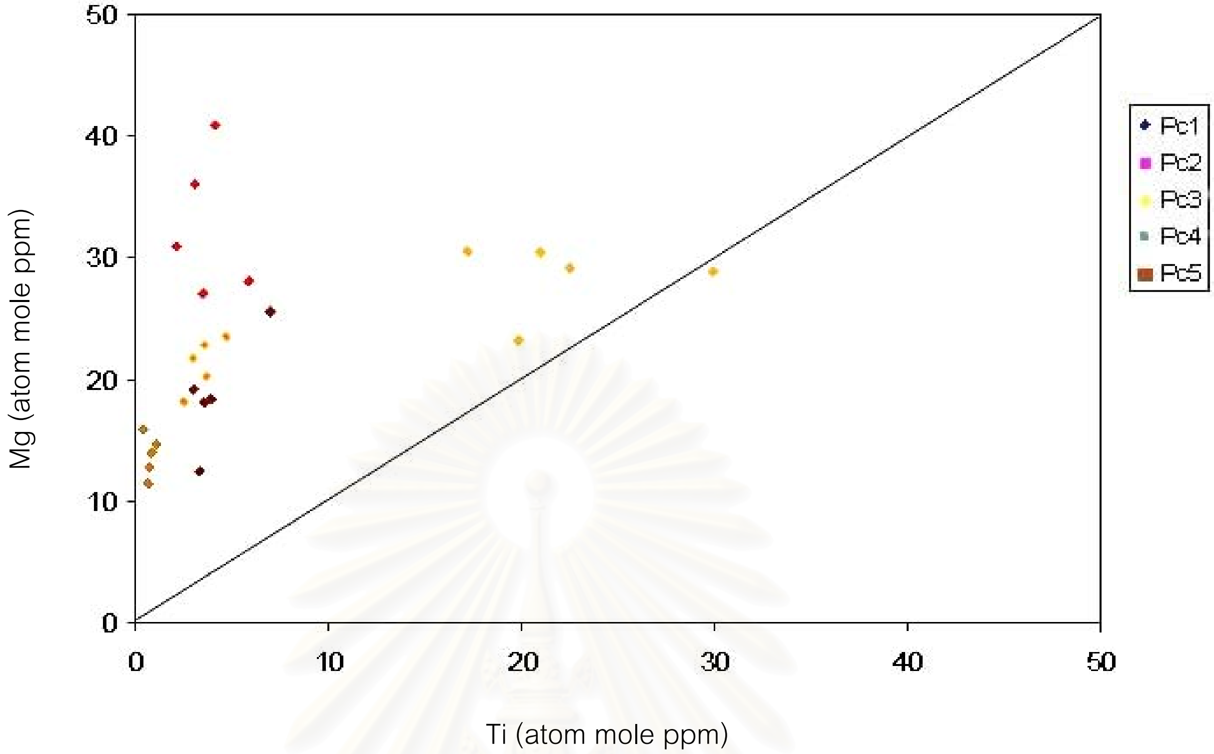


Figure 4.28 Mg-Ti cross plot of all Group 1 (PC1-5) data points of the low iron (metamorphic-type) yellow sapphires from Sri Lanka.

CHAPTER V

HIGH IRON (BASALTIC-TYPE) SAPPHIRES OF GREENISH YELLOW TO YELLOWISH GREEN VARIETY

5.1 Basic properties

The second group, the high iron sapphires or the so-called ‘basaltic-type’ sapphires of mixed yellow-green variety selected for this study, are seven untreated greenish yellow to yellowish green stones from Bang Kracha area of Changwat Chanthaburi in the eastern Thailand. The basic properties of those sapphires are summarized in Table 5.1 and their chemical compositions analysed by EDXRF are listed in Table 5.2. As shown in Table 5.2 most samples contain rather high Fe_2O_3 contents (0.8 to 1.3 wt%)

Table 5.1 Basic properties of seven greenish yellow to yellowish green sapphires (Basaltic-type) from the Bang Kracha area before experiment.

Sample no.	Weight (ct)	RI		Colour	SG	Luminescence		picture
		Min	Max			SW UV	LW UV	
Ch_1 (Chanthaburi)	0.325	1.762	1.770	Very light yellow	3.961	Inert	Weak yellow	
Ch_2 (Chanthaburi)	0.294	1.762	1.770	Light greenish yellow with blue zones	3.956	Inert	Inert	
Ch_3 (Chanthaburi)	0.217	1.762	1.770	Light greenish yellow with blue zones	3.903	Inert	Inert	
Ch_4 (Chanthaburi)	0.165	1.764	1.770	Light greenish yellow with blue patches	4.300	Inert	Inert	

Sample no.	Weight (ct)	RI		Colour	SG	Luminescence		picture
		Min	Max			SW UV	LW UV	
Ch_5 (Chanthaburi)	0.252	1.760	1.768	Very Light yellowish green with blue zones	4.029	Inert	Inert	
Ch_6 (Chanthaburi)	0.276	1.761	1.769	Light yellowish green with blue zones	3.974	Inert	Inert	
Ch_7 (Chanthaburi)	0.197	1.758	1.764	Light yellowish green with faint blue patches	3.959	Inert	Inert	

Table 5.2 Trace element contents (wt %) of seven greenish yellow to yellowish green sapphires (basaltic type) from the Bang Kracha area before treatment, obtained from EDXRF

Sample no.	Al_2O_3	Cr_2O_3	Fe_2O_3	TiO_2	V_2O_3	Ga_2O_3
Ch_1	98.2227	0.0217	1.0000	0.7173	0.0021	0.0362
Ch_2	98.2734	0.0286	1.2754	0.3862	0.0033	0.0330
Ch_3	98.7431	0.0000	0.8864	0.3243	0.0103	0.0359
Ch_4	97.9313	0.0300	1.3335	0.6370	0.0133	0.0549
Ch_5	98.6217	0.0028	1.2171	0.1175	0.0099	0.0310
Ch_6	98.6467	0.0000	1.1577	0.1495	0.0014	0.0447
Ch_7	98.3806	0.0182	1.3681	0.1910	0.0059	0.0361

5.2 Heating experiment

These greenish yellow to yellowish green sapphires were heat-treated in pure oxygen atmosphere (oxidizing condition) at 1650°C for 24 hours. The colour of all samples did not show any obvious change after the heat treatment (Figures 5.1 to 5.7).

Figure 5.1 A very light yellow sapphire (CH1) before treatment (left) does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.2 A light greenish yellow sapphire with blue zones (CH2) before treatment (left) does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.3 A light greenish yellow sapphire with blue zones (CH3) before treatment (left) does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.4 A light greenish yellow sapphire with blue patches (CH4) before treatment (left) does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.5 A light yellowish green sapphire with blue zones (CH5) before experiment (left) does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.6 A light yellowish green sapphire with blue zones (CH6) before experiment does not show any change in colour after heating at 1,650 °C in O_2 atmosphere for 24 hours (right).

Figure 5.7 A light yellowish green sapphire with blue zones (CH7) before treatment (left) does not show any change in colour after heating at 1,650 ºC in O_2 atmosphere for 24 hours (right).

5.3 UV-Vis absorption spectra

The UV-Vis absorption spectra of those seven sapphires were recorded both before and again after the heating experiment at exactly the same position and condition. As expected, the UV-Vis spectra (o-rays) of those seven samples measured before and after the treatment (Figures 5.8 to 5.21) show absorption peaks due to Fe^{3+} at 450, 388 and 377 nm which are normally present in the high iron sapphires. In addition for the samples which show blue zones or patches, the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers with the maxima about 565 nm and 900 nm, respectively also appear as well. As the colour of most samples do not show any obvious change after the heat treatment, the residue spectra (obtained by subtraction of spectra measured before treatment from that measured after the heating at the same position) show a flat line without absorption. It is apparent that the oxidation heating in this experiment could not change the intensity of the absorption peaks due to Fe^{3+} at 450, 388 and 377 nm as well as the intensity of the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers in each individual sample even if they were heated in pure O_2 atmosphere at 1650°C for 24 hours.

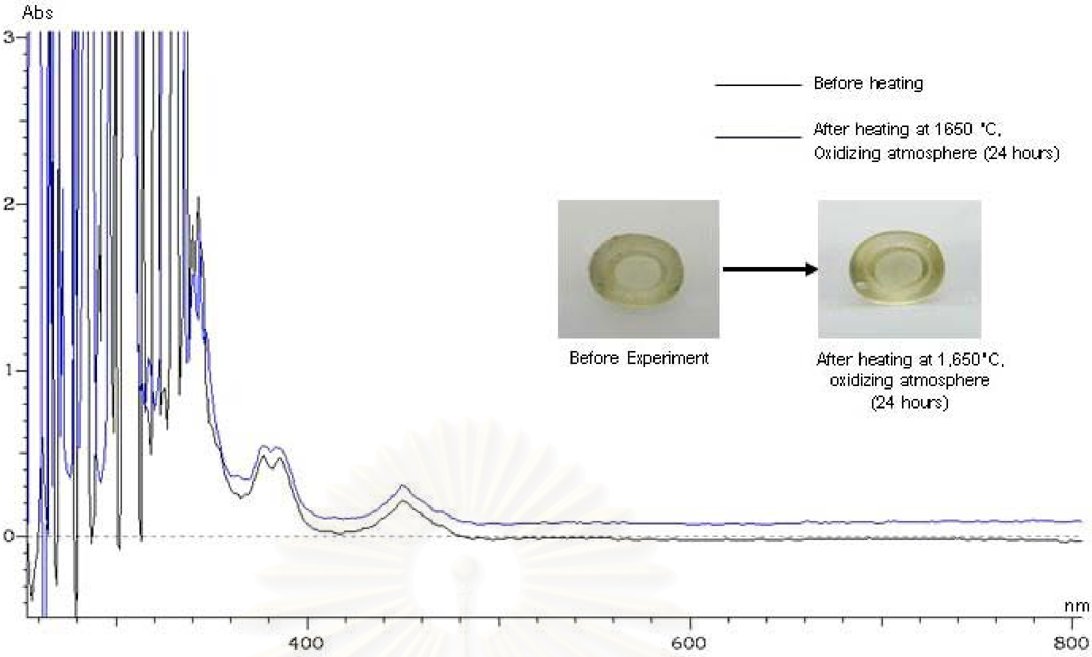


Figure 5.8 UV-Vis spectra (o-rays) of the sample CH1 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. Because the colour of this sample is light yellow without blue patch, the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers are not present.

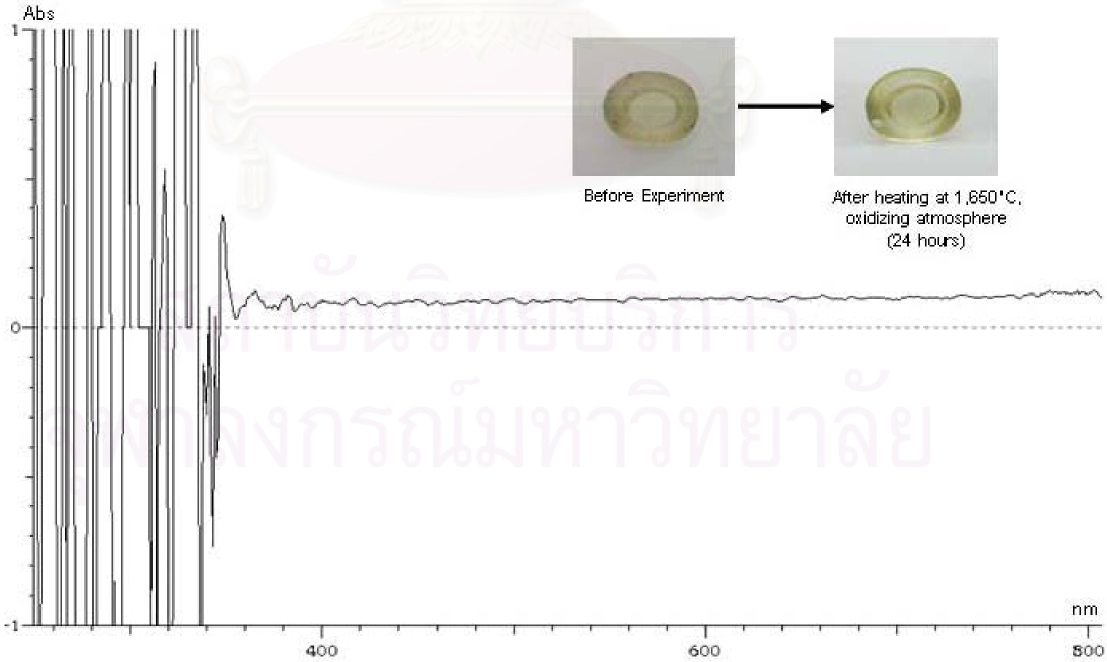


Figure 5.9 Residue spectrum of the sample CH1 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.8.

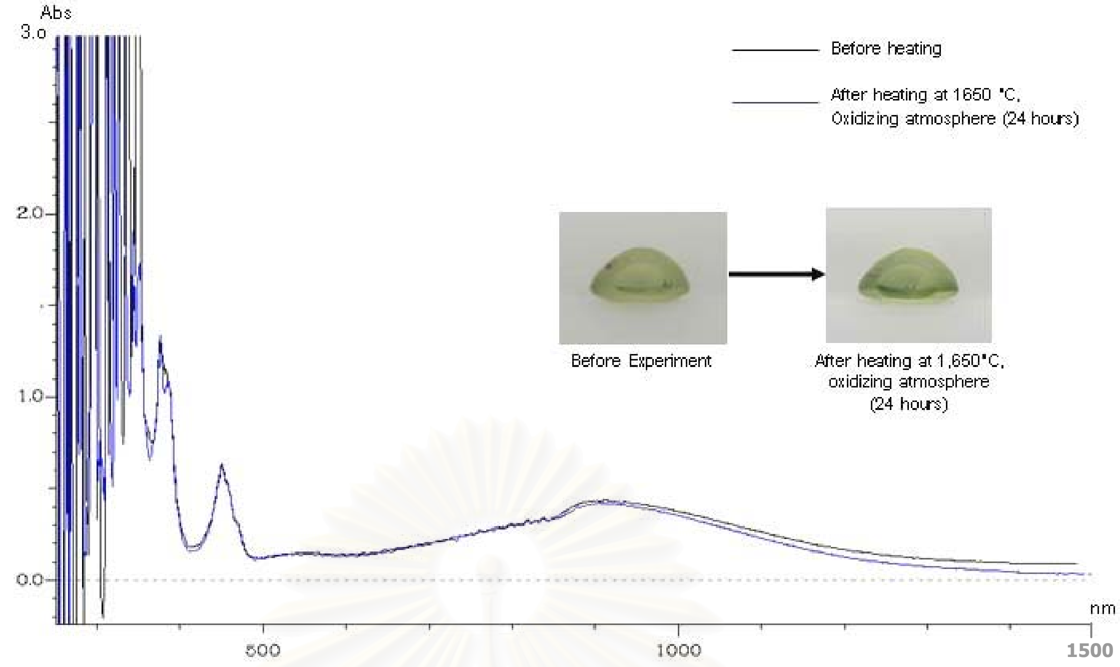


Figure 5.10 UV-Vis spectra (o-rays) of the sample CH2 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light greenish yellow with blue zones, hence the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfer are also present with the maxima about 565 nm and 900 nm, respectively .

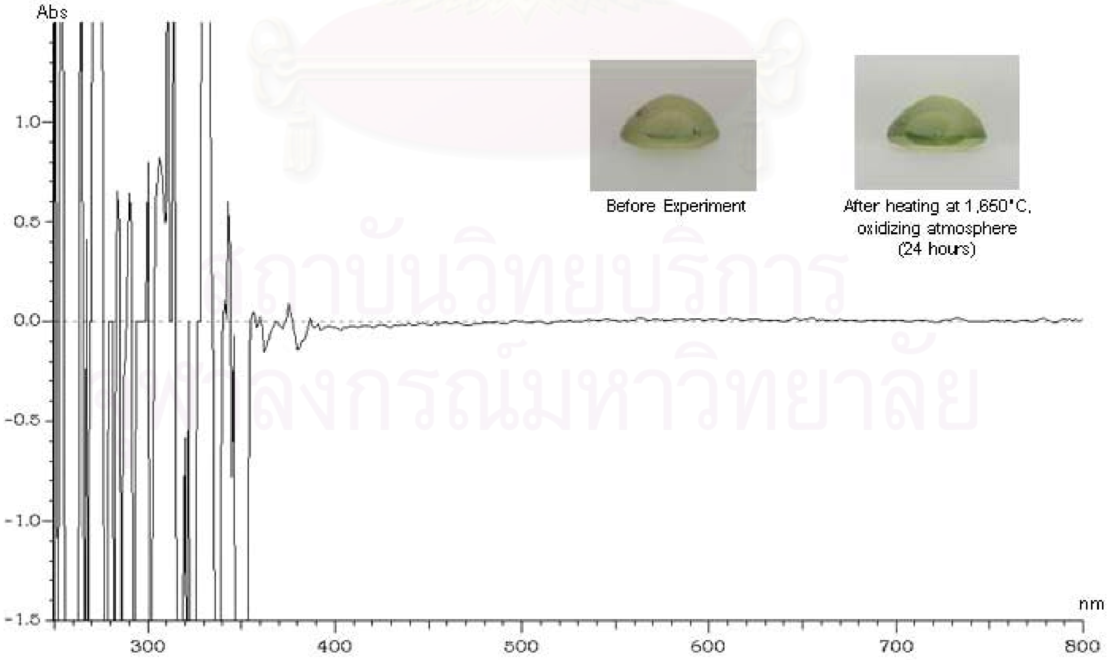


Figure 5.11 Residue spectrum of the sample CH2 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.10.

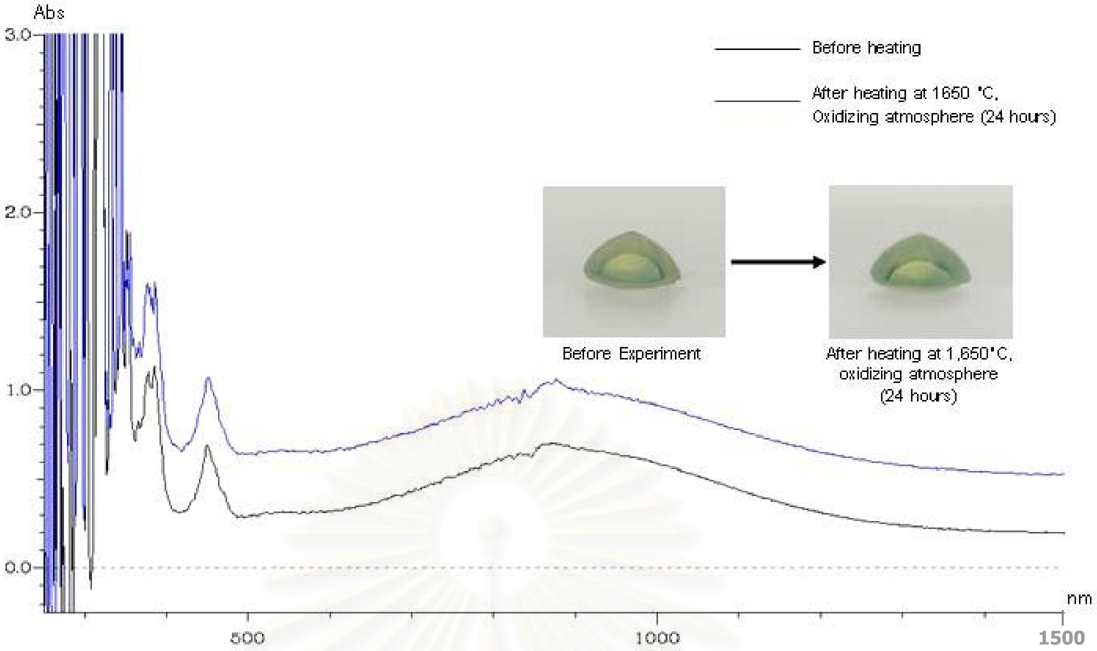


Figure 5.12 UV-Vis spectra (o-rays) of the sample CH3 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light greenish yellow with blue zones, hence the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfer are also present with the maxima about 565 nm and 900 nm, respectively .

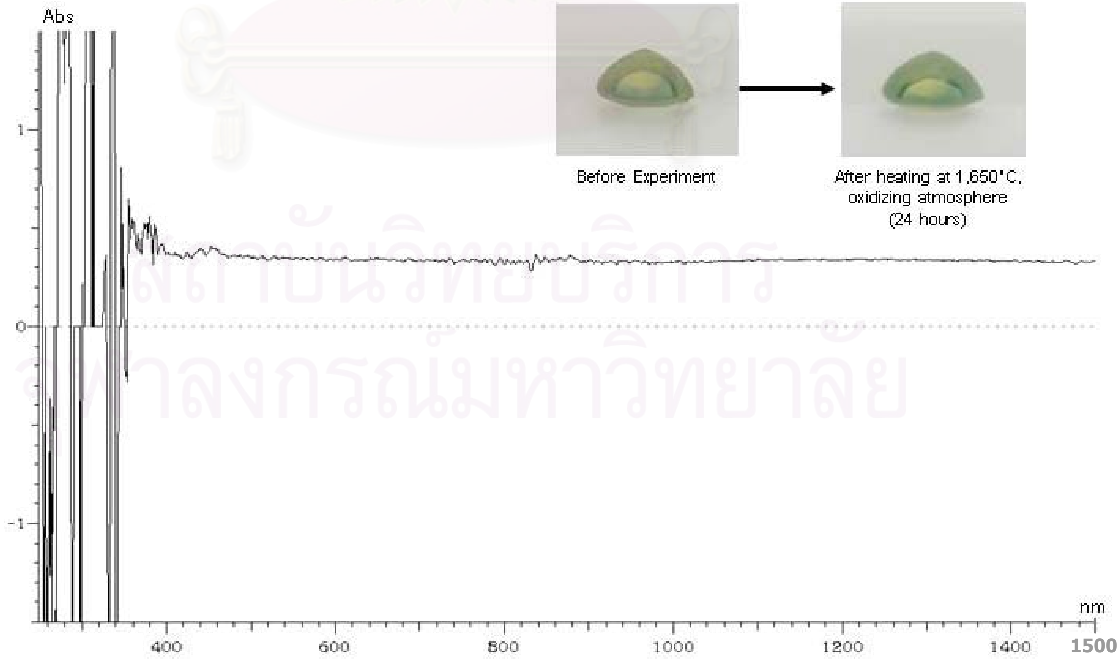


Figure 5.13 Residue spectrum of the sample CH3 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.12.

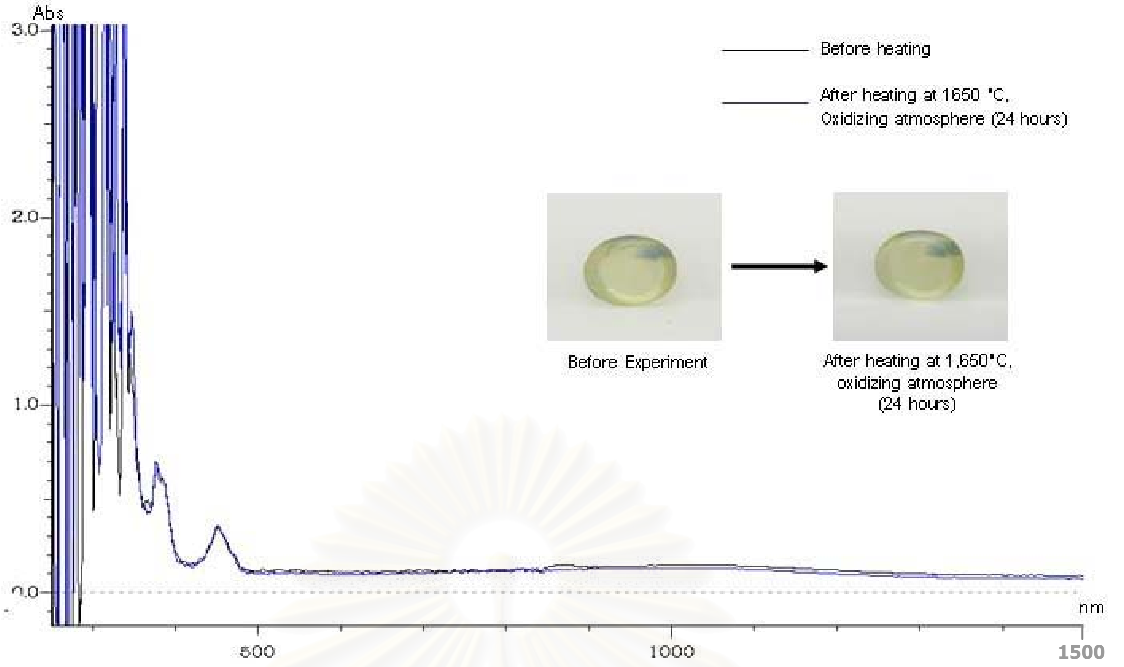


Figure 5.14 UV-Vis spectra (o-ray) of the sample CH4 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light greenish yellow with blue patches at the rim; the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers are not present because the spectra were taken in the middle of the sample.

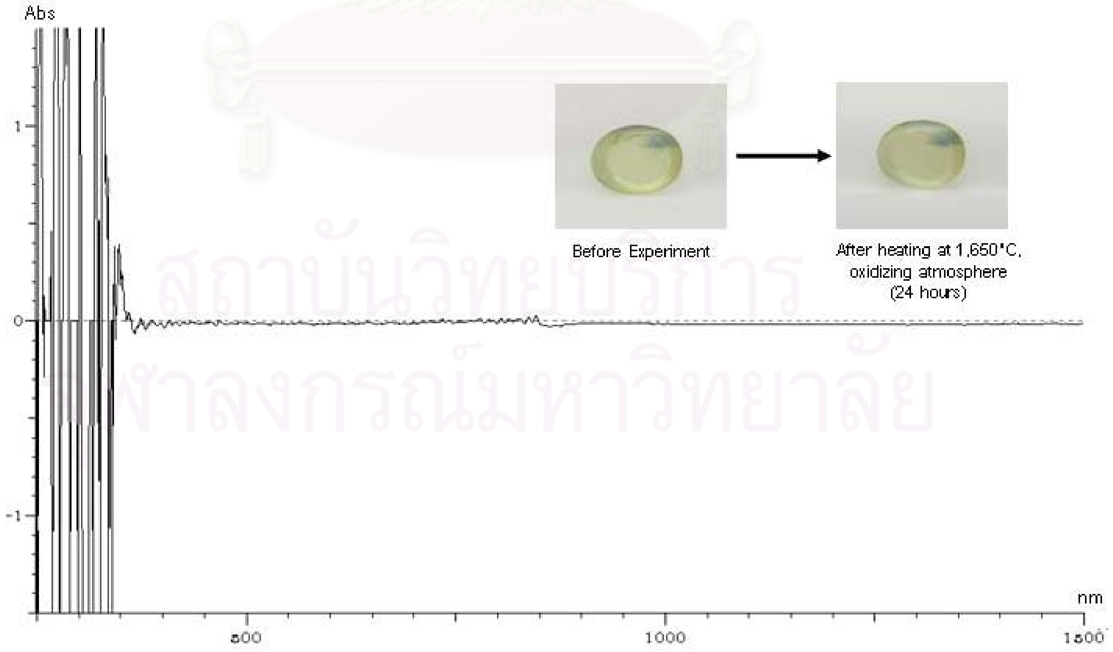


Figure 5.15 Residue spectrum of the sample CH4 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.14.

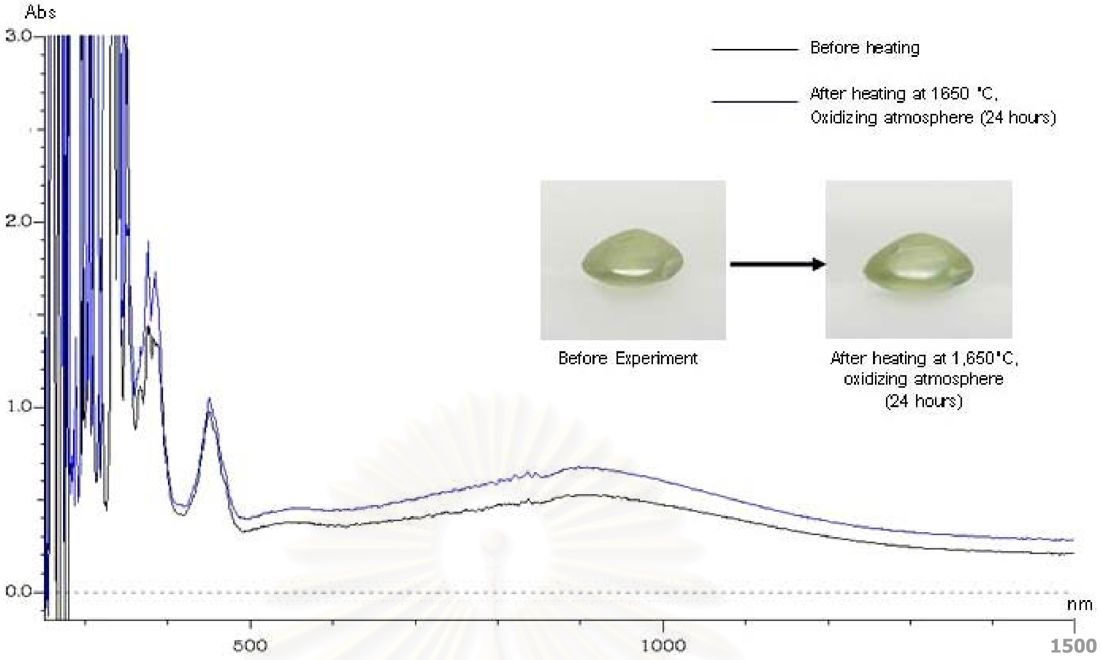


Figure 5.16 UV-Vis spectra (o-rays) of the sample CH5 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light yellowish green with faint blue zones, hence the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfer are also present with the maxima about 565 nm and 900 nm, respectively.

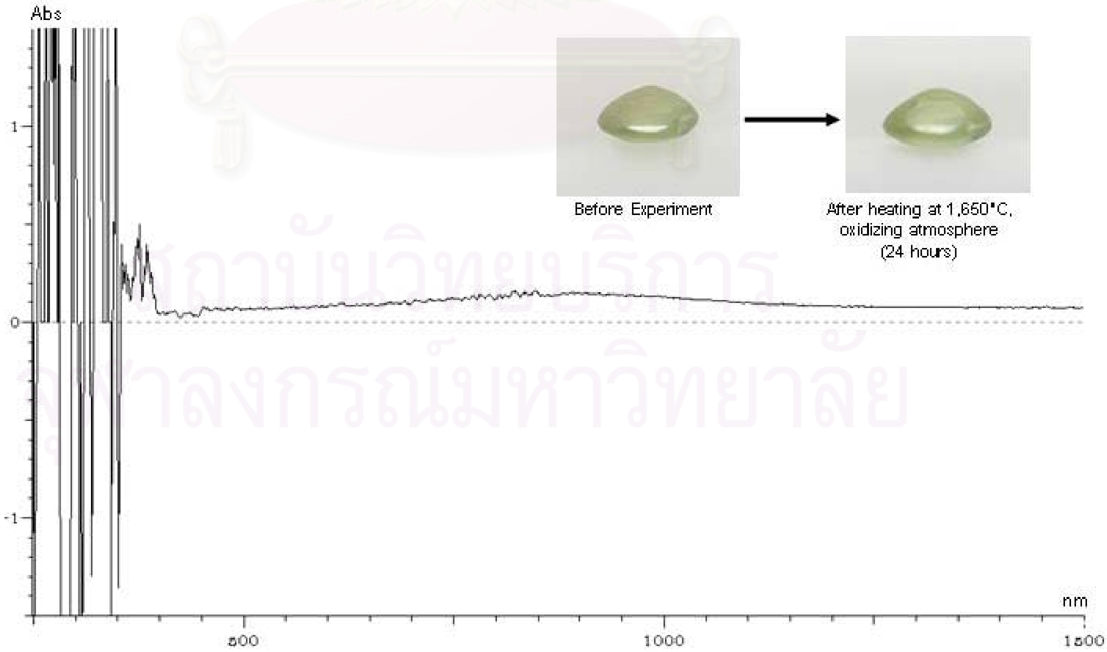


Figure 5.17 Residue spectrum of the sample CH5 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.16.

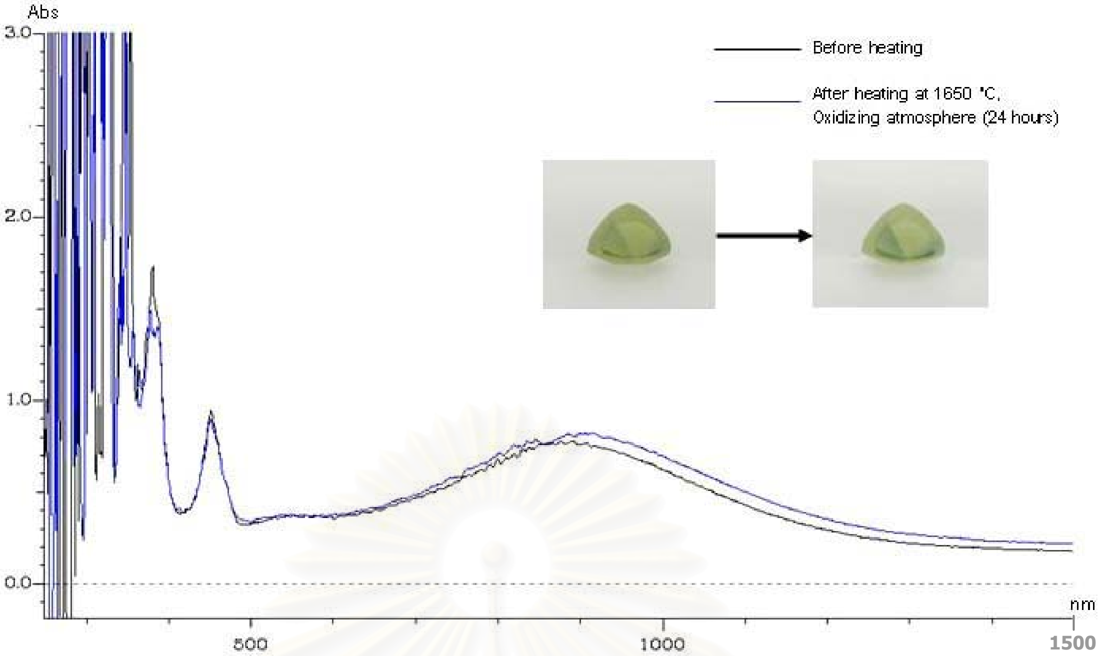


Figure 5.18 UV-Vis spectra (o-rays) of the sample CH6 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light yellowish green with obvious blue zones, hence the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfer are also present with the maxima about 565 nm and 900 nm, respectively.

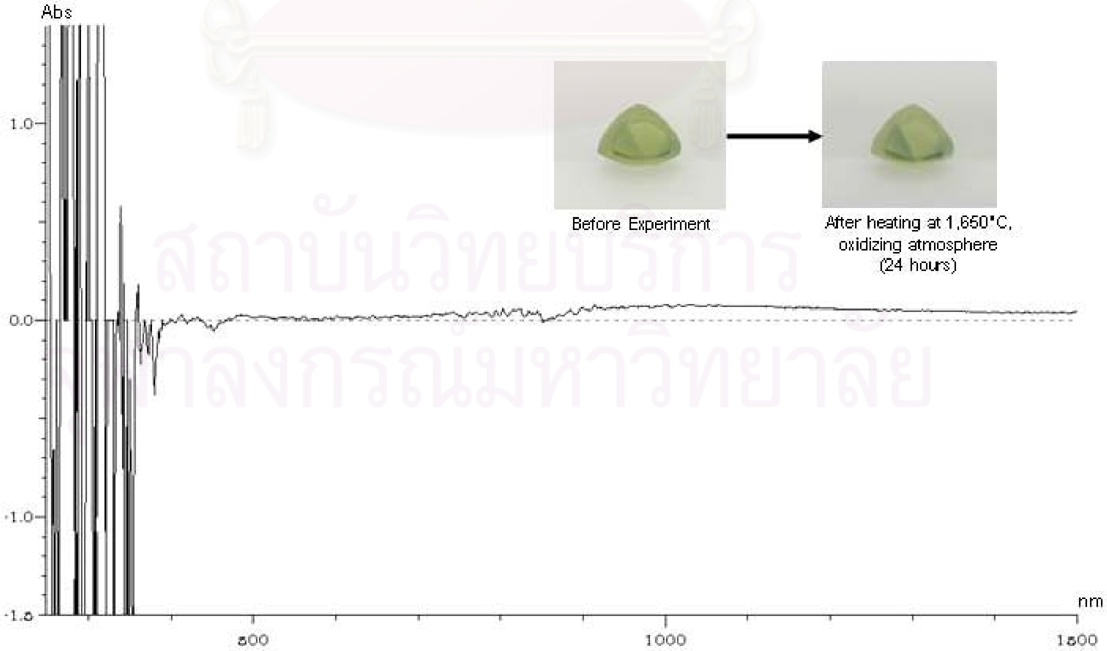


Figure 5.19 Residue spectrum of the sample CH6 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.18.

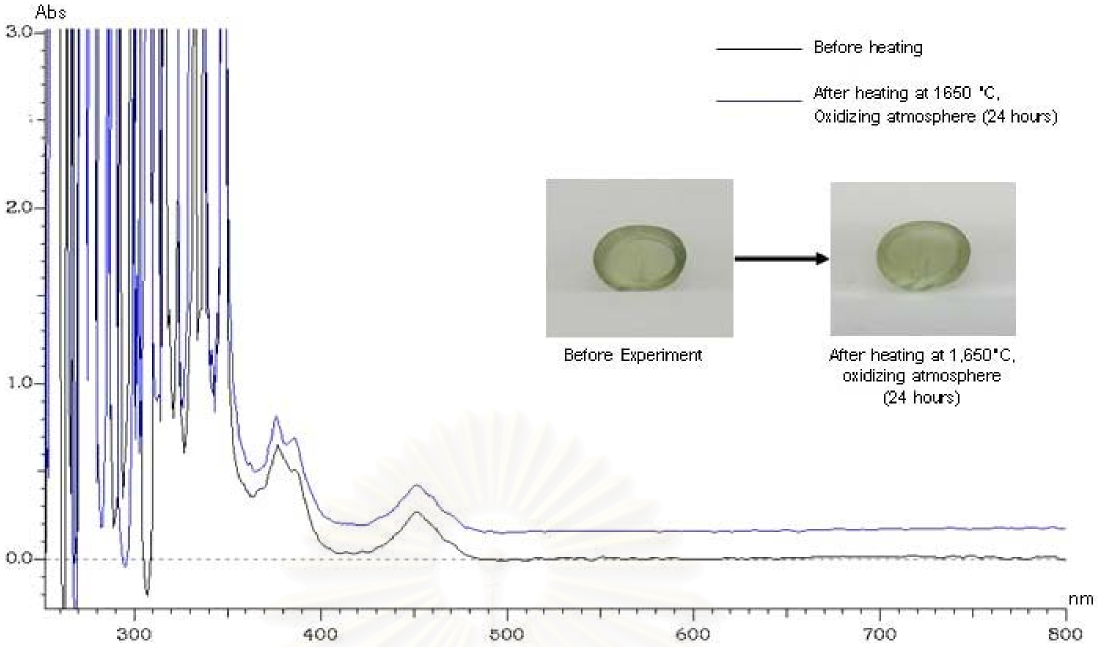


Figure 5.20 UV-Vis spectra (o-rays) of the sample CH7 measured before and after heat treatment at 1,650ºC in O_2 atmosphere for 24 hours. Note the presence of absorption peaks due to Fe^{3+} at 450, 388 and 377 nm. The colour of this sample is light yellowish green with blue patches at the rim; the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers are not present because the spectra were taken in the middle of the sample.

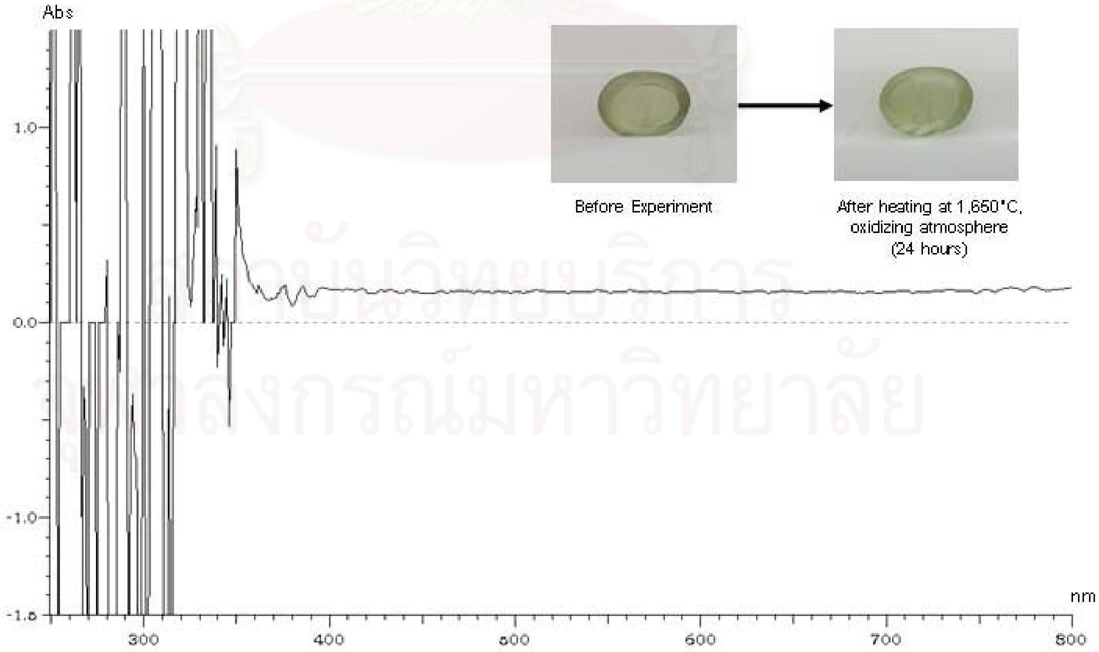


Figure 5.21 Residue spectrum of the sample CH7 obtained by subtracting the spectrum recorded before from the one after the treatment in Figure 5.20.

5.4 LA-ICP-MS Analyses

Each of those seven sapphires was measured for the important trace element concentration at five points across the polished surface by LA-ICP-MS technique to monitor the role of those elements in causing colour in those sapphires (Figures 5.22-5.34 qand Tables 5.3-5.9). As shown in those figures and tables, the analyses show rather high Fe contents in all samples. Of those seven samples, five have Ti > Mg contents and two have only minor excess contents of Mg over Ti (<~5 atom mole ppm) in all the points analysed.

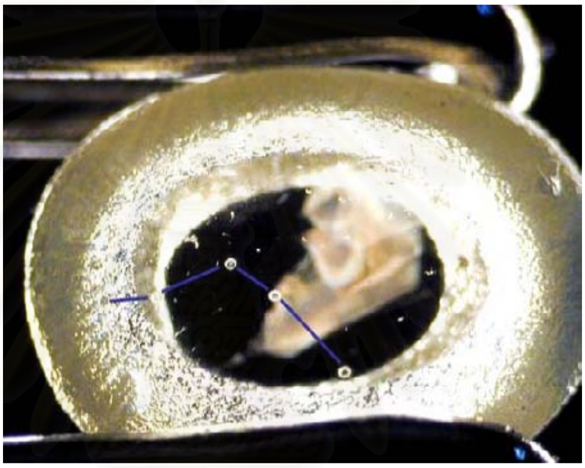


Figure 5.22 Close-up view of the polished surface of the sample CH1 showing the locations of the five point analyses from left to right by LA-ICP-MS.

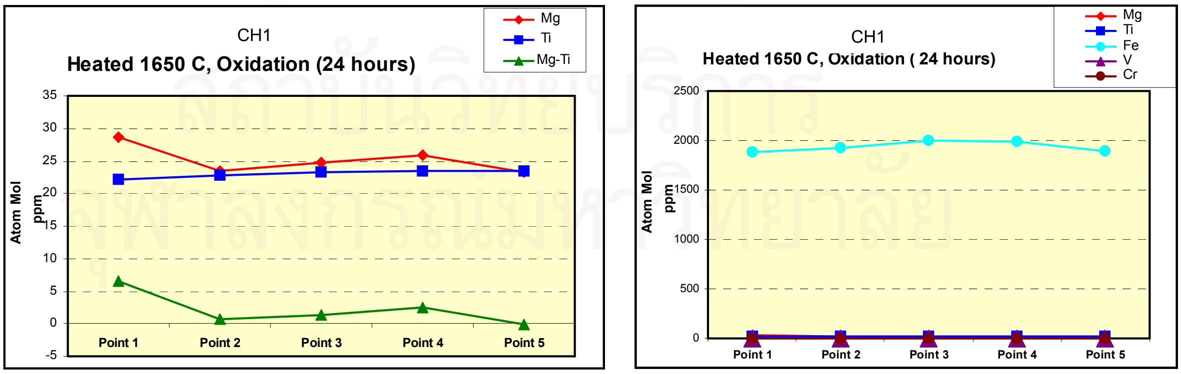


Figure 5.23 Plots of trace element contents at the points where the analyses were taken on the sample CH1 shown in Figure 5.22. The analyses show rather high Fe contents and only minor excess contents of Mg over Ti (<~5 atom mole ppm) in all the points analysed.

Table 5.3 Trace element contents of the sample CH1, obtained by LA-ICP-MS

CH1	Point 1	Point 2	Point 3	Point 4	Point 5
Cations (ppm by weight)					
Be	<0.13	<0.20	<0.18	<0.18	<0.20
Na	1.72	<0.92	<0.80	<0.81	<0.86
Mg	34.31	28.07	29.64	31.07	27.99
Al	529250.25	529250.25	529250.31	529250.25	529250.25
Ti	52.35	53.76	55.16	55.38	55.32
V	6.33	6.19	6.33	6.37	6.02
Cr	6.06	5.48	5.58	5.59	5.55
Mn	0.50	0.33	0.45	0.31	0.57
Fe	5197.60	5301.52	5504.16	5488.38	5207.01
Ga	170.43	172.16	179.56	179.79	170.57
Total %	53.47	53.48	53.50	53.50	53.47
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.00
Na	1.52	0.00	0.00	0.00	0.00
Mg	28.64	23.43	24.74	25.93	23.37
Al	398004.79	397973.18	397895.78	397900.17	398007.16
Ti	22.17	22.77	23.36	23.45	23.43
V	2.52	2.47	2.52	2.54	2.40
Cr	2.36	2.14	2.18	2.18	2.17
Mn	0.19	0.12	0.17	0.11	0.21
Fe	1888.20	1925.80	1999.02	1993.32	1891.63
Ga	37.66	40.52	35.73	37.37	37.19
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**6.47**	**0.66**	**1.38**	**2.48**	**-0.07**
Mg%	**1.48**	**1.19**	**1.21**	**1.27**	**1.21**
Ti %	**1.14**	**1.15**	**1.14**	**1.15**	**1.21**
Fe%	**97.38**	**97.66**	**97.65**	**97.58**	**97.59**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

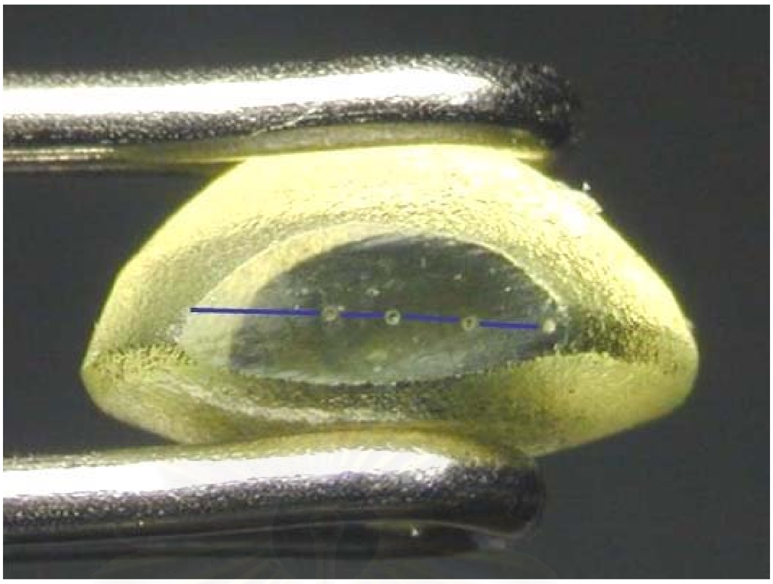


Figure 5.24 Close-up view of the polished surface of the sample CH2 showing the locations of the five point analyses from left to right by LA-ICP-MS.

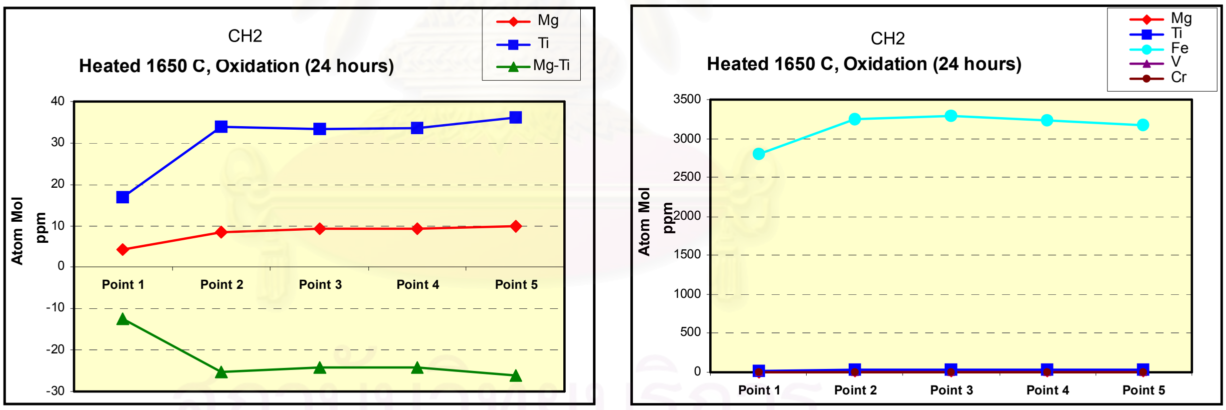


Figure 5.25 Plots of trace element contents at the points where the analyses were taken on the sample CH2 shown in Figure 5.24. The analyses show rather high Fe contents and Ti > Mg contents in all the points analysed.

Table 5.4 Trace element contents of the sample CH2, obtained by LA-ICP-MS

CH2	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.14	<0.18	<0.17	<0.16	<0.15
Na	<0.70	<0.88	<0.78	<0.72	<0.71
Mg	5.04	10.22	11.09	11.12	12.04
Al	529250.25	529250.25	529250.25	529250.25	529250.25
Ti	39.65	79.93	78.90	79.27	85.42
V	6.47	8.61	8.95	8.91	8.50
Cr	3.19	1.47	1.77	1.80	5.47
Mn	1.00	1.16	1.37	1.33	1.39
Fe	7727.55	8957.84	9111.48	8926.44	8740.77
Ga	174.21	215.21	215.05	209.44	203.34
Total %	53.72	53.85	53.87	53.85	53.83
Cations (Atom Mole ppm)					
Be	0.00	0.00	6.86	0.00	0.43
Na	0.00	0.00	0.00	0.00	0.00
Mg	4.20	8.50	9.22	9.25	10.02
Al	397123.20	396647.78	396585.26	396659.94	396723.33
Ti	16.76	33.74	33.30	33.46	36.07
V	2.57	3.42	3.55	3.54	3.37
Cr	1.24	0.57	0.69	0.70	2.13
Mn	0.37	0.43	0.50	0.49	0.51
Fe	2801.08	3243.14	3298.25	3231.87	3165.16
Ga	50.59	62.42	62.36	60.74	58.98
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**-12.56**	**-25.24**	**-24.08**	**-24.21**	**-26.05**
Mg%	**0.15**	**0.26**	**0.28**	**0.28**	**0.31**
Ti %	**0.59**	**1.03**	**0.99**	**1.02**	**1.12**
Fe%	**99.26**	**98.71**	**98.52**	**98.70**	**98.55**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

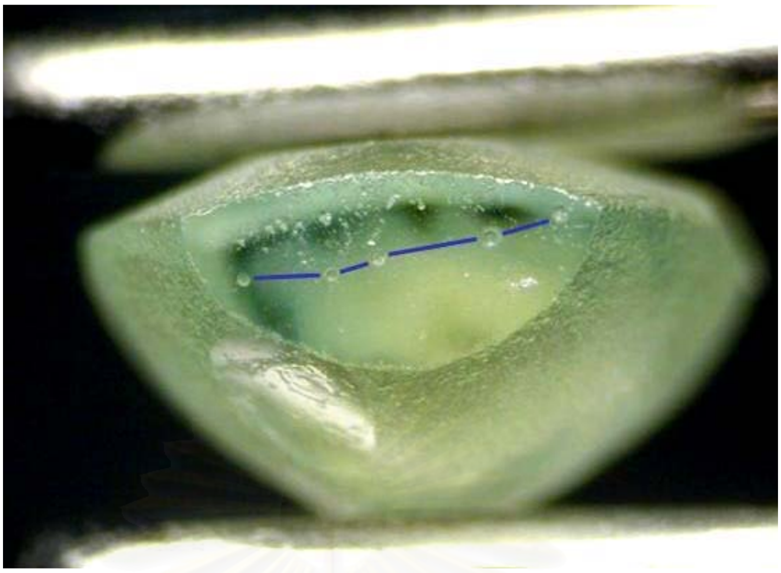


Figure 5.26 Close-up view of the polished surface of the sample CH3 showing the locations of the five point analyses from left to right by LA-ICP-MS.

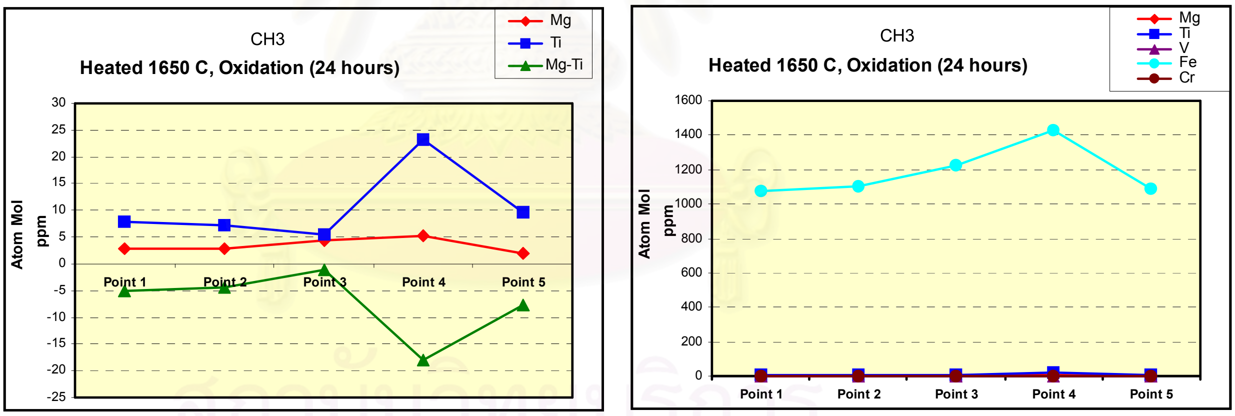


Figure 5.27 Plots of trace element contents at the points where the analyses were taken on the sample CH3 shown in Figure 5.26. The analyses show rather high Fe contents and Ti > Mg contents in all the points analysed.

Table 5.5 Trace element contents of the sample CH3, obtained by LA-ICP-MS

CH3	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.24	<0.27	<0.14	0.22	<0.11
Na	4.29	<2.85	<1.35	<1.43	<1.14
Mg	3.48	3.42	5.18	6.18	2.46
Al	529250.38	529250.38	529250.38	529250.38	529250.38
Ti	18.56	17.05	12.73	54.75	22.86
V	1.756	1.811	1.953	2.353	1.648
Cr	0	0.81	0.57	0.67	0.54
Mn	0.647	0.775	0.833	0.921	0.688
Fe	2950.52	3023	3376.35	3935.11	2993.9
Ga	185.12	188.4	198.6	205.89	170
Total %	53.24	53.25	53.28	53.35	53.24
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.50	0.00
Na	3.79	0.00	0.00	0.00	0.00
Mg	2.91	2.86	4.33	5.17	2.06
Al	398856.32	398833.14	398702.34	398478.33	398847.60
Ti	7.88	7.24	5.40	23.22	9.70
V	0.70	0.72	0.78	0.94	0.66
Cr	0.00	0.32	0.22	0.26	0.21
Mn	0.24	0.29	0.31	0.34	0.25
Fe	1074.17	1100.49	1228.72	1431.26	1089.94
Ga	53.99	54.94	57.90	59.99	49.58
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**-4.97**	**-4.38**	**-1.07**	**-18.05**	**-7.65**
Mg%	**0.27**	**0.26**	**0.35**	**0.35**	**0.19**
Ti %	**0.73**	**0.65**	**0.44**	**1.59**	**0.88**
Fe%	**99.01**	**99.09**	**99.21**	**98.02**	**98.93**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

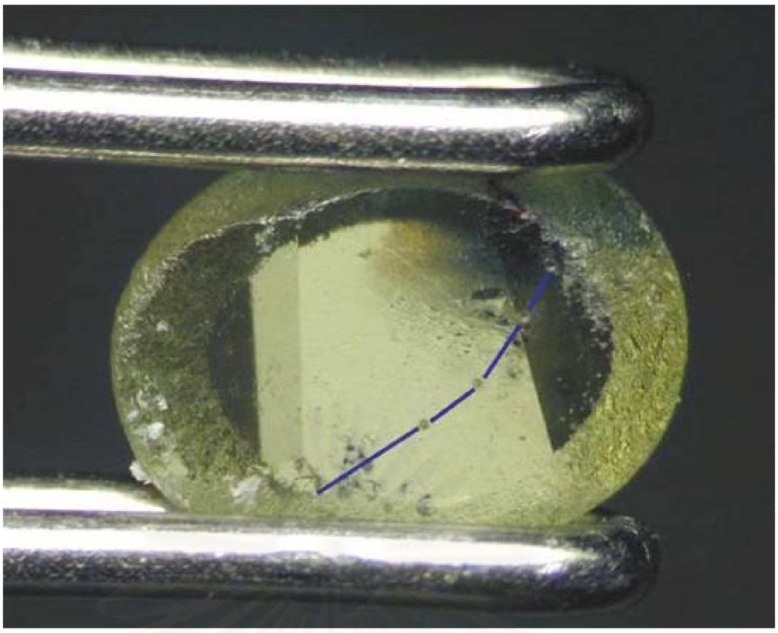


Figure 5.28 Close-up view of the polished surface of the sample CH4 showing the locations of the five point analyses from left to right by LA-ICP-MS.

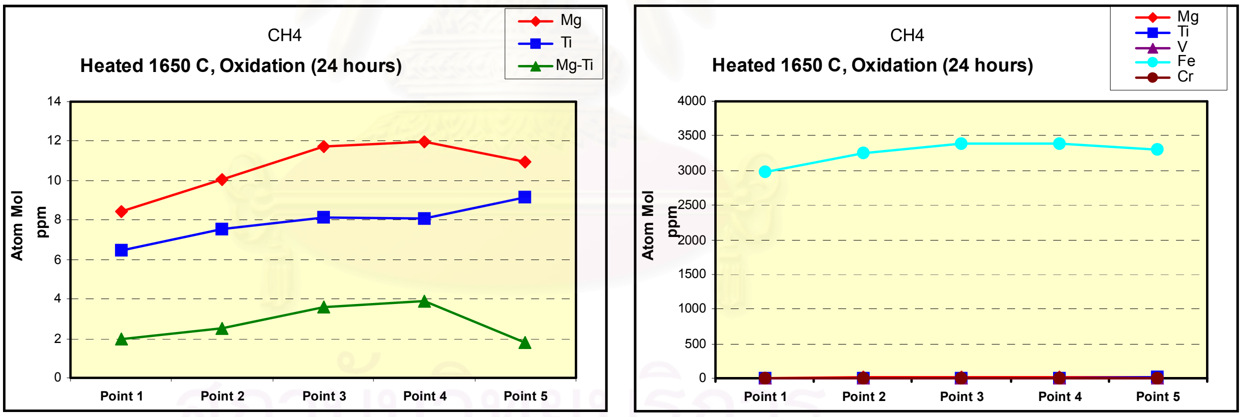


Figure 5.29 Plots of trace element contents at the points where the analyses were taken on the sample CH4 shown in Figure 5.28. The analyses show rather high Fe contents and only minor excess contents of Mg over Ti (<~4 atom mole ppm) in all the points analysed.

Table 5.6 Trace element contents of the sample CH4, obtained by LA-ICP-MS

CH4	Point 1	Point 2	Point 3	Point 4	Point 5
Cations (ppm by weight)					
Be	<0.19	<0.19	<0.18	<0.18	<0.17
Na	<0.90	<0.87	<0.80	<0.82	<0.76
Mg	10.16	12.09	14.08	14.37	13.13
Al	529250.25	529250.31	529250.31	529250.25	529250.25
Ti	15.33	17.89	19.24	19.1	21.66
V	7.08	7.49	5.49	5.53	5.85
Cr	0	0	0.62	0.49	0
Mn	0.813	0.942	1.146	1.185	1.128
Fe	8208.57	9001.8	9374.87	9342.82	9119.53
Ga	211.74	225.25	232.91	233.88	220.13
Total %	53.77	53.85	53.89	53.89	53.86
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00
Mg	8.46	10.06	11.71	11.95	10.92
Al	396946.39	396654.63	396516.80	396527.86	396611.98
Ti	6.48	7.55	8.12	8.06	9.14
V	2.81	2.97	2.18	2.19	2.32
Cr	0.00	0.00	0.24	0.19	0.00
Mn	0.30	0.35	0.42	0.44	0.42
Fe	2974.11	3259.11	3393.00	3381.50	3301.38
Ga	61.46	65.33	67.53	67.81	63.84
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**1.98**	**2.51**	**3.59**	**3.89**	**1.78**
Mg%	**0.28**	**0.31**	**0.34**	**0.35**	**0.33**
Ti %	**0.22**	**0.23**	**0.24**	**0.24**	**0.28**
Fe%	**99.50**	**99.46**	**99.42**	**99.41**	**99.40**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

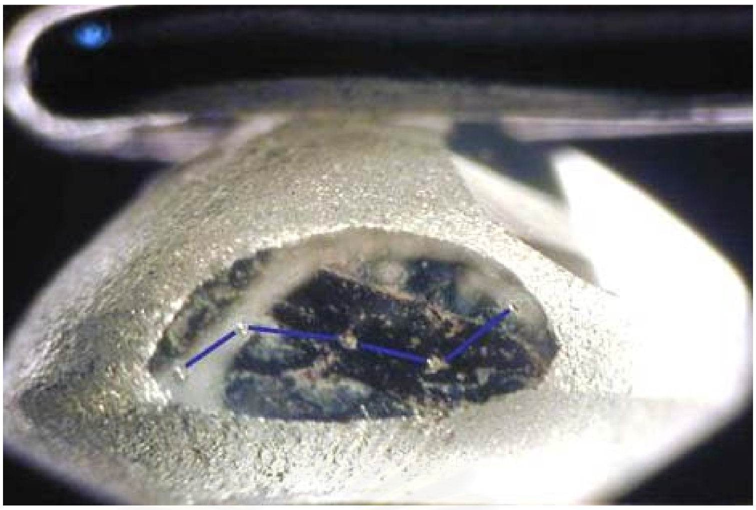


Figure 5.30 Close-up view of the polished surface of the sample CH5 showing the locations of the five point analyses from left to right by LA-ICP-MS. The two points on the left are at the blue zones while the three points on the right are in the yellowish green area.

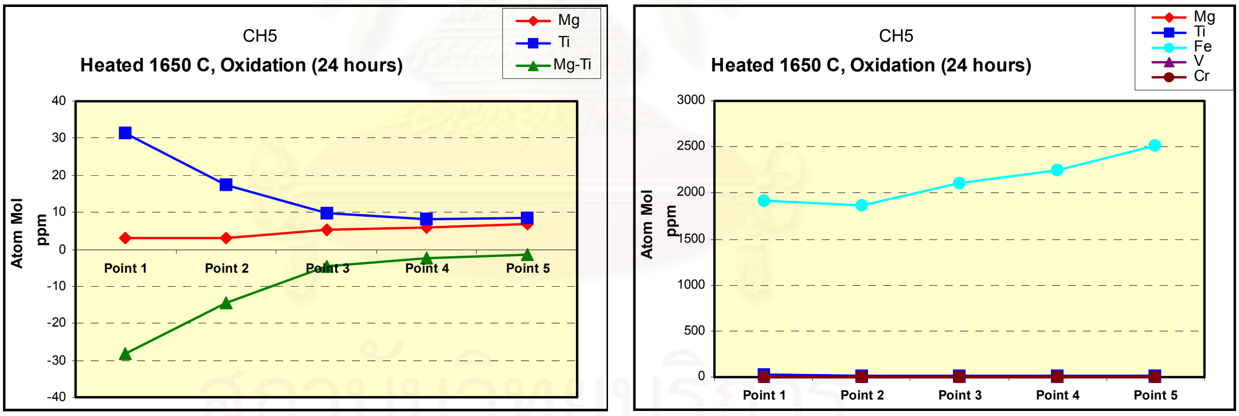


Figure 5.31 Plots of trace element contents at the points where the analyses were taken on the sample CH5 shown in Figure 5.30. The analyses show rather high Fe contents and Ti > Mg contents in all the points analysed. The point 1 and 2 which are on the blue zones show large excess contents of Ti over Mg.

Table 5.7 Trace element contents of the sample CH5, obtained by LA-ICP-MS

CH5	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.13	<0.12	<0.12	<0.13	<0.12
Na	<1.34	<1.22	<1.18	<1.26	<1.25
Mg	3.78	3.77	6.35	6.88	8.25
Al	529250.44	529250.44	529250.44	529250.44	529250.44
Ti	73.86	41.29	23.13	19.51	19.6
V	3.5	3.01	2.98	3.06	3.26
Cr	0.49	0.98	0.46	0.34	0
Mn	0.615	0.528	0.545	0.596	0.531
Fe	5273.31	5113.49	5812.94	6192.11	6939.56
Ga	164.91	165.07	162.6	164.62	171.32
Total %	53.48	53.46	53.53	53.56	53.64
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00
Mg	3.16	3.15	5.30	5.74	6.88
Al	398000.07	398071.58	397825.25	397688.86	397416.26
Ti	31.29	17.49	9.79	8.26	8.29
V	1.39	1.20	1.19	1.22	1.30
Cr	0.19	0.38	0.18	0.13	0.00
Mn	0.23	0.20	0.20	0.22	0.20
Fe	1915.68	1857.96	2110.79	2247.71	2517.30
Ga	47.99	48.05	47.30	47.87	49.78
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**-28.13**	**-14.34**	**-4.49**	**-2.52**	**-1.41**
Mg%	**0.16**	**0.17**	**0.25**	**0.25**	**0.27**
Ti %	**1.60**	**0.93**	**0.46**	**0.37**	**0.33**
Fe%	**98.23**	**98.90**	**99.29**	**99.38**	**99.40**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

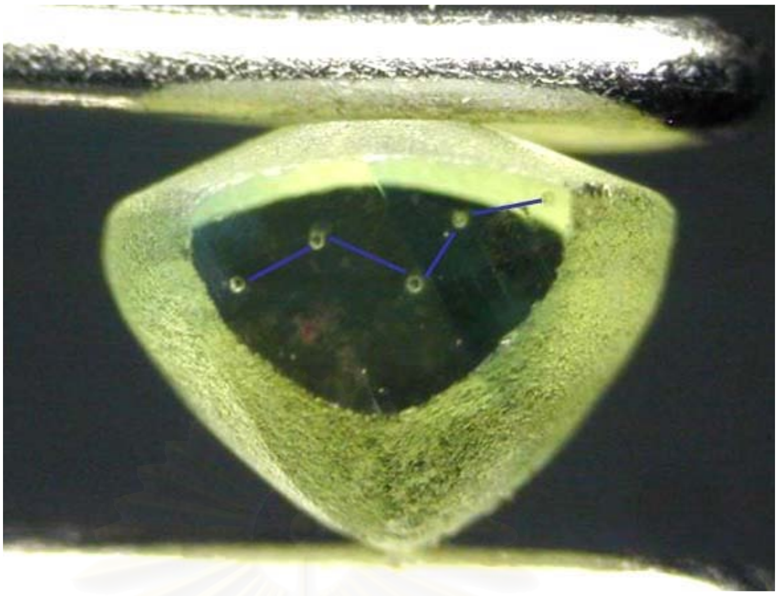


Figure 5.32 Close-up view of the polished surface of the sample CH6 showing the locations of the five point analyses from left to right by LA-ICP-MS.

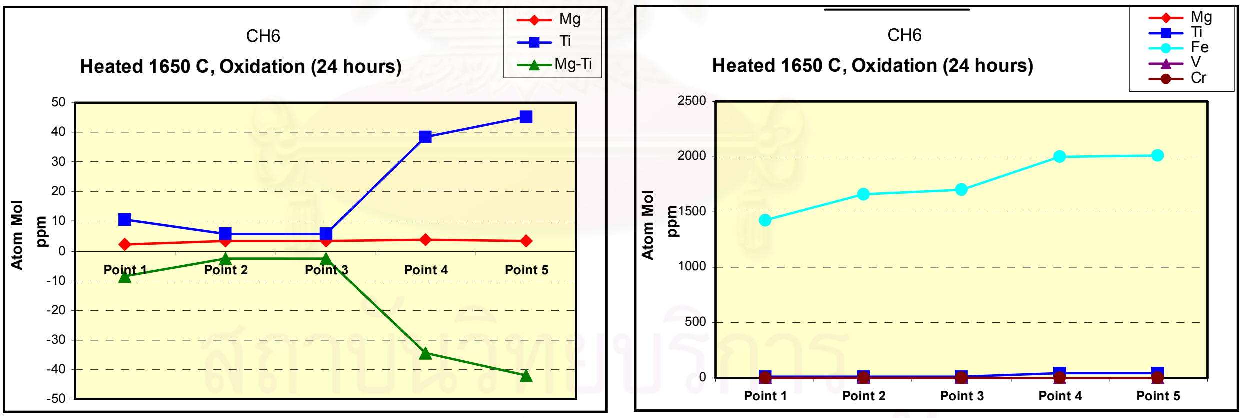


Figure 5.33 Plots of trace element contents at the points where the analyses were taken on the sample CH6 shown in Figure 5.32. The analyses show rather high Fe contents and Ti > Mg contents in all the points analysed.

Table 5.8 Trace element contents of the sample CH6, obtained by LA-ICP-MS

CH6	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	0.125	<0.13	<0.13	0.713	0.976
Na	<1.38	<1.35	<1.42	<1.40	<1.06
Mg	2.65	3.87	3.83	4.75	3.93
Al	529250.44	529250.44	529250.44	529250.44	529250.44
Ti	25	14	13.54	90.76	106.82
V	0.592	0.66	0.662	0.965	0.98
Cr	0	0	0	0	0
Mn	1.058	1.268	1.158	1.399	1.336
Fe	3913.83	4552.62	4689.58	5503.53	5548.59
Ga	243.03	268.09	270.82	280.57	269.41
Total %	53.34	53.41	53.42	53.51	53.52
Cations (Atom Mole ppm)					
Be	0.28	0.00	0.00	1.60	2.20
Na	0.00	0.00	0.00	0.00	0.00
Mg	2.21	3.23	3.20	3.96	3.28
Al	398491.89	398257.09	398207.01	397874.79	397855.09
Ti	10.60	5.93	5.74	38.43	45.23
V	0.24	0.26	0.26	0.38	0.39
Cr	0.00	0.00	0.00	0.00	0.00
Mn	0.39	0.47	0.43	0.52	0.49
Fe	1423.57	1654.94	1704.51	1998.69	2014.95
Ga	70.81	78.07	78.85	81.62	78.37
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**-8.39**	**-2.70**	**-2.54**	**-34.47**	**-41.95**
Mg%	**0.15**	**0.19**	**0.19**	**0.19**	**0.16**
Ti %	**0.74**	**0.36**	**0.33**	**1.88**	**2.19**
Fe%	**99.11**	**99.45**	**99.48**	**97.85**	**97.55**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

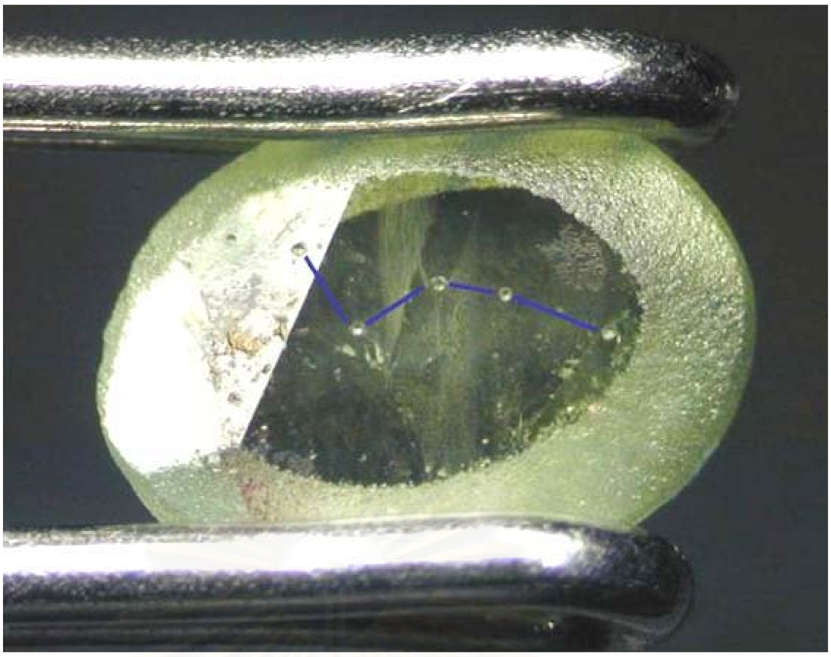


Figure 5.34 Close-up view of the polished surface of the sample CH7 showing the locations of the five point analyses from left to right by LA-ICP-MS.

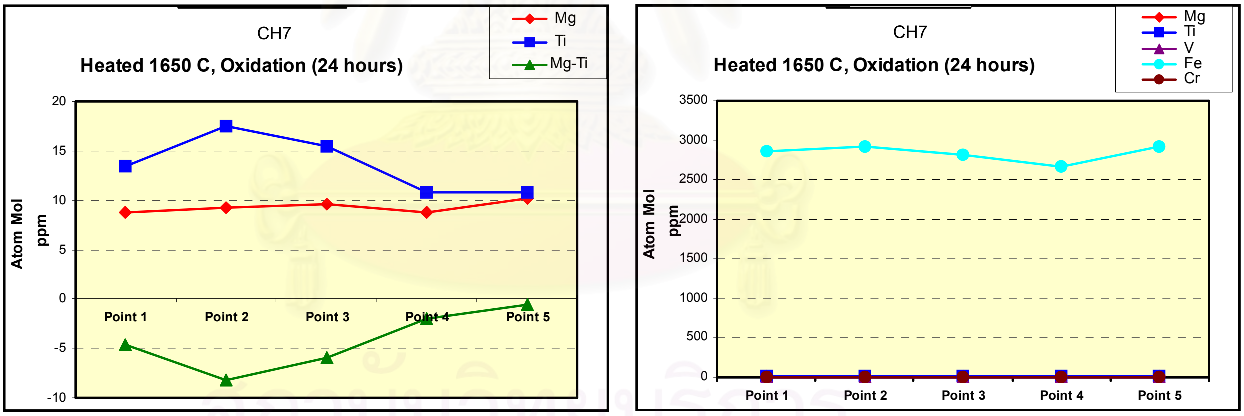


Figure 5.35 Plots of trace element contents at the points where the analyses were taken on the sample CH7 shown in Figure 5.33. The analyses show rather high Fe contents and Ti > Mg contents in all the points analysed.

Table 5.9 Trace element contents of the sample CH7, obtained by LA-ICP-MS

CH7	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.30	0.22	<0.17	<0.19	<0.17
Na	<3.00	<1.43	<1.71	<1.87	<1.72
Mg	10.54	11.12	11.5	10.51	12.3
Al	529250.31	529250.31	529250.31	529250.31	529250.31
Ti	31.75	41.36	36.65	25.43	25.55
V	6.38	6.46	5.95	6.12	5.51
Cr	1.09	0	0	0.52	0.77
Mn	0.582	0.609	0.662	0.609	0.646
Fe	7894.85	8074.62	7769.17	7339.12	8052.94
Ga	171.14	173.45	167.18	161.38	170.64
Total %	53.74	53.76	53.72	53.68	53.75
Cations (Atom Mole ppm)					
Be9	0.00	0.50	0.00	0.00	0.00
Na23	0.00	0.00	0.00	0.00	0.00
Mg24	8.78	9.26	9.58	8.76	10.24
Al27	397063.66	396993.70	397107.73	397269.50	397008.52
Ti47	13.42	17.47	15.49	10.75	10.80
V51	2.54	2.57	2.36	2.43	2.19
Cr53	0.42	0.00	0.00	0.20	0.30
Mn55	0.21	0.22	0.24	0.22	0.24
Fe57	2861.29	2925.93	2816.05	2661.26	2918.18
Ga71	49.69	50.35	48.54	46.88	49.53
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	**-4.64**	**-8.22**	**-5.91**	**-1.99**	**-0.55**
Mg%	**0.30**	**0.31**	**0.34**	**0.33**	**0.35**
Ti %	**0.47**	**0.59**	**0.55**	**0.40**	**0.37**
Fe%	**99.23**	**99.08**	**99.12**	**99.27**	**99.28**

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

5.5 Discussions

These seven untreated sapphires of greenish yellow to yellowish green variety from Bang Kracha area, Chanthaburi, Thailand are of the high iron sapphires or the so-called ‘basaltic-type’. The stones were heated at 1,650ºC in pure O_2 atmosphere for 24 hours. After the treatment the colour of most samples did not show any obvious change. The UV-Vis-NIR spectra recorded both before and after the treatment show similar absorption peaks due to Fe^{3+} at 450, 388 and 377 nm and additional absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers in the samples containing blue zones or patches. The residue spectra (obtained by subtraction of spectra measured before from that after the treatment at the same position) show a flat line without absorption. It is apparent that the oxidation heating in this experiment could not have any noticeable effect on the intensity of the absorption peaks due to Fe^{3+} at 450, 388 and 377 nm as well as the intensity of the absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers in each individual sample.

The trace element analyses by LA-ICP-MS show rather high Fe contents in all the seven samples (∼1000 to ∼3,300 atom mole ppm Fe) and five of those have Ti > Mg contents while two have only minor excess contents of Mg over Ti (<∼5 atom mole ppm) in all the points analysed. Because of the high iron concentrations of these basaltic sapphires, all the data points, when plotted in Mg-Ti-Fe diagram, are clustered at the Fe apex (Figure 5.35). Hence the diagram is not applicable in understanding the cause of colour for the high iron sapphires. However when all the data points are plotted in Mg-Ti cross plot (Figure 5.36), majority of the points are below 1:1 line with only a few are at or slightly above. These data seem to suggest that there is not enough excess Mg to stabilize the yellow ‘colour centres’. Hence the light yellow hues present in those high Fe samples are mainly due to Fe^{3+} spin forbidden transition.

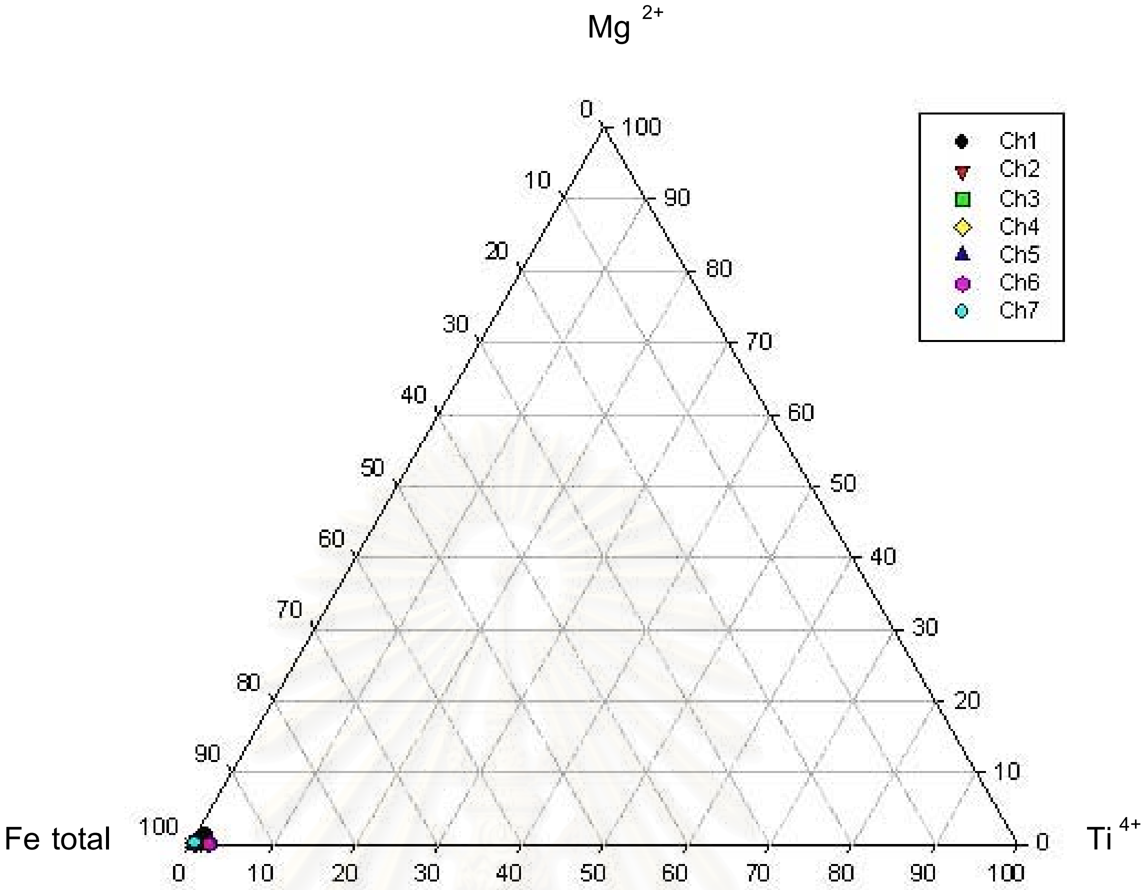


Figure 5.36 Triangular plot of all Group 2 (CH1-7) data points of the high iron (basaltic-type) sapphires of greenish yellow to yellowish green variety from Bang Kracha area, Chanthaburi, Thailand.

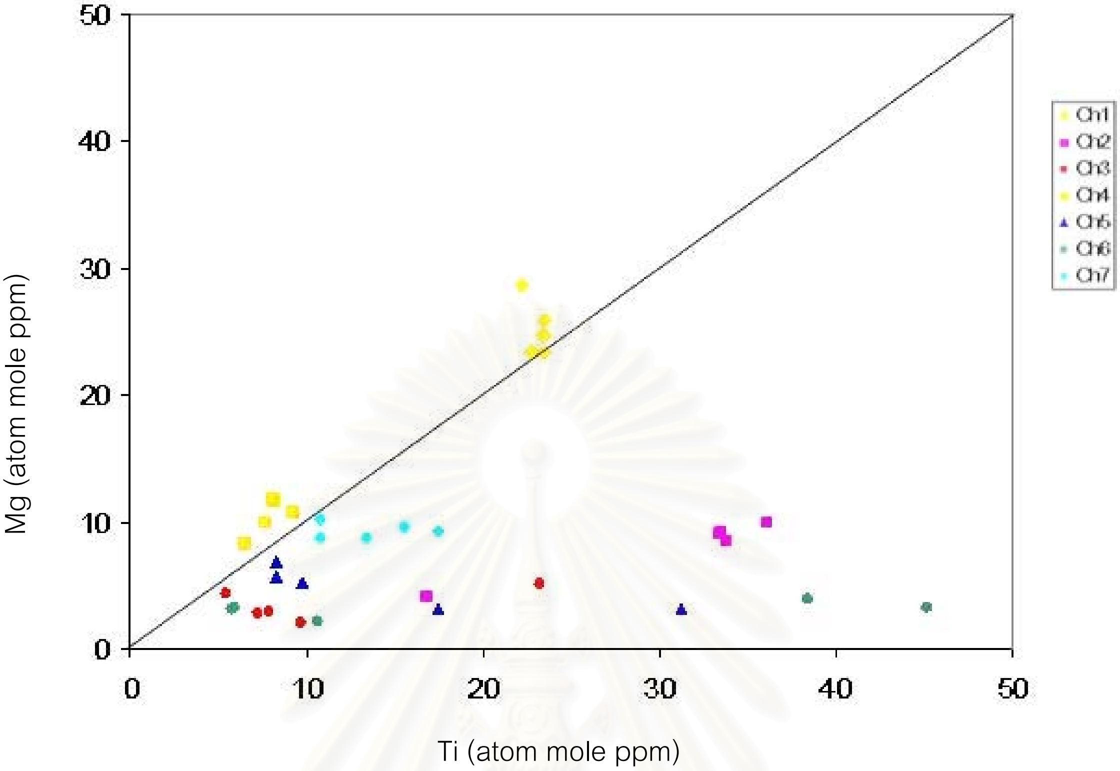


Figure 5.37 Mg-Ti cross plot of all Group 2 (CH1-7) data points of the high iron (basaltic-type) sapphires of greenish yellow to yellowish green variety from Bang Kracha area, Chanthaburi, Thailand.

CHAPTER VI

HIGH IRON (BASALTIC-TYPE) SAPPHIRES OF YELLOW VARIETY

6.1 Basic properties

The third group, the high iron sapphires or the so-called ‘basaltic-type’ sapphires of yellow variety selected for this study, are two untreated pale yellow stones from Bang Kracha area of Changwat Chanthaburi in the eastern Thailand. The basic properties of those sapphires are summarized in Table 6.1 and their chemical compositions analysed by EDXRF are listed in Table 6.2.

Table 6.1 Basic properties of two pale yellow sapphires with high Fe content (Basaltic-type) from Bang Kracha area before experiment

Sample no.	Weight (ct)	RI		Colour	SG	Luminescence		Picture
		Min	Max			SW UV	LW UV	
YCH1 (Chanthaburi, Thailand)	1.909	1.763	1.769	Light yellow	3.990	Inert	Weak orange	
YCH2 (Chanthaburi, Thailand)	1.460	1.763	1.770	Light yellow	3.964	Inert	Inert	

Table 6.2 Trace element contents (wt %) of two pale yellow sapphires with high Fe contents (basaltic type) from Bang Kracha area, obtained from EDXRF

Sample no.	Al_2O_3	Cr_2O_3	Fe_2O_3	TiO_2	V_2O_3	Ga_2O_3
YCH1	99.6188	0.0116	0.3325	0.0239	0.0000	0.0132
YCH2	99.3957	0.0084	0.5577	0.0185	0.0029	0.0168

6.2 Experiments on the sample YCH1

This rough pale yellow sapphire sample was cut into two pieces. The smaller piece was kept as the reference while the larger piece was used for the heating experiment. The larger sample had turned from pale yellow before treatment into brownish yellow after heating at high temperature reportedly in an oxidizing atmosphere in an electric furnace for several hours. The comparison of the colour before treatment with that after heat treatment is shown in Figure 6.1. The brownish yellow coloration after treatment was stable after the fading test. The UV-Vis absorption spectra of the large piece measured before and after heating are displayed in Figure 6.2. As seen in the figure, both spectra show strong absorption due to Fe^{3+} at 450 nm and the spectrum after treatment shows a continuously elevated absorption towards the shorter wavelengths. The residue spectrum (obtained by subtraction of the absorption measured before treatment from that of after heating) shows a continuous increase in absorption towards the UV part of the spectrum with a small shoulder or hump at around 450 nm. The small irregularity of the hump at 450 nm was probably due to a slight error during measurement. The oxidation heating was unable to change the oxidation state of iron from Fe^{2+} (if there were originally present before treatment) into Fe^{3+} to have any significant effect on the yellow coloration as seen from the height of 450 nm peak was barely unchanged by the heating experiment.

Figure 6.1 Comparison of the colour of sample YCH1 before treatment (the smaller reference sample on the left) with that (the larger sample on the right) after heat treatment at high temperature in an oxidizing condition

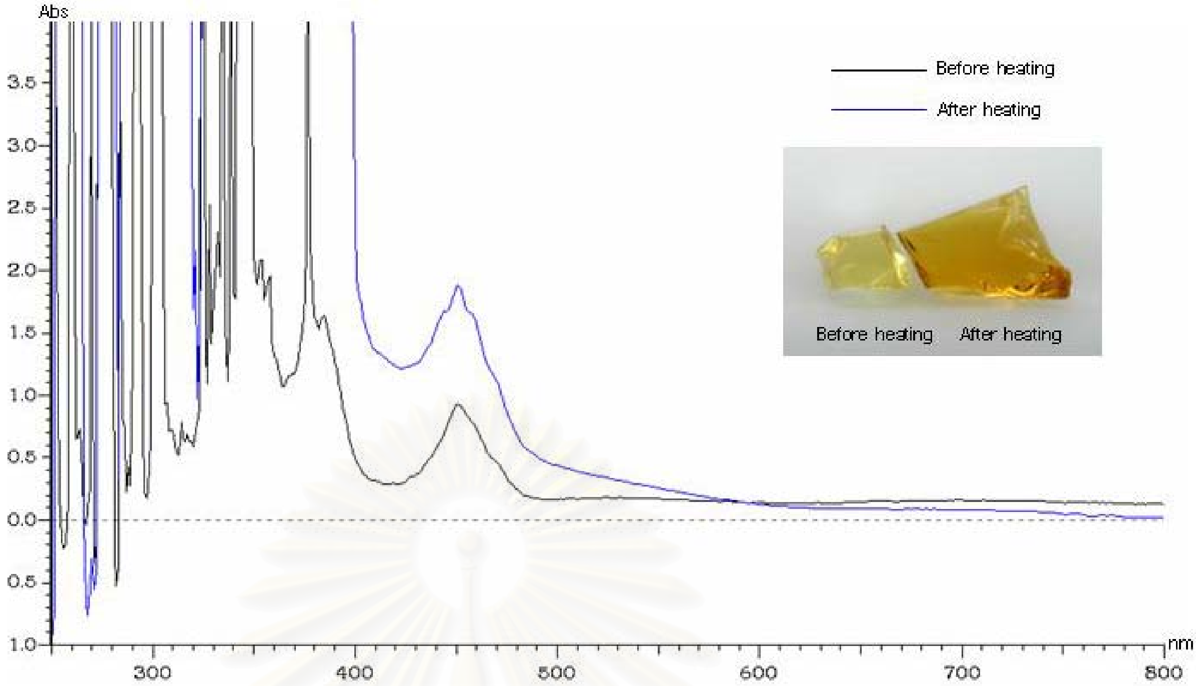


Figure 6.2 UV-Vis spectra (o-rays) of sample YCH1 recorded before and after heating experiment reportedly at high temperature in the oxidizing condition

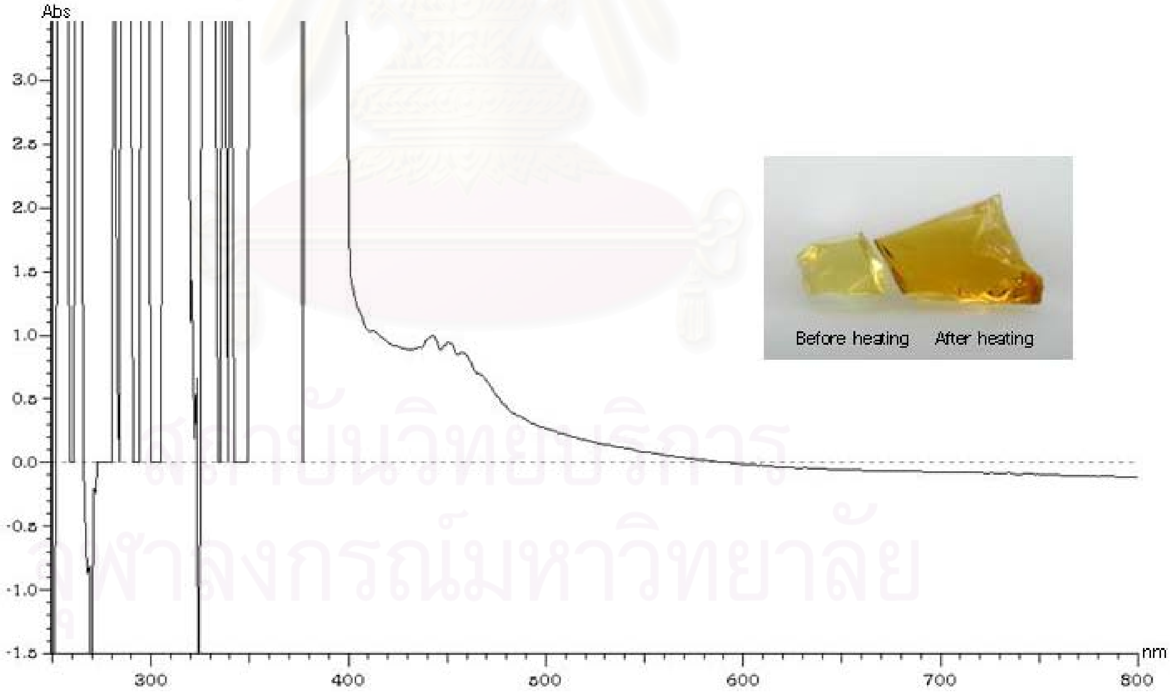


Figure 6.3 Residue UV-Vis spectrum of the sample YCH1 obtained by subtracting the absorption spectrum taken before experiment from the one taken after heat treatment in Fig. 6.2.

The sample YCH1 was also measured for the important trace element concentration at six points across a polished surface by LA-ICP-MS technique (Figures 6.4 and 6.5 and Table 6.3). As shown in those figures and table, all the points analysed show rather high Fe contents (~2700- 2900 atom mole ppm) and the excess contents of Mg over Ti (~8 atom mole ppm).

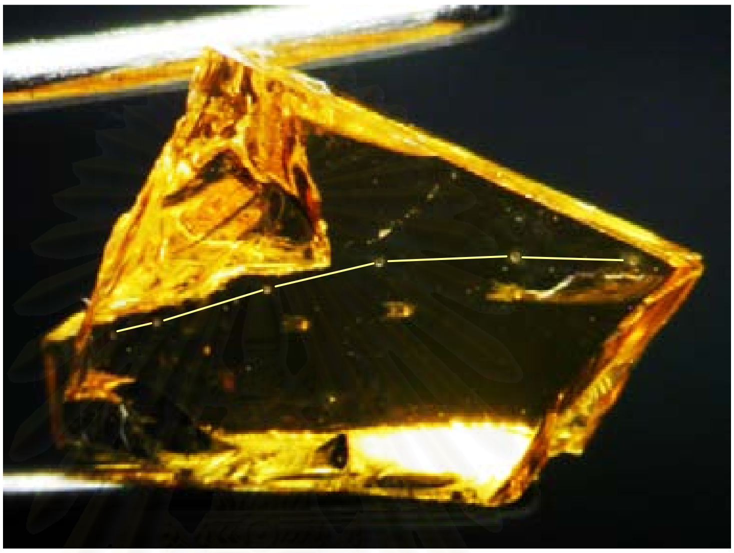


Figure 6.4 Close-up view of the polished surface of the sample YCH1 showing the approximate locations of the six point analyses from left to right by LA-ICP-MS.

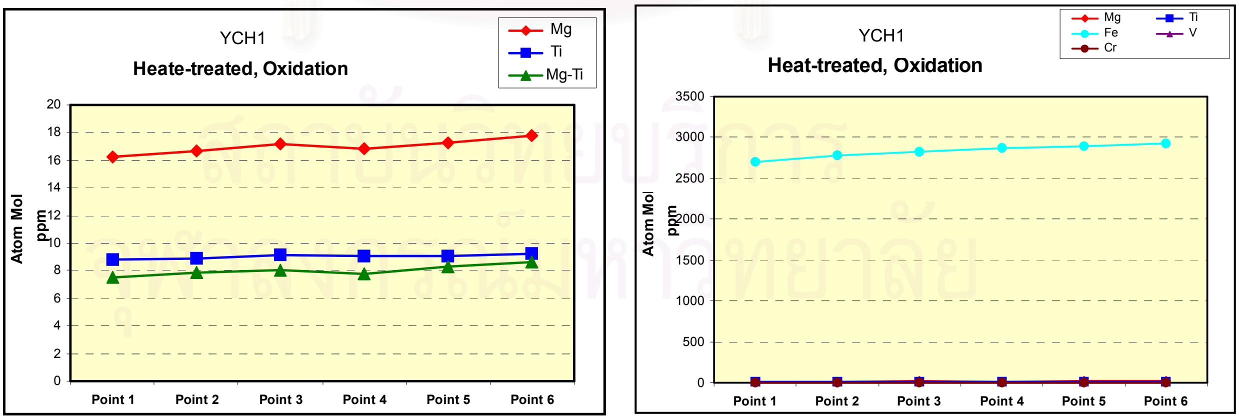


Figure 6.5 Plots of trace element contents at the points where the analyses were taken on the sample YCH1 shown in Figure 6.4. The analyses show rather high Fe contents and some excess contents of Mg over Ti in all the points analysed.

Table 6.3 Trace element contents of the yellow sapphires from Chanthaburi: YCH1, obtained by LA-ICP-MS

	Point 1	**Point 2**	**Point 3**	**Point 4**	**Point 5**	**Point 6**
Cations (ppm by weight)						
Be	<0.19	<0.21	<0.25	<0.25	<0.27	<0.22
Na	<1.51	<1.83	<1.98	<1.87	<2.02	<1.68
Mg	19.54	20.04	20.60	20.18	20.78	21.39
Al	529250.44	529250.44	529250.38	529250.44	529250.44	529250.44
Ti	20.78	20.97	21.57	21.38	21.38	21.80
V	1.29	1.27	1.25	1.28	1.31	1.37
Cr	0.00	2.33	1.08	0.00	0.00	0.00
Mn	1.06	1.07	1.60	1.17	1.28	1.20
Fe	7434.45	7668.98	7801.47	7924.47	7987.12	8065.40
Ga	130.70	134.81	136.76	136.85	137.36	132.56
Total %	53.69	53.71	53.72	53.74	53.74	53.75
Cations (Atom Mole ppm)						
Be	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00
Mg	16.28	16.69	17.16	16.81	17.30	17.81
Al	397240.44	397153.43	397104.77	397061.48	397038.25	397010.80
Ti	8.79	8.86	9.12	9.03	9.03	9.21
V	0.51	0.50	0.50	0.51	0.52	0.54
Cr	0.00	0.91	0.42	0.00	0.00	0.00
Mn	0.39	0.40	0.59	0.43	0.47	0.44
Fe	2695.63	2780.06	2827.74	2872.01	2894.54	2922.71
Ga	37.96	39.15	39.71	39.73	39.88	38.48
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00	40.00
Mg-Ti	7.50	7.83	8.04	7.77	8.27	8.60
Mg%	0.60	0.59	0.60	0.58	0.59	0.60
Ti %	0.32	0.32	0.32	0.31	0.31	0.31
Fe%	99.08	99.09	99.08	99.11	99.10	99.08

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

6.3 Experiments on the sample YCH2

Similar results were also obtained from the experiments on the sample YCH2. The sample had turned from pale yellow before treatment (not shown here) into brownish yellow (Figure 6.6) after heating at high temperature reportedly treated under the same condition as the sample YCH1. The brownish yellow coloration after treatment was stable after fading test. The UV-Vis absorption spectra of the sample YCH2 measured before and after heating are displayed in Figure 6.7. As seen in the figure, both spectra show strong absorption due to Fe^{3+} at 450 nm and the spectrum after treatment shows a continuously elevated absorption towards the shorter wavelengths. The residue spectrum shows a continuous increase in absorption towards the UV part of the spectrum with a negative peak at around 450 nm. The negative peak at 450 nm was probably due to the measurement error rather than a real peak. This is because the experiment was undertaken in the oxidizing condition which should increase the Fe^{3+} absorption at 450 nm rather than decreasing.

Figure 6.6 Comparison of the colour of sample YCH2 before treatment (left) with that (right) after heat treatment at high temperature in an oxidizing condition

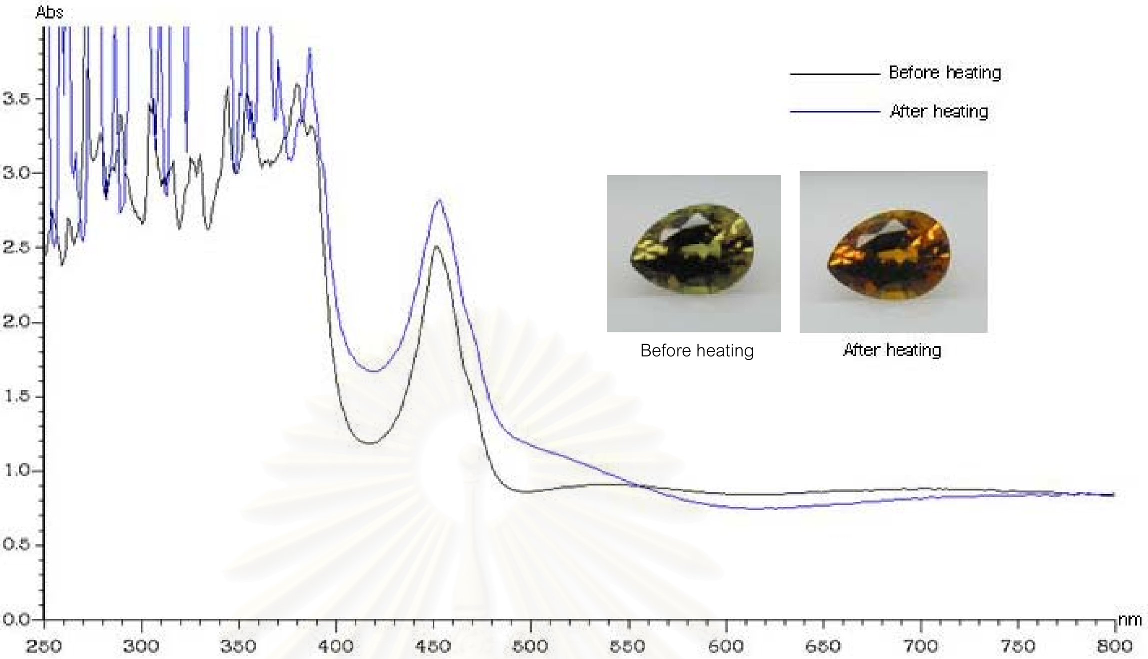


Figure 6.7 UV-Vis spectra (o-ray) of sample YCH2 recorded before and after heating experiment reportedly at high temperature in the oxidizing condition

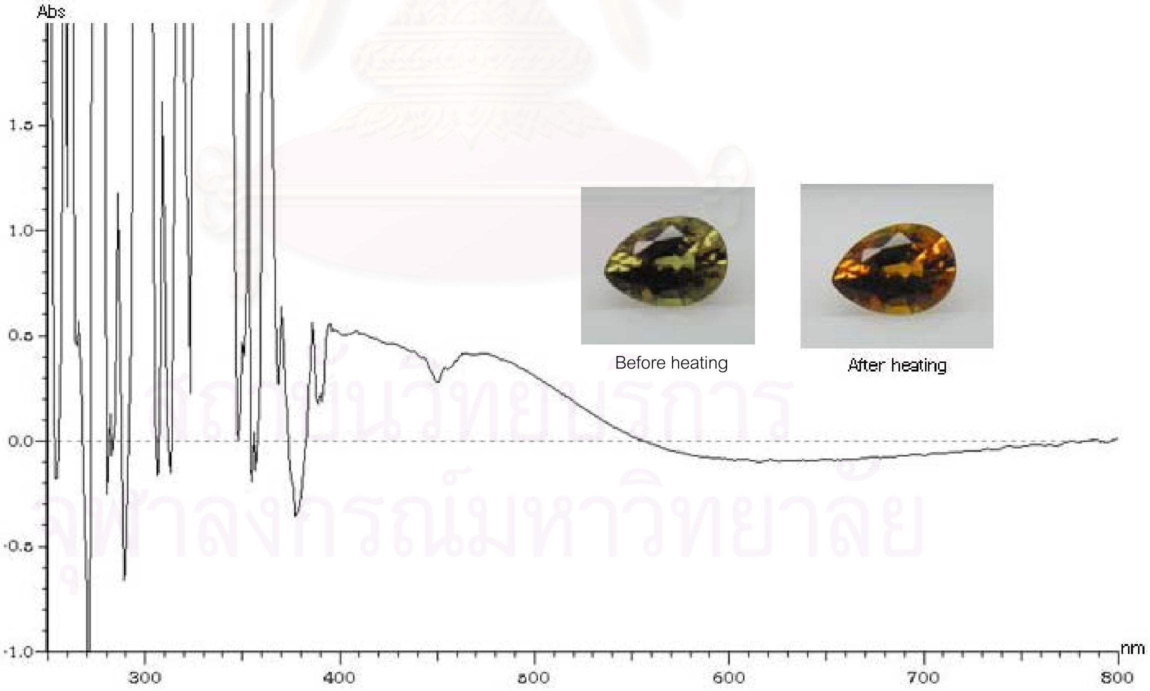


Figure 6.8 Residue UV-Vis spectrum of the sample YCH2 obtained by subtracting the absorption spectrum taken before experiment from the one taken after heat treatment in Figure 6.5.

The important trace element concentrations analysed by LA-ICP-MS technique at five points across the table facets of the sample YCH1 are shown in Figures 6.9 and 6.10 and Table 6.4. All the points analysed show rather high Fe contents (∼3100-3300 atom mole ppm) and the excess contents of Mg over Ti (∼9 atom mole ppm).

Figure 6.9 Close-up view of the sample YCH2 showing the approximate locations of the five point analyses from left to right by LA-ICP-MS.

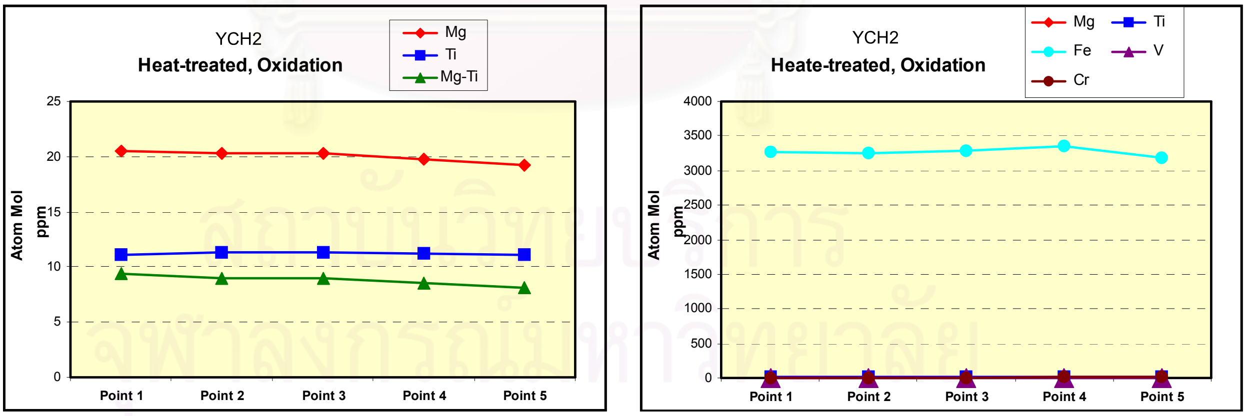


Figure 6.10 Plots of trace element contents at the points where the analyses were taken on the sample YCH2 shown in Figure 6.9. The analyses show rather high Fe contents and some excess contents of Mg over Ti in all the points analysed.

Table 6.4 Trace element contents of the yellow sapphires from Chantaburi: YCH2, obtained by LA-ICP-MS

YCH2	**Point 1**	**Point 2**	**Point 3**	**Point 4**	**Point 5**
Cations (ppm by weight)					
Be	<0.20	<0.21	<0.15	<0.17	<0.16
Na	<1.33	<1.28	<0.93	1.48	<0.91
Mg	24.65	24.38	24.37	23.81	23.12
Al	529250.31	529250.31	529250.31	529250.31	529250.31
Ti	26.33	26.73	26.74	26.57	26.38
V	2.28	2.30	2.32	2.42	2.46
Cr	15.10	16.97	15.03	39.90	23.67
Mn	1.15	1.17	1.14	1.11	1.05
Fe	9006.14	8964.56	9086.20	9263.64	8777.32
Ga	139.37	140.10	135.08	138.73	134.56
Total %	53.85	53.84	53.85	53.87	53.82
Cations (Atom Mole ppm)					
Be	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	1.30	0.00
Mg	20.51	20.28	20.27	19.80	19.24
Al	396660.03	396674.06	396632.59	396557.48	396741.48
Ti	11.12	11.28	11.29	11.21	11.14
V	0.91	0.91	0.92	0.96	0.98
Cr	5.87	6.60	5.84	15.51	9.21
Mn	0.42	0.43	0.42	0.41	0.39
Fe	3260.73	3245.79	3289.49	3353.09	3178.54
Ga	37.66	40.52	35.73	37.37	37.19
Total (Atom Mole %)	40.00	40.00	40.00	40.00	40.00
Mg-Ti	9.39	9.00	8.99	8.59	8.10
Mg%	0.62	0.62	0.61	0.59	0.60
Ti %	0.34	0.34	0.34	0.33	0.35
Fe%	99.04	99.04	99.05	99.08	99.05

< = below the detection limit of which 0.00 value is used for calculation of atom mole ppm

6.4 Discussions

These two untreated sapphires of yellow variety are also from Bang Kracha area (or the high iron 'basaltic-type' sapphires). They were reportedly heat-treated at high temperature in an oxidizing atmosphere. The colour of the samples did change from pale yellow before treatment to brownish yellow after the heat treatment. The brownish yellow coloration after treatment was stable after a fading test. The UV-Vis absorption spectra measured before and after the treatment again show strong absorption peak due to Fe^{3+} at 450 nm and the spectrum after treatment shows a continuously elevated absorption towards the shorter wavelengths. The residue spectrum (obtained by subtraction of the absorption measured before treatment from that of after heating) shows a continuous increase in absorption towards the UV part of the spectrum with a small shoulder or hump at around 460 nm. This spectral pattern is similar to those observed in both untreated and heat-treated yellow metamorphic sapphires with low iron contents such as from Sri Lankan. This data therefore seems to suggest that the brownish yellow coloration induced by heat treatment of these 'basaltic' sapphires is mainly caused by defect centre in the corundum lattice or the so-called 'colour centres'.

The trace element concentration by LA-ICP-MS show rather higher Fe contents (two samples, ∼2700 to ∼3300 atom mole ppm Fe) and Mg > Ti contents (> ∼8 atom mole ppm) at all the points analysed across the polished surface. Again because of the high iron concentrations of these two basaltic sapphires, all the data points are clustered at the Fe apex in Mg-Ti-Fe diagram (Figure 6.11). However when the data points of these two yellow samples including those of the second group are plotted in Mg-Ti cross plot (Figure 6.12), the points of these two yellow samples are well above 1:1 line in contrast to those of the second group. Hence, these data reveal that the excess Mg in those two yellow samples is able to stabilize the yellow 'colour centres'. Therefore based on this preliminary result, the overall brownish yellow colour appearance after the heat-treatment of these 'basaltic' sapphires is mainly caused by the combination of Fe^{3+} spin forbidden transition and the 'stable colour centres' or the 'Mg-trapped hole colour centres'.

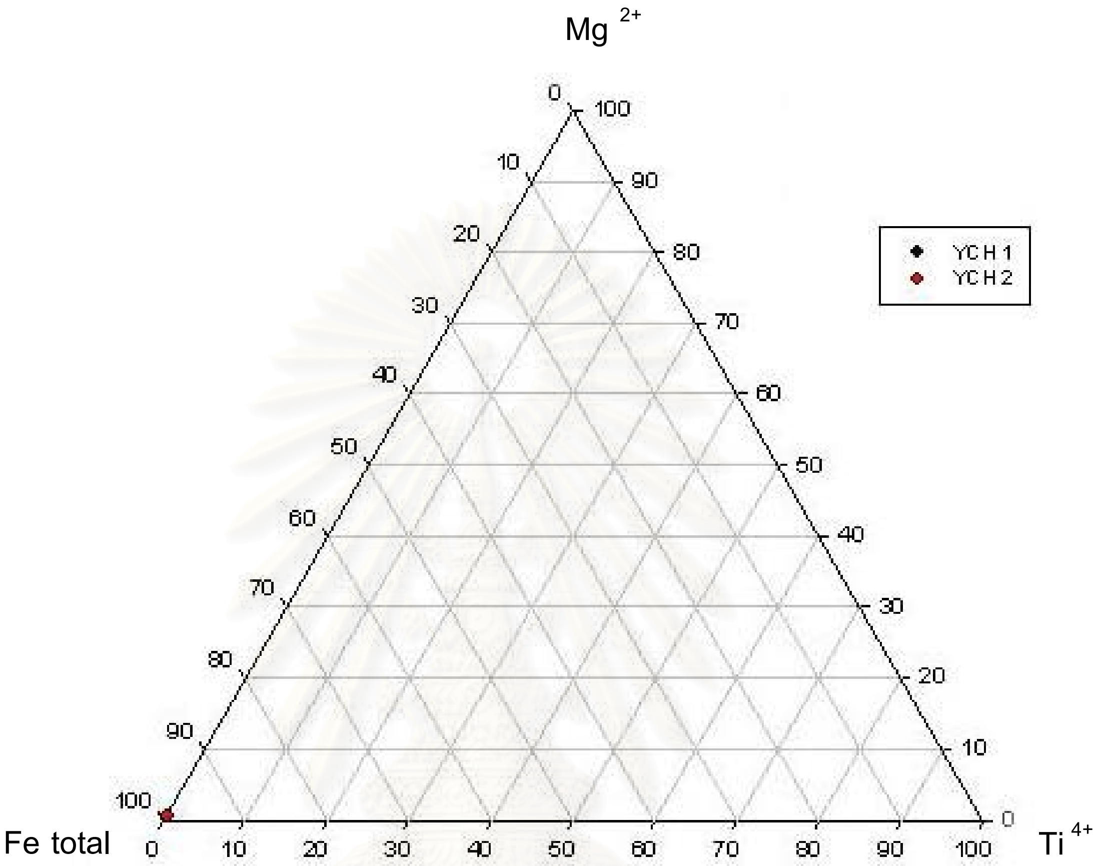


Figure 6.11 Triangular plot of all Group 3 (YCH1-2) data points of the high iron (basaltic-type) sapphires of greenish yellow to yellowish green variety from Bang Kracha area, Chanthaburi, Thailand.

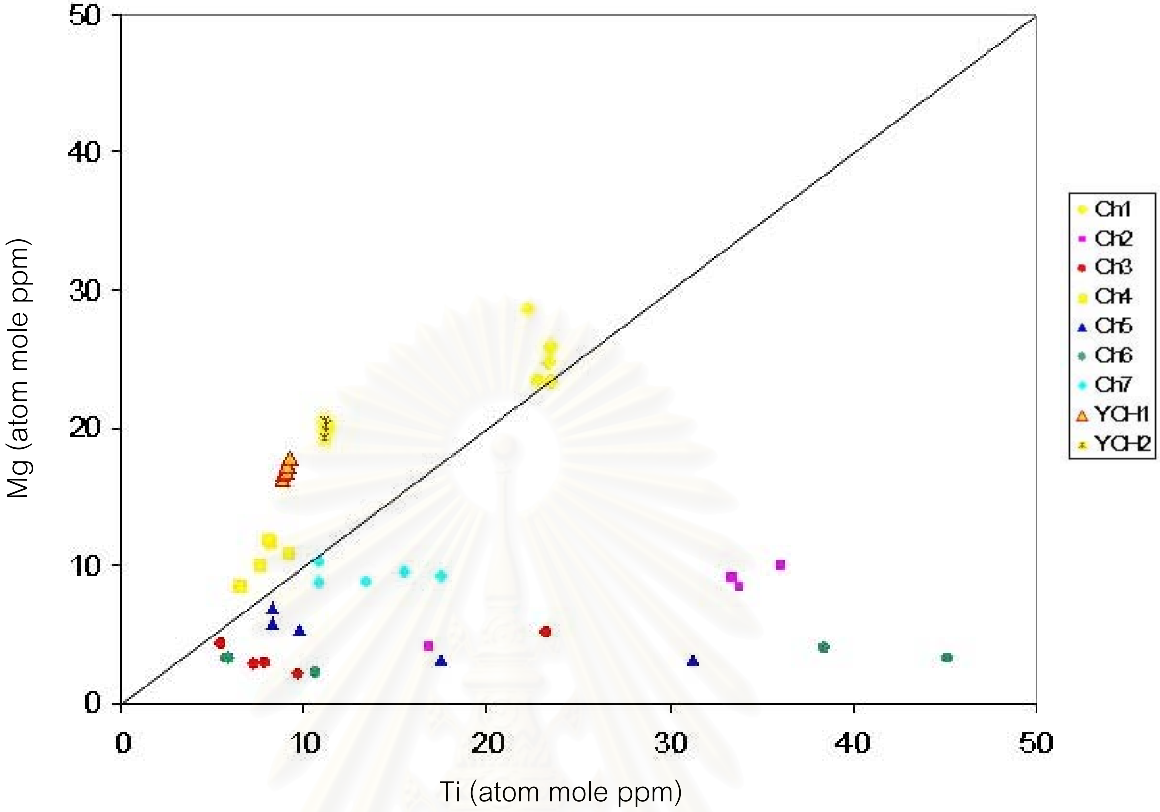


Figure 6.12 Mg-Ti cross plot of all Group 2 (CH1-7) and Group 3 (YCH1-2) data points of the high iron (basaltic-type) sapphires of greenish yellow to yellowish green and yellow varieties from Bang Kracha area, Chanthaburi, Thailand.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The experiments described from the chapters before on the three groups of yellow sapphire samples on the basis of their colour modification by heat treatment, UV-Vis-NIR spectra recorded before and after the treatment and the trace element contents, it can be concluded as follows:

1. In the first group of samples, the low iron (metamorphic-type) yellow sapphires, the yellow coloration created during the heating process is caused by defect centres which are stabilized by Mg in the Al_2O_3 structure or the so-called 'stable colour centres or Mg-trapped hole colour centres'. This yellow coloration is easily eliminated under a reducing heating.

2. In the second group of samples, the high iron (basaltic-type) sapphires of greenish yellow to yellowish green variety from Bang Kracha area, Chanthaburi, Thailand, all the samples do not have enough excess Mg to stabilize the yellow 'colour centres'. Hence the light yellow hues present in those high Fe samples are mainly due to Fe^{3+} spin forbidden transition. The green hue or blue zones or patches in those sapphires are the result of additional absorption bands due to Fe^{2+} - Ti^{4+} and Fe^{2+} - Fe^{3+} charge transfers.

3. In the third group of samples, the high iron (basaltic-type) sapphires of yellow variety from Bang Kracha area, Chanthaburi, Thailand, the brownish yellow coloration induced by heat treatment is mainly due to the defect centre in the corundum lattice or the so-called 'colour centres'. Hence the overall brownish yellow colour appearance of the samples after the heat treatment is mainly caused by the combination of Fe^{3+} spin forbidden transition and the 'stable colour centres' or the 'Mg-trapped hole colour centres'.

7.2 Recommendations for gem testing

The result form this study has provided us with a useful and applicable guideline for laboratory testing of yellow sapphires in the following manner.

1. After the study of the colour modification and UV-Vis-NIR spectra of yellow sapphires recorded before and after the heat treatment, it is possible to separate heat treated and unheated yellow sapphires by observing the characteristic of UV-Vis-NIR spectra. The heat-treated spectra tend to have a rather strong and continuous increase in the absorption toward shorter wavelength in particular those of the yellow sapphires undergone Be treatment as compared with those of the untreated ones.

2. The chemical data gained from this study can also provide as database in the laboratory for origin determination of the yellow sapphires from the basaltic-type sapphires of Chanthaburi, Thailand and from the metamorphic-type sapphires of Sri Lanka.

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