APPRAISAL OF HEAT TREATMENT OF *“GEUDA”* GEMSTONES USING GAS-FIRED AND ELECTRICALLY OPERATED FURNACE

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Thesis submitted in partial fulfilment of the requirements for the degree of Master of Philosophy in Gemmology

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Sri Lanka

February 2021

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Abstract

"Geuda" gemstones are less valuable corundum variety that has the potential to alter into blue sapphire. *"Geuda"* is found abundantly in Sri Lanka and it is translucent to opaque corundum with a milky or silky appearance in reflected light and brownish honey colour (or diesel colour) in transmitted light with a basic body colour of a bluish, yellowish or reddish colour. At present, Sri Lankan gem industry commonly adapts gas-fired furnaces for heat-treating *"Geuda"*, to obtain the desired blue colour, yet recently introduced electric furnaces have also shown potential. It is widely believed that electric furnaces are superior to gas furnaces in achieving the anticipated colour, yet no proper evaluation has been done in this regard. Thus, revealed the optimum conditions and the colouring mechanism for electric furnace heat treatment compare to gas furnace heat treatment, twenty (20) *"Geuda"* samples were selected and each stone is cut into three similar pieces to compare the colour changes more accurately. The *"Lakmini"* furnace was used as the gas furnace and the maximum chamber temperature used was 1750°C with a soaking time of 30 min under reducing environmental condition inside the gas furnace. Electric heat treatment carried out at three different temperatures (1300°C, 1500°C,1700°C) and with different soaking times (three days, five days, ten days and one month). Colour enhancement after heat treatment was observed using the GIA colour grading system. Samples were subjected to XRD, FTIR and UV-visible spectrum analysis before and after the heat treatments and XRF for the identification of elements present in the gemstones.

The optimum colour alteration occurred in combined heat treatment (1700°C in electrically operated furnace after gas furnace at 1750°C, 30 min). There was a significant peak height drop at 3309 cm^{-1} in FTIR spectroscopy after the thermal treatment in all samples tested. This peak height drop corresponded to O-H stretching mode water molecules inside *"Geuda"* stone and it was imperceptible with one month of soaking time. The UV-Visible analysis showed a peak development after heat treatments at 550 nm-650 nm. This is due to the development of blue colour inside the stone as a result of the formation of $[FeTi]^{+6}$ complex and it was conspicuous in combined heat treatment. d-spaces of the lattice structure in the *"Geuda"* stones have changed in the stones when analyzed using XRD. XRF analysis emphasized that the Fe:Ti ratio is a critical determiner of blue colour development with combine heat treatment. Geuda stones with a Fe:Ti ratio of 1:7 to 1: 13 produced the desired blue colour. Presence of increased Ti in the stone produced a dark blue colour. The results reported in this study suggest the method of heat treatment, Fe:Ti ratio of the stones and reduced environment inside the furnace are the critical determiners of blue colour development in geuda gemstones.

Key Words: “Geuda” Heat treatment, “Geuda”, Gemstone Enhancement, Gemstone Characterization

Acknowledgements

First, I would like to express my deepest gratitude to my supervisors, Prof. P.G.R Dharmaratne and Prof. K.B Wijesekara for their excellent support and guidance and also providing me with a conducive environment to complete my research successfully.

Special thanks go to the Dr. G. V. I. Samaradivakara (Head, Department of Earth Resources Engineering, University of Moratuwa), Prof. H. M. R. Premasiri (Former Head, Department of Earth Resources Engineering, University of Moratuwa), Prof. H.M.J.C. Pitawala (Former Head, Department of Science and Technology, Uva Wellassa University) and Dr. Preshan Francis (Former Director-General of the Gem and Jewelry Research and Training Institute) for providing me with the necessary analytical instruments to carry out my research work

I convey a special thanks for all the respondents who support and especially Mr. Punsiri Tennakoon, Mr. Vihanga Wijerathna and Mr. Chamith Kumarasinghe who supported me to conduct heat treatments using electrically operated furnace and. Miss. Chulodha Wickramarathna for providing some photos.

Finally, I would like to offer my heartiest gratitude to all the people whose names were not mentioned, yet were behind the success of this research.

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List of abbreviations

UN - Unheated

GH - Gas Heated

EH - Electrically operated furnace heated

CH - Combined Heated (Electrically operated furnace heated after gas heated)

XRF - X-ray Fluorescence

XRD - X-ray Diffraction

FTIR - Fourier-Transform Infrared Spectroscopy

UV-Visible Spectroscopy - Ultraviolet-Visible Spectroscopy

LPG - Liquid Petroleum Gas

GIA - Gemmological Institute of America

^{o}C - Celsius

nm - nanometre

Å - Angstrom

cm^{-1} - Per centimetre

B.C – before Christ

CHAPTER 01

1. INTRODUCTION

Sri Lankan history illustrates that gemstones were discovered on this charming island as early as 500 B.C. According to chronicle, the Aryans who travelled to Ceylon (old name for Sri Lanka) from an upper region of Bharat (old name of India) near to Himalaya found some precious colourful stones in the streams of this island. The erosion of the rocks resulted in elongated placer deposits laden with precious gemstones in the beds of the flowing streams in the valleys which were located in the lower altitudes. The traders set these attractive colourful stones in their rings and other forms of jewellery like bracelets and armlets frequently worn during those days. During their travels, they traded these stones in the different markets of Asia and Europe. In this manner, Sri Lankan gemstones reached new destinations in different parts of the globe. Marco Polo wrote that the island had the best, sapphires, topazes, amethysts, and other gems in the world.

Records from middle – eastern and Persian sailors who visited the island states that they brought back "Jewels of Serendib". Serendib was the ancient name given to Sri Lanka by middle – eastern and Persian traders that crossed the Indian Ocean to trade gems, ivory, spicy food from Sri Lanka to the East during the 4th and 5th century.

1.1 Statement of the problem

Sri Lanka encompasses thousands of gem pits. Gem mining has been practised for centuries in the island and most of the gemstones originate in Sri Lanka can be put into the corundum family. *"Geuda"* is one of the varieties of Corundum that is found in Sri Lanka abundantly and has a less marketable value because of the attractiveness of the *"Geuda"* stone not enough to stand with other gem varieties. Nevertheless, with the different types of treatments, these *"Geuda"* stones could be converted into sapphire varieties.

Modification of colour of gemstones by dying, oiling, and heating goes back to at least 2000 B.C. (Nassau, 1997). With the enhancements like lattice diffusion, surface diffusion, heat treatment and irradiation, identification of gemstones become tougher to even experienced gemmologists. Over the last few decades, quality enhancement methods for the *“Geuda”* were carried out using the heat treatment method. Gas furnaces and the electrically operated furnaces were used for the heat treatment process. However, studies on heat treatment with electric furnaces are seldom carried out due to less active engagement of educated professionals in this field and until very recently only a few Sri Lankans have endeavoured heat-treating using modern electrically operated furnaces.

Contemporary Sri Lankan gem dealers do the electric heat treatment for “*“Geuda”*” without any precise and appropriate knowledge of the underlying science of it. Thus, this study is to assess the *“Geuda”*, before and after electric heat treatment and establish the optimum temperature and soaking time for electric furnace heat treatment using chemical analysis as well as optical spectra analysis.

1.2 Research objectives

The main objective of this research is to assess the *“Geuda”*, before and after gas furnace heat, electrically operated furnace heat and combined (electric furnace after gas furnace) heat treatment to establish the optimum method of heat treatment, temperature and soaking time for colour alteration using chemical and optical spectra analysis.

The main objective is supported with the following secondary objectives;

- To identify the modern heat treatment techniques.
- To discover the chemical reactions, occur within the *“Geuda”* heat treatment.
- To discover the identification methods of the treated *“Geuda”*.

1.3 Significant of the study

Heat treatment of *“Geuda”* has become more prominent in Sri Lanka since late 1970 with enhanced knowledge to convert *“Geuda”* into premium blue colour sapphire (Rupasinghe et al., 1993). The gas furnace was the instrument used for the heat treatment and the recently identified instrument is electrically operated furnace. With compare to a gas furnace, electrically operated furnaces have produced more desired blue hues on the *“Geuda”* stones.

Only a few of Sri Lankan merchants use electrically operated furnaces for heat treatment as they believe it produces more profit for them compare with gas furnaces treated *"Geuda"* gemstones. Nevertheless, the time and cost for the electrically operated furnace are higher than the gas furnace and the outcome of this study will identify the most feasible method and conditions for the *"Geuda"* gemstone heat treatment that will uncover the knowledge gap of heat treatment using electrically operated furnaces.

CHAPTER 02

2. LITERATURE REVIEW

2.1 Gem minerals of Sri Lanka

Gemstones are defined by their colour, beauty, durability and rarity. Some of these factors should be satisfied for a mineral to be considered as a gemstone. From the earth’s greatest concentration of gems, about 75 varieties are found within the country’s land area (Dissanayake et al., 2000). Gem mining has been practised for centuries in Sri Lanka and nearly 25% of the landmass is gem bearing (Dissanayake et al., 1995). In the past, '*“Geuda”*' and 'Ottu' (kind of corundum) were not considered as gemstones in Sri Lanka. However, after introducing the heat treatment process for value addition, its market price has increased significantly. According to Gemstones Found in Sri Lanka, (2017), there are 10 main species of Gemstones found in Sri Lanka. They are as follows:

- Corundum
- Beryl
- Chrysoberyl
- Zircon
- Spinel
- Quartz
- Garnet
- Topaz
- Tourmaline
- Feldspar

Among them, Corundum is the most valuable stone among the Sri Lankan gemstones since it is considered as one of the precious gemstones in the world with a wide range of colours such as blue, red, green, yellow and some of the corundum varieties are rare like Padparadscha sapphire. According to Rupasinghe et al., (1993), “*“Geuda”*” consist of semi-transparent, whitish, or semi-brownish, milky or silky corundum with a characteristic ‘Diesel-effect’ (Colour of diesel fuel)/ white cloudiness, in transmitted light. *“Geuda”* can enhance the colour using different methods like Heat treatment, (Peiris, 1993).

2.2 Classification of *“Geuda”* gemstones

Gem dealers classify different varieties of *“Geuda”* based on the external characteristics. Because of the lack of scientific basis, the classification may differ from place to place. The following classification is based on (Rupasinghe et al., 1993).

Diesel *“Geuda”*:

Define because of its colour, further classified as “Young”, “Normal”, “Thick”, “Very Thick” depend on the degree of diesel appearance.

Milky *“Geuda”*:

This variety shows ‘milkiness’ appearance.

Silky *“Geuda”*:

In reflected light, this variety shows ‘silkiness’ appearance on the surface while in transmitted light shows ‘milkiness’ appearance.

Athul Ottu:

Irregular blue patches can be seen inside of the stone.

Pita Ottu:

Blue patches can be seen on the surface of the stone.

Dot Ottu:

Blue areas can be seen as points/dots inside the stone.

Iri Ottu:

In the Sinhala Language ‘Iri’ indicates lines or bands. The Iri Ottu consist of the blue band inside the stone.

Kalu Ottu:

Translucent areas can be seen inside the stone, under the powerful transmitted light those opaque areas show blue colour.

Dun *“Geuda”*:

In normal light shows a pale blue colour while under in water container, the smoky areas will appear to have a bluish tint.

Kowangu Pushparaga:

Clear in normal Light, Jelly-like consistency can be seen inside the stone if viewed at right angles using the strong light beam.

Ural Ottu:

A light blue colour normally while more bluish along the C-Axis of the stone

2.3 Definition of the colour of a gemstone

Definition of the colour of gemstones was one of the difficult tasks in the past days since the colour get change when it gets to the assortment with different other hues and this may produce a vast range of colures for given hue. Apart from that same colours may contain different shades (lightness or darkness) and on the other hand, the ambient lighting conditions directly affect to the identification of the colour, for an example, the colour that produces from the direct sunlight may differ from the colour that produces with the incandescent light.

When describing the colour of a gemstone, there are two concepts used in the gem industry (GIA, 2002), the colour range and the fine colour. Colour range is the assortment of colours in which a gemstone occurs. For an example peridot has a yellowish-green in colour and difficult to find other range of colours, while sapphire has a more diverse colour range like red, blue, green, yellow, violet, pink, orange. Fine colour is the colour or colours in a gemstone’s colour array that considered by the industry to be the utmost desirable. For instance, violet-blue to pure blue sapphires are generally considered as the highest valued sapphires compare with the greenish-blue hue sapphires.

2.4 Cause of colour in Blue Sapphire

Colour of blue in sapphire mainly due to the presence of Titanium (Ti) and Iron (Fe) (Ileperuma, 1993). The process of colouring is called as “Intervalence Charge Transfer”, which means the motion of an electron from one transition metal to other (Nassau, 2001).

According to Ileperuma, (1993), the above process absorbs some part of the white light energy and produce a blue colour. Furthermore, that research concludes with UV-visible spectra of the corundum. Absorption bands of 14500, 22200, 25800, 26600 produced upon dropping iron (III), absorption bands of 17880,14330 are due to charge transfer from iron (II) to titanium (III) and vice versa.

In the Al_2O_3 structure, aluminium can be replaced by both iron and titanium. Iron can be a present as Fe^{2+} or as Fe^{3+} and normally titanium is present as Ti^{4+}. If both Fe^{2+} and Ti^{4+} are located in an adjacent way, orbits of these irons overlap to each other since the distance between Fe^{2+} and Ti^{4+} are fairly small (2.65 Å). This configuration makes it possible for an electron to pass from one ion to the other.

By losing an electron Fe^{2+} converts to Fe^{3+} and by gaining an electron Ti^{4+} converts to Ti^{3+}.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$Ti^{4+} + e^- \rightarrow Ti^{3+}$$

By combining the equations

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

The energy of the right-hand side is higher than the left-hand side by 2.11 eV. The energy for the reaction absorbs by the white light and produce blue colour along the C-axis of the stone.

There is another arrangement that occurs perpendicular to the C-axis. In this arrangement, two atoms of Fe^{2+} and Ti^{4+} are further apart than earlier arrangement (2.79 Å). Due to that, the overlapping amount is less and energy difference also less than 2.11 eV. Resulting absorption spectra produce bluish-green dichroism of blue sapphire.

2.5 Different types of *"Geuda"* heat treatment methods

According to Ileperuma, (1993), the Melting point of Al_2O_3 is 2050°C. Nevertheless, with the impurities present in the corundum cause slight changes in the melting point. Thus, the temperature used for the heat treatment may vary within 1600°C –1800°C depending on the appearance/or impurities.

- **Enhancement of Blue Colour**

Presence of Fe^{3+} reduces the blue colour in the stone. Therefore, heat treatment under reducing environment convert Iron(III) into Iron(II) and the chemical reaction occur around the temperature of 1600°C.

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

- **Lightening of dark blue sapphire**

Due to a large amount of Iron(II) the stone can get the dark blue colour and under oxidizing environment, Iron(III) becomes Iron(II) oxide and hence light the blue colour present in the stone.

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

- **Development of Potential asterism**

An asterism is due to the presence of Titanium(IV) oxide as needles that six side edges of the crystal system. When the heat is about 1850°C, Titanium(IV) oxide dissolves inside the crystal and form Ti_2O_3.

$$4TiO_2 \rightarrow 2Ti_2O_3 + O_2$$

This Ti_2O_3 replace some Al_2O_3. With the slow rate of cooling Ti_2O_3 reconvert into TiO_2 and form rutile needles within the corundum to produce star effect.

- **Removal of Silk**

$$4TiO_2 \rightarrow 2Ti_2O_3 + O_2$$

The procedure is as same as the development of asterism and the difference is when cooled at fairly rapid rate, Ti_2O_3 may remain in the same form without reconverting into TiO_2.

2.5 Sri Lankan traditional methods and instruments of *"Geuda"* heat treatment

Sri Lanka is one of the famous countries for an abundance of *"Geuda"* gemstones and there are several types of *"Geuda"* varieties and their subcategories present in Sri Lanka (for an example Diesel *"Geuda"* could subdivide into young, normal thick, very thick depending on its appearance under transmitted light). Table 01 shows different types of *"Geuda"* varieties and their optimum temperatures and environmental conditions for blue colour enhancement.

Table 1: Optimum temperatures and soaking times for different kinds of "Geuda"

Type of *"Geuda"*	**Heating Temperature (^oC)**	**Condition**	**Colour after the heat treatment**
Ottu	1600 – 1650	Reducing	Blue
Dum *"Geuda"*	1600 – 1650		
Diesel *"Geuda"*	1750 – 1800		
Milky *"Geuda"*	1750 – 1800		
Silky *"Geuda"*	1800 – 1900		
Deguna Stones	1050 – 1500	Oxidizing	Red
Kowangu Pushparaga	1800 – 1900		Yellow

Source : (*"Geuda"* Heat Treatment, n.d.)

Sri Lanka gem traders had used various types of furnaces and instruments for the *"Geuda"* heat treatment from the latter part of 90s with the knowledge of heat treatment. In the past, furnaces were very simple in structure and with the advancement of research and development process, even programmable electric furnaces are available at present for *"Geuda"* heat treatment. As illustrated in Table 02, before the invention of "*"Lakmini"* gas furnace", Thai gas furnace, Toda Furnace and Condor furnace had been used in Sri Lankan gem industry (Munasinghe, 1993).

Table 2: Various types of furnaces

Type of Furnace	**Type of Fuel**	**Source of Thermal Energy**	**Maximum Temperature (^oC)**
Open-Flame	Gas	Gas + Air	1600 – 1700
		Oxygen + LPG	1700 – 1750+
		Oxygen + LPG + Air	1800 – 1850+
		Acetylene + Oxygen	2800 +
	Solid	Coke + Air	1000 – 1200

		Lignite + Air	1400 – 1600
		Charcoal + Air	900 – 100
	Liquid	Diesel + Air	1600 – 1700
		Diesel + Air + Oxygen	1750 – 1800+
Electric Resistance		Molybdenum Disilicide	1700
		Graphite	2250
Other		RF (radio frequency) Induction	1900+

Source: (Themelis, 1992)

2.5.1 Traditional methods and Instruments

Blow Pipe

Most conventional equipment for *"Geuda"* heat treatment is the blowpipe and it uses the injector principle. Although this method is one of the oldest methods of heat treatment, Sri Lankan traditional heat treaters still use this for various types of gemstones. The blowpipe is used to reduce the blue colour and blue related hue, which causes purplish tint in pink sapphires and rubies since blowpipe produces an oxidizing environment around the crucible. Moreover, it may be used to intensifying the weak yellow colour of Pushparaga sapphires into golden-yellow colour.

The instrument is very simple and consist of:

- A small metal or bamboo pipe about 2-3 feet in length and about 30 mm in diameter.
- A bowl made out of clay which has a diameter of about 30 cm.
- Another small shallow depth bowl with around 10 cm diameter.

The energy source of the blowpipe is usually charcoal. The large bowl and also small bowls are filled halfway with sand (SiO_2) and the rest with charcoal. In some areas Lime ($CaCO_3$) use as the filling material of bowls. Then, the gemstones are placed in the small bowl install on top of the larger bowl. The maximum temperature claimed about 900^{o}C and the treatment time varies according to the colour of the stone and the type of stone used (Table 03). Nevertheless, if the stone has more intensified blue overtone, the heat treatment process may require over two days without interruptions. In the conventional operation, one person (Fig. 01) or two (Fig. 02) need to provide the air to the furnace using a tube/ blowpipe. Nevertheless, there are some modified blowpipes with a mechanism to provide air without any interruption using a mechanical system nowadays (Fig. 03).

Table 3: Soaking time for different types of "Geuda" under Blowpipe

Variety	**Time**
Ottu	0.5 hrs
'Deguna' Stone	4-5 or 1-3 hrs
Zircon	15-10 Min
Green Tourmaline	1-3 hrs

Source : (Blow Pipe Heat Treatment, 2019)

Figure 1:operation of Blow Pipe with one person

Figure 2: Operation of the Blow Pipe with two people

Figure 3: Mechanical Blowpipe

Toda Furnace

Japanese made Toda furnace was used for the ceramic industry and laboratory thermo-chemical experiments in Japan. Sri Lankan Export Development Board imported Toda furnace to Sri Lanka in 1984 for the experiments of heat treatments of *"Geuda"* (Munasinghe, 1993).

The furnace uses oxygen and LPG as the fuel which can be controlled by a set of regulators to produces different temperatures and environmental conditions inside the furnace. Combination of oxygen and LPG and their different ratios adequate to produce about 1800°C temperature inside the furnace within two hours and a thermocouple is used to measure the temperature.

Toda furnace was very popular in Sri Lanka before the "*"Lakmini"*" furnace and used to heat treat every type of *"Geuda"* since it can change the atmospheric condition (Oxidizing and Reducing) by changing the oxygen to LPG ratio.

Condor Furnace

The most common type of furnace uses in Thailand and introduced to Sri Lanka in the late 90s and still been used by some of the gem traders due to its simple configuration and convenience of handling (Fig. 4). Diesel mixed with air or oxygen used as the fuel and a set of propellers that connected to a motor control the fuel and air volumes injection to the furnace. Two concrete blocks work as a shield from contamination from ambient air (Fig. 05).

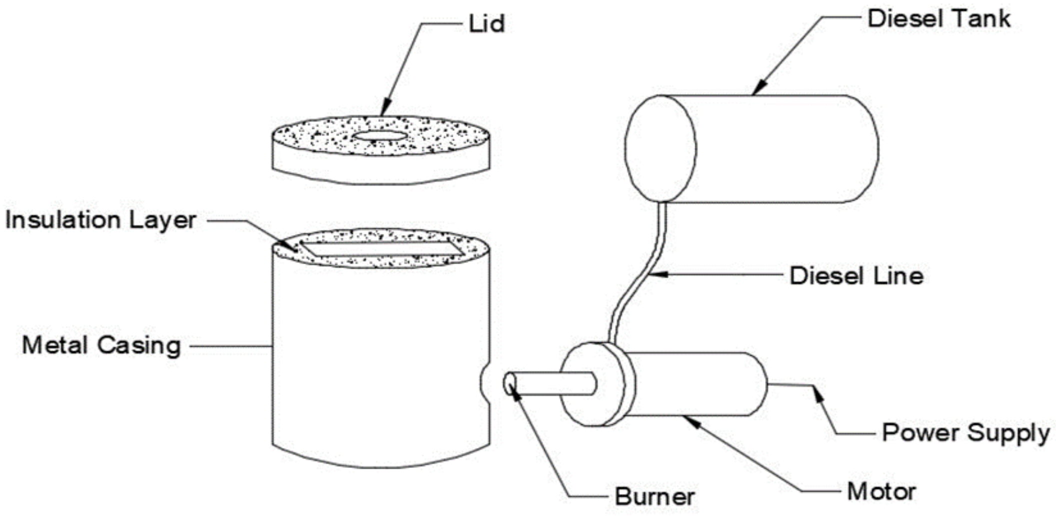


Figure 4: Structure of the Condor furnace

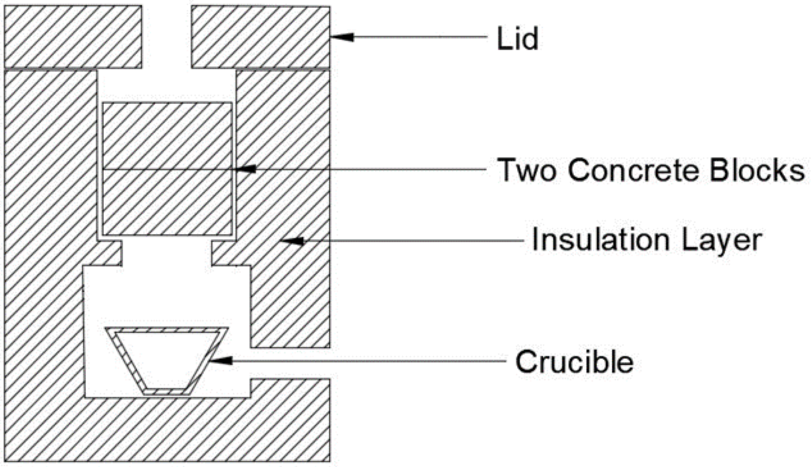


Figure 5: Cross-section of the Condor furnace

Measurement of the temperature inside the furnace is very difficult, as there is no inbuilt mechanism to do that and well-experienced people could identify the temperature inside the furnace by the looking at the colour of the flame. The fan inside the motor provides sufficient turbulence inside the burner to mix oxygen with diesel and oxygen to diesel ratio can change by using the lever near the motor (Fig. 06). The maximum temperature that can reach through the furnace is about 1700^{o}C.

Since crucible used in the condor furnace is comparatively small to the furnace, the manufacturer has made two concrete blocks to keep reducing conditions inside the furnace (Fig. 07).

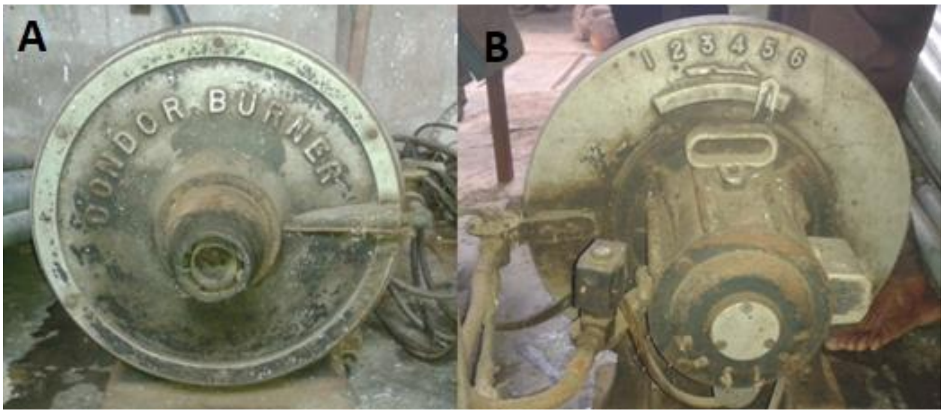


Figure 6: Front view (A) and Back view (B) of the Condor Burner

Figure 7: Top view of two concrete blocks (Condor Furnace)

"Lakmini" **Furnace**

Since Toda Furnace and Condor furnace has some downsides in terms of importing to Sri Lanka and they were not designed especially for gemstones heat treatments, Sri Lankan government together with universities, research institutes and private sector manufactured a gas furnace call '*"Lakmini"*' which can heat treat *"Geuda"* gemstones under high oxidizing and high reducing conditions (Fig. 08). *"Lakmini"* furnace manufactured by the Lanka Refractories Limited and is very similar to the Japanese

Toda furnace nevertheless, water-cooling dual burners is positioned in horizontally while in Toda furnace contain one vertically oriented water-cooling burner. Oxygen and LPG (Liquid Petroleum Gas) are the fuel for the *"Lakmini"* and with the proper combination of both gases can provide the temperature above 1800^{o}C within 2-3 hours.

Construction of the *"Lakmini"* Furnace

The *"Lakmini"* furnace consist of six main segments namely;

a. The cylindrical part that consists of the furnace chamber
b. Box-shaped base
c. Two Lids
d. Crucibles
e. Thermal couple for temperature measurement
f. Cooling system

The base consists of about 3 cm thickness water cooling layer and hollow metal part. The air trapped inside a hollow metal part act as an insulation layer hence prevents overheat of the basement. Water cooling system provides sufficient cooling power to the two burners. The burners consist of two-needle valves for LPG and Oxygen with the embedded cooling system.

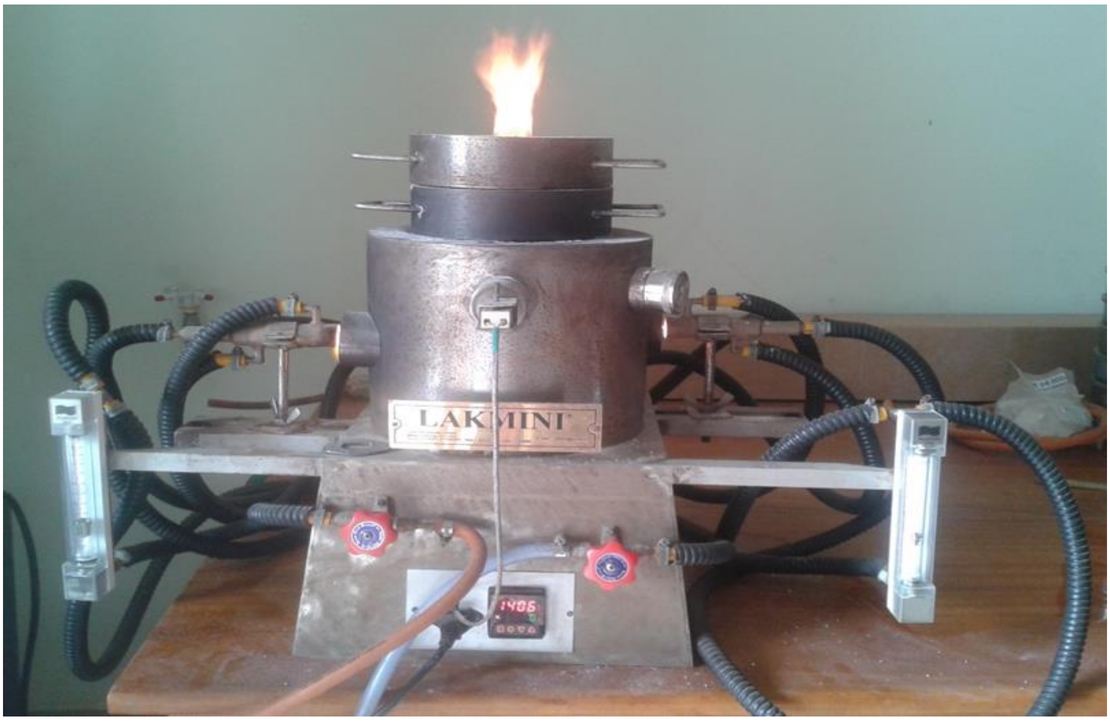


Figure 8: "Lakmini" furnace

Advantages and Limitation of the *"Lakmini"* Furnace

Although *"Lakmini"* furnace has the highest popularity among gem traders in Sri Lanka for the convenience of *"Geuda"* heat treatment, there are advantages as well as some drawbacks in the furnace. When considering the advantages, they can be listed out as follows:

- Durability is high since it constructed with durable metals and materials.
- Price is comparatively low in Sri Lanka compared with other imported gas furnaces.
- Could achieve oxidizing and reducing conditions with proper control of LPG and Oxygen.
- The maximum temperature is above 1800°C
- Heat loss is minimized due to 3-4 cm width insulation layer and that reduces fuel consumption in the long run.

The first and most affected drawback in the furnace is uneven temperature distribution in vertical profile inside the furnace (Fig. 09) and temperature measurement errors. Since burners located close to the bottom of the chamber the temperature at the uppermost parts has less temperature than we expected. If two or more crucibles are placed inside the furnace the non-uniform distribution of temperature effect more significantly and hence colour improvement may not occur precisely. Thermo-couple is located in the upper part of the furnace and it is mounted on the furnace wall. Because of its location, the temperature indicates in the display has a deviation from actual temperature inside the furnace.

The next issue occurs when trying to measure the flow rates in each flow meters as they are not calibrated for the oxygen and LP but for the normal air. According to Rupasinghe et al., (1993) if the oxygen flow meter shows 40 l/min, the actual value is about 36.5 l/min and for LPG, if the meter reading is 6 l/min, the real value is around 4.25 l/min.

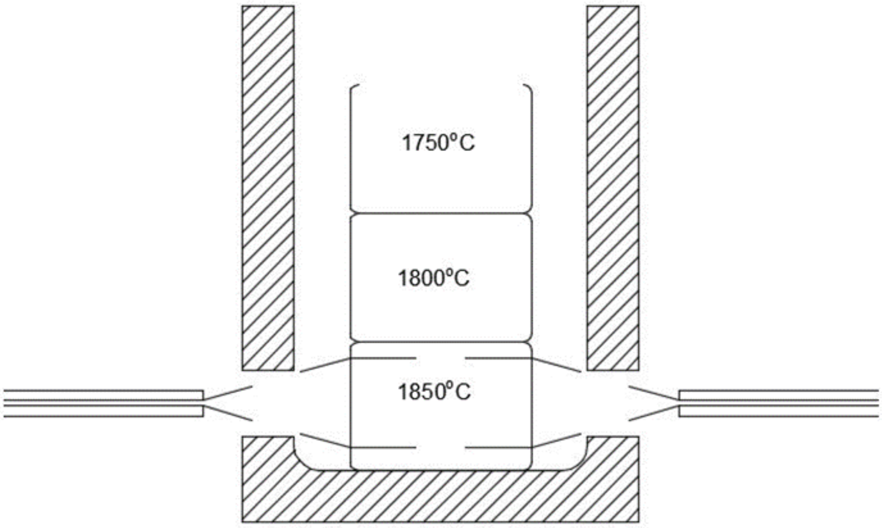


Figure 9: Illustration of temperature distribution in "Lakmini" Furnace

Electric resistance furnaces

Electric resistance or electrically operated furnaces has been used for gemstones heat treatment in various countries such as USA, Japan, Thailand and Germany and recently adopted to Sri Lanka for *"Geuda"* heat-treatment process. The main difference between the electrically operated furnaces is the electric resistance element. Table 04 shows the different types of heating elements and their operating temperatures. In the table, Kanthal denotes for iron-chromium-aluminium (FeCrAl) alloys used in the heating element.

Table 4: Different types of Electric Heating Elements

Type of element		Max Temp (^{o}C)	
		Element	Delivered
Graphite		3000	2850
Molybdenum Disilicate	- Kanthal Super 33	1800	1700
	- Kanthal Super 33+	1900	1800
Silicon Carbide		1550	1500
Nickel Chrome		1200	1150

Source: (Themelis, 1992)

Electrically operated furnaces generally consists of two integrated modules namely heating unit/chamber and control unit with power supply. The heating chamber consists of heat resistant fibre insulation or layer of clay in inner layer and galvanized steel in the outmost layer. Inner layer utilizes several heating elements, typically fitted through the furnace roof, and organized parallel to the side walls. There are two types of heating chambers box-type and tube type. In the box type chambers, crucibles can be introduced to the furnace through a properly fabricated door that fixed in a horizontal or vertical axis and these types of furnaces are common in the gem heat treatment. In any kind of electrically operated furnaces, an appropriate port has been installed for the thermocouple which provides the information about temperature inside the chamber.

Control model consists of a transformer and other necessary electronic equipment that facilitate a reliable temperature control with time. Most of the furnaces include digital meters and control switches to regulate the temperature and how the temperature would change with the time. The programming felicity may vary with the type and the manufacturer, it may perform a single loop and having a single deviation segment or it may feature multiple loops with deviation segments.

3. METHODOLOGY

3.1 Conceptualization and conceptual framework of the study

The study was based on an experimental research methodology and the main parameters of the study that affect the final result (colour and the clarity of the *"Geuda"* stone) were:

1. Type of the furnace
2. Soaking Time
3. Maximum Temperature
4. Chemical Nature of the *"Geuda"* Stone

There are two types of furnaces used in Sri Lanka for the *"Geuda"* heat treatment, The *"Lakmini"* furnace and the electrically operated furnace. The *"Lakmini"* furnace is gas operated furnace which is manufacture in Sri Lanka, especially for *"Geuda"* heat treatment. The maximum temperature that could be achieved with *"Lakmini"* furnace is about 1900^{o}C. There are various manufacturers for the electric furnaced and all electrically operated furnaces use the same basic principle to generate thermal energy inside the furnace. Lenton EHF 17/3 was selected as the electrically operated furnace in this research. Different temperatures and soaking times (soaking time refers to the time that keeps the maximum temperature constantly) were used to identify optimum conditions for electric furnace. X-Ray Fluorescence (XRF) used to determine the element composition of *Geuda* gemstones and Fourier-transform infrared (FTIR) and UV-Visible spectroscopy methods were used to identify spectral changes in the stone with the different heat treatments. X-ray powder diffraction (XRD) analysis was performed to identify the possible changes in crystallinity and lattice structure after heat treatment.

Based on the main factors affecting final colour alteration of the stone, the following hypothesis was made as to the conceptual framework given in Fig. 10.

H_0: Colour enhancement after heat treatment is not affected by the type of furnace used, temperature inside the heating chamber, soaking time and chemical nature of the Geuda gemstone.

H_1: There is a relationship between the type of the furnace and the optimum colour.

H_2: There is a relationship between the maximum temperature inside the heating chamber and optimum colour development.

H_3: There is a relationship between the soaking time and optimum colour

H_4: There is a combined effect from soaking time and maximum temperature used inside the heating chamber to the optimum colour

H_5: There is a combined effect from soaking time and type of furnace used to the optimum colour

H_6: There is a combined effect from the maximum temperature inside the heating chamber and type of the furnace used to the optimum colour

H_7: There is a combined effect from soaking time, maximum temperature inside the heating chamber and type of furnace used to the optimum colour

H_8: There is a relationship between the chemical nature of Geuda gemstone and optimum colour

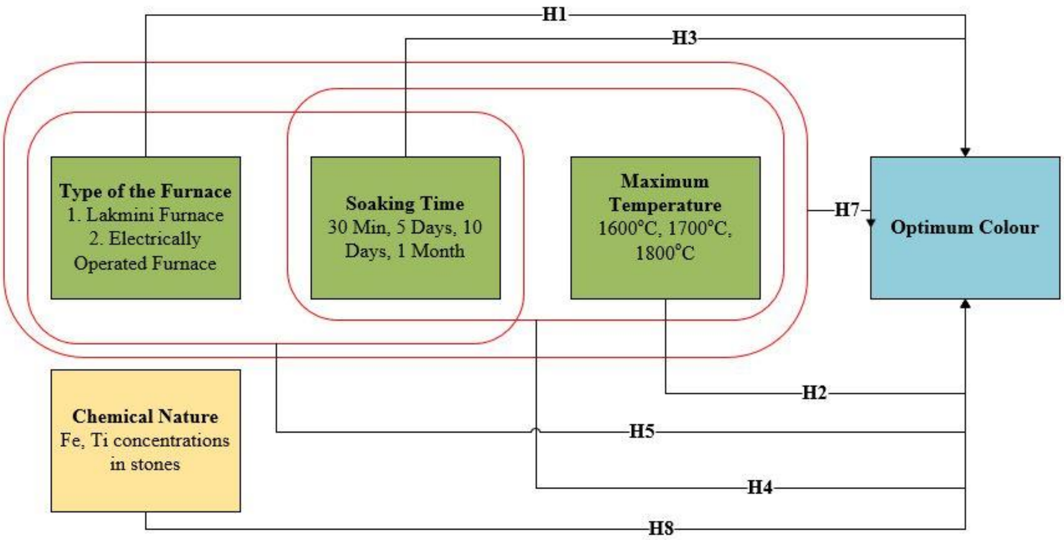


Figure 10: Conceptual Framework of the study

The flow diagram below (Fig. 11) illustrates the research methodology that followed to reach objectives while considering the hypothesis corroboration.

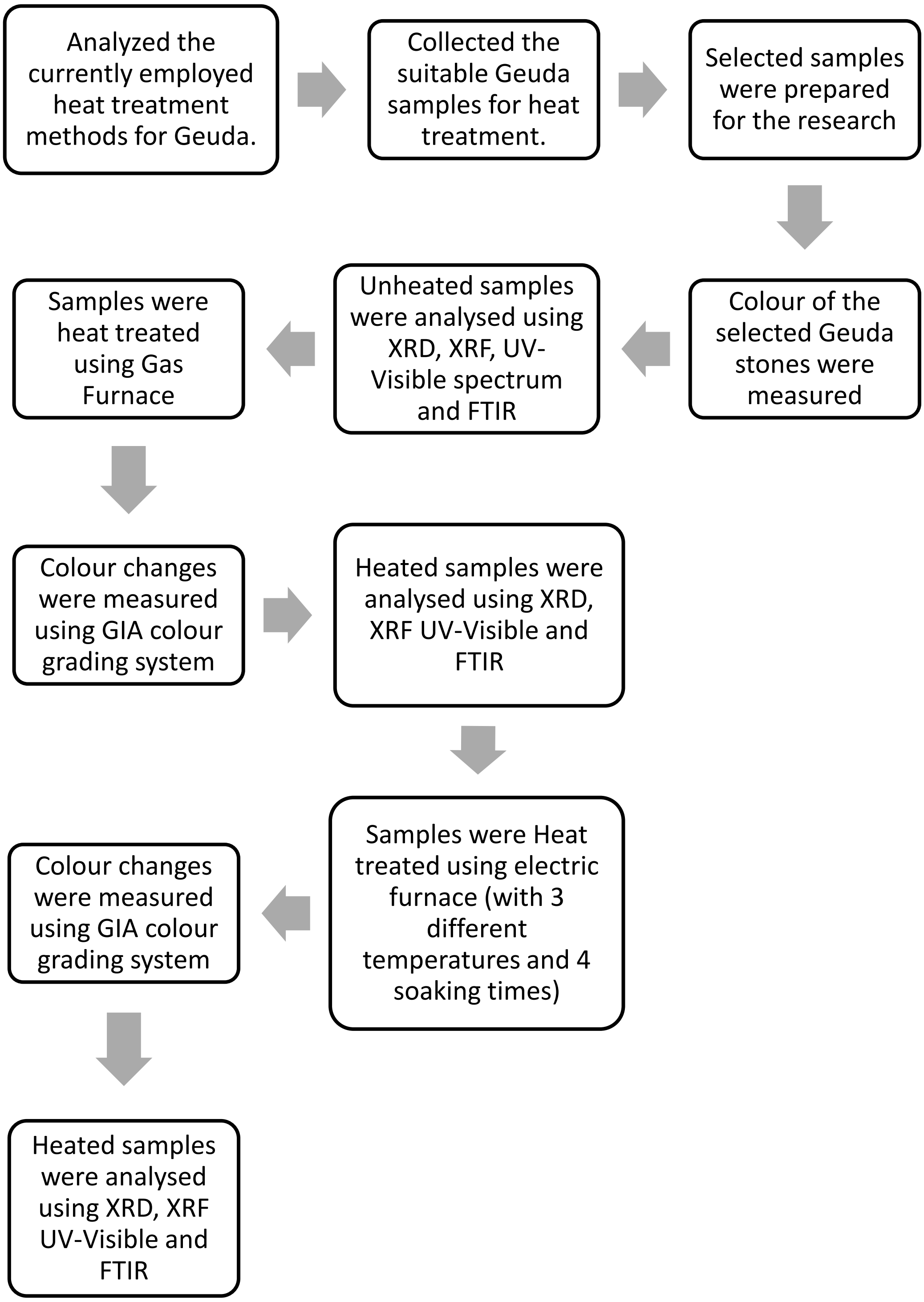


Figure 11: The schematic representation of the methodology adapted in the research.

3.2 Analysis of the currently available methods for heat treatment of *“Geuda”*

A detailed study was carried out on presently available heat treatment methods, commonly employed in Sri Lanka and other countries, where Geuda heat treatment is performed as a business.

3.3 Sample collection and preparation

Fourty Geuda gemstones were collected from gem markets of Ratnapura, Niwithigala, Lunugala and Ambalangoda of Sri Lanka. Next, samples that demonstrated typical "Diesel effect" (color of Diesel fuel) under transmitted light were separated. The stones ranged from 0.2 to 1.0 carats (ct), with most of the samples ranged between 0.5 to 1.0 ct. Chosen stones were then observed under the darkfield illumination of a gemological microscope (Kruss, KSW8000 model under 10x magnification) to remove stones with fractures and air bubbles that could adversely affect the subsequent heat treatment process. Sample stones were then randomized and assigned with the catalog number. After that samples were cut into three similar pieces.

3.5 Heat treatment of selected samples

One piece from each sample were subjected to a heat-treated using gas fired furnace (GF) “Lakmini” (Lanka Refractories Limited, Sri Lanka) at 1750^{O}C for 30 min. A reducing environment inside the furnace was maintained by balancing Liquid Petroleum Gas and oxygen supply to the furnace. After the second piece from each sample was subjected to heat treatment using an electrically operated furnace (EF) (Lenton, EHF 17/3, Carbolite Gero Limited, United Kingdom). EF Heat treatment was performed with three different temperatures and four different soaking times without purging or inserting gases. The third piece of each sample served as the unheated control.

3.6 Color Determination of heat-treated stones

Colour development in the heat-treated stones were determined with the aid of GIA colour grading system (Gemological Institute of America).

3.7 Analysis of unheated samples using XRD, XRF, UV- Visible spectrum and FTIR

- **Crystallinity and phase analysis using X-Ray Diffraction (XRD) Spectrum**

All samples were analysed using a Rigaku Ultima IV, XRD machine for identification of phase changes and d-space changes with 40 kV, 40 mA power, D/teX Ultra Detector and copper (Cu) target. Samples were mounted on the sample holder and scan rate was 3 degree per min. Full range 2θ values (0 – 90) were measured to identify the peak developments and their changes. Peak position, shape of the peak and peak intensity changes considered for the Crystallinity and phase analysis.

- **Chemical bond analysis using Furiour Tranceform Infared (FTIR) Spectrometer**

Bruker, ALPHA II was used for the FTIR analysis under scan rate of (signal to noise ratio) 64 with the wavelength resolution of 4 cm^{-1}. ATR (Attenuated Total Reflectance) method was used to identify the spectrum.

- **Absorbance spectrum changes analysis using UV- Visible Spectrophotometer**

Multiskan™ GO Microplate Spectrophotometer under absorbance mode was used for the analysis. Absorption spectrums were obtained for the range of 200 nm to 800 nm with 1 nm steps. Wavelength selection was monochromator with xenon flash lamp light source (Fig. 15).

- **Element analysis using X-Ray Florescence (XRF) Spectrometer**

Trace elemental analysis of heat treated Geuda gemstones was done using an Energy Dispersive X-Ray Fluorescence Spectroscopy (EDXRF) elemental analyzer (Rigaku NEX CG) (Fig. 12). Small gemstones were mounted on a custom-built sample holder and sealed with a 4 µm thick polypropylene film before measuring. Analytical settings of the EDXRF elemental analyzer are as given in table 01. Spectra derived from EDXRF procedures we generated data for the elements Al, Zr, Si, Cr, V, Fe, and Ti. Elements profile in each sample was given as a percentage (Wt.%). Multiple analysis of three randomly selected samples were performed to check the repeatability of trace element profile.

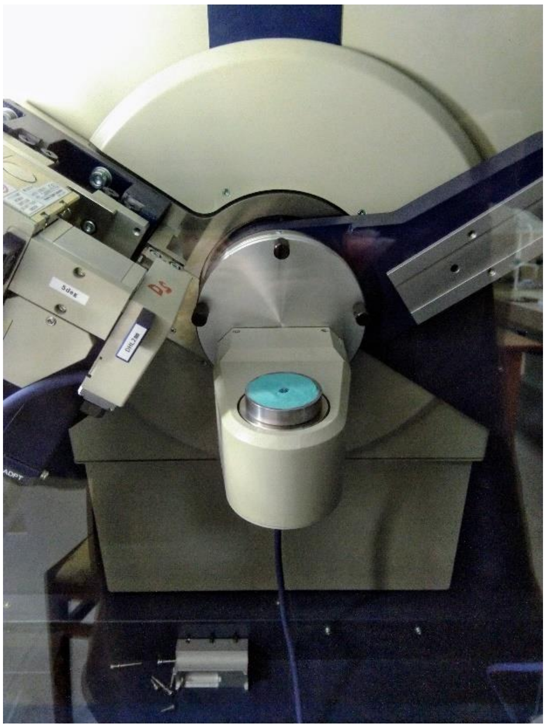


Figure 12: XRD analysis of "Geuda" gemstones:

3.8 Heat-treatment using a gas furnace

The foremost phase of the heat treatment is the heat treatment using a gas furnace. The extensively available gas furnace is "*"Lakmini"*" furnace. "*"Lakmini"*" gas furnace used under reducing environment (LPG: Oxygen =1:5) and maximum temperature of 1750^{o}C for the heat treatment. 18 *"Geuda"* samples were subjected to the gas heat treatment, Fig. 13 and Fig. 14 illustrate the oxygen and LPG (liquid petroleum gas) changes with the time.

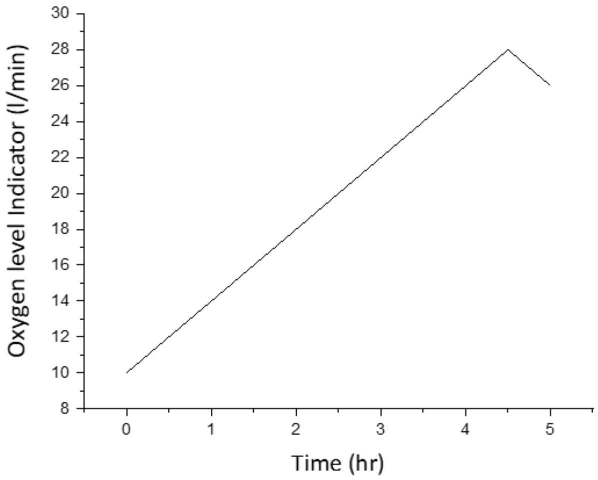


Figure 13: Oxygen variation with time

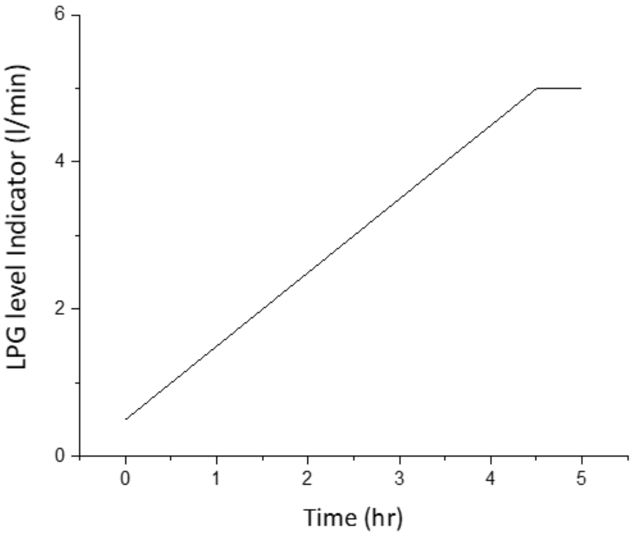


Figure 14: LPG variation with time

3.9 Measurement of colour changes

Measured the colour changes after the gas heat treatment using the same GIA colour grading system by comparing the given standard samples with the heat-treated specimens.

3.10 Analysis of the gas heated sample using XRD, UV-Visible and FTIR

The gas furnace heat-treated samples were subject to XRD, FTIR and UV-Visible spectroscopy analysis to observe the lattice structure changes, phase changes, bond formations, colour enhancement. Here XRF analysis ware not conducted since in the treatment process there was not any lattice diffusion or surface diffusion has occurred (did not provide foreign materials with heat treatment).

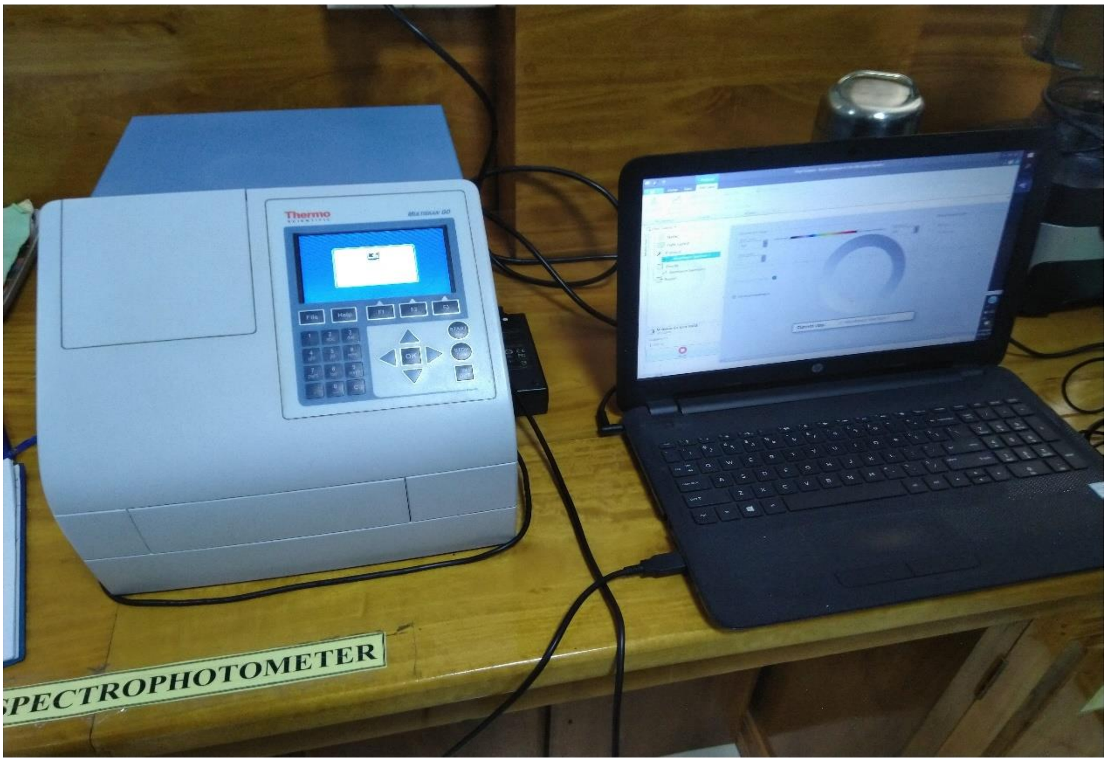


Figure 15: UV Visible spectrophotometer

3.11 Heat-treatment using electric furnace (3 different maximum temperatures and soaking times)

Lenton, EHF 17/3 (Carbolite Gero Limited, United Kingdom) was used as the electrically operated furnace since the Lenton elevator hearth furnaces (EHF) is suitable for operation in air or inert gas atmospheres with a maximum operating temperature of 1700°C. To obtain optimum temperature and soaking time for the heat treatment using an electrically operated furnace needed to observe the quality of the colour of stone while changing the temperature and soaking time. Thus, the maximum temperatures were selected as 1500°C, 1600°C and 1700°C respectively with soaking times of 3 days, 5 days and 1 month. One set was only electric heated while other gas heated set also subjected to electric furnace heat treatment to identify the differences between electric heat treatment and combined heat treatment (electric furnace heat treatment after gas furnace heat treatment) that practice in the industry.

3.12 Determination of colour after electrically operated furnace heat treatment

Colour changes of the stones after electrical furnace heat treatment was determined using GIA colour grading system (Fig. 16) and tabulated all the data (Table 07) and assigned a weighted average heading value (Table 06) based on colour and the clarity of the heated and unheated *"Geuda"* for the convenience of the analysis using Minitab 17 software.

Figure 16: GIA colour grading system

3.13 Analysis of the electrically heated samples using XRD, XRF UV-Visible and FTIR

The electrically operated furnace heat-treated samples also were subject to XRD, FTIR and UV-Visible spectroscopy analysis to observe the lattice structure changes, phase changes, bond formations, colour enhancement. Here also XRF analysis ware not conducted since in the treatment process there was not any lattice diffusion or surface diffusion has occurred (did not provide foreign materials with heat treatment).

3.14 Summary of the heat treatments

Twenty *"Geuda"* samples were subjected to the heat treatment process as follows. First, samples were heat-treated for three different temperatures (1300^{o}C, 1500^{o}C and

1700°C) with three different soaking times (3 days, 5 days, 1 month) for the sake of identification of optimum temperature as showed in Fig. 17. After that, 10 days of soaking time was applied for another two samples under 1700°C since 1700°C temperature *"Geuda"* has produced the desired blue colour alteration and using these data could identify the best soaking time for that temperature.

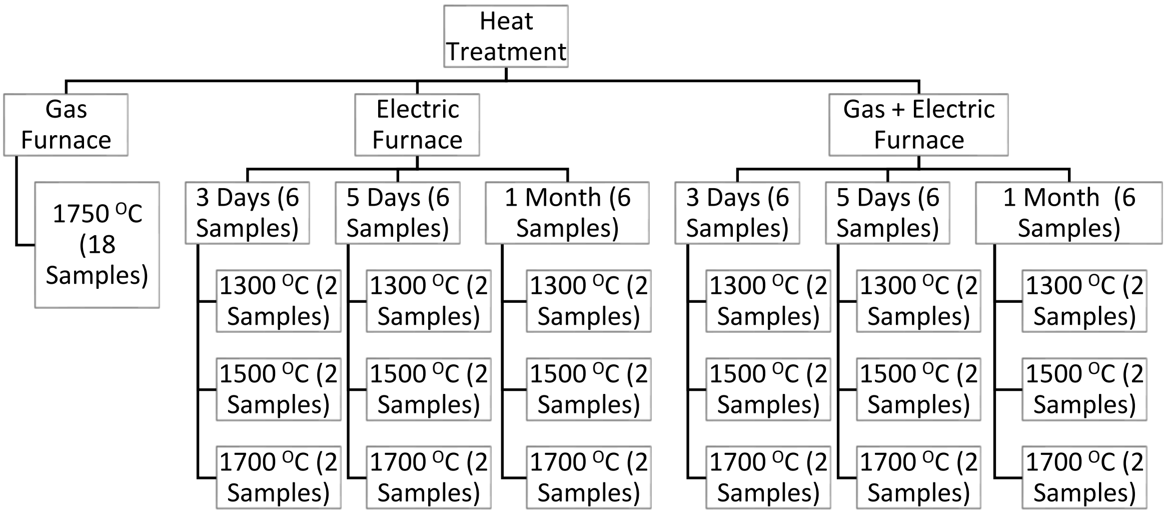


Figure 17: Heat treatment process

The research process went through the stages as follows

- Heat treatment experiments with the aid of gas furnace and electrically operated furnace.
- Chemical analysis using XRD and the XRF.
- Optical colour and clarity changes analysis using GIA colour grading tools.
- Statistical analysis based on GIA colour grading data.
- Spectral analysis using FTIR and UV-Visible spectroscopy.

CHAPTER 04

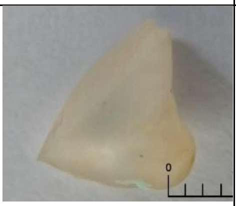
3 RESULTS AND DISCUSSION

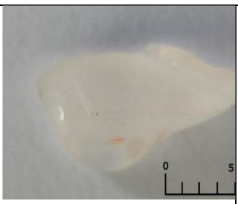
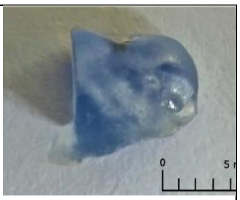
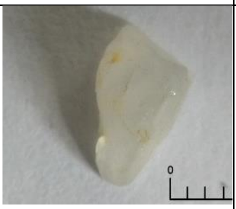
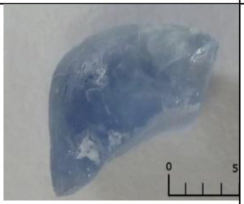
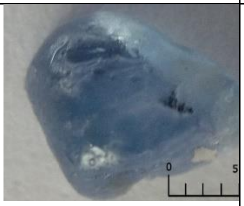
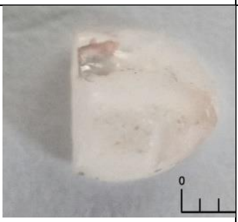
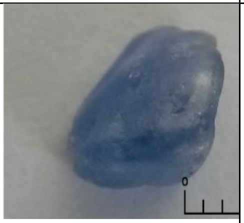
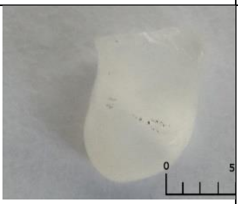
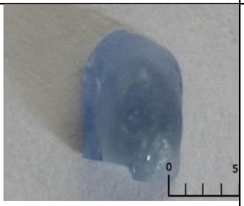
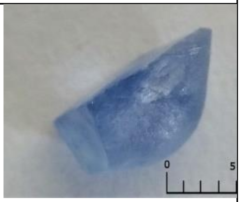
3.1 Heat treatment and colour changes

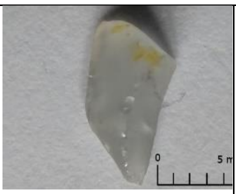
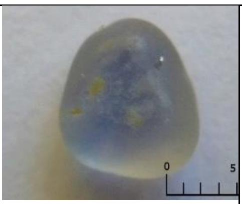
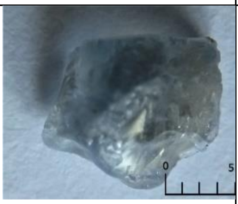
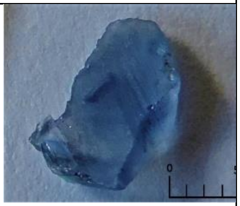
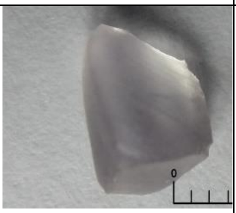
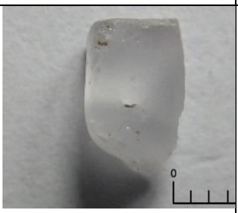
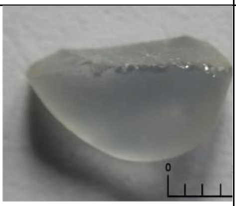
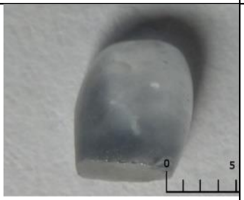
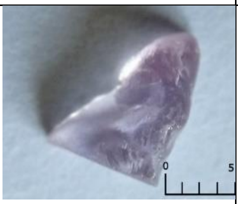
Heat Treatments were conducted under three different soaking times and three different temperatures as mentioned in methodology (Fig. 17). The observed colour alteration was tabulated in Table 05 with the aid of images. With the 3 days of soaking time in CH could not observe a significant difference. EH has not provided much colour improvement compare with GH and CH. When considering the CH, with the increase of soaking time intensity of colour alteration could be observed. Furthermore, with the maximum temperature increase, same behaviour could observe for CH. Apart from that, 1 month and 5 days with the maximum temperature of 1700^{o}C has produced similar like colour alteration in some gemstones (G_04 and G_16 in Table 05). Thus, as mentioned in methodology 10 days of soaking time was adopted for the 1700^{o}C to compare the colour alteration with soaking time at optimum temperature.

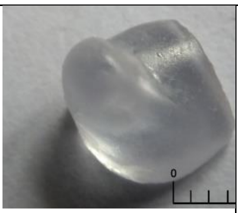
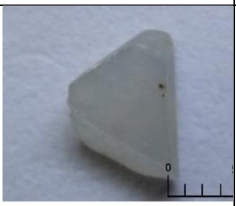
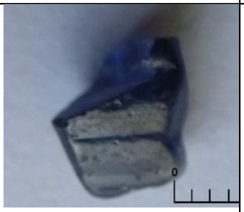
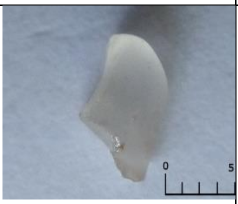
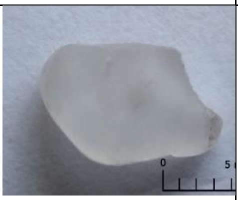
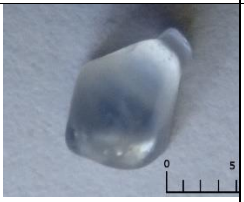
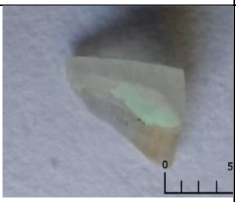
Since the visual observations are not reliable in analysis, the colour of all the samples (UH, GH, EH and CH) were measured using the GIA colour grading system (Table 07). GIA colour grading observations were converted into numerical values using the author defined ranking system (Table 06) based on grading values for the convenience of statistical analysis (Table 07).

Table 5: Colour alteration of "Geuda" samples with different temperature and soaking times

Sample No	Unheated	Electric heated	Gas heated	Combined Heated
G_01				
		1700 ^{o}C – 3 Days	1750^{o}C	1700 ^{o}C – 3 Days

G_02				
		1700 °C – 3 Days	1750°C	1700 °C – 3 Days
G_03				
		1700 °C – 5 Days	1750°C	1700 °C – 5 Days
G_04				
		1700 °C – 5 Days	1750°C	1700 °C – 5 Days
G_05				
		1500 °C – 3 Days	1750°C	1500 °C – 3 Days
G_06				
		1500 °C – 3 Days	1750°C	1500 °C – 3 Days

G_07				
		1500 °C – 5 Days	1750°C	1500 °C – 5 Days
G_08				
		1500 °C – 5 Days	1750°C	1500 °C – 5 Days
G_09				
		1300 °C – 3 Days	1750°C	1300 °C – 3 Days
G_10				
		1300 °C – 3 Days	1750°C	1300 °C – 3 Days
G_11				
		1300 °C – 5 Days	1750°C	1300 °C – 5 Days

G_12				
		1300 °C – 5 Days	1750°C	1300 °C – 5 Days
G_13				
		1700 °C – 1 Month	1750°C	1700 °C – 1 Month
G_14				
		1300 °C – 1 Month	1750°C	1300 °C – 1 Month
G_15				
		1300 °C – 1 Month	1750°C	1300 °C – 1 Month
G_16				

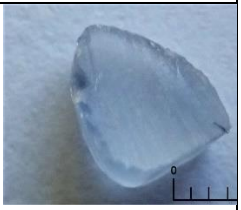
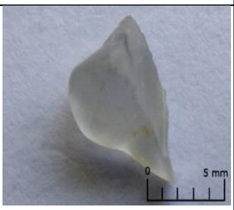
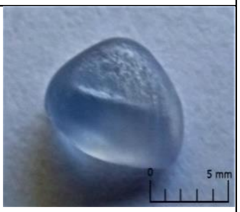
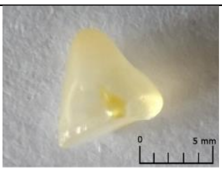
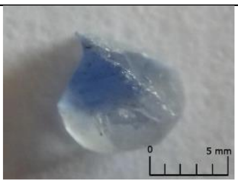
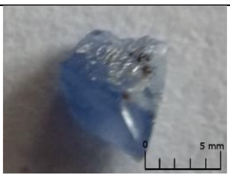
		1700 °C – 1 Month	1750°C	1700 °C – 1 Month
G_17				
		1500 °C – 1 Month	1750°C	1500 °C – 1 Month
G_18				
		1500 °C – 1 Month	1750°C	1500 °C – 1 Month
G_19				
			1750°C	1700 °C – 10 Days
G_20				
			1750°C	1700 °C – 10 Days

Table 6: Assigned a weighted average heading value for "Geuda" samples

Weighted Number	Meaning
1	No blue colour, No clarity
2	Little blue colour, Little clarity
3	Little blue colour, No clarity
4	Little or No blue colour, Good clarity
5	Moderate blue colour, Moderate clarity
6	Good blue colour, Moderate clarity

Table 7: Colour and clarity measurements of "Geuda" samples using GIA colour grading system

Sample No	**Sub Category (Instrument/ Method)**	**Max Temp (°C)**	**Soaking Time**	**Colour**	**Clarity**	**Weighted Colour (Quality)**
G_01	UH	-	-	B 3/1	vd-8	1
	GH	1750	30 min	B 4/6	m-5	5
	EH	1700	3 days	B 2/2	m-5	3
	GH+EH	1700	3 days	B 3/4	m-6	5
G_02	UH	-	-	B 3/1	md-6	1
	GH	1750	30 min	B 4/4	m-5	5
	EH	1700	3 days	B 4/2	ml-4	3
	GH+EH	1700	3 days	B 4/4	ml-4	5
G_03	UH	-	-	B 3/1	d-7	1
	GH	1750	30 min	B 7/2	ml-4	5
	EH	1700	1 week	B 3/3	ml-4	3
	GH+EH	1700	1 week	bV 5/4	ml-4	6
G_04	UH	-	-	B 3/1	vd-8	1

	GH	1750	30 min	bV 4/5	ml-4	5
	EH	1700	1 week	B 3/3	ml-4	4
	GH+EH	1700	1 week	bV 5/4	ml-4	5
G_05	UH	-	-	B 3/1	d-7	1
	GH	1750	30 min	bV 3/4	m-5	5
	EH	1500	3days	B 2/2	m-5	3
	GH+EH	1500	3days	B 5/3	I-3	5
G_06	UH	-	-	B 3/1	vd-8	1
	GH	1750	30 min	B 3/3	I-3	4
	EH	1500	3days	B 3/1	I-3	3
	GH+EH	1500	3days	VB 5/3	ml-4	5
G_07	UH	-	-	B 3/1	vd-8	1
	GH	1750	30 min	B 3/3	I-3	4
	EH	1500	1 week	B 3/1	I-3	3
	GH+EH	1500	1 week	B 3/3	ml-4	4
G_08	UH	-	-	B 3/1	d-7	1
	GH	1750	30 min	bV 3/3	I-3	4
	EH	1500	1 week	B 5/1	m-5	3
	GH+EH	1500	1 week	B 3/3	ml-4	5
G_09	UH	-	-	B 3/1	vd-8	1
	GH	1750	30 min	B 3/3	ml-4	4
	EH	1300	3 days	B 3/1	I-3	3
	GH+EH	1300	3 days	vb 4/3	ml-4	4
G_10	UH	-	-	B 3/1	d-7	1
	GH	1750	30 min	B 3/3	ml-4	3
	EH	1300	3 days	B 3/1	d-7	3
	GH+EH	1300	3 days	B 3/1	m-5	4
G_11	UH	-	-	V 3/2	ml-4	2

	GH	1750	30 min	bV 4/3	I-3	4
	EH	1300	1 week	V 3/2	I-3	3
	GH+EH	1300	1 week	bp 2/3	I-3	4
G_12	UH	-	-	B 3/1	vd-8	2
	GH	1750	30 min	bV 4/3	I-3	4
	EH	1300	1 week	V 3/1	I-3	3
	GH+EH	1300	1 week	bp 2/3	I-3	4
G_13	UH	-	-	B 3/2	md-6	2
	GH	1750	30 min	bV 5/5	md-6	4
	EH	1700	1 month	v 2/2	md-6	3
	GH+EH	1700	1 month	bV 6/4	md-6	5
G_14	UH	-	-	B 3/1	ml-4	1
	GH	1750	30 min	B 3/2	ml-4	3
	EH	1300	1 month	B 3/1	ml-4	3
	GH+EH	1300	1 month	vs/g B 2/2	vl-2	4
G_15	UH	-	-	B 3/1	ml-4	1
	GH	1750	30 min	B 3/1	ml-4	4
	EH	1300	1 month	B 3/1	ml-4	4
	GH+EH	1300	1 month	B 4/2	ml-4	4
G_16	UH	-	-	B 3/1	m-5	1
	GH	1750	30 min	B 4/4	ml-4	4
	EH	1700	1 month	B 2/2	ml-4	3
	GH+EH	1700	1 month	bv 6/5	ml-4	6
G_17	UH	-	-	Y 2/2	md-6	2
	GH	1750	30 min	B 3/2	ml-4	5
	EH	1500	1 month	B 3/1	m-5	4
	GH+EH	1500	1 month	B 4/4	ml-4	5

G_18	UH	-	-	B 3/1	ml-4	1
	GH	1750	30 min	B 3/2	I-3	4
	EH	1500	1 month	B 3/1	ml-4	4
	GH+EH	1500	1 month	vB 2/3	I-3	5
G_19	UH	-	-	B 3/1	m-5	1
	GH	1750	30 min	B 3/4	ml-4	5
	GH+EH	1700	10 Days	B 4/4	I-3	5
G_19	UH	-	-	B 3/1	ml-4	1
	GH	1750	30 min	vB 3/3	ml-4	4
	GH+EH	1700	10 Days	B 3/4	I-3	5

3.1.1 Statistical analysis of colour change

Changes of the colour were statistically analysed before the move to the other analysis to verify whether there is a significant difference in the method of heat treatment, maximum temperatures and soaking time for the development of colour. The Minitab 17 statistical software used to identify the relationships between variables as shown in Fig. 10. Table 09 and Table 10 illustrates the average weighted values of the colour (obtained from Table 07) variation with the temperature for electric heated and gas heated *"Geuda"* samples respectively. Fig. 18 and Fig. 19 shows the visual representation of Table 09 and Table 10 data.

When considering about Fig. 17, the colour development variation for electric heat treatment hasn't produced significant change over different temperatures. Furthermore, it appears like the one-month soaking time has enhanced the clarity of the stone compared with the other two cases. 1700^{o}C - five days of soaking time also produced the same average weighted colour development and as discussed in page 110 this may due to the chemical nature of the samples. In the combined heat treatment (Fig. 18) could observe a significant colour development with the maximum average colour grade of 5.5 for the 1700^{o}C, one month of soaking time. For 1700^{o}C - 5 days and 3 days have produced the same average colour development with a numerical value of 5. Apart from that 1300^{o}C has produced the least colour development with the average grade of 4.

Table 1: Average weighted colour variation with temperature for electric heat treatment for three soaking times

Soaking time	Temperature		
	1300^{o}C	1500^{o}C	1700^{o}C
3 Days	3	3	3
5 Days	3	3	3.5
1 Month	3.5	4	3.5

Table 2: Average weighted colour variation with temperature for combined heat treatment for three soaking times

Soaking time	Temperature		
	1300^{o}C	1500^{o}C	1700^{o}C
3 Days	4	5	5
5 Days	4	4.5	5.5
1 Month	4	5	5.5

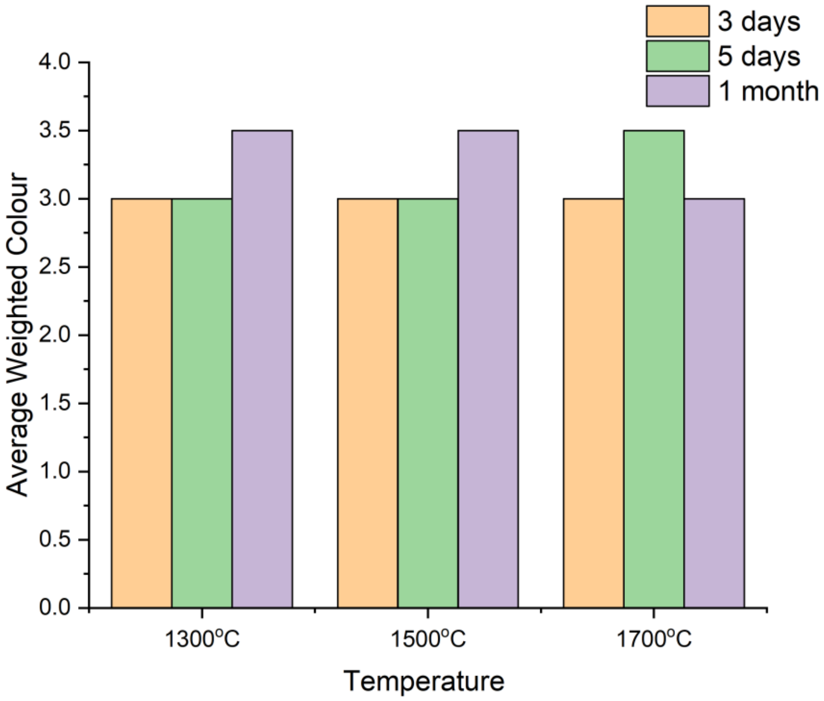


Figure 18: Average weighted colour changes of electrically heated "Geuda" gemstones

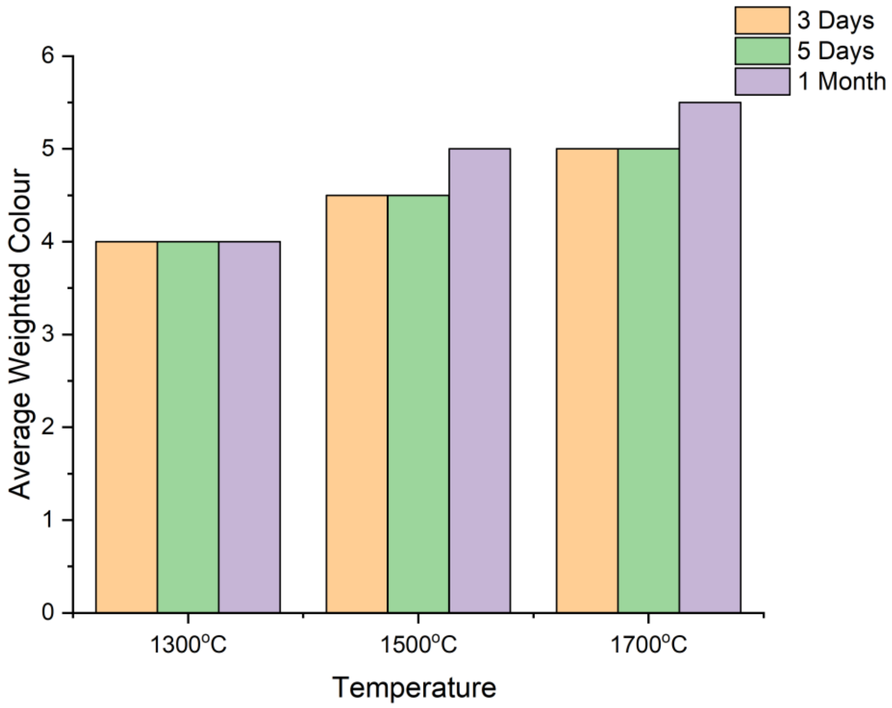


Figure 19: Average weighted colour combined heated "Geuda" gemstones

The changes in the average colour grading with the soaking time has also produced some observations. Table 10 and Table 11 demonstrate the colour value variation with the different soaking time and their graphical representations are illustrated in Fig. 19 and Fig. 20. For the electric heat treatment, average colour variation range occurred from 3 to 3.5 and thus can conclude that electric heat treatment couldn't produce the desired colour development and within the range, one month of soaking time has produced the best colour and clarity enhancement for electric heat treatment.

Table 3: Average weighted colour variation with soaking time for electric heat treatment for three temperatures

Temperature	Soaking time		
	3 Days	5 Days	1 Month
1300°C	3	3	3.5
1500°C	3	3	3.5
1700°C	3	3.5	3

Table 4: Average weighted colour variation with soaking time for combined heat treatment for three temperatures

Temperature	Soaking time		
	3 Days	5 Days	1 Month
1300°C	4	4	4
1500°C	4.5	4.5	5
1700°C	5	5	5.5

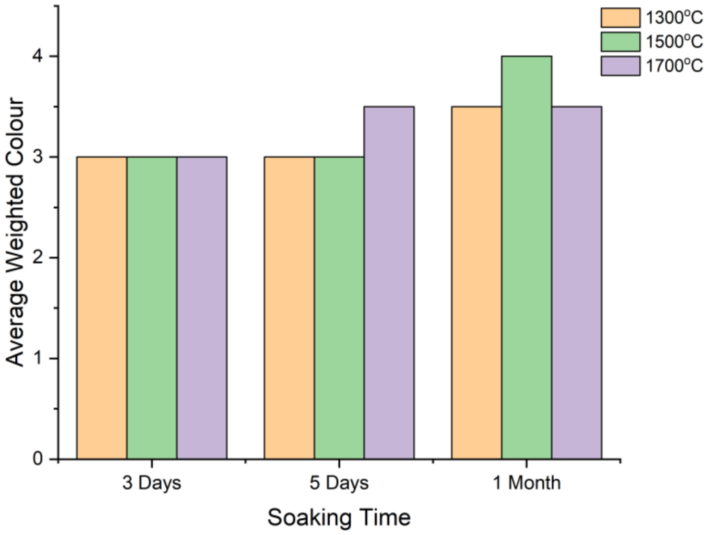


Figure 20: Average weighted colour distribution of combined heated stones for different soaking times and temperatures

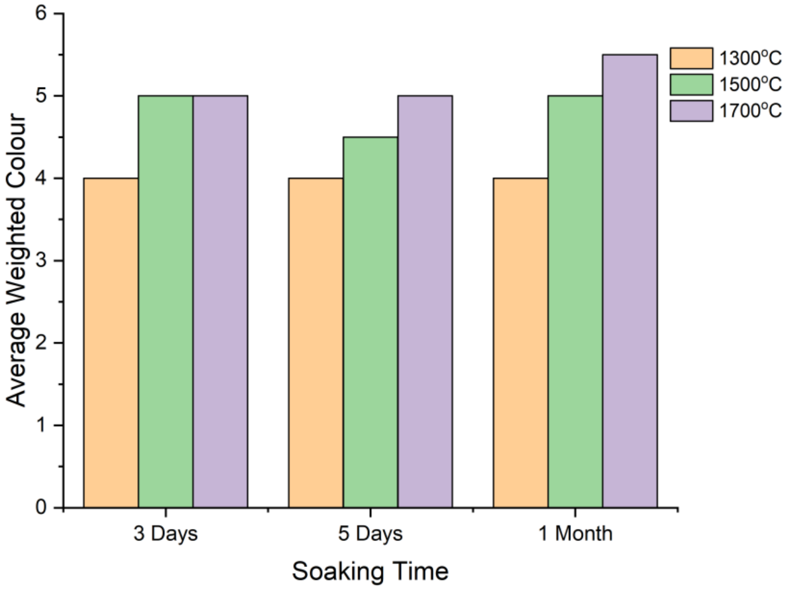


Figure 21: Average weighted colour distribution of electrically heated stones for different soaking times and temperatures

In addition to the above mention, average weighted colour value analysis data obtained from the GIA colour grading system, samples were analyzed using Minitab 17 software and following observations could obtain. First, all the weighted colour used for analysis using a general linear model to identify the relationship between weighted colour and the type of treatment and the following hypotheses were considered.

H0: There is no difference between treatments on weighted colour

H1: At least two treatments are different

Table 12 illustrate the calculated data of the 'Analysis of Variance' and Table 13 illustrates the model summary of the Analysis of Variance. In the Table, DF denotes the degrees of freedom of the population, Adj SS is the adjusted summation of the square, Adj MS is the mean sum of square values, F-Value is the ratio of MS and the MS error and P-Value is the probability value.

Table 5: Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	18	29.46	1.6369	5.91	0.000

Error	37	10.25	0.2770		
Total	55	39.71			

Table 6: Model Summary of Analysis of Variance

S	R-sq	R-sq(adj)	R-sq(pred)
0.526334	74.19%	61.63%	53.20%

Since P-value, less than .05 ((0.00) <0.05), with 95% of confidence can reject H0 hypothesis or at least two treatments are different at 0.05 level of significance. That means there is a difference between treatments and the final colour. In here treatments means the

- difference between gas heat treatment, electric heat treatment and combined heat treatment,
- difference combinations of temperatures for electric heat treatment and combined heat treatment
- difference combinations of soaking times for electric heat treatment and combined heat treatment.

Thus, the above analysis can conclude that the final colour get affected by the temperature, soaking time and the method of heat treatment as a combination. Fig. 22 shows the Residual Plots for weighted colour. In the Normal Probability Plot, it could be observed that all the data were normally distributed along the normalized line. Versus Fits and the Histogram provide an idea about mean values distribution and Verses Order gives information about error distribution pattern. With all these results, it could be concluded that analysis of variance could apply for the colour variation data set.

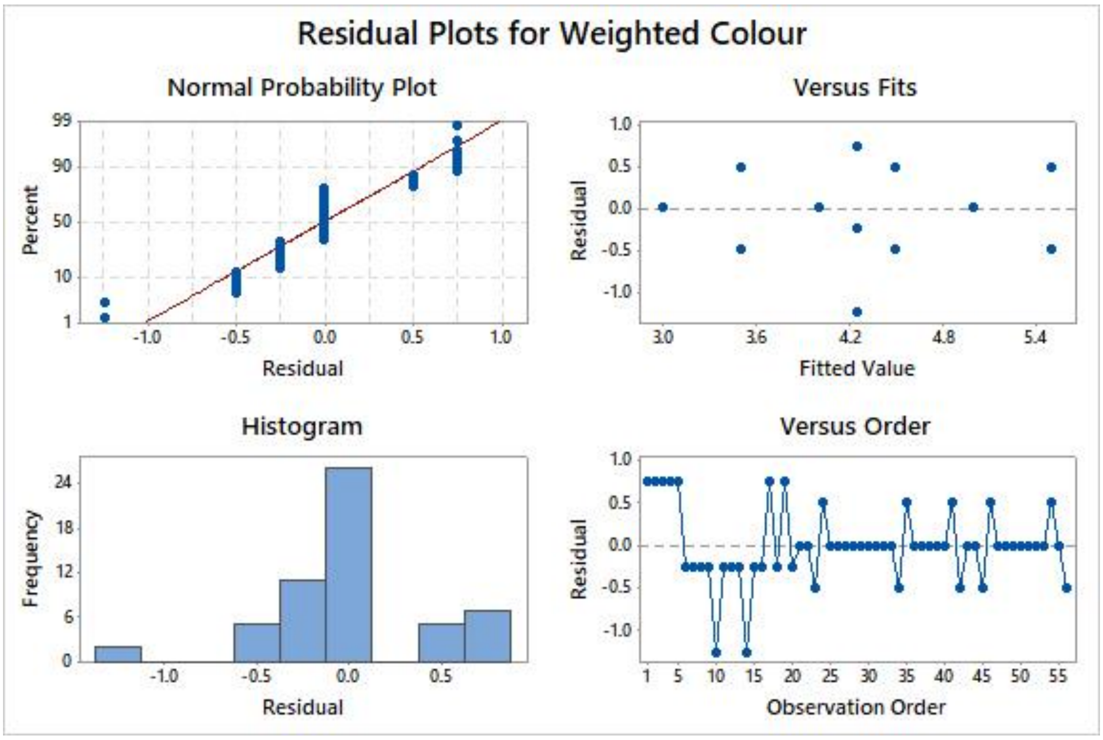


Figure 22: Residual plots for weighted Colour

After individual comparison, pairwise comparison was carried out to identify the relationship between the treatment methods and the final colour. Therefore, Tukey Pairwise Comparison was carried out for the dataset and the following observations were obtained (Table 15). In the table, N means the number of replicates for given treatment and three groups were considered as A, B and C for the comparison of significant of variance.

Table 7: Tukey Pairwise Comparison

Treatment	N	Mean	Grouping		
CH-1700°C-1 Week	2	5.5	A		
CH-1700°C-1 Month	2	5.5	A		
CH-1700°C-3 Days	2	5	A	B	
CH-1500°C-1 Month	2	5	A	B	
CH-1500°C-3 Days	2	5	A	B	
CH-1500°C-1 Week	2	4.5	A	B	C
GH-1750°C-30 min	20	4.25	A	B	C
EH-1500°C-1 Month	2	4	A	B	C

CH 1300^{o}C-3 Days	2	4	A	B	C
CH 1300^{o}C-1 Week	2	4	A	B	C
CH 1300^{o}C-1 Month	2	4	A	B	C
EH-1700^{o}C-1 Week	2	3.5		B	C
EH-1300^{o}C-1 Month	2	3.5		B	C
EH-1300^{o}C-3days	2	3			C
EH-1500^{o}C-3 Days	2	3			C
EH-1500^{o}C-1 Week	2	3			C
EH-1300^{o}C-1 Week	2	3			C
EH-1300^{o}C-3 Days	2	3			C
EH-1700^{o}C-1 Month	2	3			C

Then Kruskal-Wallis test was conducted to identify significant different of pairwise comparison and to further conformed about the obtained results (Table 16). N is the number of replicants and median got change from 3 to 5 with the maximum mean value at ‘CH-1700^{o}C -1 Month’ variable. Z means the s the number of standard deviations from the mean value of the reference population.

Thus, Treatment combinations come with Combined Heat and maximum temperature 1700^{o}C perform well compare to other treatments. Consequently, the second experiment was done by changing soaking time (3 days, 1 week, 10 days and 1 month) to identify the best treatment combination Table 17.

Table 8: Kruskal-Wallis Test on Weighted Colour

Treatment	N	Median	Average Rank	Z
EH-1700^{o}C-3 Days	2	3	8.5	-1.77
EH-1700^{o}C-1 Week	2	3.5	18	-0.93
EH-1500^{o}C-3 Days	2	3	8.5	-1.77
EH-1500^{o}C-1 Week	2	3	8.5	-1.77
EH-1300^{o}C-3 Days	2	3	8.5	-1.77
EH-1300^{o}C-1 Week	2	3	8.5	-1.77
EH-1700^{o}C-1 Month	2	3	8.5	-1.77

EH-1300^{o}C-1 Month	2	3.5	18	-0.93
EH-1500^{o}C-1 Month	2	4	27.5	-0.09
CH-1700^{o}C-3 Days	2	5	46.5	1.59
CH-1700^{o}C-1 Week	2	5	51	1.99
CH-1500^{o}C-3 Days	2	5	46.5	1.59
CH-1500^{o}C-1 Week	2	4.5	37	0.75
CH-1300^{o}C-3 Days	2	4	27.5	-0.09
CH-1300^{o}C-1 Week	2	4	27.5	-0.09
CH-1700^{o}C-1 Month	2	5.5	51	1.99
CH-1300^{o}C-1 Month	2	4	27.5	-0.09
CH-1500^{o}C-1 Month	2	5	46.5	1.59
GH-1750^{o}C-30min	20	4	32.3	1.28
Overall	56		28.5	

Table 9: Analysis variance of Kruskal-Wallis Test

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Soaking time	3	0.5	0.1667	0.67	0.615
Error	4	1.0	0.2500		
Total	7	1.5			

Table 17 shows the summary of the Kruskal-Wallis Test on Weighted Colour for the soaking time. P-value got 0.615 (> .5) with F-value of .067 means that there is no significant difference for the soaking time with the confident interval of 0.5 even.

Finally, the Kruskal-Wallis Test was conducted to identify the relationship between Weighted Colour versus Soaking Time for 1700^{o}C temperature since with above analysis could observe that combined heat treatment with 1700^{o}C maximum temperature has produced the desired colour. Nevertheless, it could not identify the soaking time relationship for the final colour. Thus, to identify the relationship between soaking time and the final colour, another set of samples were thermally treated with a soaking time of 10 days apart from previous three (3 days, 5 days and 1 month). Table 18 shows the results of the Kruskal-Wallis Test.

Table 10: Results of the Kruskal-Wallis Test

Soaking Time	N	Median	Avg Rank	Z
1 month	2	5.5	5.5	0.67
10 days	2	5	3.5	-0.67
1 week	2	5.5	5.5	0.67
3 days	2	5	3.5	-0.67
Overall	8		4.5	

3.1.2 Discussion of the statistical analysis

One month of soaking time and the one week of soaking time has produced the same average weighted colour and median weighted colour results. Soaking time of 10 days and 3 days have produced 3.5 value of average ranks. Therefore, with the results of the Kruskal-Wallis Test could not identify the best soaking time because one month and one week have the same acceptable results for the analysis. In simply there is a contradiction about the soaking time for the colour alteration. All the statistical analysis was based on the average colour ranked values of each category. This may be one of the reasons for getting this observation. To do further analysis of the obtained statistical analysis result XRF spectroscopy analysis was conducted and discussed in Pg. 86.

3.2 UV-Visible Analysis

UV-Visible spectrum widely uses in gemstone identification – specially treated gemstones since with the colour alteration intensity of the peaks get change significantly and these changes correspond to the various reactions that occurred inside the gemstone. Samples were analysed for absorption under various treatment methods and could observe a broad peak after 550 nm that corresponds for the formation of $[FeTi]^{+6}$ complex (Karl et al., 1983; Perera, 1993; Karl et al., 1999) and this could use as the indicator of the formation of blue colour. Apart from that most of the samples showed peaks at 388 nm and 450 nm which corresponded to Fe^{3+}(Lhuaamporn et al., 2017; Perera, 1993). Fig. 23 shows the UV-Visible spectrums of a one specimen and all the other specimens available in the annex 01(Fig. 113 to Fig.132).

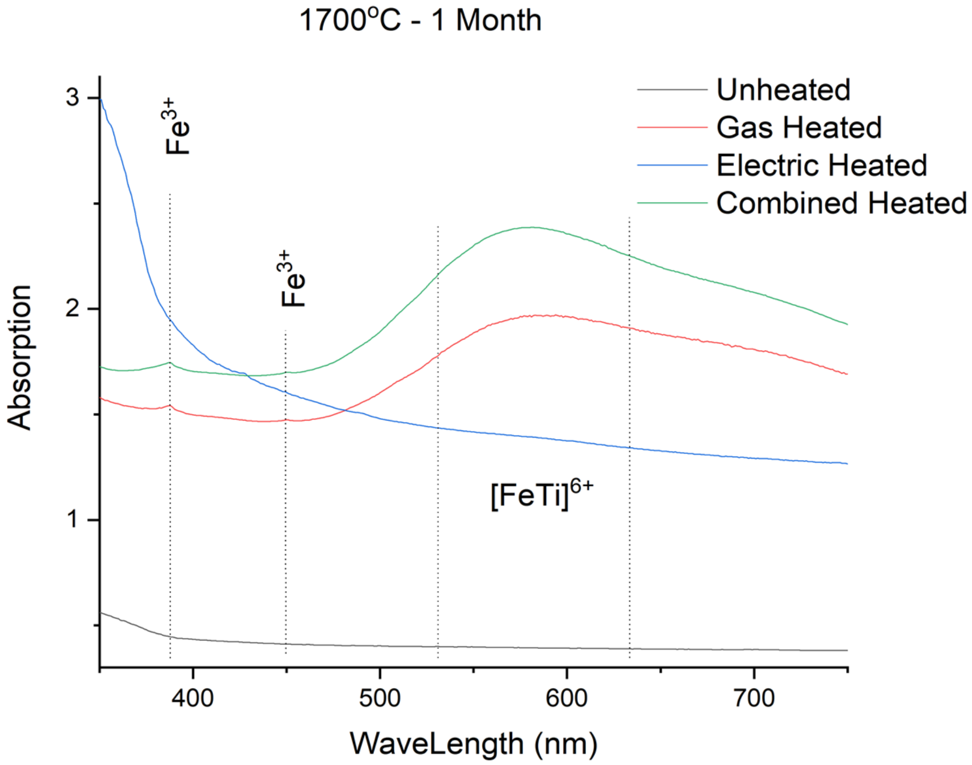


Figure 23: UV-Visible Spectrum G-01 1700°C – 1 month of soaking time

The Fig. 29 illustrate the general behavior of the treated "*Geuda*". Combined heat treatment has produced the highest peak development and gas furnace treated stone also showed potential significant peak development after 550 nm. Electric furnace heat treatment and the combined heat treatment has not provided that peak and this is also supported by the visual observations (there was no any colour development for electric furnace treatment only). Table 19 illustrates the peak positions of the UV-Visible absorption spectrum observed with encompassing elements, irons or complexes. It is very clear that along with the heat treatment process the peak development at 550 nm – 650 nm got increased except in electric heat treatment.

Table 11: UV-Visible analysis: Peak Position and their Responsible chemical group

Absorption peak position (nm)	Name of the chemical group	References
388	Fe^{3+}	(Lhuaamporn et al., 2017; Perera, 1993)
450	Fe^{3+}	(Lhuaamporn et al., 2017; Perera, 1993)
485	Ti^{3+}	(Keig, 1968; K. Schmetzer & Bank, 1980)
After 550	$[FeTi]^{+6}$	(Ediriweera & Perera, 1989; Karl et al., 1983; Lhuaamporn et al., 2017; Perera, 1993; Karl Schmetzer & Peretti, 1999)

there were some special cases (Fig. 114, Fig. 115, Fig. 117, Fig. 119, Fig. 122, Fig. 124) that didn't show any significant peak development and it may due to chemical composition changes within the gemstones (it has been discussed in details in page 86. When increased the maximum temperature from 1300°C to 1700°C in combined heat treatment could observe peak development that emphasizes the enhancement of blue colour. There were three soaking times (3 days, 5 days and 1 month) for a one heating temperature and observed 1700°C as the optimum temperature for the colour change using GIA-Colour Grading System. Thus, apart from above mention three soaking times, to keep consistency gap within soaking times, 10 days was adopted for 1700°C heat treatment. Fig. 131 and Fig. 132 illustrate the UV-Visible variation of 10 days of soaking time. When compared with the 3 days of soaking time (Fig. 113 and Fig. 114) and 5 days of soaking time (Fig. 115 and Fig. 116), 10 days of soaking time showed an improvement of blue colour at 1700^{o}C.

3.2.1 UV Visible Spectroscopy changes with temperature

Fig.43 to Fig.48 illustrated the effect of temperature when change the soaking time for CH, EH. With the increment of the temperature in combined heat treatment there is a tendency to develop the peak near 550 nm (Fig. 46, Fig. 47 and Fig. 48). Furthermore, in the electric heat treatment could not identify any peak development even with the change of temperature (Fig. 43, Fig. 44 and Fig. 45).

In the EH there is no significant differences for the UV- spectrums since the colour development has not changed during the heat treatment process. Nevertheless, combined heat treatments showed significant difference with heat treatment. Furthermore, within the combined heat treatments the highest peak development near 550nm has occurred in 1 month of soaking time (Fig.48).

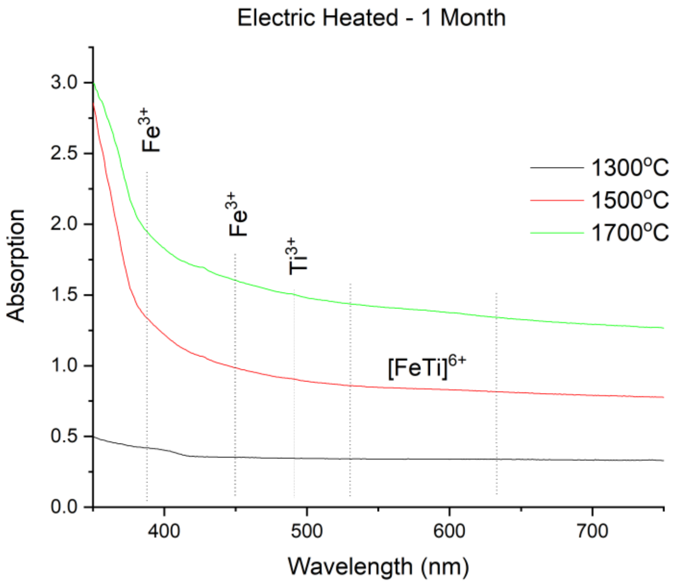


Figure 24:UV-Visible spectrum changes for 1 month of soaking of electric heat treatment

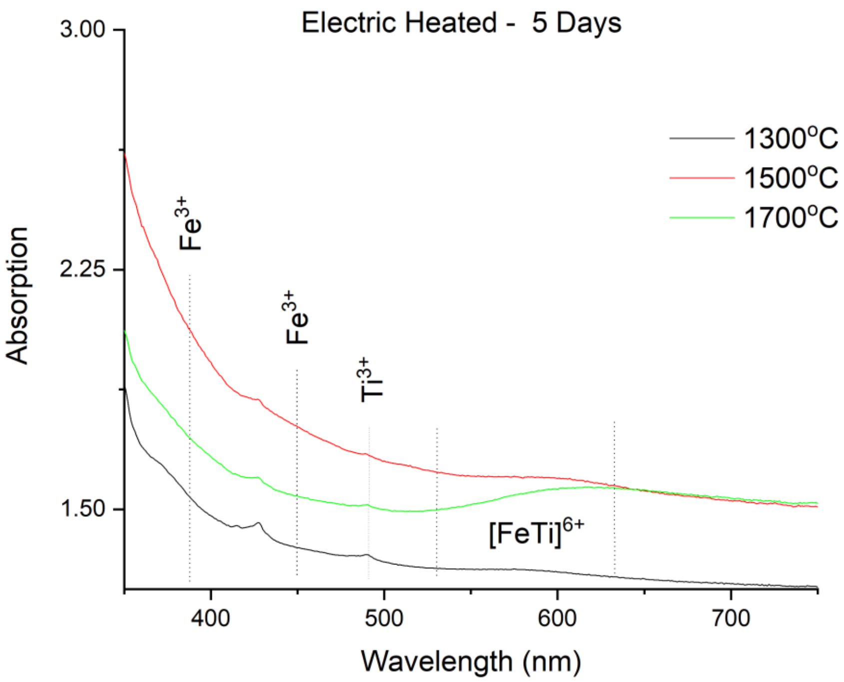


Figure 25: UV-Visible spectrum changes for 5 days of soaking of electric heat treatment

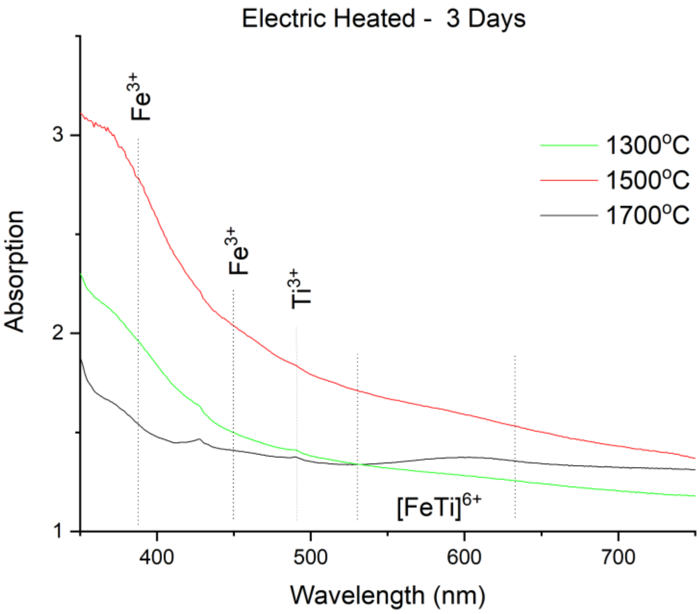


Figure 26: UV-Visible spectrum changes for 3 days of soaking of electric heat treatment

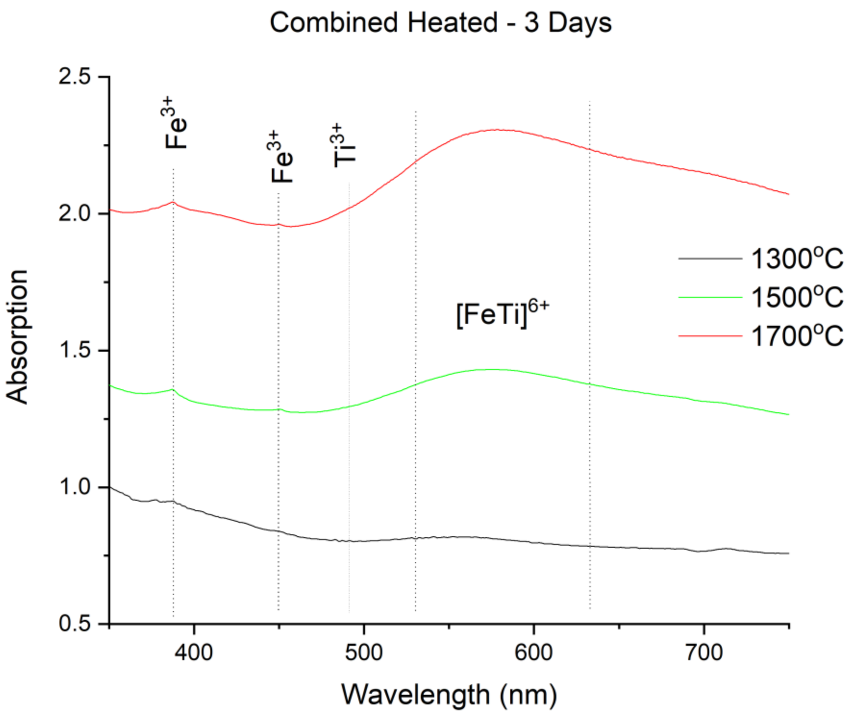


Figure 27: UV-Visible spectrum changes for 3 days of soaking of combined heat treatment

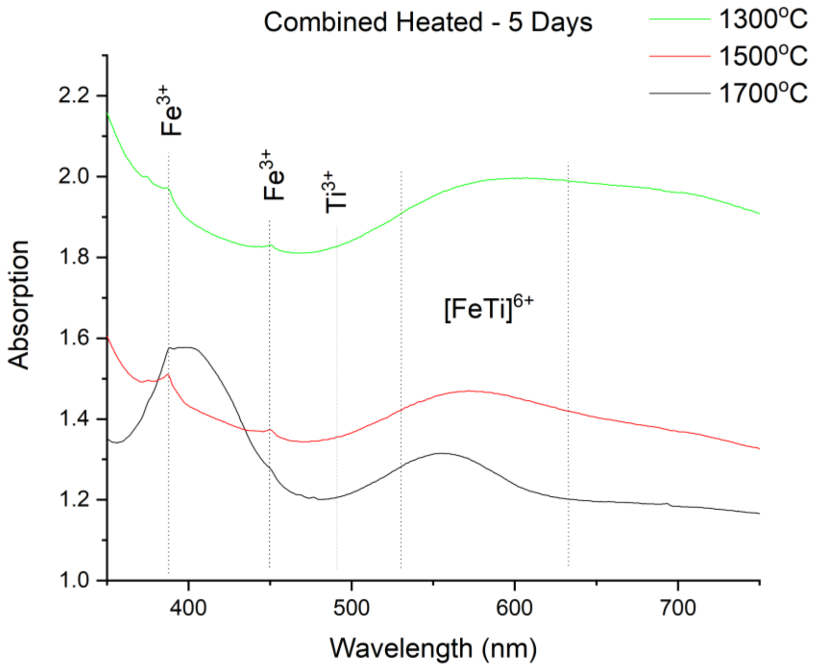


Figure 28: UV-Visible spectrum changes for 5 days of soaking of combined heat treatment

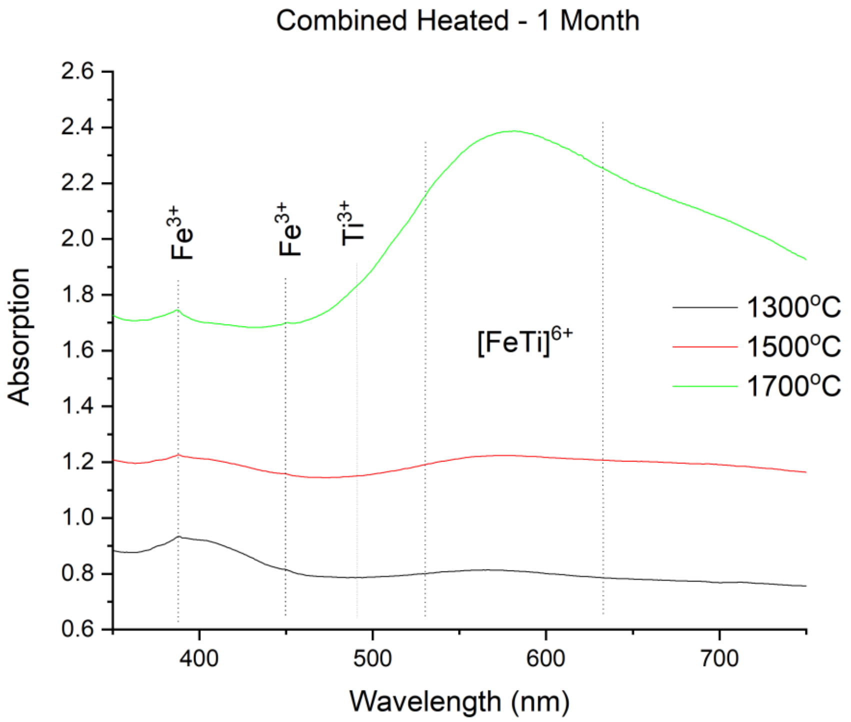


Figure 29: UV-Visible spectrum changes for 1 month of soaking of combined heat treatment

3.2.2 UV Visible Spectroscopy changes with soaking time

Fig. 49 to Fig. 54 illustrates the UV-Visible spectrums changes with the soaking time when changing the temperature and the method of heat treatment. With EH, under different soaking times could not observe any significant differences in the patterns (Fig. 49 to Fig. 51) though, the CH has produced a peak development after 550 nm due to blue colour development inside the stones (Fig. 52, Fig. 53 and Fig. 54). When considering the CH graphs not could observe any significant colour development with respect to soaking time for a given temperature (Fig. 52, Fig. 53 and Fig. 54).

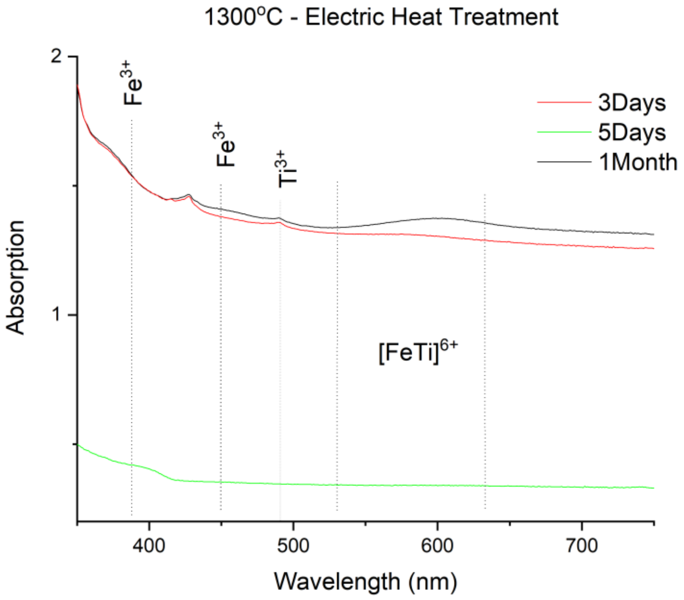


Figure 30: UV-Visible spectrum changes of electric heat treatment under 1300°C temperature

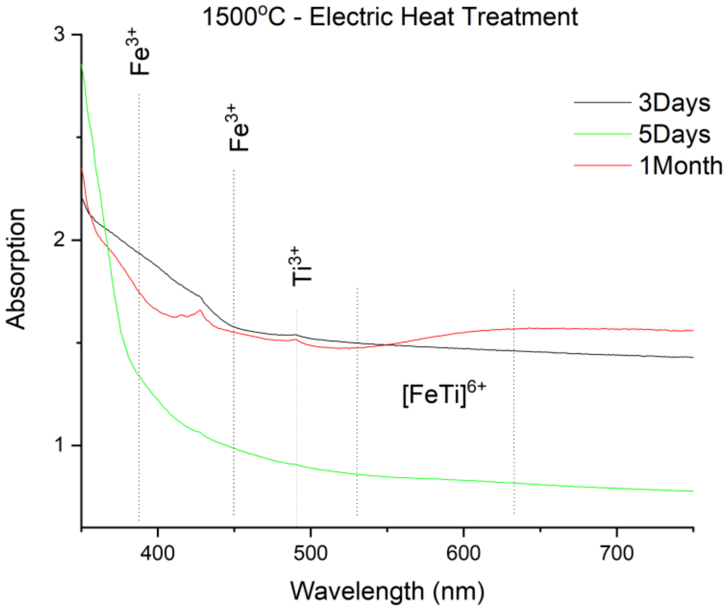


Figure 31: UV-Visible spectrum changes of electric heat treatment under 1500°C temperature

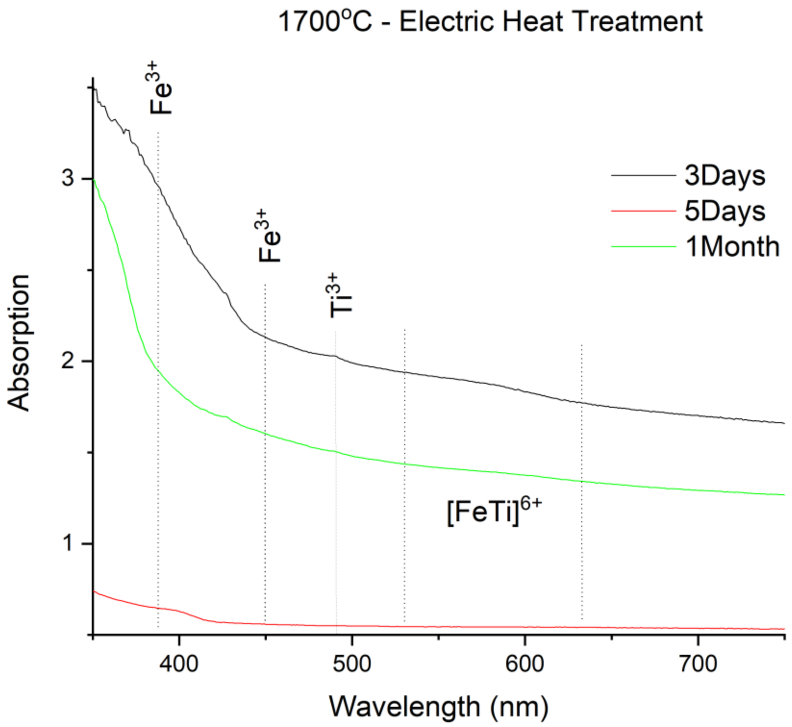


Figure 32: UV-Visible spectrum changes of electric heat treatment under 1700°C temperature

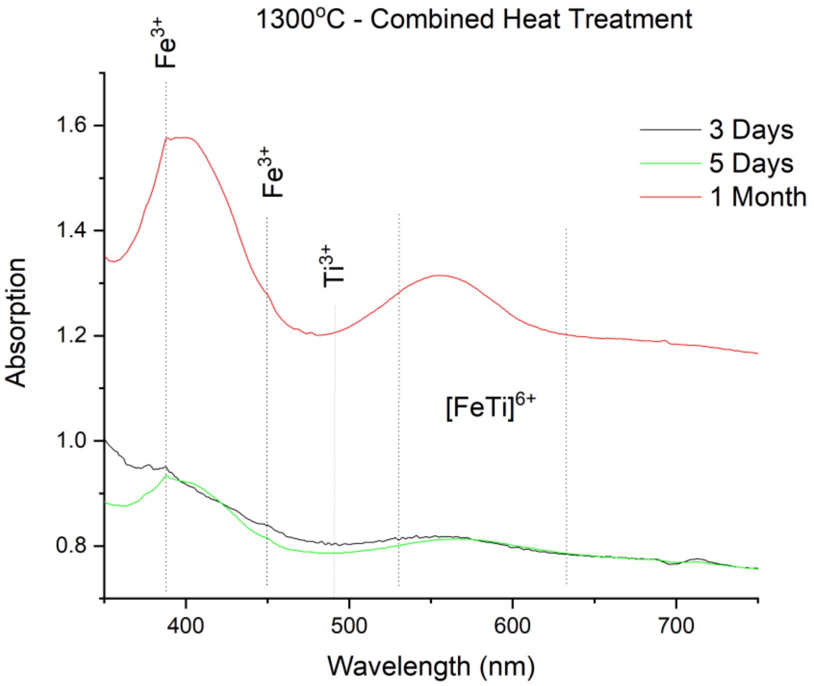


Figure 33: UV-Visible spectrum changes of combined heat treatment under 1300°C temperature

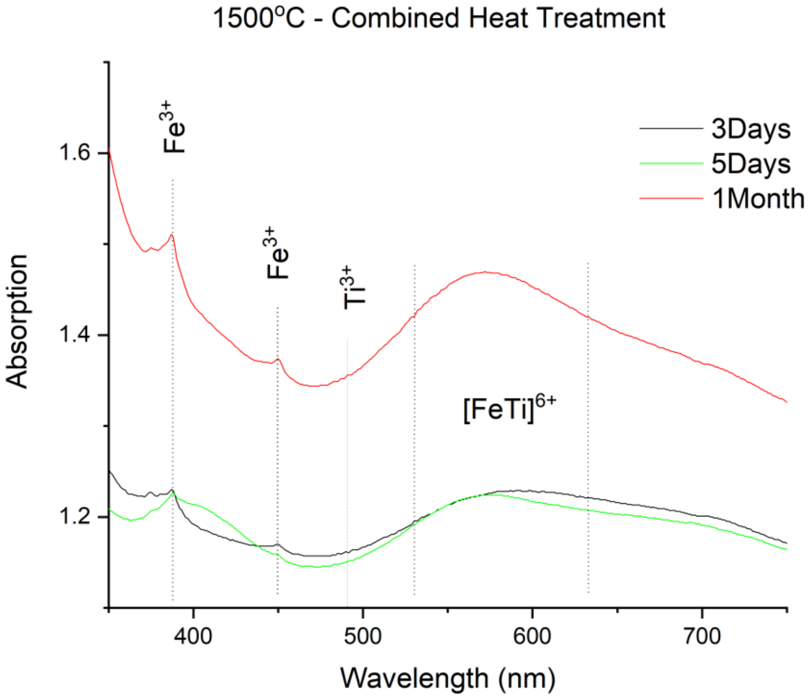


Figure 34: UV-Visible spectrum changes of combined heat treatment under 1500°C temperature

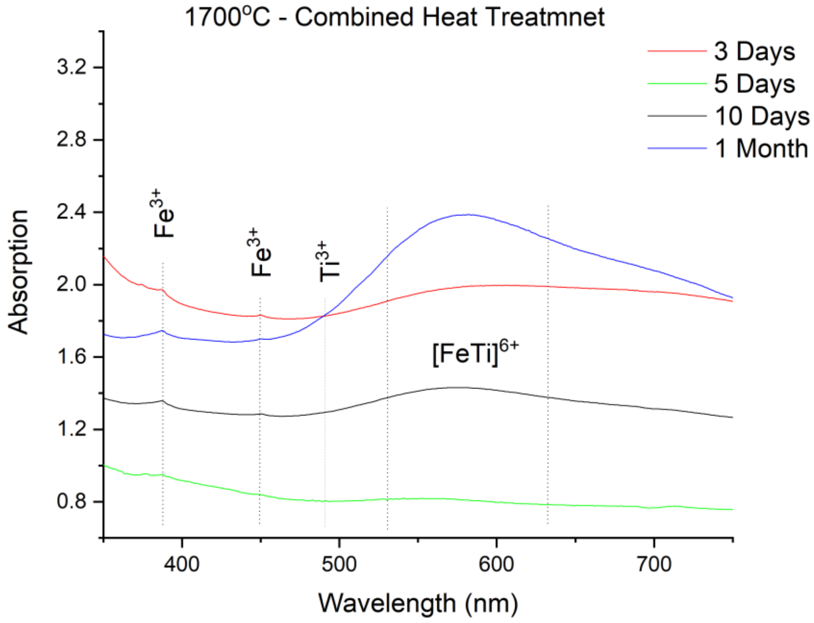


Figure 35: UV-Visible spectrum changes of combined heat treatment under 1700°C temperature

3.2.3 Discussion of UV-Visible analysis

With the above-mentioned observation following conclusions could be made;

- Peak height development occurred from unheated to combined heated regarding the method of heat treatment to as follows
  - Unheated < Electric heated < Gas Heated < Combined Heated
- The desired blue colour development concerning the temperature in combined heat treatment occurred as follows
  - 1300°C < 1500°C < 1700°C
- For soaking time could not identify any significant pattern
- Electric heat treatment hasn’t produced significant blue colour under any temperature or soaking time nevertheless, has enhanced the clarity compared with unheated *“Geuda”* stones.
- There were some exceptional of the spectrums due to colour development variations (Fig. 114, Fig. 115, Fig. 117, Fig. 119, Fig. 122, Fig. 124) and it has explained in page 86 under the XRF analysis topic.

3.3 FTIR Analysis

FTIR (Fourier-Transform Infra-Red) Spectrophotometer is a use to identify bond vibration of materials when it exposes to the infrared beam. The peaks indicate the type of bond that presents in the medium or the mode of vibration of a particular bond (Smith, 2011) and this would be a good indication for identification of treated gemstones since with the treatment method there are some bond changes in the atomic structure. Most of the naturally formed gemstones contain some amount of water or OH^- at its formation (Roger & Rossman, 1984). The heat treatment process may reduce the number of water molecules inside the gemstones. Thus, a variation of the peaks of FTIR indicates whether the gemstone being tested has been thermally enhanced or not.

In FTIR absorption spectroscopy, samples showed a peak at 3309 cm^{-1}. According to (Loretta et al., 2012), (Lowry, 2002), (Diep, 2015) and (Phlayrahan et al., 2018), the peak at 3309 cm^{-1} in the Fourier transform spectroscopy corresponds to the O-H stretching and vibration mode of water. Changes in temperatures and time cause development or decline of the peaks. The band associated with the OH^- (3309 cm^{-1}) in *"Geuda"* samples has been reduced in a significant amount.

Apart from the 3309 cm^{-1} peak, there were another two peaks appeared at 2920 cm^{-1} and 2850 cm^{-1}. According to (Cartier, 2009), two peaks nearby 2853 cm^{-1} and 2924 cm^{-1} correspond to oils or fats, which were probably due to the contaminations from handling. All the spectrum values for *"Geuda"* gemstone heat treatment are summarized in Table 20.

Table 12: The peak positions of the absorption bands of FTIR

Absorption band Frequency (cm^{-1})	Name of the chemical group/ reason	Reference
~2350	Atmospheric CO_2	(Ortiz et al., 1995)
2853 and 2924	Oil or fat	(Cartier, 2009)
3309	OH^-	(Loretta et al., 2012), (Lowry 2002), (Diep 2015),(Moon & Phillips, 1991, 1994; Smith & Van der Bogert, 2006)

In annex 02, Fig. 133 to Fig. 153 illustrate the FTIR variation of individual *"Geuda"* samples and a figure contains a variation of Unheated, Gas heated, Electric heated and Combined heated specimens of the same sample. A sample graph illustrated in Fig. 55. The peak at 3309 cm^{-1} is the identification factor of the *"Geuda"* gemstones since with the different methods of heat treatment produced different peak heights. When comparing the type of heat treatment, combined heat treatment (CH) has received the smallest peak compared to the unheated (UH) stone and also electric heat treatment (EH) has smaller peak compared to gas heated (GH) stones. Furthermore, the same trend was observed when the soaking time increased. One-month soaking time has produced the smallest peak at 3309 cm^{-1} compared to 3 days, 5 days and 10 days of soaking times in electric heat treatment and the combined heat treatment. Combine heat treatment has produced the shortest peak development compared to electric heat treatment. There was a relationship between peak height at 3309 cm^{-1} and the soaking time. When increasing the soaking time, the peak height got shortened since the peak represents the OH^- vibration mode of water and when increasing the soaking time, trapped water inside the stone may get evaporated.

Peak positions at 2920 cm^{-1} and 2850 cm^{-1} were changed haphazardly throughout the samples since it was due to contamination from handling (oils and fats). Height of the peak corresponded to the amount of oil/fat present on the surface of the gemstones.

Apart from above mention two peaks there is a noise type, fluctuation set of peaks near 2350 cm^{-1} due to the atmospheric CO_2 contamination (Ortiz et al., 1995).

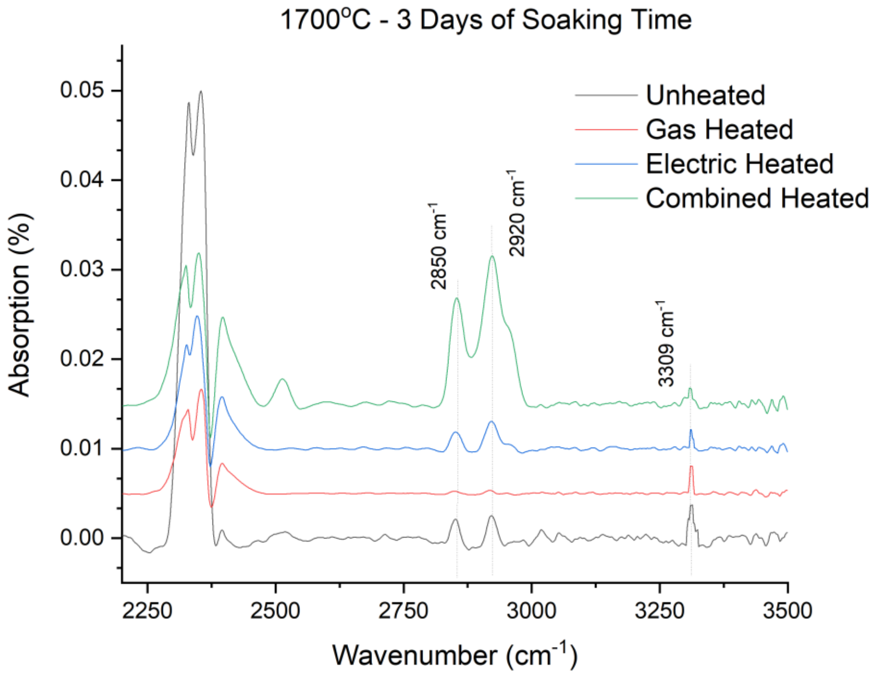


Figure 36: FTIR Spectrum – G-01_1700°C – 3 Days of the Soaking time

3.3.1 FTIR variation with soaking time

When comparing the FTIR variation with soaking time, 3309 cm^{-1} has shown a substantial difference with the height of the peak. There wasn't a significant difference between electric heat treatment and the combined heat treatment in the observations with the change of soaking time since the peak height may be a function of temperature and the soaking time. And it has not any difference with the method of treatment. Nevertheless, within the given temperature and the method, could observe a peak height variation at 3309 cm^{-1}. 3 days soaking time has the highest peak height while one month of soaking time showed the least peak height. Fig. 75 to Fig. 80 illustrates the observation changes with the soaking time.

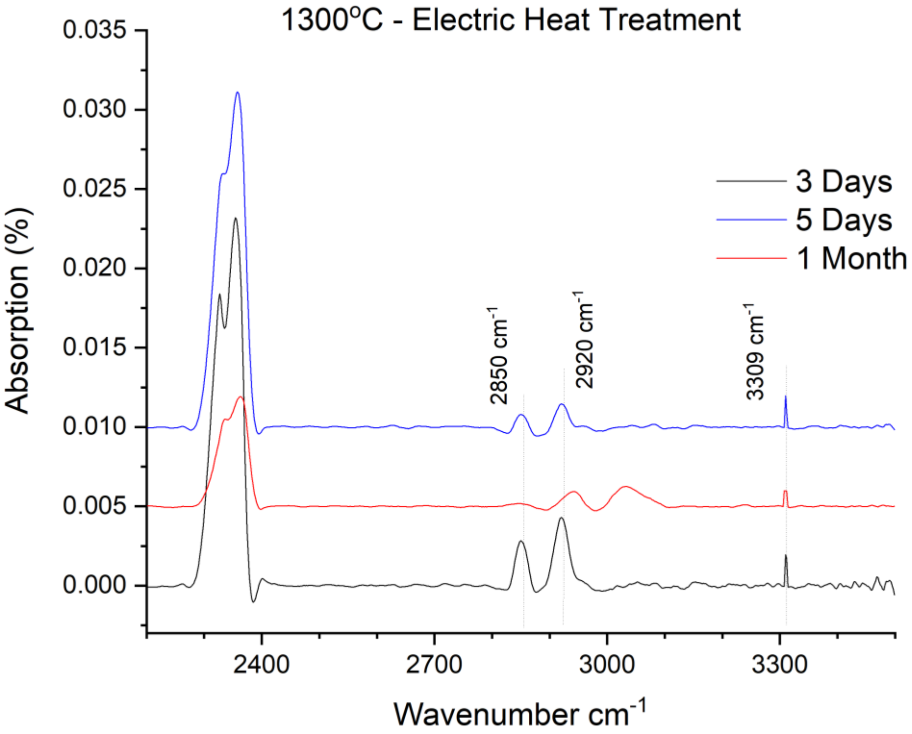


Figure 37: FTIR Spectroscopy_ 1300ºC_Electric heat treatment under different soaking times

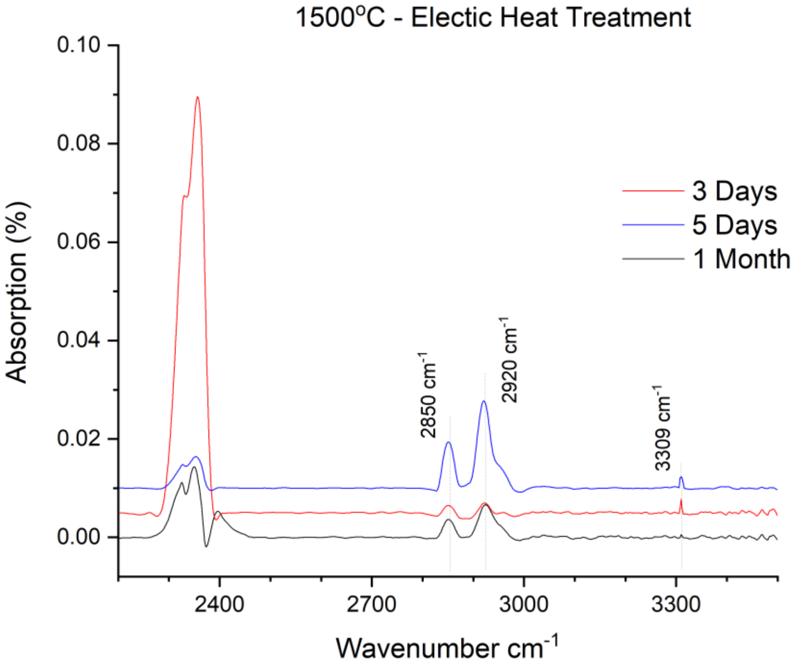


Figure 38: FTIR Spectroscopy_ 1500ºC_Electric heat treatment under different soaking times

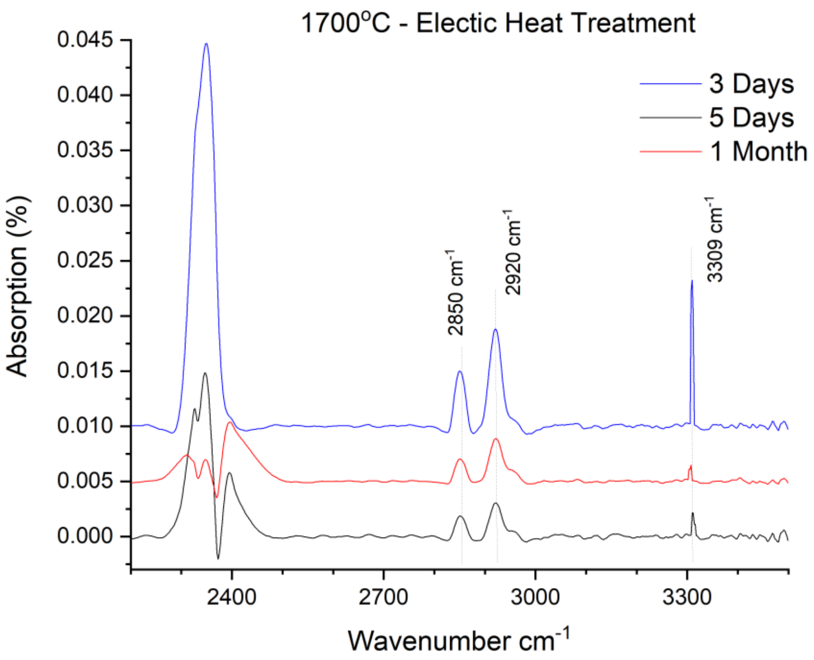


Figure 39: FTIR Spectroscopy_ 1700ºC_Electric heat treatment under different soaking times

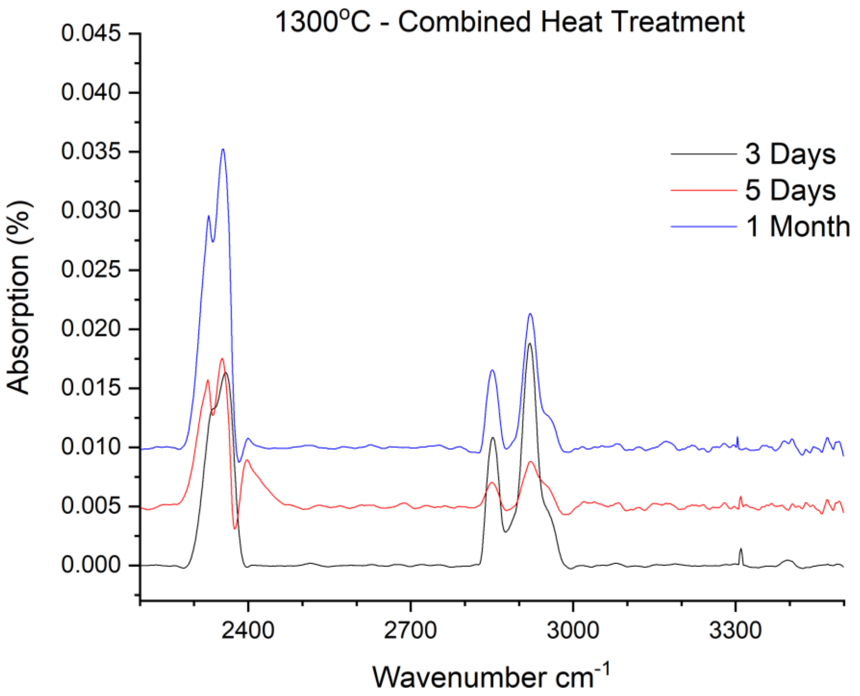


Figure 40: FTIR Spectroscopy_ 1300ºC_Combined heat treatment under different soaking times

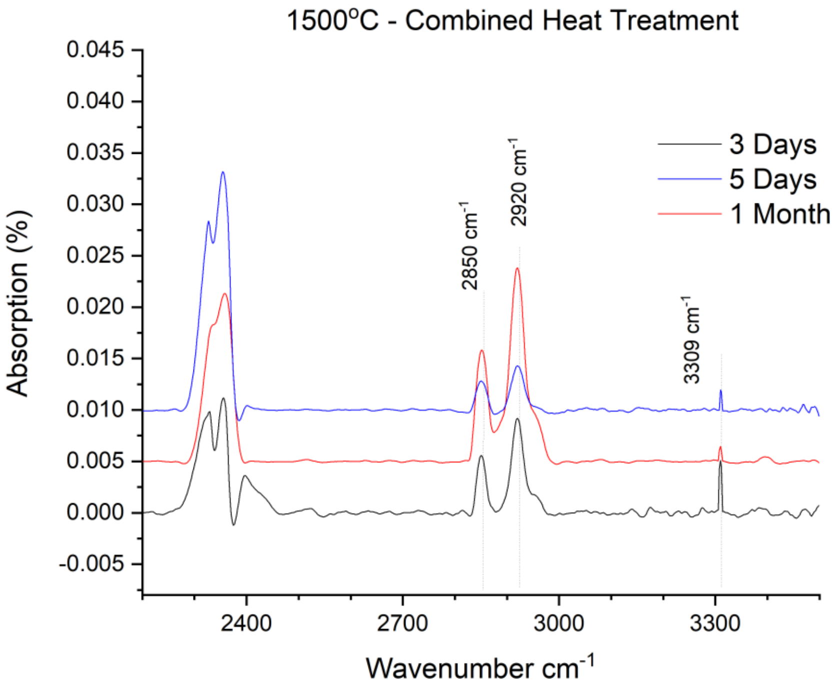


Figure 41: FTIR Spectroscopy_ 1500ºC_Combined heat treatment under different soaking times

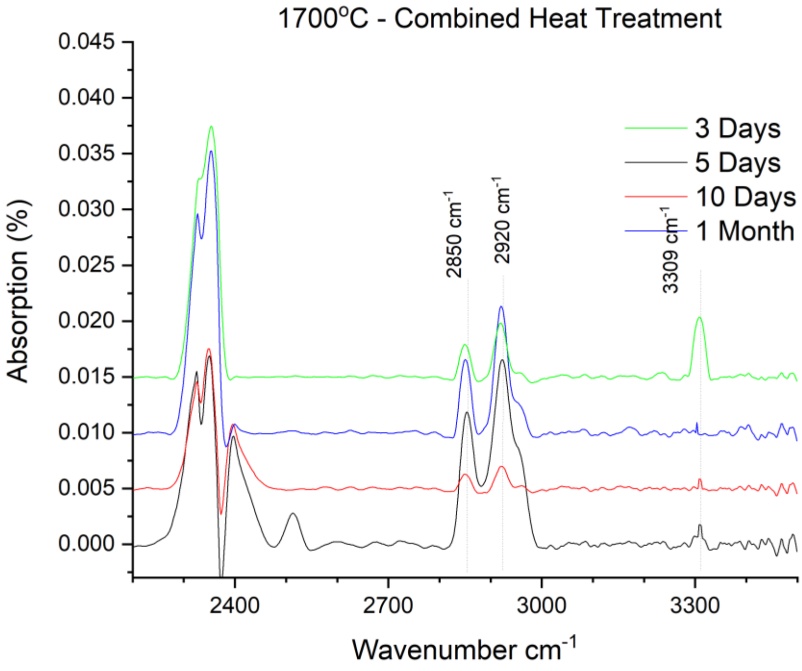


Figure 42: FTIR Spectroscopy_ 1700ºC_Combined heat treatment under different soaking times

3.3.2 FTIR variation with temperature

FTIR variation with the temperature showed the effect to the peak at 3309 cm^{-1} and could observe some pattern with the temperature. There wasn't any significant difference at the 3309 cm^{-1} peaks with the change of method (electric heat treatment and electric heat treatment after gas heat treatment) as discussed in the previous topic (Topic 3.3.1). 1300°C has produced the highest peak and when increased the temperature from 1300°C to 1700°C, observed peak height drop and this pattern could notice throughout in the all the graphs (Fig. 81 to Fig. 86).

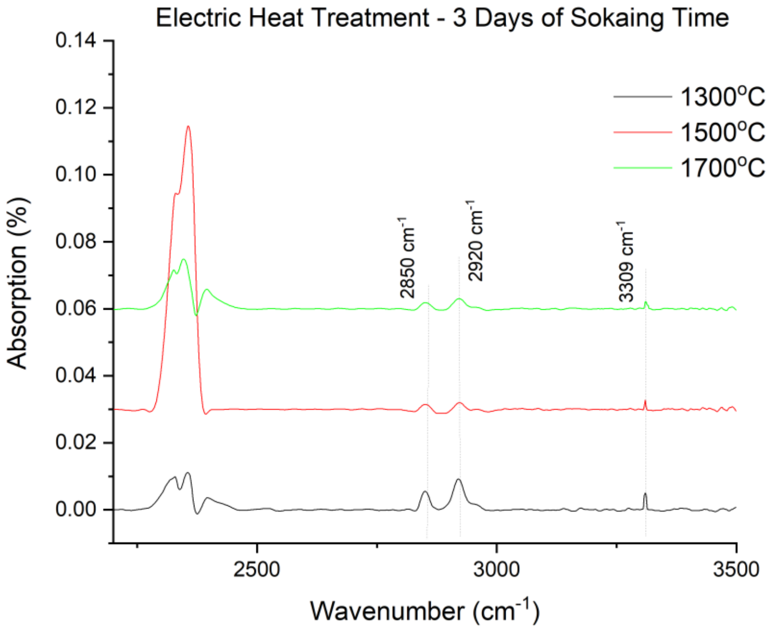


Figure 43: FTIR Spectroscopy_ 3 Days of soaking time_Electric heat treatment under different Temperatures

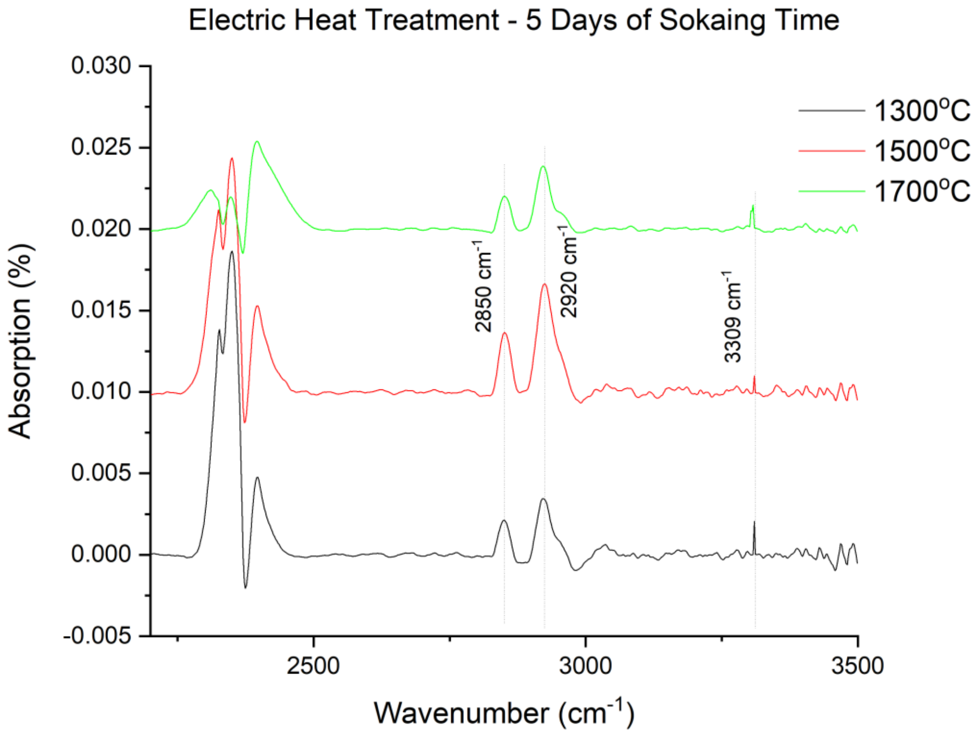


Figure 44: FTIR Spectroscopy_ 5 Days of soaking time_Electric heat treatment under different Temperatures

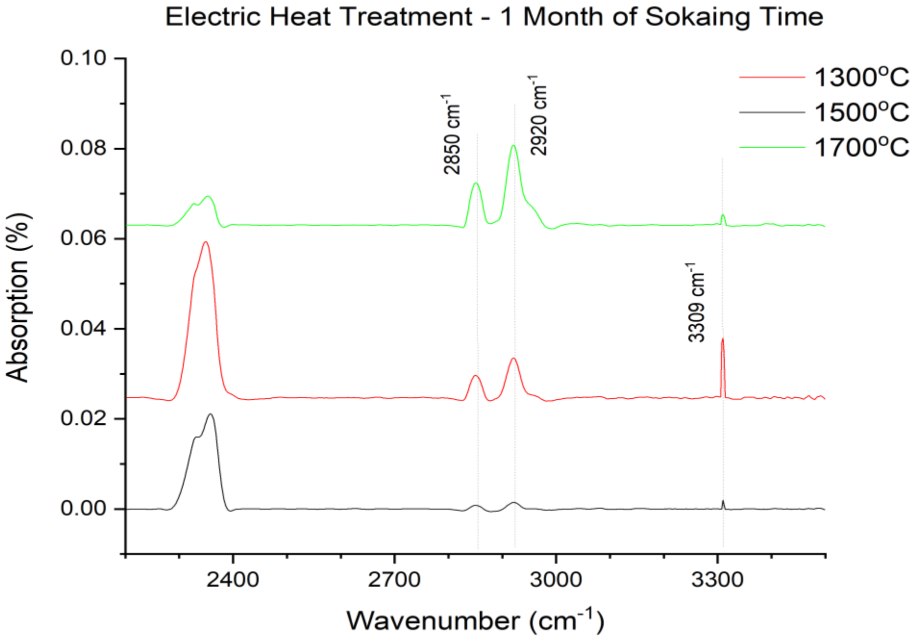


Figure 45: FTIR Spectroscopy_1 month of soaking time_Electric heat treatment under different Temperatures

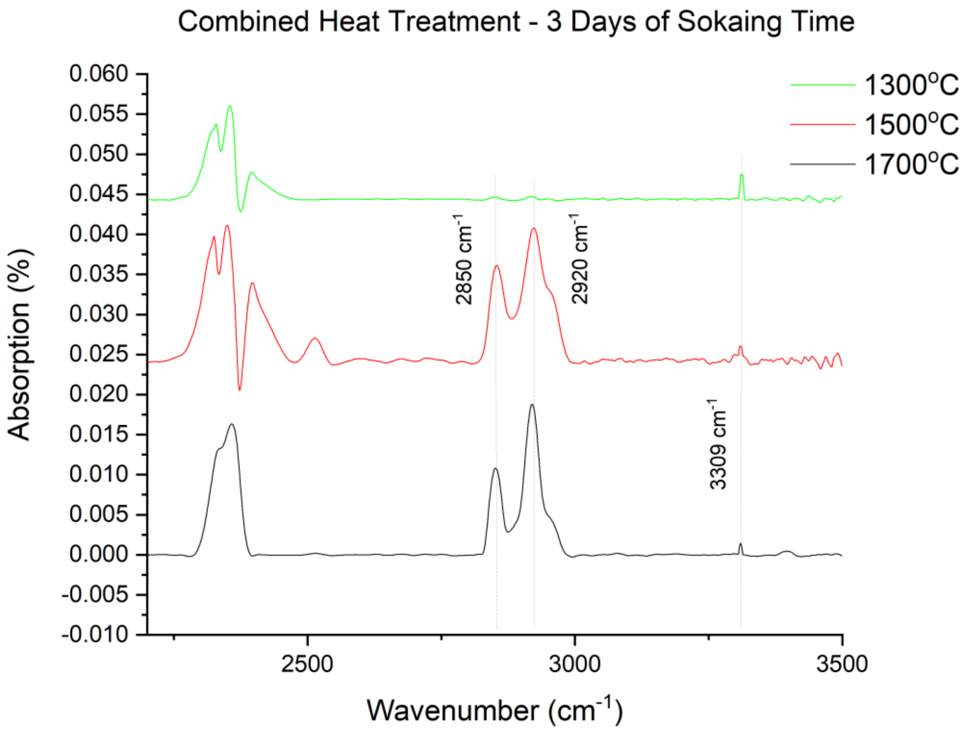


Figure 46: FTIR Spectroscopy_ 3 Days of soaking time_Combined heat treatment under different Temperatures

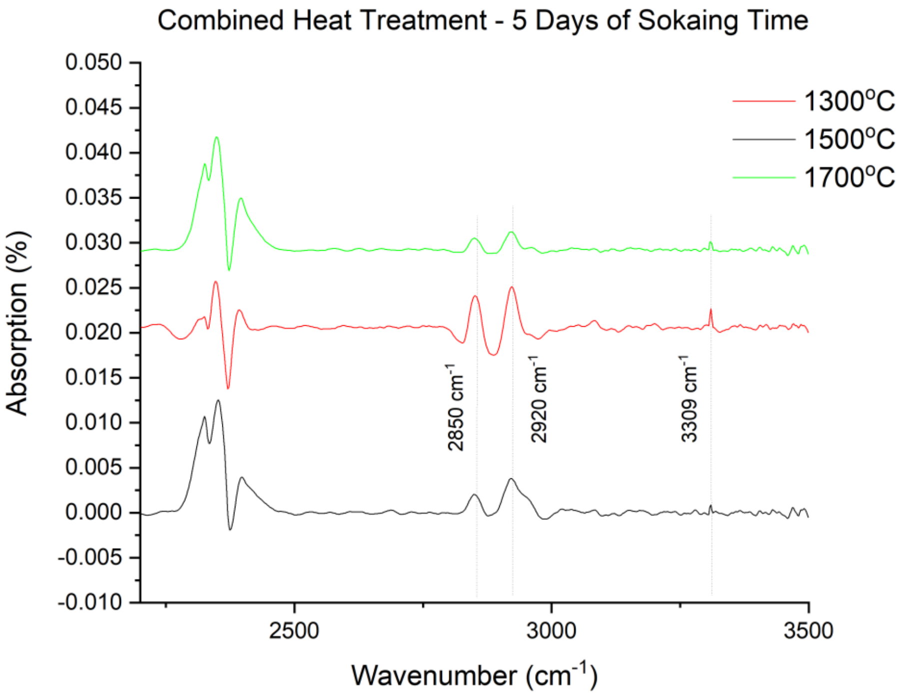


Figure 47: FTIR Spectroscopy_ 5 Days of soaking time_Combined heat treatment under different Temperatures

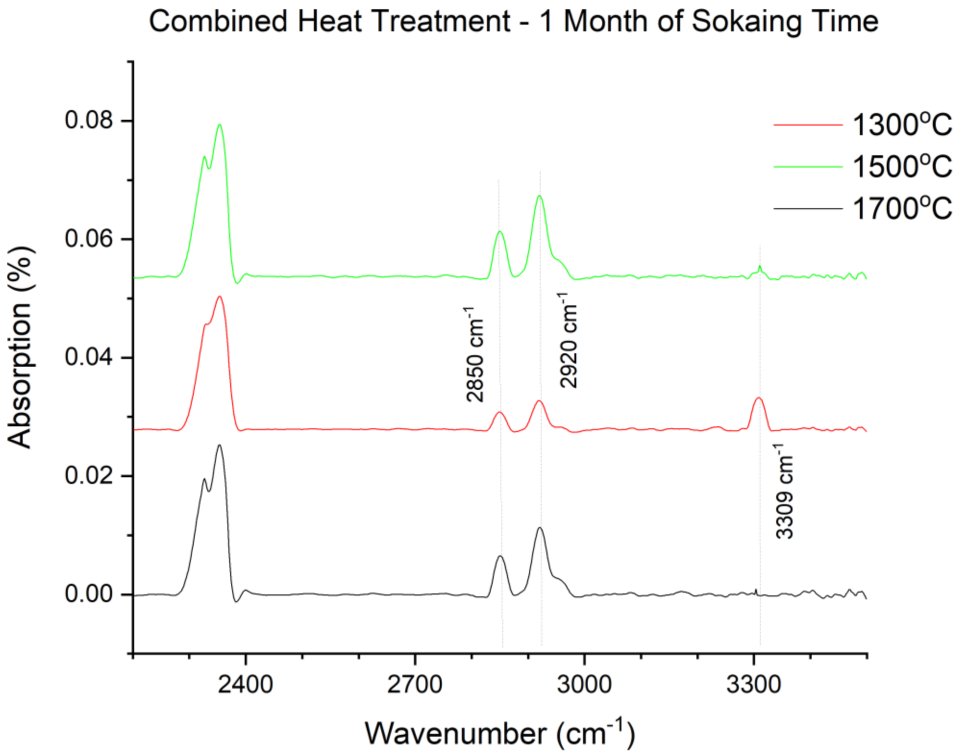


Figure 48: FTIR Spectroscopy_ 1 Month of soaking time_Combined heat treatment under different Temperatures

3.3.3 Discussion of FTIR analysis

There were four major peaks could observe in the FTIR spectrum for three different chemical compositions. The noise type, set of peaks near 2350 cm^{-1} due to the atmospheric CO_2 infection while measuring the samples and atmospheric CO_2 in the measuring chamber of the instrument may get changed with the time. Peak positions at 2920 cm^{-1} and 2850 cm^{-1} due to contamination from handling (oils and fats). The peak at 3309 cm^{-1} is due to the vibration pattern of OH^- in the *"Geuda"* gemstones and this is the identification factor of the *"Geuda"* gemstones since with the different methods of heat treatment, produced different peak heights. Peak positions at 2920 cm^{-1} and 2850 cm^{-1} have not produced recognized pattern since the amount of oil and fat may change with the way of handling.

At 3309 cm^{-1}, combined heat treatment has produced least peak height compared to unheated, gas heated and electrically operated furnace heated for *"Geuda"* stones. The peak height observation could summarize as follows;

Unheated > Gas Heated > Electrically operated furnace heated ≥ Combined Heated

That may due to the increment of soaking time and time produce more possibilities to evaporate the water inside the gemstones.

When comparing the peak height at 3309 cm^{-1} with the soaking time the following observation was noted;

3 Days > 5 Days > 10 Days > 1 Month

ten days of soaking time applicable only to the 1700^{o}C. the above observation pattern was not changed with the temperature and the type of method of heat treatment. Temperature variation showed a similar type of variation pattern. When increased the temperature peak height at 3309 cm^{-1} got reduced as follows.

1300^{o}C > 1500^{o}C > 1700^{o}C

Increased temperature results the increase of thermal energy and the thermal energy could convert into kinetic energy of the atoms or the thermal energy may get absorbed by the atoms in the structure. As explained in pages 100-110, these energies produce possibilities to change the lattice parameters of the *"Geuda"* gemstones and OH^- may get released to the atmosphere through these defects.

Some of the *"Geuda"* stones did not show a peak at 3309 cm^{-1} (Fig. 140, Fig. 142, Fig. 143, Fig. 149 and Fig 151) even at unheated conditions and by the reason of that no any peak could be observed in the gas heated, electrically operated furnace heated and combined heated stones. Sometimes stones may not get trap water at their formation and due to that reason stones haven not produced any peak development at 3309 cm^{-1}.

3.4. XRD Analysis

XRD (X-ray diffraction) is one of the non-destructive analytical techniques which can deliver the unique fingerprint of a material crystal structure when associated Bragg law and Scherrer equation.

About 95% of all solid materials can be described as crystalline, means that material has a proper repeating unit cell. When X-rays interact with a crystalline substance (more accurately with the phase), produces diffraction patterns. The X-ray yield constructive interferences at specific angles when they get diffracted in the atoms of a crystal and that corresponded to the atomic arrangement of the crystal structure. Thus, XRD is one of the methods that can use in the gem identification of chemical composition changes, phase changes and d-space changes. In the research, samples were subjected to the XRD analysis and peaks intensity were obtained for 2-theta values under 30.0000 deg./min scan speed. Sharp peaks were obtained through the analysis and the shapes of the peaks were remain through the various soaking time and hence, could conclude that the crystallinity of the samples has remained with the thermal treatment. The peak positions indicated that *"Geuda"* gemstones contain aluminium(III) oxide in alpha phase, titanium(IV) oxide in anatase phase and Iron(III) oxide in alpha phase (Table 21).

Table 13: XRD Peak positions of "Geuda" gemstones

Chemical Composition	2θ Value	Miller Indices (h k l)	References
α-Al_2O_3	37.9	(1 1 1)	(Adamiak et al., 2017; Ayieko et al., 2015; Chattopadhyay et al., 2014; Kouam et al., 2012; Krishna & Xavior, 2015; Lei & Ma, 2010; Ravichandran et al., 2014)
	45.9	(2 0 0)	
	64.3	(2 2 0)	
α-Fe_2O_3	41.6	(1 1 0)	(Han et al., 2014; Majid & Farzaneh, 2014)

Anatase TiO_2	47	(2 0 0)	(Duan et al., 2016; Lü et al., 2019; Mishra & Ahrenkiel, 2012; Nirmala et al., 2011; Ravichandran et al., 2014)
	27.9	(1 0 1)	

IN XRD peak shift along the x-axis without any significant pattern was observed. In annex 03, Fig. 153 to Fig. 172 shows the XRD pattern of standard *"Geuda"* samples and one illustration has shown in Fig. 87. The peak shift may be due to the random movements of the atoms inside the atomic structure with the heat treatment process.

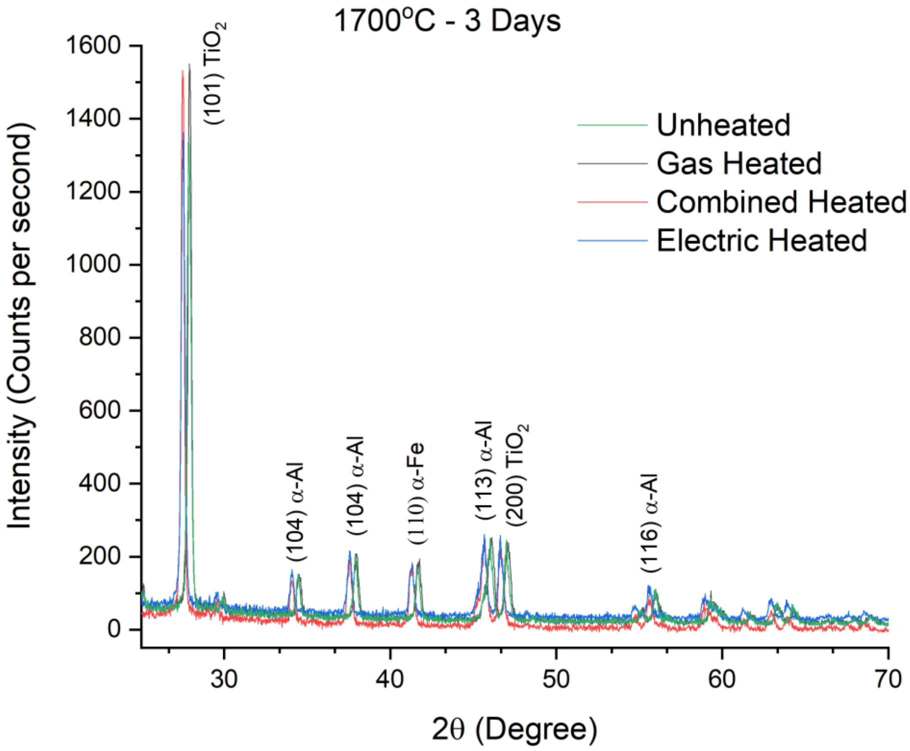


Figure 49: XRD Spectruscopy_G-01_1700°C 3 Days of soaking time

Fig. 87 shows the difference peaks with their corresponding chemical compositions. With the heat treatment, there was not any significant peak shift along the x-axis to change the phase of the compounds. Furthermore, the shape of the peaks remains unchanged with the heat treatment and thus can conclude that the crystallinity has not changed with the heat treatment process.

One of the advantages of getting XRD data is to calculate the spacing of the crystal layers or in other meaning, the path difference of diffracted and contractive- interfered X-Rays. A crystalline material comprises of a periodic arrangement of the unit cell into a lattice and the unit cell can contain a single atom or set of atoms in a fixed arrangement. Crystals consist of planes of atoms that are spaced a distance' apart. However, crystals can be resolved into many atomic planes, each with a different d-spacing (Fig. 108).

Fig. 107 illustrates the crystal structure of NaCl and red colour represent the Cl^- and Blue colour for the Na^+. (200) the plane has different d- space while (220) plane has another value for the d-space. With d-space changes within given planes could observe in the graphs with the peak shift along the x-axis and these peak shifts may due to the following causes.

- changes in stoichiometric composition by doping.
- Instrumentations (Doppler effect during counts)
- Microstructure parameters changes (crystallize size and lattice strain) due to thermal annealing

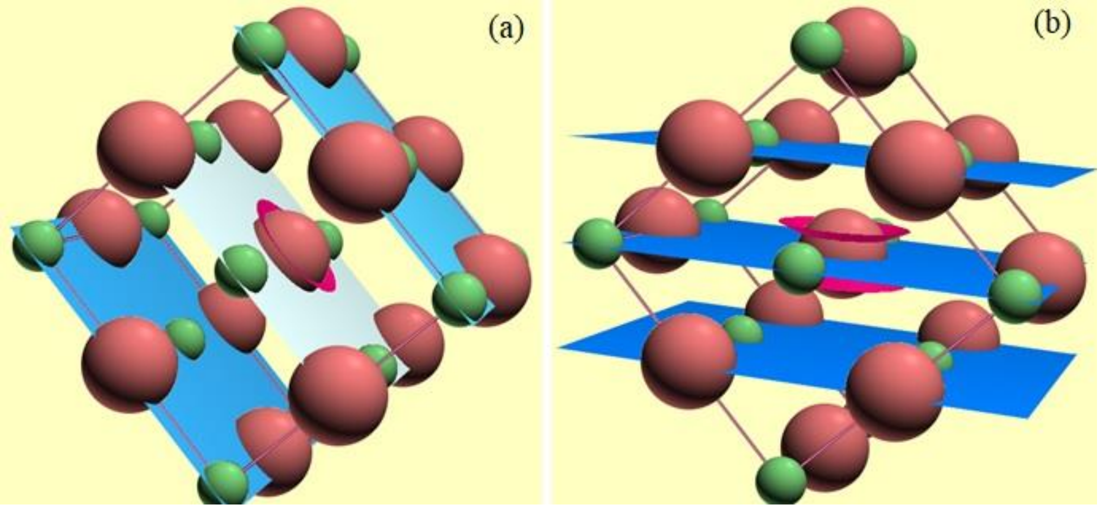


Figure 50: NaCl Structure (a) The (200) planes of atoms in NaCl (b) The (220) planes of atoms in NaCl (Source: https://www.slideshare.net/msakhan61/xray-diffraction-analysis-for-material-characterization)

In the research, did not insert any foreign materials with the heat treatment, thus changes in stoichiometric is not possible. Furthermore, at every measuring time instrument was calibrated using known sample and therefore instrumentation error has the least effect to the peak shift along the x-axis. The only possible reason is the microstructure parameters changes due to thermal annealing and due to that d-spaces got changed. To produce a blue colour in the *"Geuda"* gemstones there are three conditions to be fulfilled.

- *"Geuda"* gemstone should consist of Fe and Ti as impurities
- These Fe should in Fe^{2+} and Ti in Ti^{4+} valency state
- Fe^{+2} and the Ti^{4+} should in an adjacent way and due to that electron clouds of these atoms may get overlap

Therefore, could suggest that enhancement of blue colour means the overlap of Fe^{2+} and Ti^{4+} electron clouds. To overlap Fe and Ti, they should be in an adjacent way and thermal treatment produce kinetic energy to move these atoms inside the lattice structure.

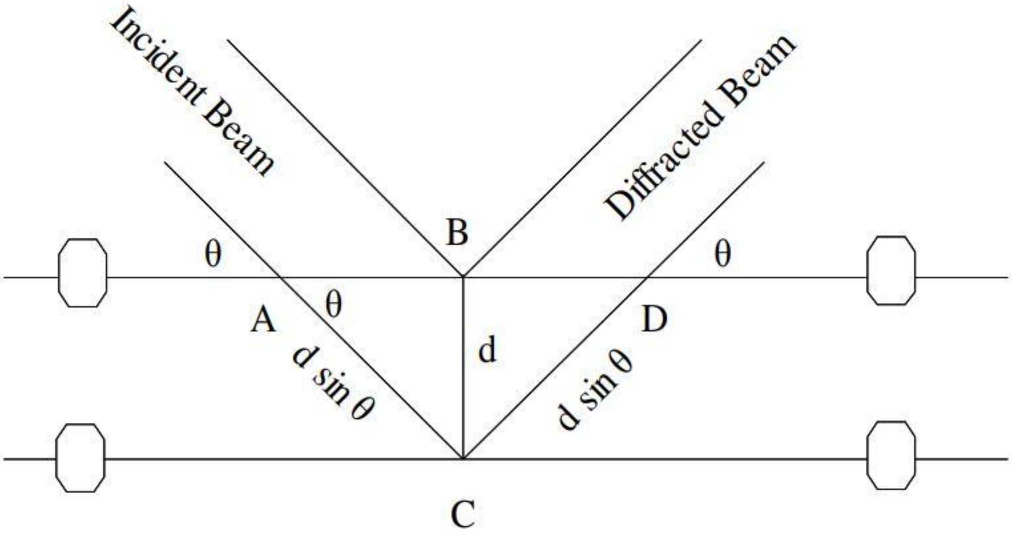


Figure 51: Brags Law illustration

3.4.1 d-spaces calculation base on XRD data

d- space was calculated using Bragg's law.

$$2d\sin\theta = n\lambda$$

Where,

λ is the wavelength of the x-ray (the incident wave), d is the spacing of the crystal layers (path difference),

θ is the incident angle (the angle between the incident ray and the scattering plane), and

n is the order of the equation (an integer)

the incident wavelength was 1.5406 Å since target material was Cu (K-α) and consider for the first-order equation for the calculations. Since the differences between this d – spaces are too small to illustrate using graphs. One example calculated d- spaces for different heat treatment methods are shown in Table 22 and all the other tables are in the annex 04 (Table 26 to Table 44)

Table 14: XRD d space vales G_01

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.150	38.117	37.825	2.371	2.357	2.359	2.377
α Al_2O_3 [2 0 0]	45.981	46.232	45.381	45.781	1.972	1.962	1.997	1.980
α Al_2O_3 [2 2 0]	64.300	64.865	63.982	64.547	1.448	1.436	1.454	1.443
Anatase TiO2 [2 0 0]	47.029	46.934	47.979	47.261	1.931	1.934	1.895	1.922
Anatase TiO2 [1 0 1]	27.893	28.213	27.997	27.698	3.196	3.161	3.184	3.218
α Fe2O3 [1 1 0]	41.633	41.984	41.973	41.473	2.168	2.150	2.151	2.176
α Fe2O3 [3 0 0]	65.300	65.102	65.398	65.589	1.428	1.432	1.426	1.422

There were small changes in the dimension of the lattice structure when changing the treatment method or the soaking time and these changes were not visible even in the graphs. For an example 2θ value of 37.917, d-spaces are 2.371 Å, 2.357 Å, 2.359 Å and 2.377 Å for unheated, gas heated, electric heated and combined heated respectively. Therefore, only the 3rd decimal place of the d-space has changed with the type of heat treatment method. The atomic radius of Al, Fe and Ti are 1.18 Å,1.25 Å and 1.36 Å correspondingly. The arbitrary peak shift along the X-axis may be due to the thermal energy transforms into kinetic energy and increased the mobility of the atoms inside the *"Geuda"* gemstone and that produced small destructions in the lattice structure.

3.4.2 Discussion of XRD analysis

With the XRD data could observe three important factors about heat treatment.

1. The crystallinity has remained unchanged with the heat treatment
   All the graphs showed (before and after heat treatments) same peak height and width without changing the shape. That is a distinguishing factor emphasizes the crystallinity of the structure. Although some *"Geuda"* specimens subjected to 1700°C temperature even for one month of soaking time the crystallinity has not changed.
2. Phase change has not occurred due to heat treatment
   Although there is small peak shift has occurred with the heat treatments due to d-space changes, the position of the peak remains in the regions within the defined phase.
3. d-space changed arbitrarily with heat treatment
   As illustrated in Table 22 (and all the tables of annex 04) d-spaces for different peaks have got different values with the maximum of second decimal place change and the important thing is these numbers haven't any significant pattern. d-space change means there are some disturbances has occurred inside the lattice structure. With high temperatures near to meting point, the atoms get excited and according to the colour formation theory of blue sapphire (Nassau, 2001), Fe and Ti atoms should be in an adjacent way. Since there is a colour improvement occurred inside the *"Geuda"* conclude that a random movement of atoms has happened inside the atomic structure. Due to the random movement d-space values got changed accordingly without any significant pattern.

3.4 XRF Analysis

XRF (X-Ray Fluorescence) is one of the latest technologies that adopt in the gem industry to identify gemstones chemical composition and various treatment techniques such as lattice diffusion, surface diffusion, fracture filling, surface filling etc (Smith & McClure, 2002). Since some of the gemstones were provided with the desired colour, some of them were didn’t produces a blue colour under the same conditions (heat treatment methods, maximum temperature, soaking time). Thus, 30 heat-treated samples (10 - light blue, 10 - medium blue and 10 - dark blue) were subjected to the XRF analysis to identify element percentages. Table 23 to Table 25 illustrate the percentage variation of major elements present in the *“Geuda”* stones under three categories.

According to the XRF analysis of *“Geuda”* stones, more than 90% consists of aluminium and the most abundant impurity is zircon (Zr) which corresponds to the 2%-4%. Other impurities are Si, Cr and V. colouring agents (Fe and Ti) are present in very low amounts 0.3-0.7% iron and 0.03 to 0.09% titanium respectively. The variation of iron content is not very much fluctuating within Light Blue, Medium Blue and Dark Blue, nevertheless, titanium may change according to the intensity of blue colour.

Table 23: XRF analysis of Light Blue Sapphire

Element (%)	LB_01	LB_02	LB_03	LB_04	LB_05	LB_06	LB_07	LB_08	LB_09	LB_10
Al	95.2	94.8	92.8	96.8	94.6	95.5	93.8	96.5	92.7	93.3
Zr	3.3	3.9	2.31	3.02	2.22	2.83	2.74	3.3	4.3	3.12
Si	2.05	4.89	0.885	1.84	1.18	2.84	1.76	1.22	1.64	1.43
Cr	.0149	.0012	.0264	.0287	.0071	.0033	.0471	.0351	.0071	.0419
V	.0116	.0051	.007	.0247	.0111	.0124	.0375	.0114	.0154	.0224
Fe	.645	.775	.468	.753	.756	.663	.782	.601	.759	.684
Ti	.042	.048	.037	.068	.049	.067	.056	.042	.041	.054

Table 24: XRF analysis of Medium Blue Sapphire

Element (%)	MB_01	MB_02	MB_03	MB_04	MB_05	MB_06	MB_07	MB_08	MB_09	MB_10
Al	93.2	94.1	96.8	94.4	95.3	92.7	94.1	93.3	92.8	93.2
Zr	2.98	3.53	1.53	0	5.42	4.47	1.91	1.09	2.78	2.89
Si	.895	3.13	3.17	1.33	0.478	1.34	1.17	3.92	1.62	2.9
Cr	.0087	.0169	.0062	.194	0	.0245	.0214	.001	.0424	.0122
V	.011	.0236	.0137	.633	.0217	.013	.0071	.0009	.0987	0.0291
Fe	.54	.555	.48	.587	.456	.568	.456	.563	.382	.601
Ti	.082	.078	.067	.062	.091	.087	.056	.062	.071	.068

Table 25: XRF analysis of Dark Blue Sapphire

Element (%)	DB_01	DB_02	DB_03	DB_04	DB_05	DB_06	DB_07	DB_08	DB_09	DB_10
Al	93.4	92.2	94.4	96.7	93.8	92.6	92.8	91.4	92.5	91.8
Zr	3.09	3.01	3.39	3.31	4.25	3.55	4.41	7.8	4.21	3.84
Si	1.31	1.44	1.18	2.06	2.78	1.58	2.71	4.96	2.67	1.45
Cr	.0445	.0149	.0262	.0308	.0153	.0168	.0704	.0301	.0452	.0367
V	.0420	.0229	.0263	.0183	.0208	.0144	.0190	.0186	.0153	.0174
Fe	.351	.454	.365	.385	.493	.386	.443	.382	.401	.359
Ti	.075	.082	.078	.067	.068	.091	.087	.056	.062	.071

Fig. 109 to Fig. 112 illustrate the relationships between colour and the Ti, Fe and Al percentages and Fig. 112 shows the comparison between light blue, medium blue and the dark blue with the content of Al, Ti and Fe. There is a relationship for the blue colour enhancement and the amount of Ti present in the gemstone. When increased the Ti content in the gemstone there is a tendency to produce dark blue with the heat treatment process (Fig. 112).

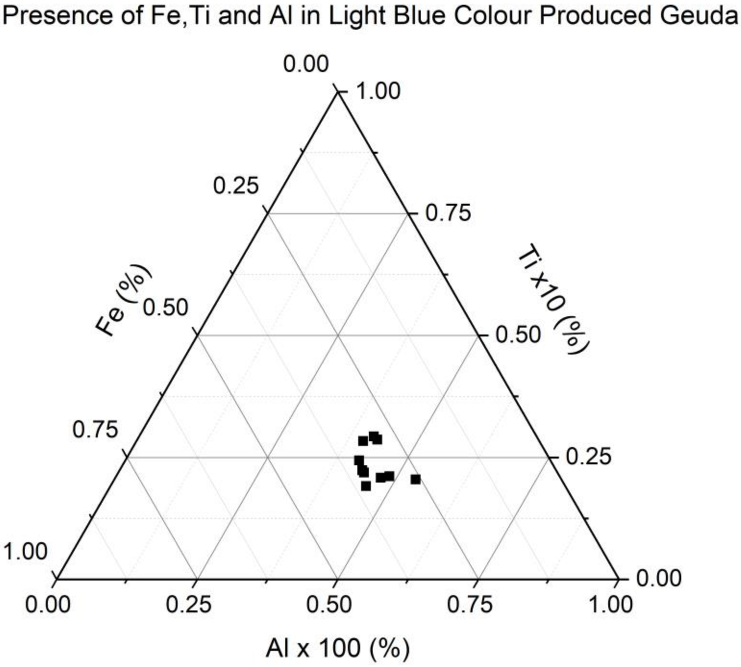


Figure 52: Presence of Fe, Ti and Al in Light Blue colour produced "Geuda"

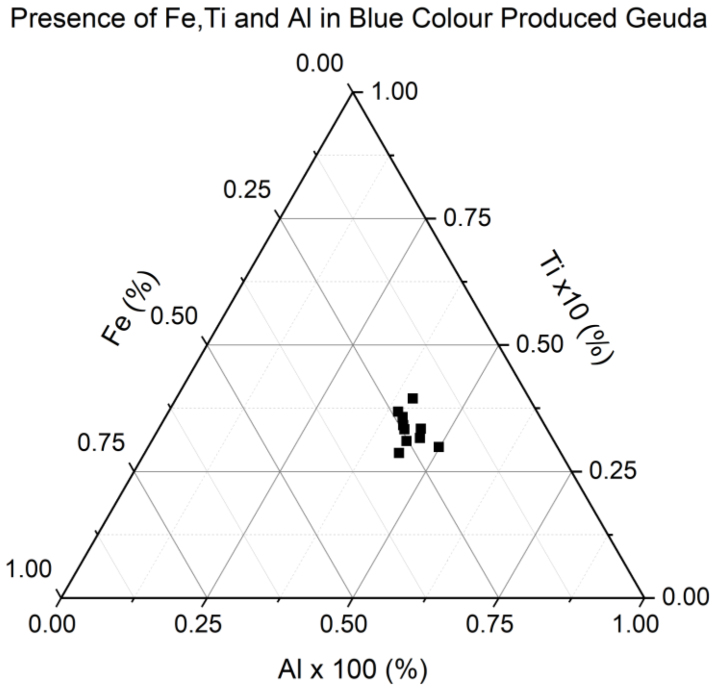


Figure 53: Presence of Fe, Ti and Al in Medium Blue colour produced "Geuda"

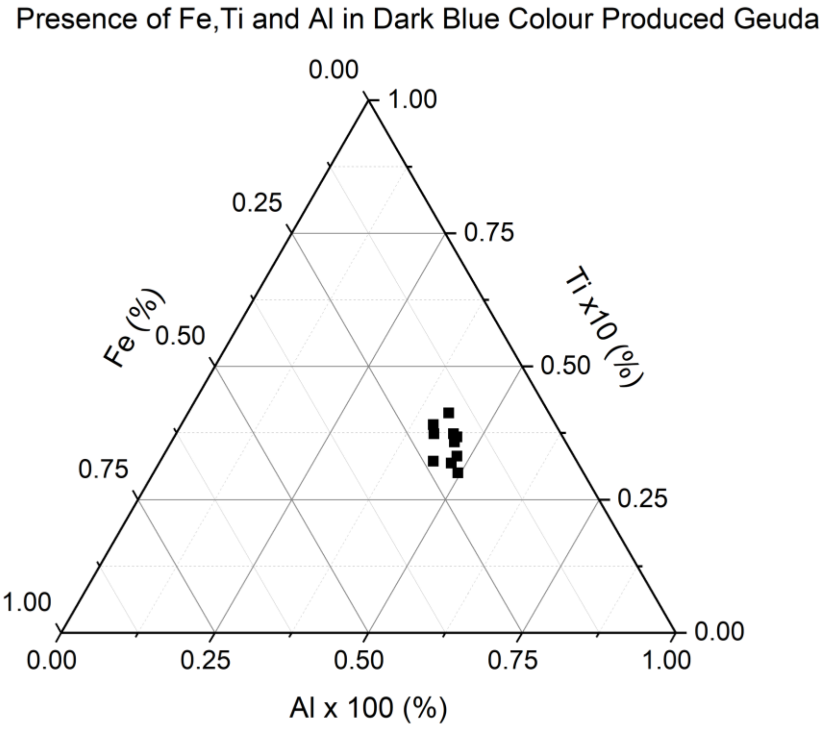


Figure 54: Presence of Fe, Ti and Al in Dark Blue colour produced "Geuda"

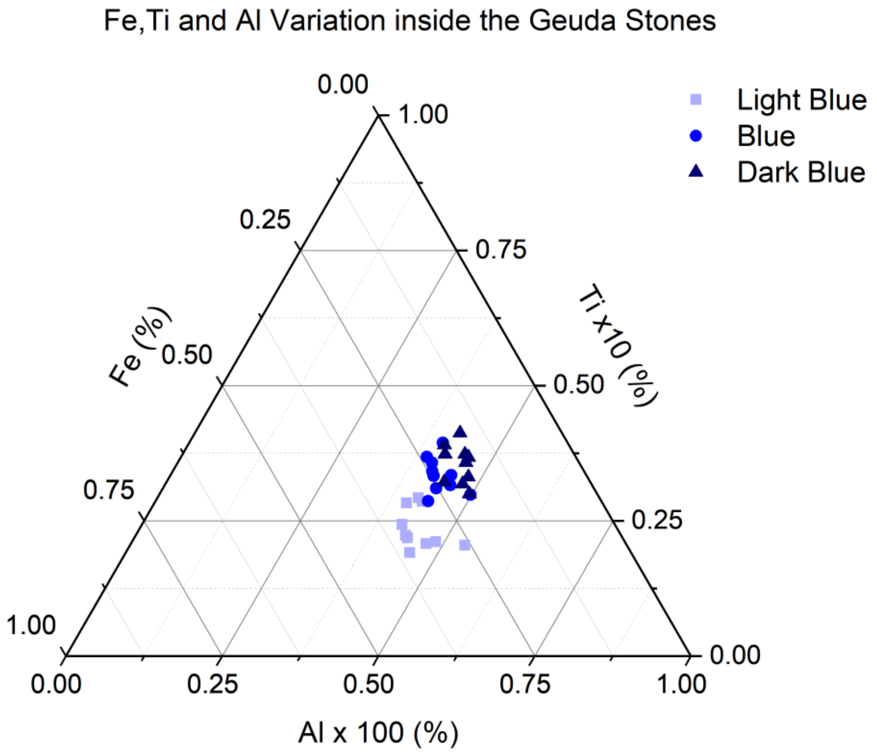


Figure 55: Fe, Ti and Al variation inside the "Geuda" stones

3.4.1 Discussion of the XRF analysis

Thirty *"Geuda"* samples heat-treated under different conditions as mentioned in Fig. 17 were categorized cording to their blur hue (Dark Blue, Medium Blue and Light Blue). With the XRF obtained data, Fe and Ti affect the colour alteration. Furthermore, there is a relationship between blue colour enhancement and the amount of Ti present in the gemstone. When increased the Ti content in the gemstone there is a tendency to produce dark blue with the heat treatment process. Thus, only with the temperature and soaking time cannot predict the blue colour alteration.

4 CONCLUSION

- Combined heat treatment (1750^{o}C, 30 min at gas furnace and 1700^{o}C in an electric furnace) can produce more colour and clarity enhancement over gas furnace heat treatment or electrically operated furnace heat treatment.
- There was no significant effect to the colour alteration from the soaking time.
- Chemical nature also directly affects to the final colour alteration and Fe: Ti ratio in between 1:13 to 1: 7 would provide the optimum blue colour inside the geuda stones.
- FTIR and UV-Visible spectroscopy methods can use to identify heat treated "*Geuda*".
- XRD can use to identify crystallinity changes, phase changes and d-space changes of gemstones.

The summery of the conclusion could illustrate as follows (Fig. 113), method of heat treatment, furnace condition and the chemical nature directly affected to the colour enhancement in “*Geuda*” gemstone.

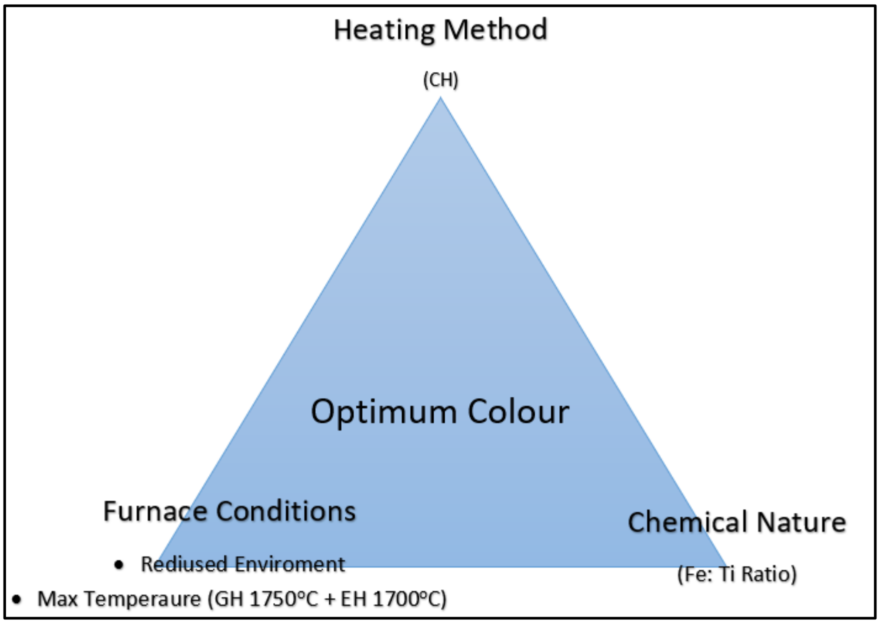


Figure 113: Final Conclusion of the research

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ANNEXURE 01 (UV-VISIBLE SPECTRUMS OF *“GEUDA”*)

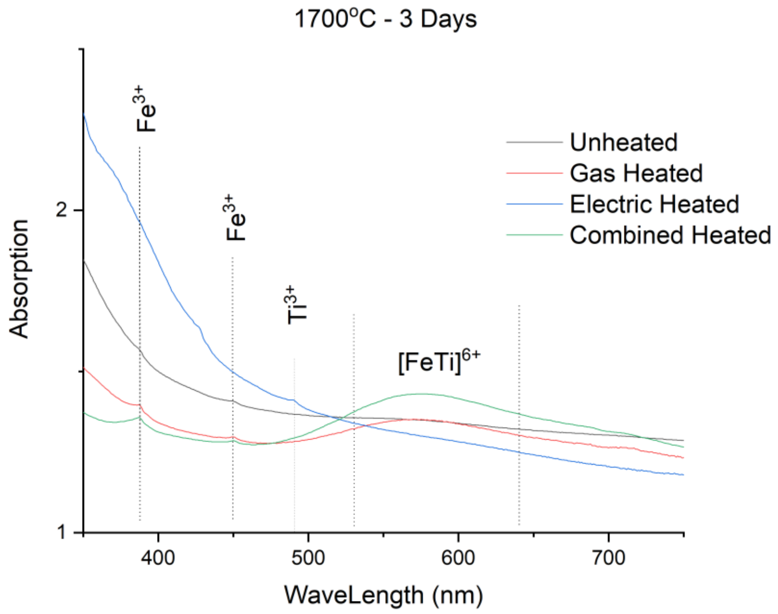

Figure 56: UV-Visible Spectrum G-01 1700ºC - 3 Days of soaking time

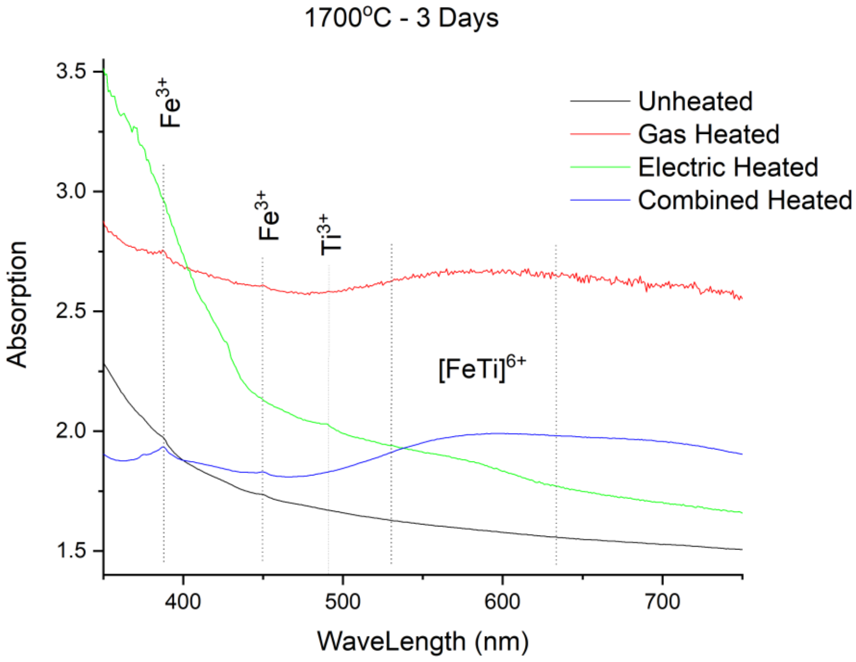

Figure 57: UV-Visible Spectrum G-02 1700ºC - 3 Days of soaking time

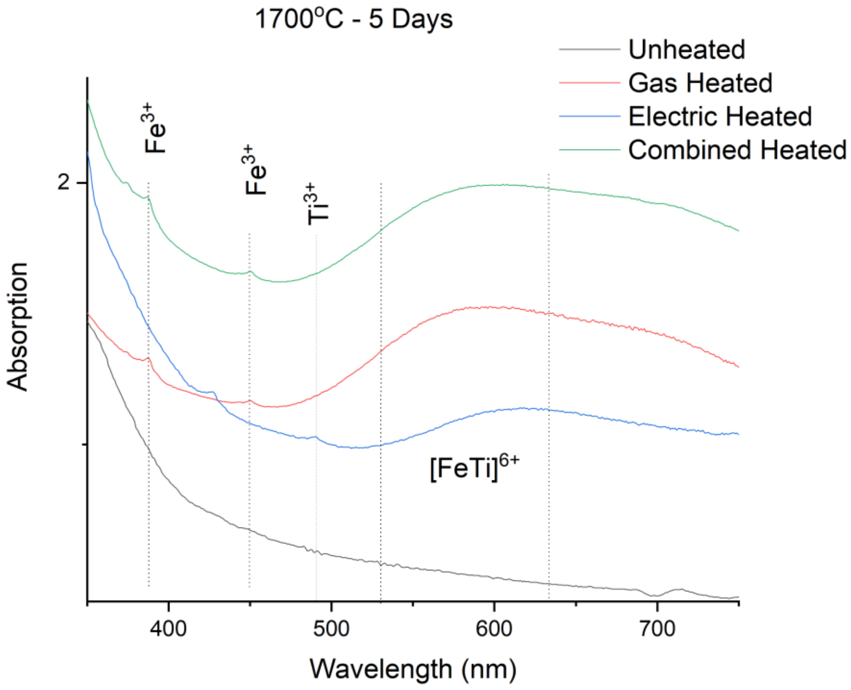

Figure 58:UV-Visible Spectrum G-03 1700°C -5 Days of soaking time

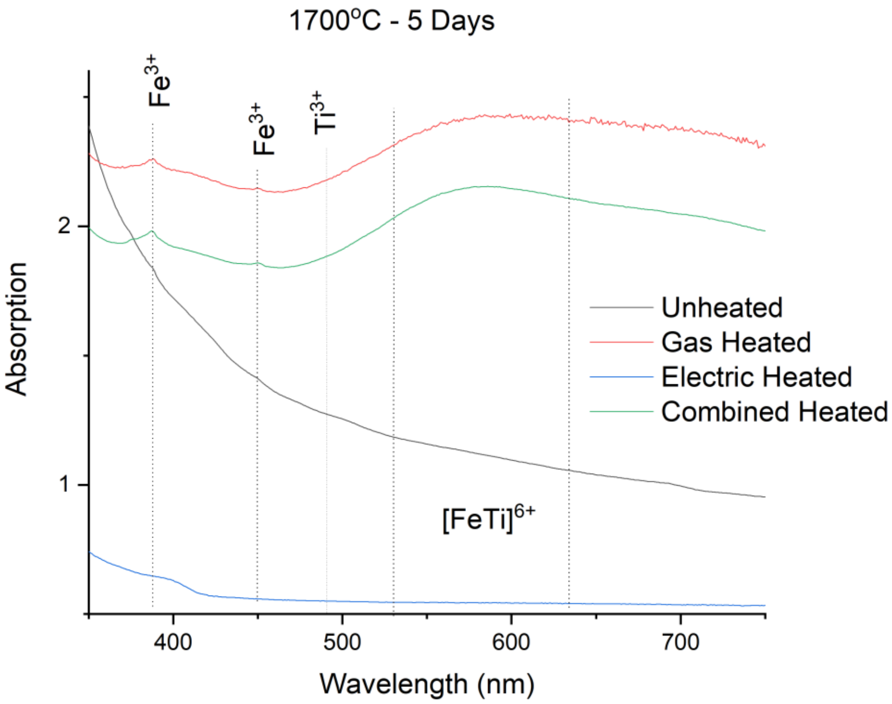

Figure 59: UV-Visible Spectrum G-04 1700°C -5 Days of soaking time

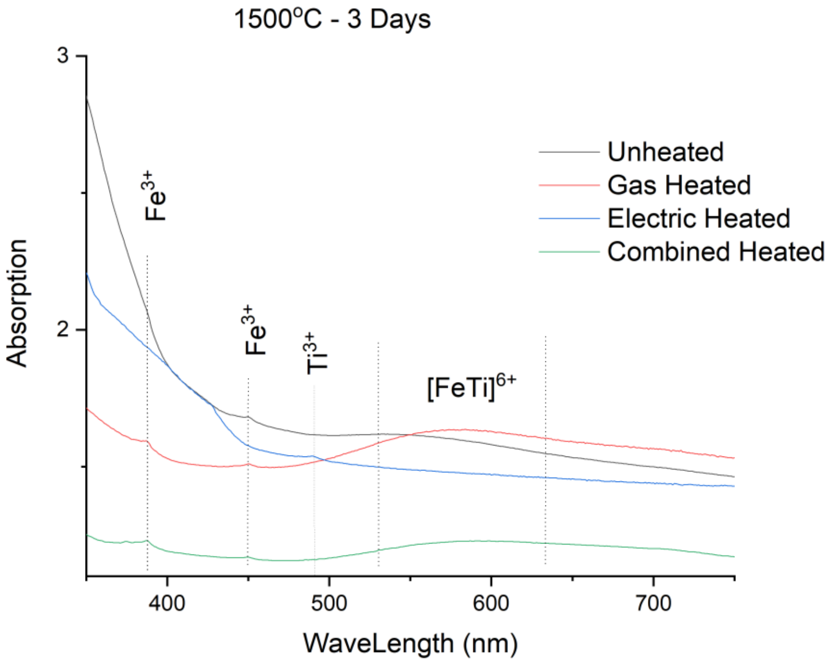

Figure 60: UV-Visible Spectrum G-06 1500°C - 3 Days of soaking time

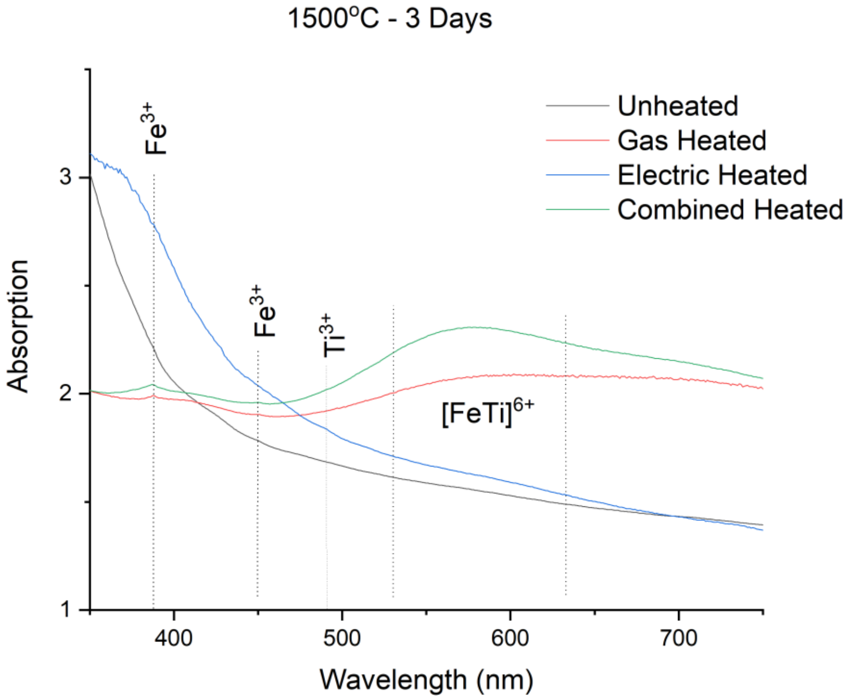

Figure 61: UV-Visible Spectrum G-05 1500°C - 3 Days of soaking time

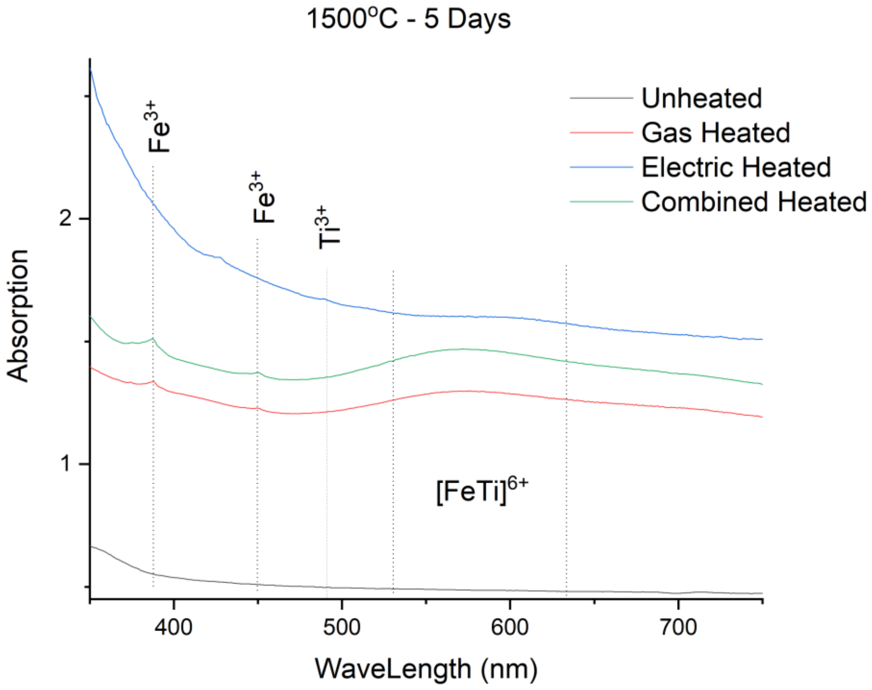

Figure 62: UV-Visible Spectrum G-07 1500ºC - 5 Days of soaking time

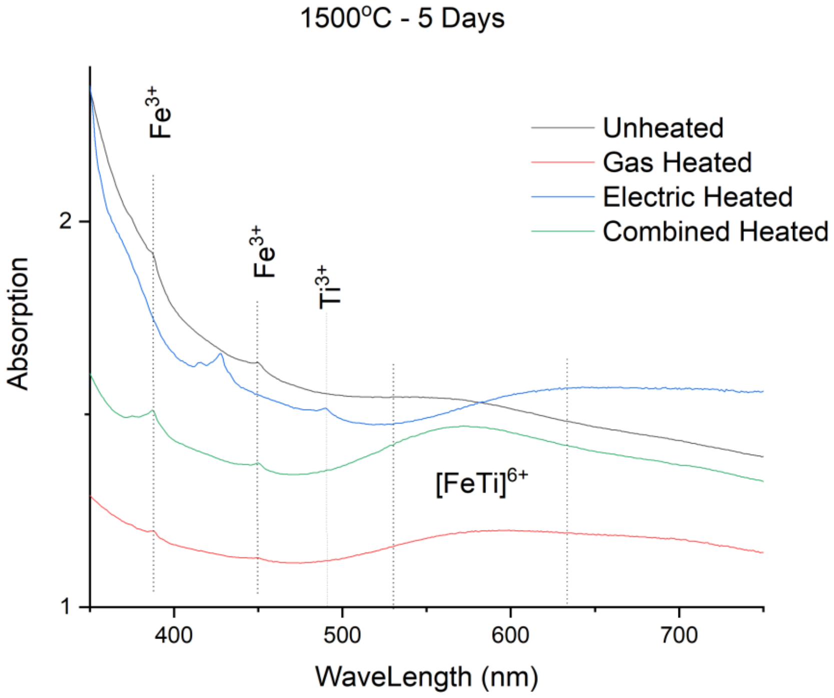

Figure 63: UV-Visible Spectrum G-08 1500ºC - 5 Days of soaking time

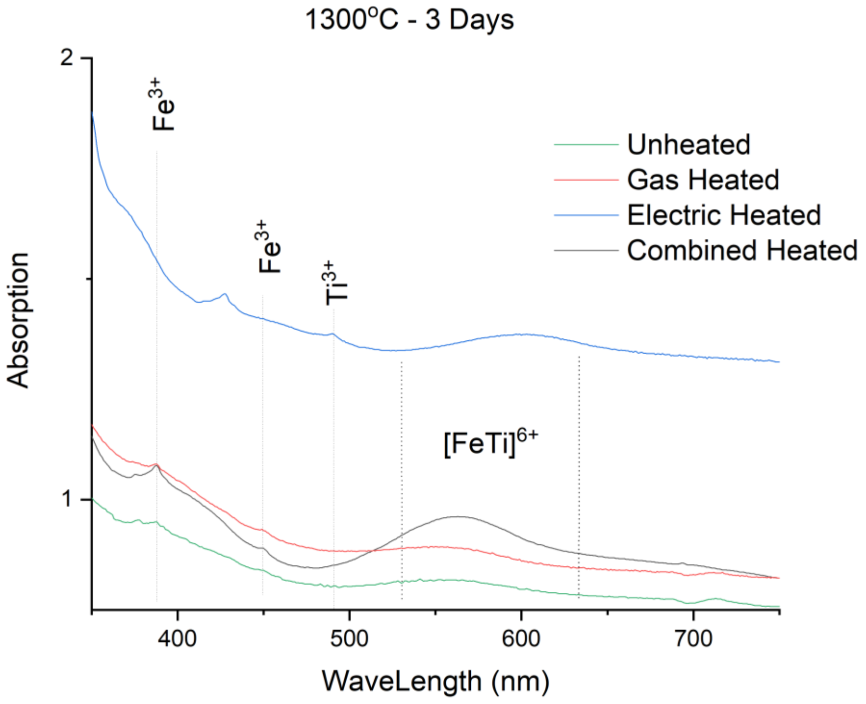

Figure 64: UV-Visible Spectrum G-08 1500ºC - 5 Days of soaking time

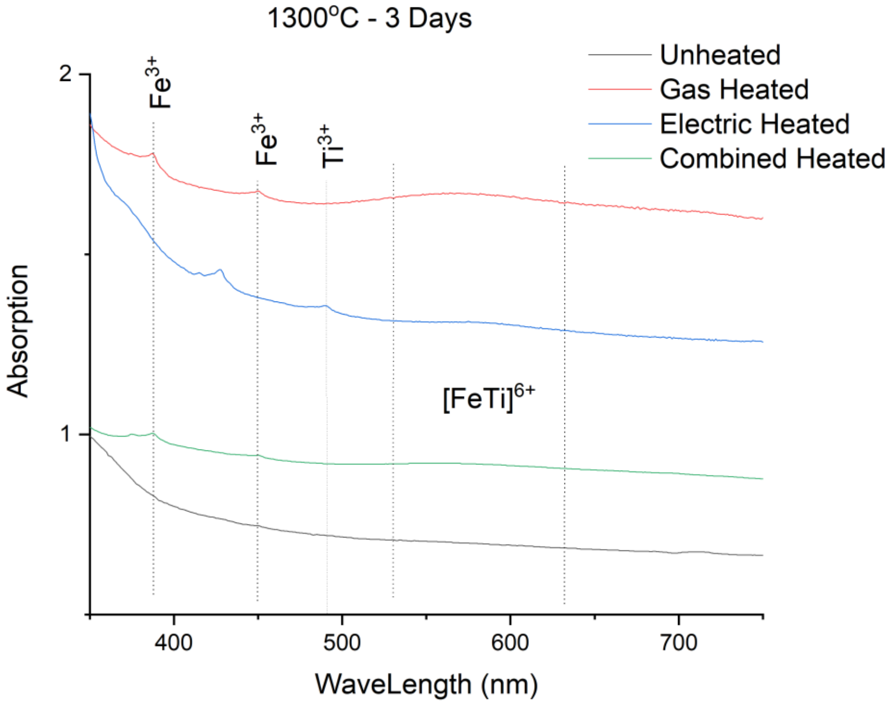

Figure 65: UV-Visible Spectrum G-09 1300ºC - 3 Days of soaking time

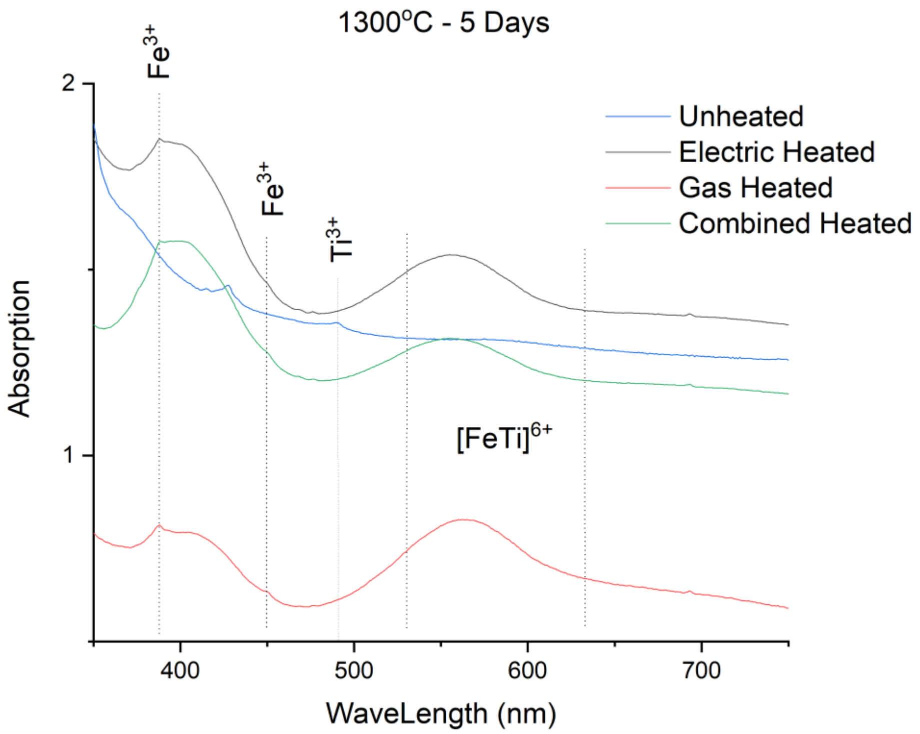

Figure 66: UV-Visible Spectrum G-10 1300ºC - 3 Days of soaking time

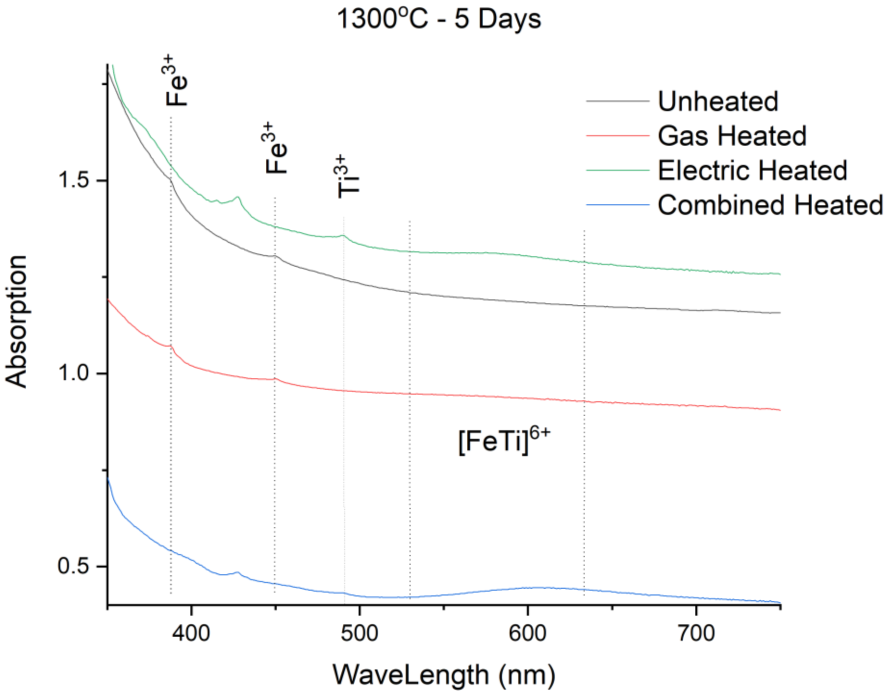

Figure 67: UV-Visible Spectrum G-11 1300ºC - 5 Days of soaking time

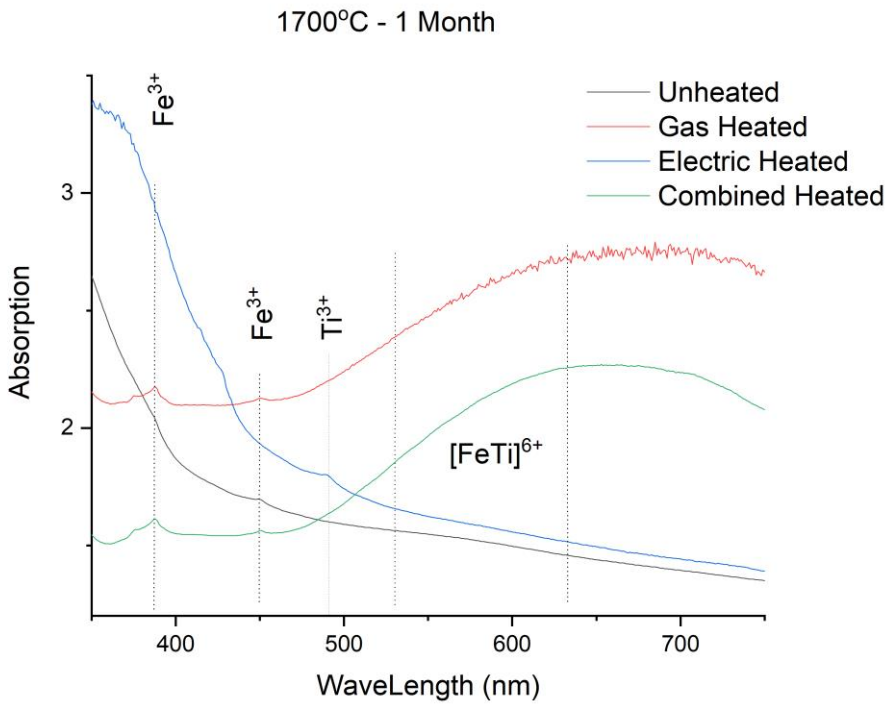

Figure 68:UV-Visible Spectrum G-13 1700ºC – 1 month of soaking time

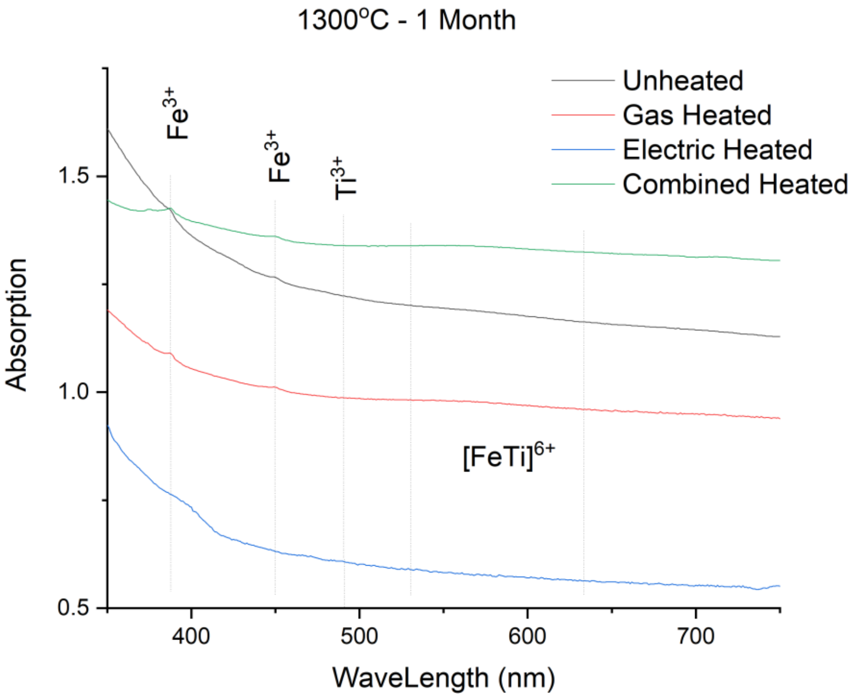

Figure 69: UV-Visible Spectrum G-14 1300ºC – 1 month of soaking time

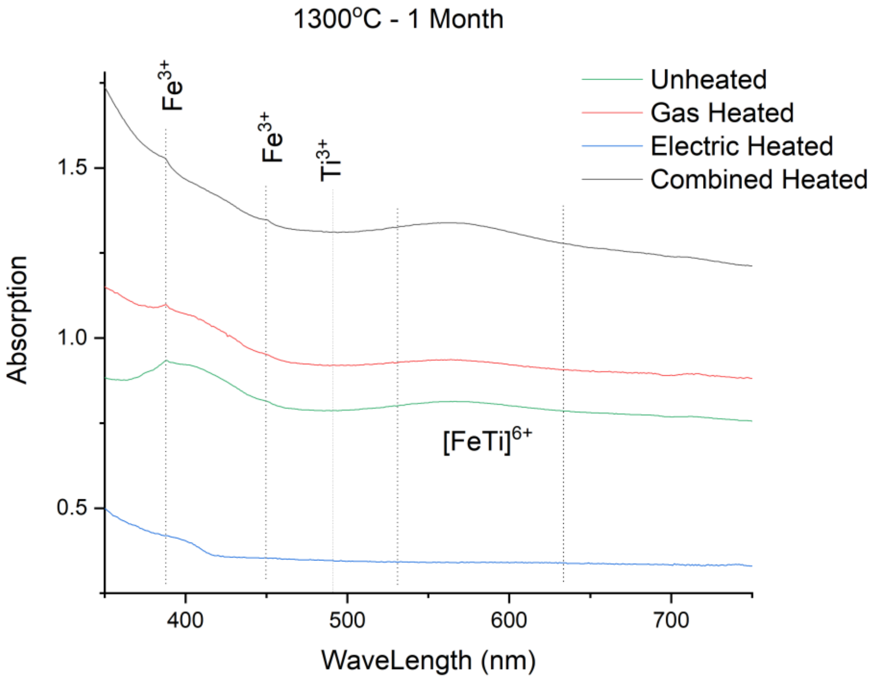

Figure 70: UV-Visible Spectrum G-15 1300ºC – 1 month of soaking time

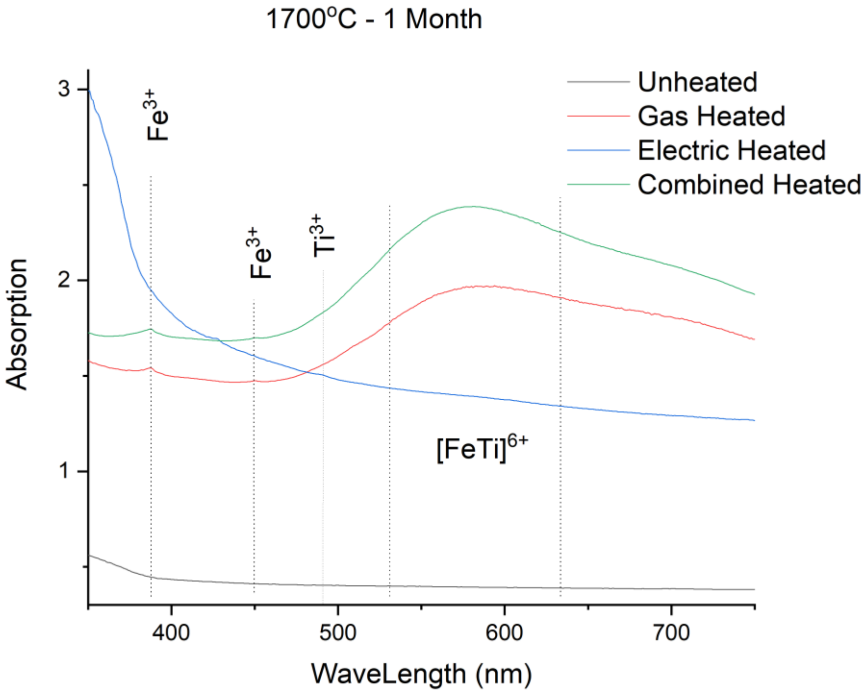

Figure 71: UV-Visible Spectrum G-16 1700ºC – 1 month of soaking time

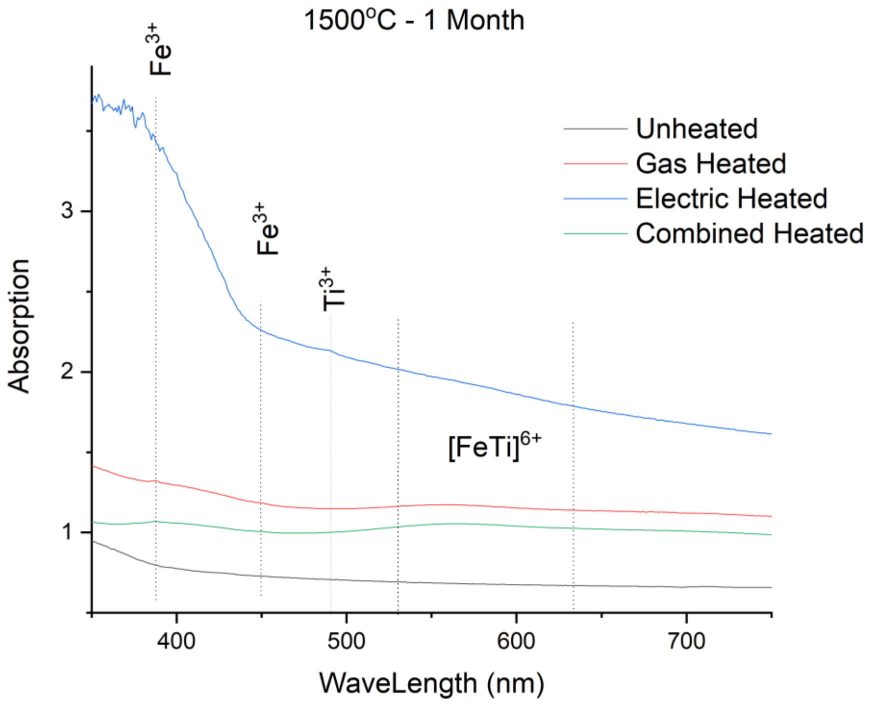

Figure 72: UV-Visible Spectrum G-17 1500ºC – 1 month of soaking time

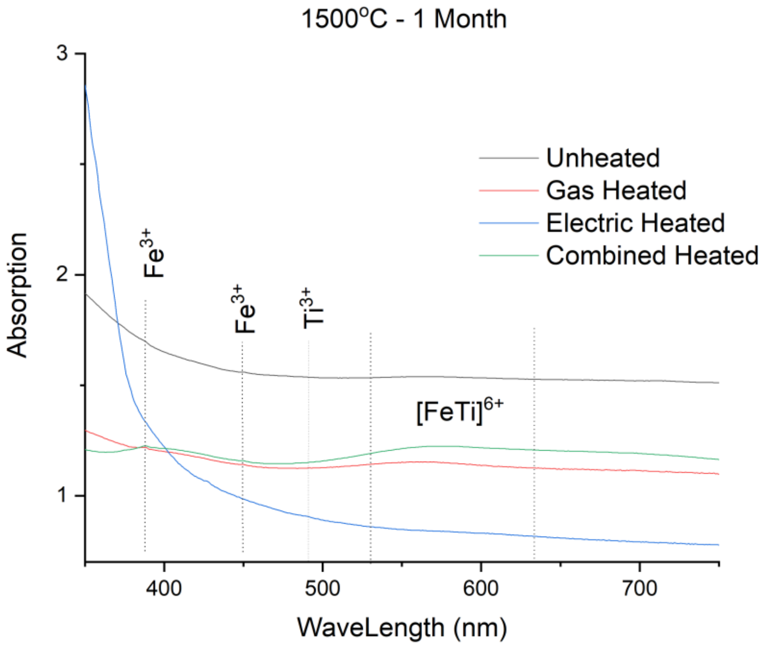

Figure 73: UV-Visible Spectrum G-18 1500ºC – 1 month of soaking time

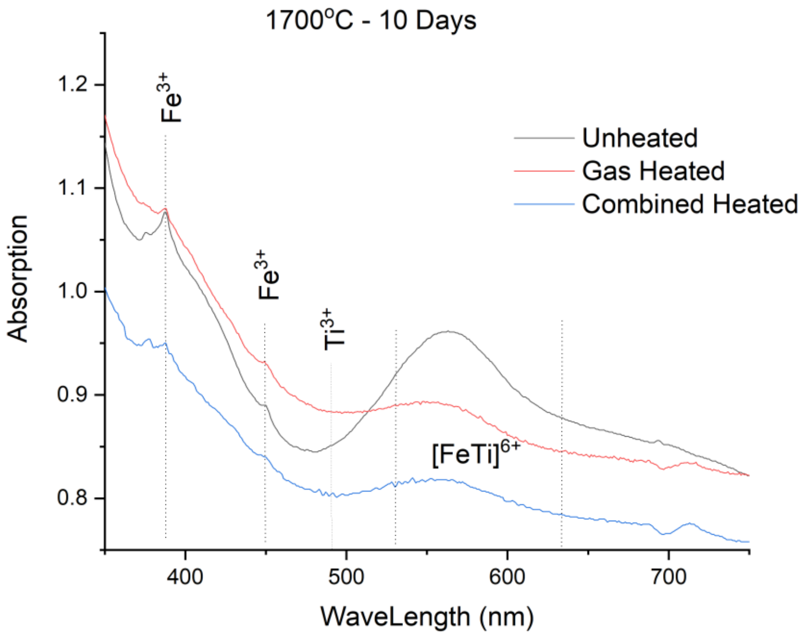

Figure 74: UV-Visible Spectrum G-19 1700ºC – 10 days of soaking time

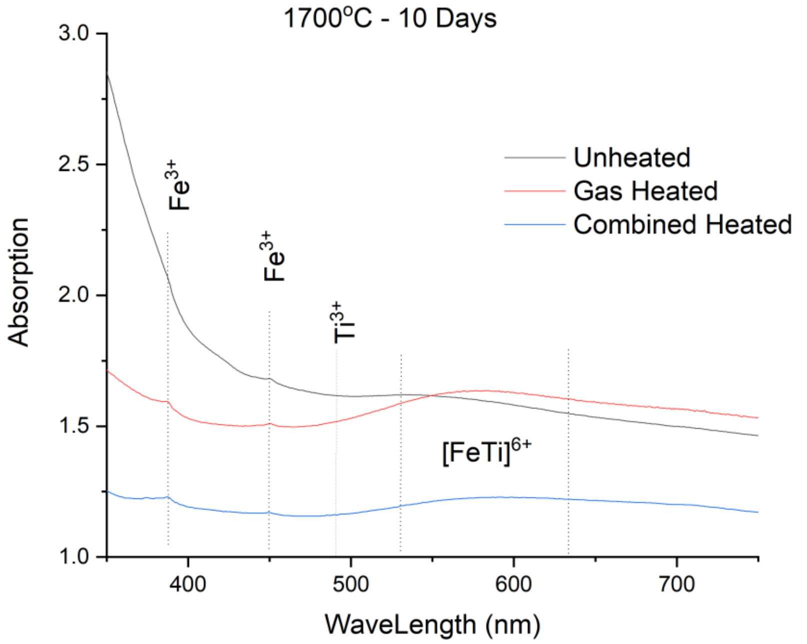

Figure 75: UV-Visible Spectrum G-20 1700ºC – 10 days of soaking time

ANNEXURE 02 (FTIR SPECTRUMS OF *"GEUDA"*)

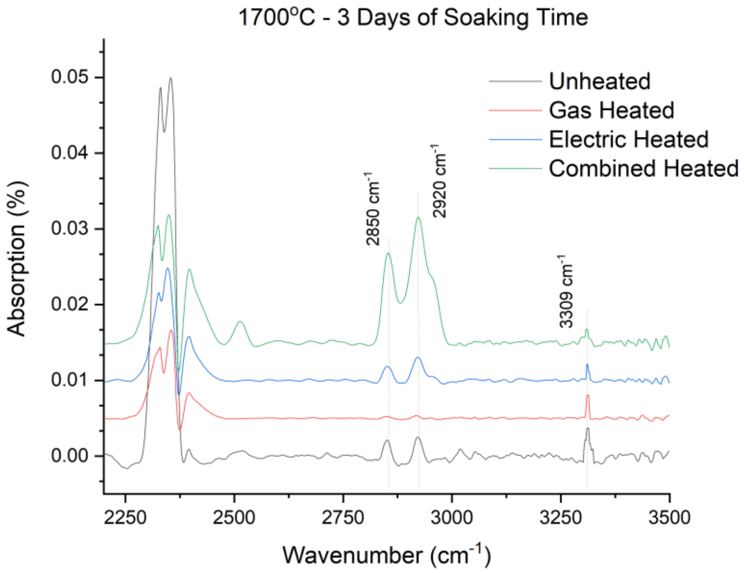

Figure 76: FTIR Spectrum – G-01_1700°C – 3 Days of the Soaking time

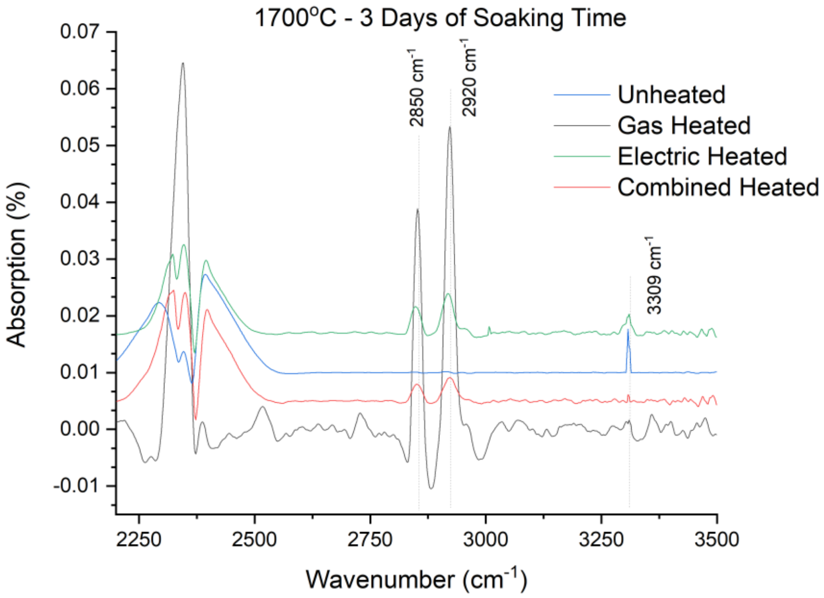

Figure 77: FTIR Spectrum – G-02_1700°C – 3 Days of the Soaking time

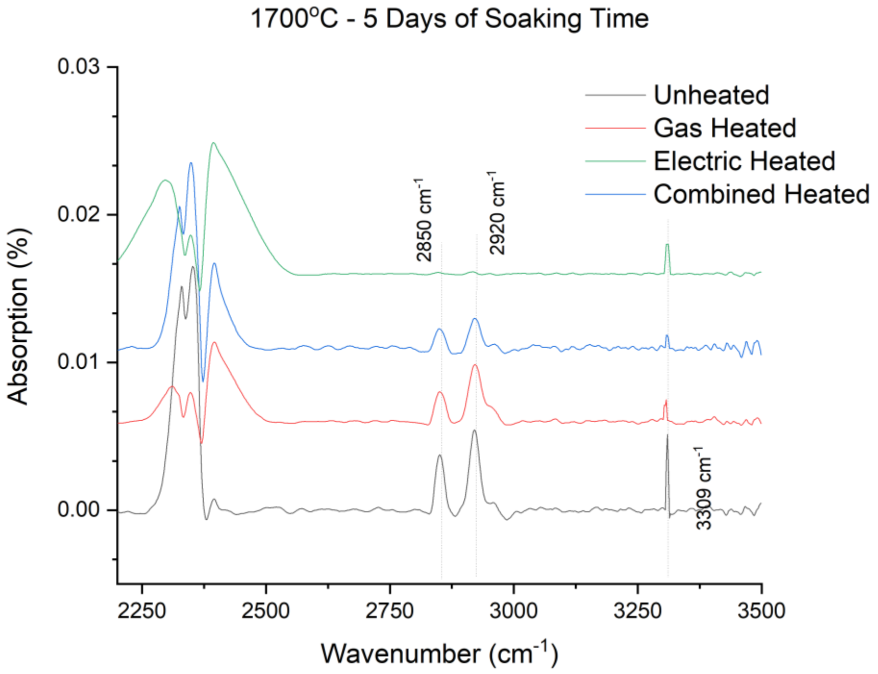

Figure 78: FTIR Spectrum – G-03_1700°C –5 Days of the Soaking time

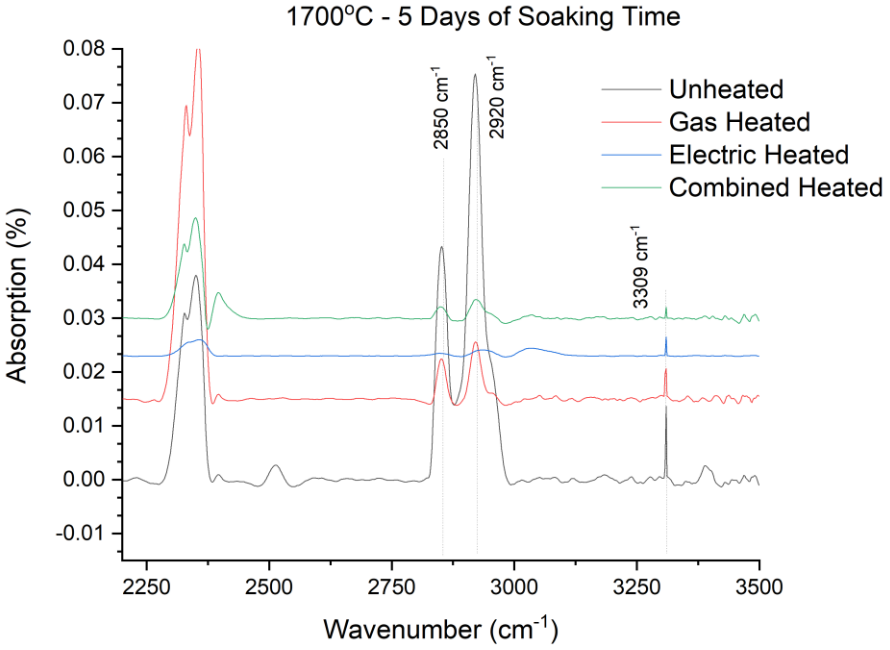

Figure 79: FTIR Spectrum – G-04_1700°C –5 Days of the Soaking time

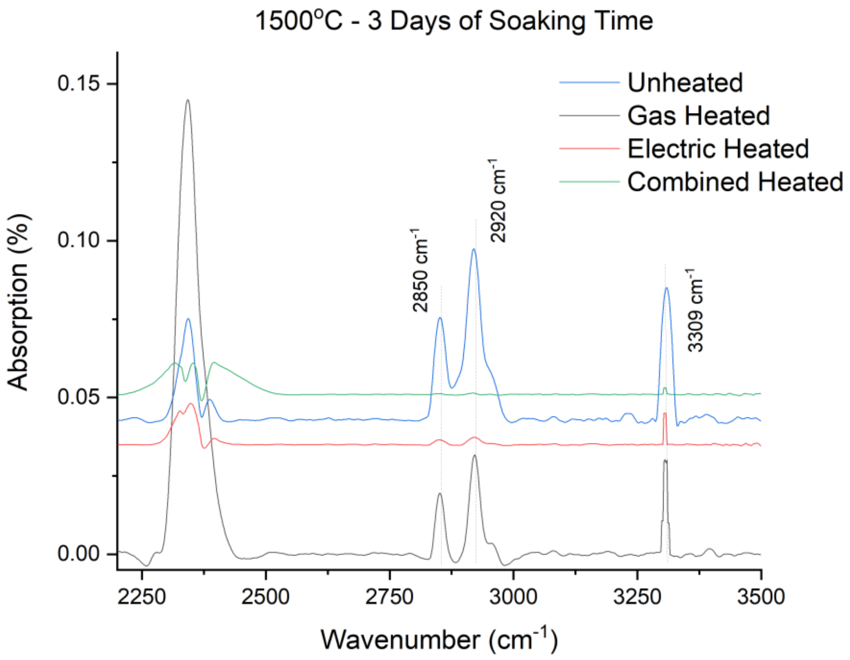

Figure 80: FTIR Spectrum – G-05_1500°C – 3 Days of the Soaking time

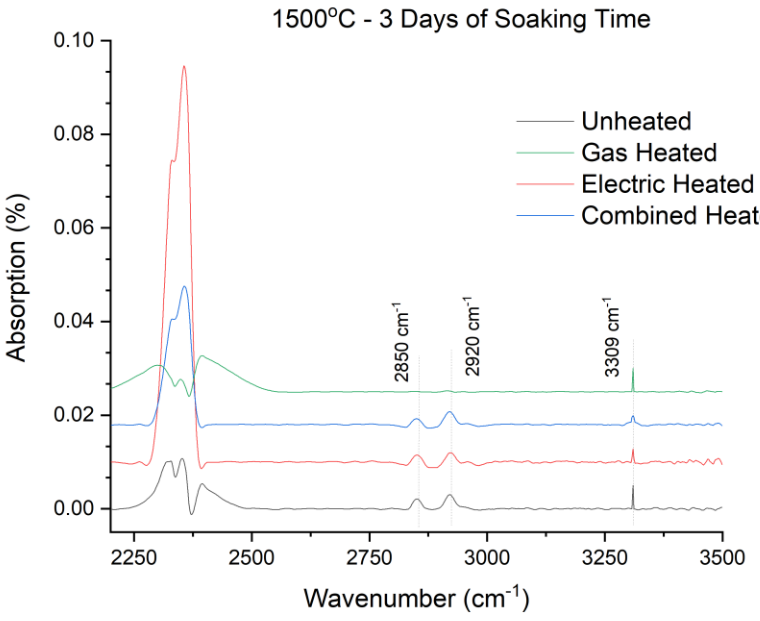

Figure 81: FTIR Spectrum – G-06_1500°C – 3 Days of the Soaking time

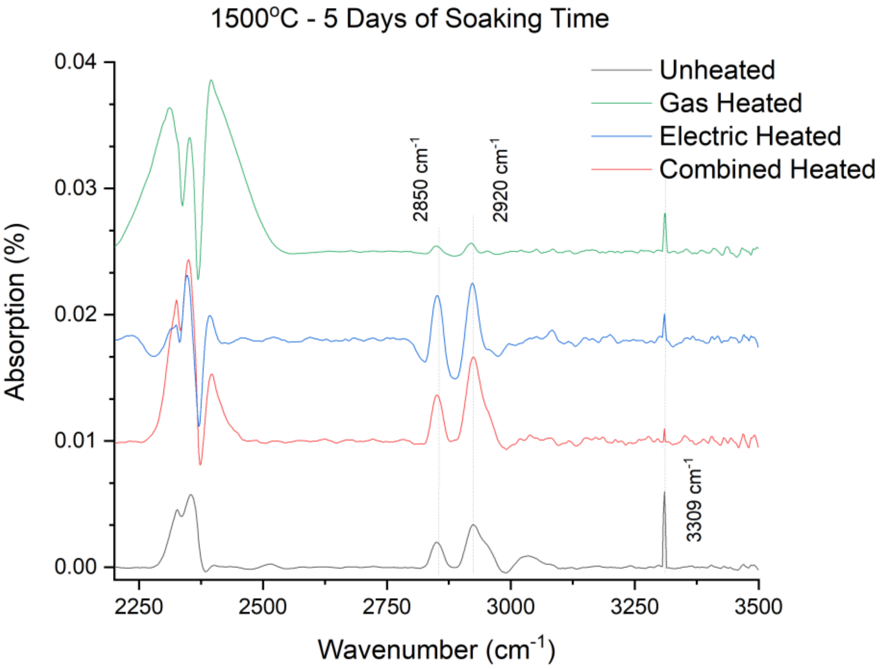

Figure 82: FTIR Spectrum – G-07_1500°C – 5 Days of the Soaking time

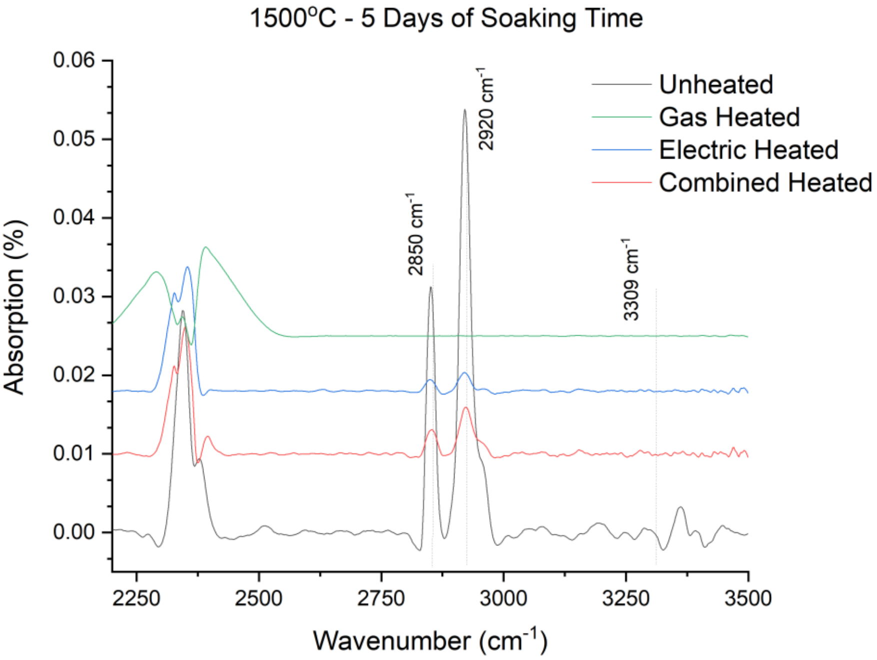

Figure 83: FTIR Spectrum – G-08_1500°C – 5 Days of the Soaking time

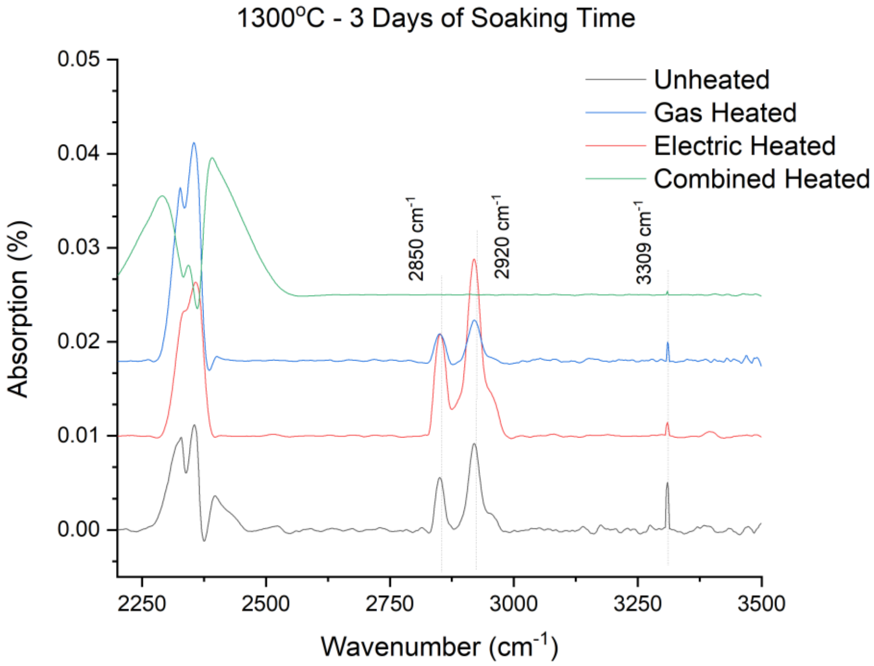

Figure 84: FTIR Spectrum – G-09_1300°C –3 Days of the Soaking time

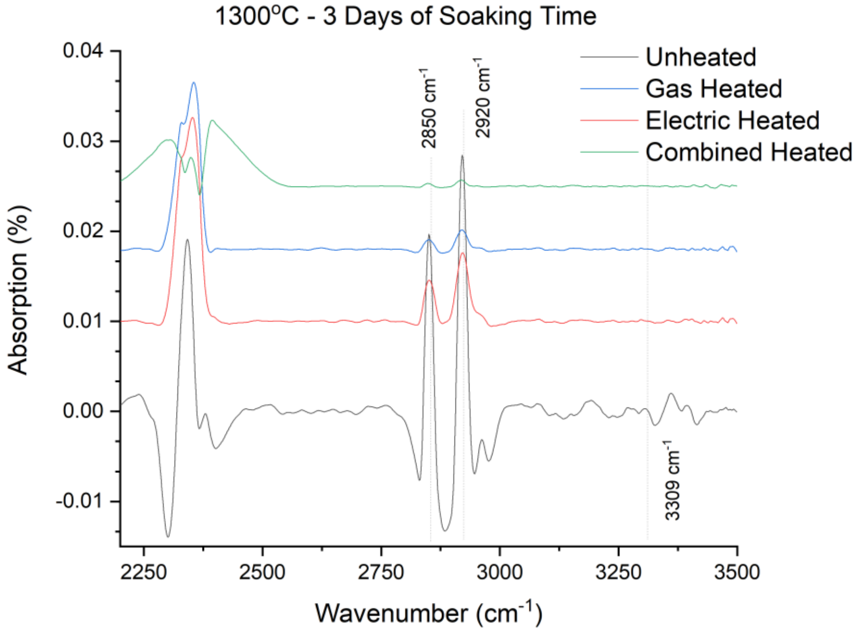

Figure 85: FTIR Spectrum – G-10_1300°C –3 Days of the Soaking time

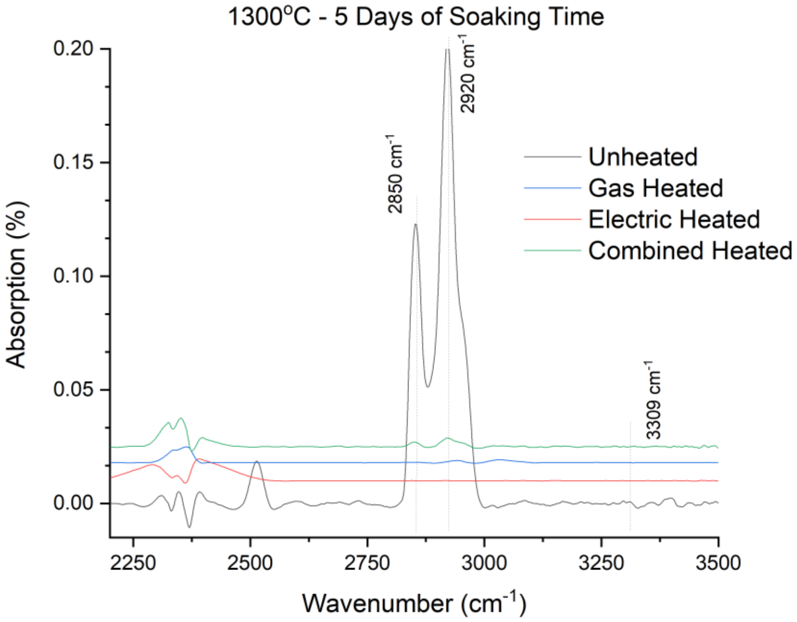

Figure 86: FTIR Spectrum – G-11_1300ºC 5 Days of the Soaking time

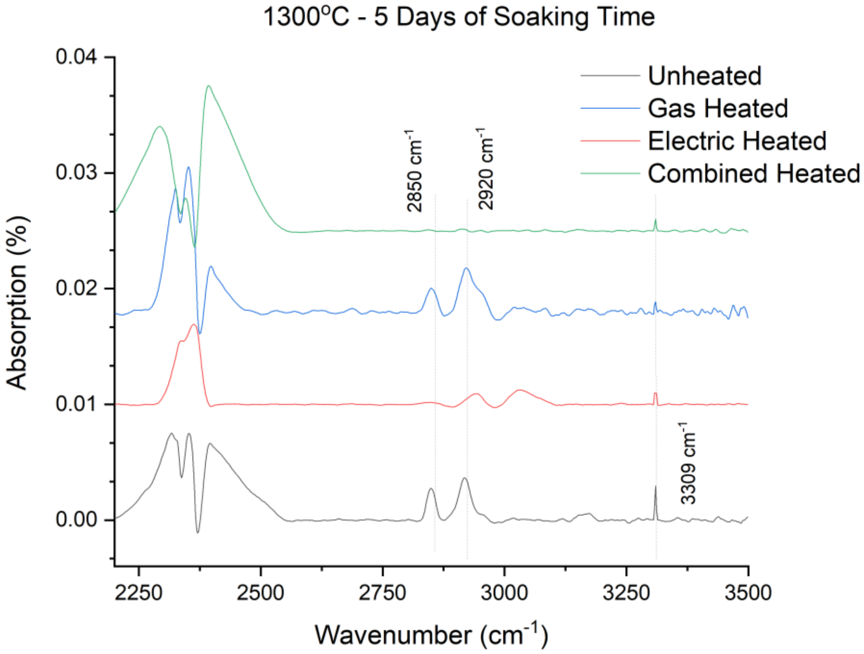

Figure 87: FTIR Spectrum – G-12_1300ºC 5 Days of the Soaking time

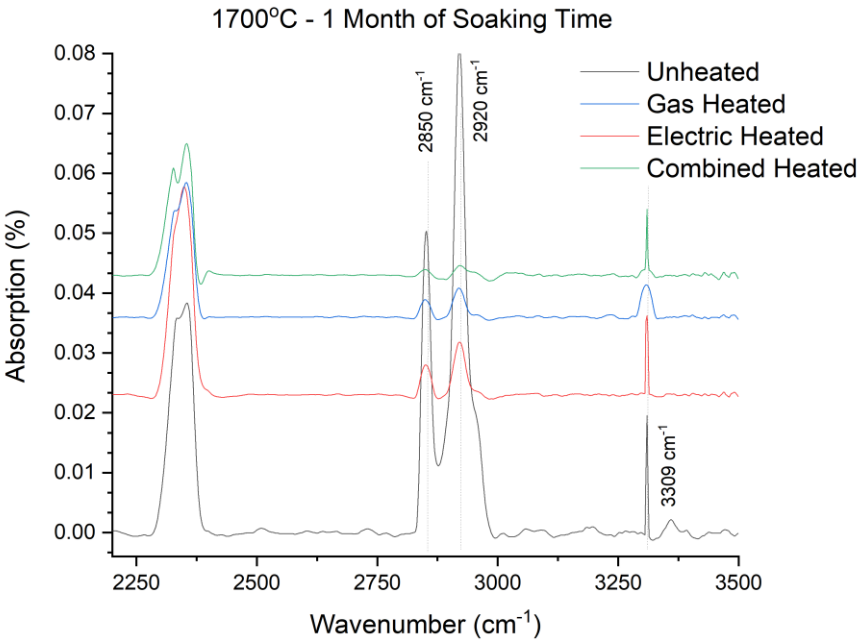

Figure 88: FTIR Spectrum – G-13_1700ºC 1 month of Soaking time

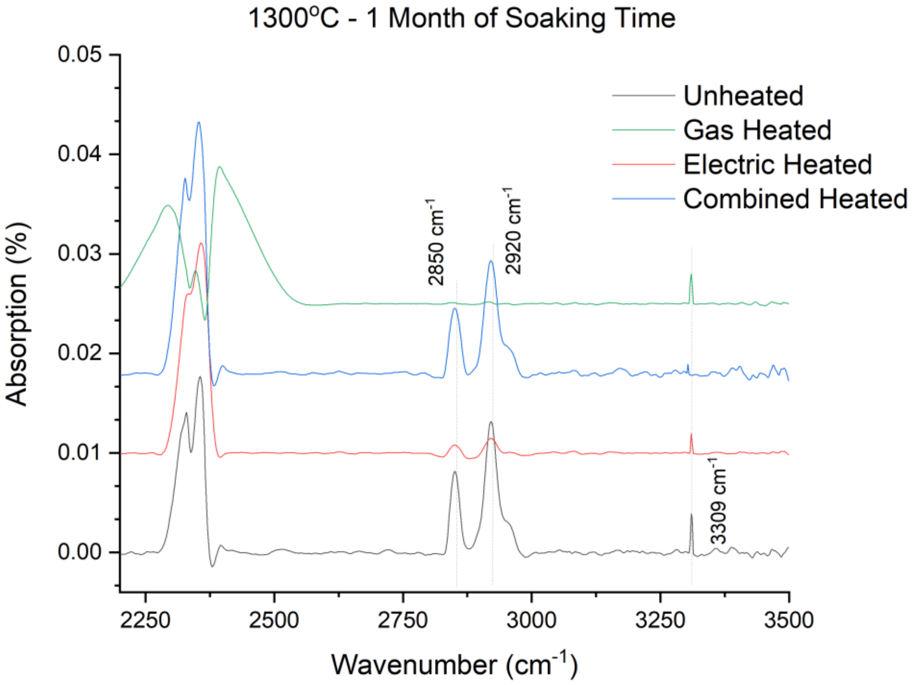

Figure 89: FTIR Spectrum – G-14_1700ºC 1 month of Soaking time

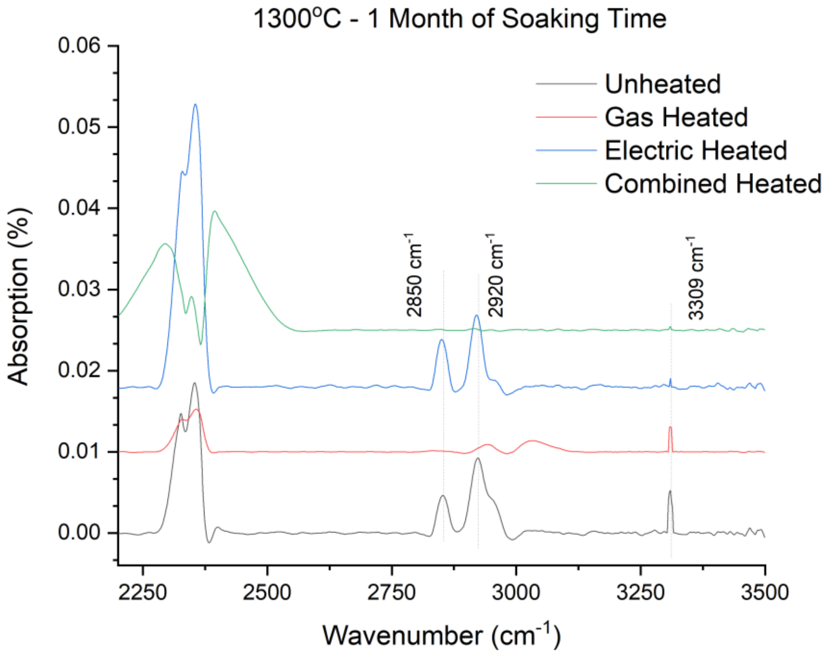

Figure 90: FTIR Spectrum – G-15_1300°C 1 month of Soaking time

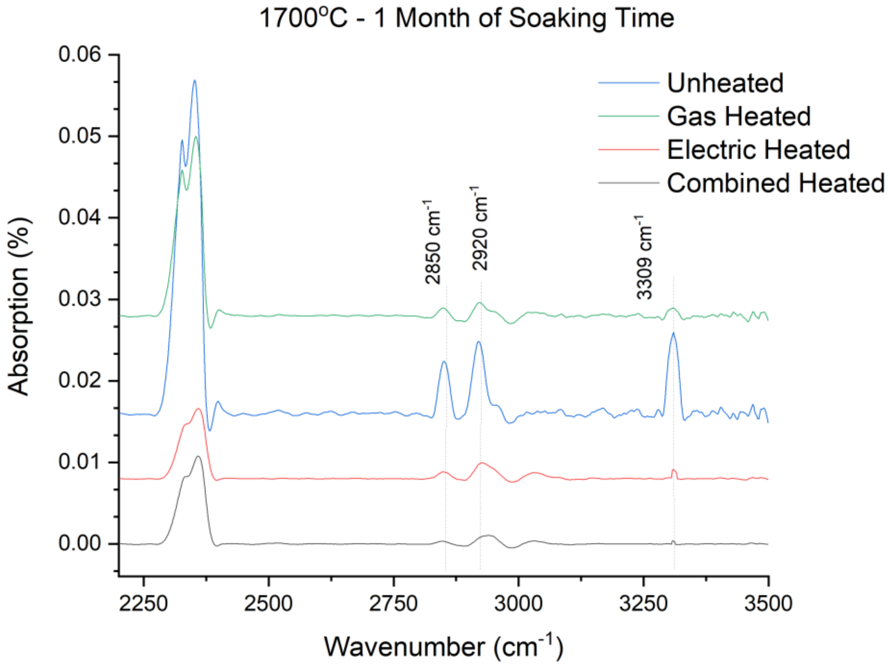

Figure 91: FTIR Spectrum – G-16_1700°C 1 month of Soaking time

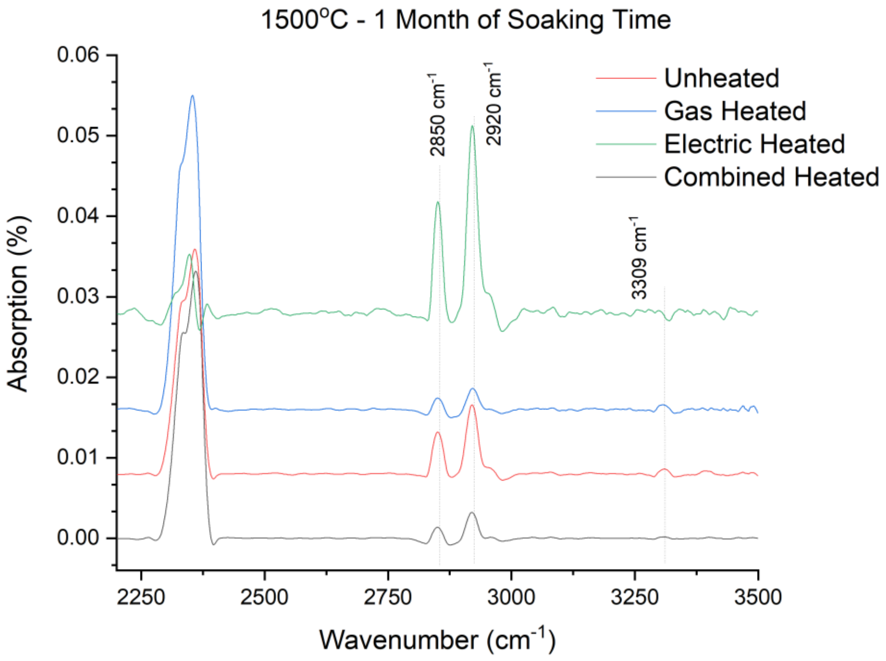

Figure 92: FTIR Spectrum – G-17_1500°C 1 month of Soaking time

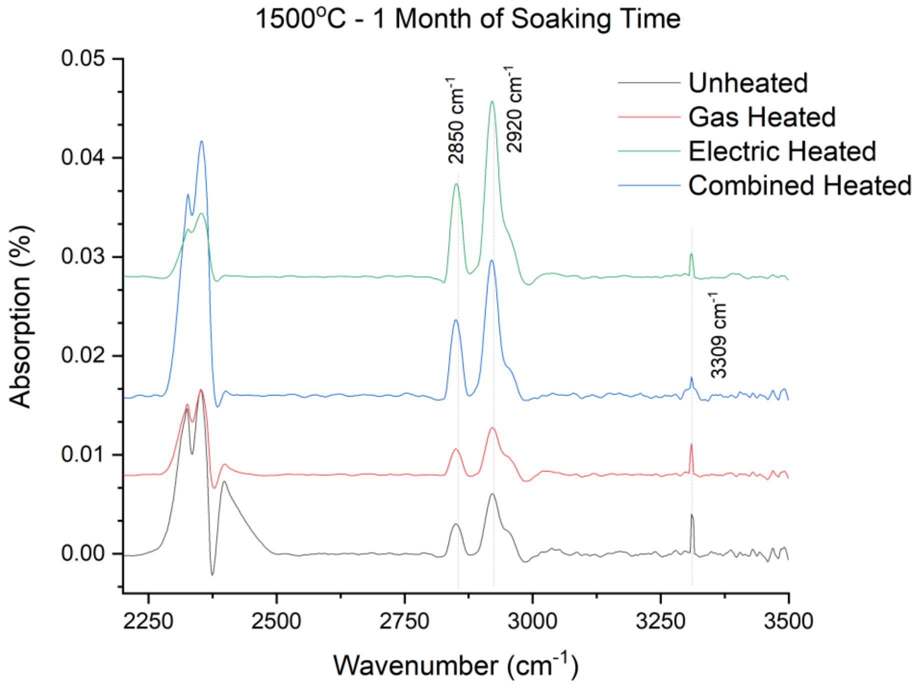

Figure 93: FTIR Spectrum – G-18_1500°C 1 month of Soaking time

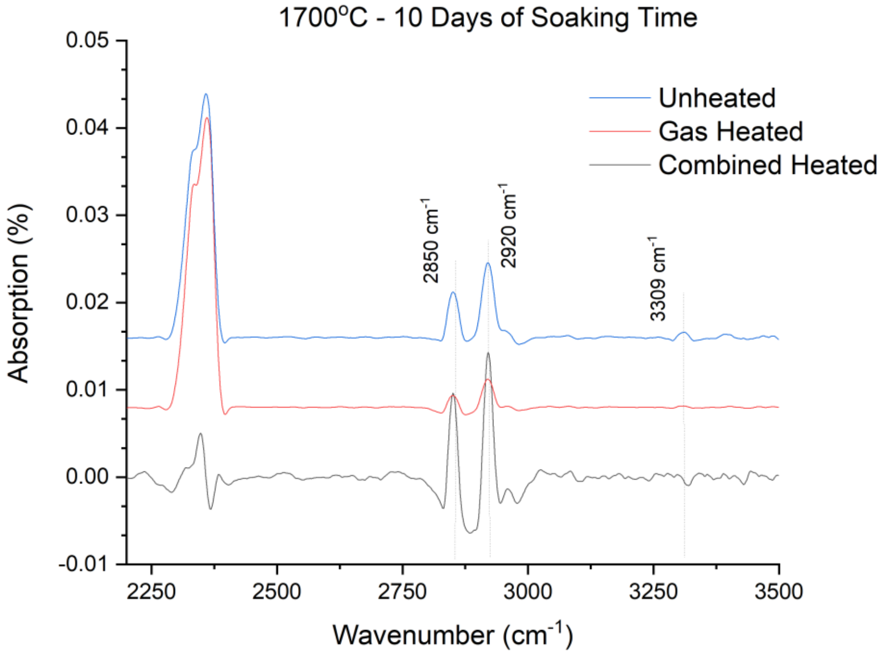

Figure 94: FTIR Spectrum – G-19_1700ºC 10 days of Soaking time

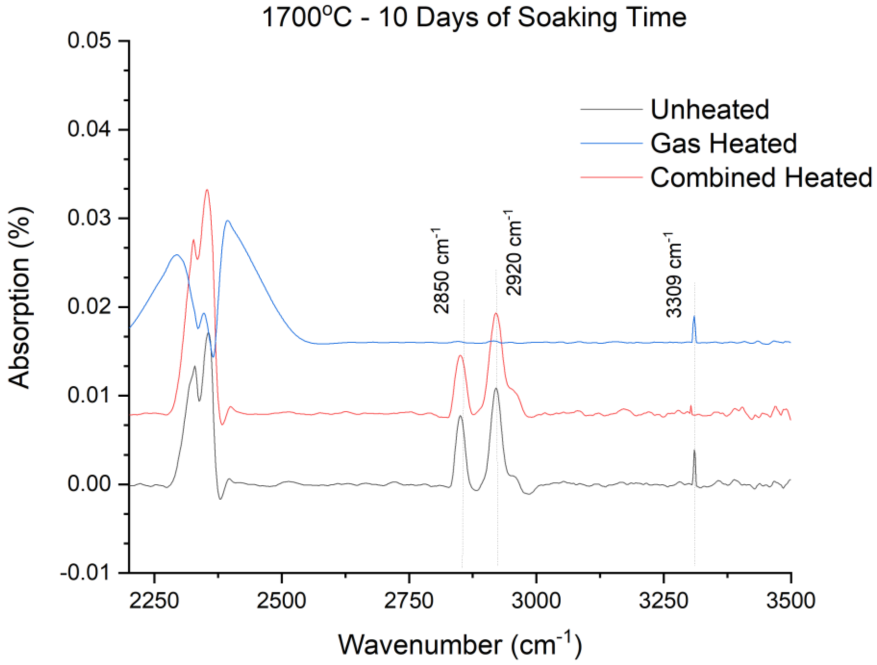

Figure 95: FTIR Spectrum – G-20_1700ºC 10 days of Soaking time

ANNEXURE 03 (XRD GRAPHS OF *"GEUDA"*)

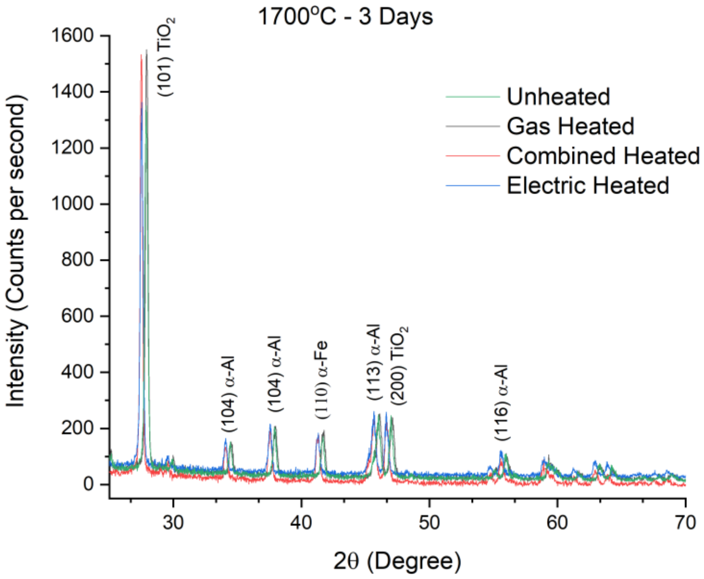

Figure 96: XRD Spectruscopy_G-01_1700°C 3 Days of soaking time

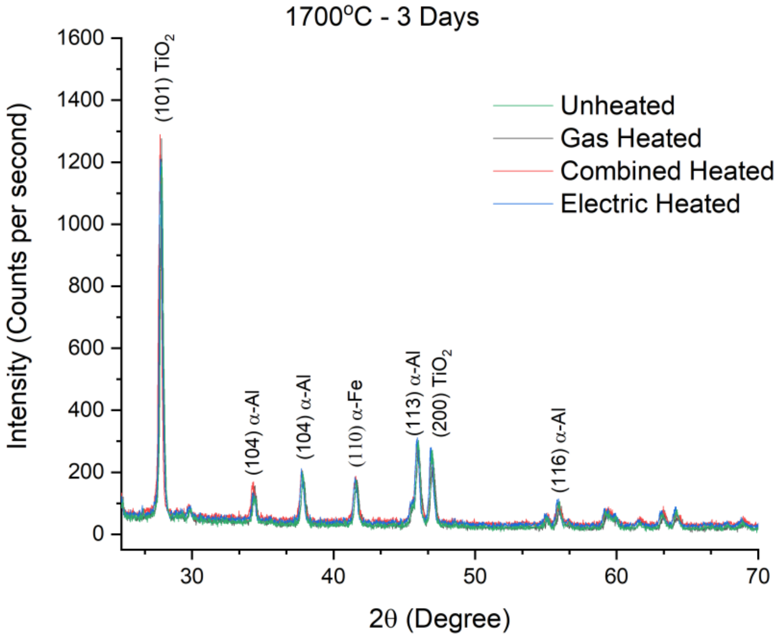

Figure 97: XRD Spectruscopy_G-02_1700°C 3 Days of soaking time

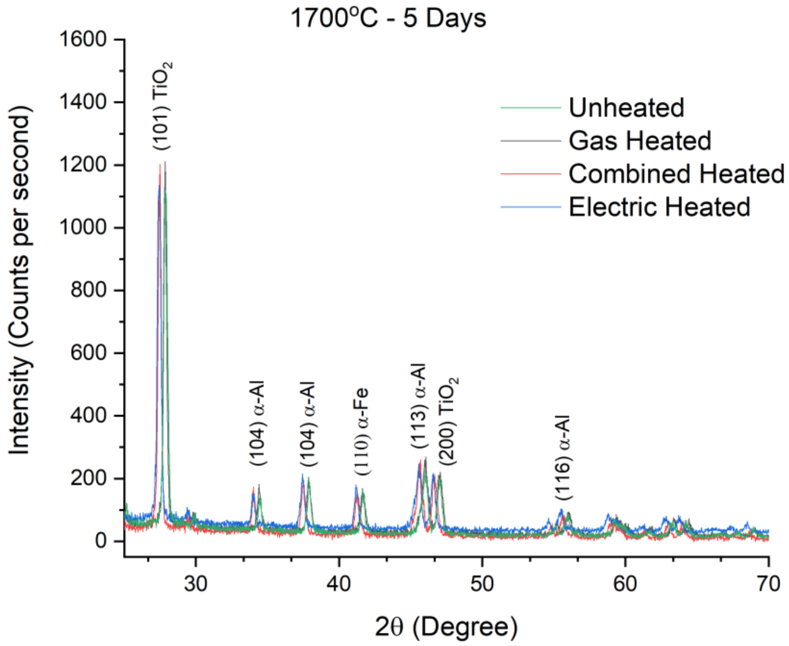

Figure 98: XRD Spectruscopy_G-03_1700ºC 5 Days of soaking time

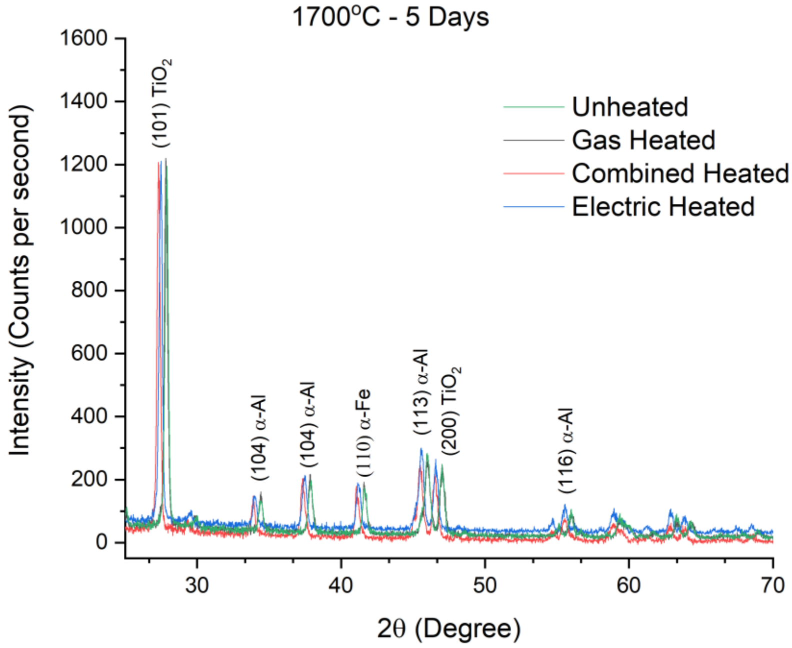

Figure 99: XRD Spectruscopy_G-04_1700ºC 5 Days of soaking time

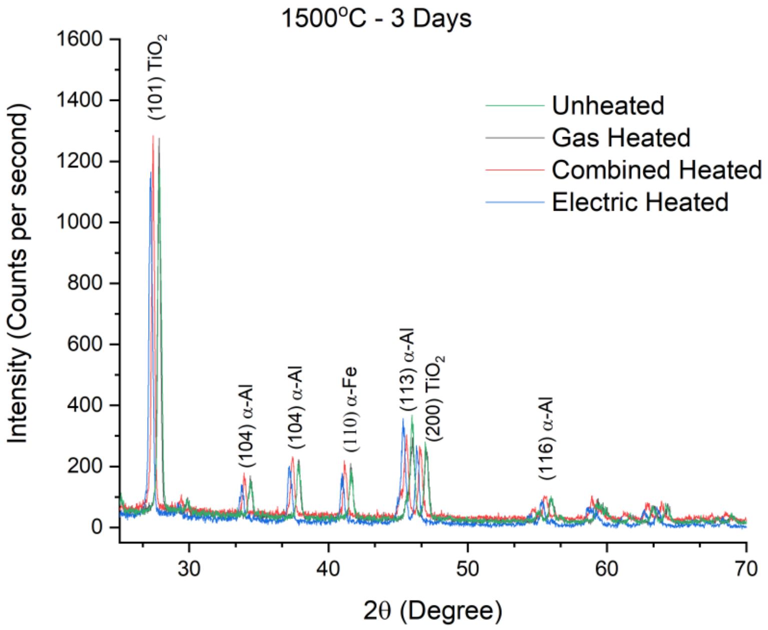

Figure 100: XRD Spectruscopy_G-05_1500ºC 3 Days of soaking time

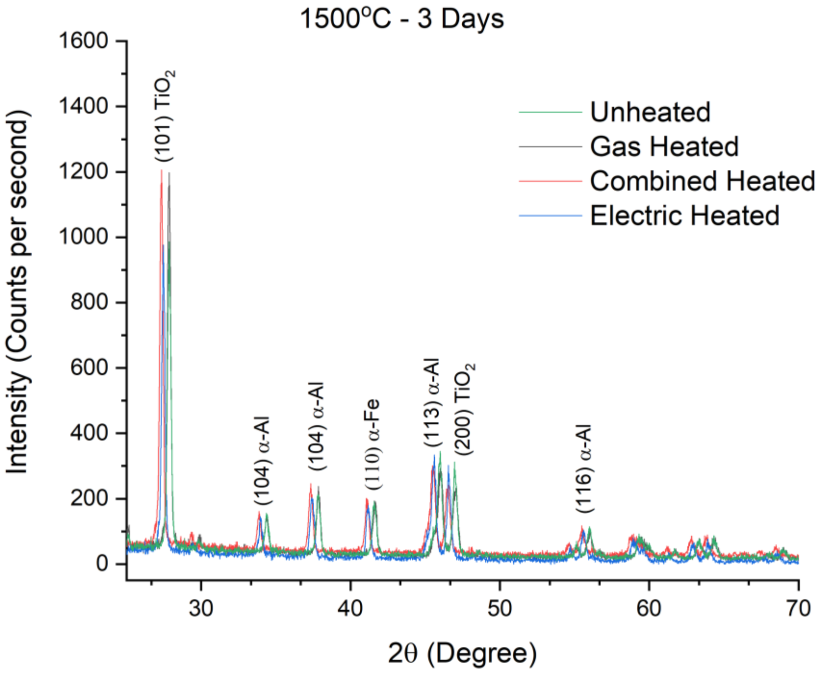

Figure 101: XRD Spectruscopy_G-06_1500ºC 3 Days of soaking time

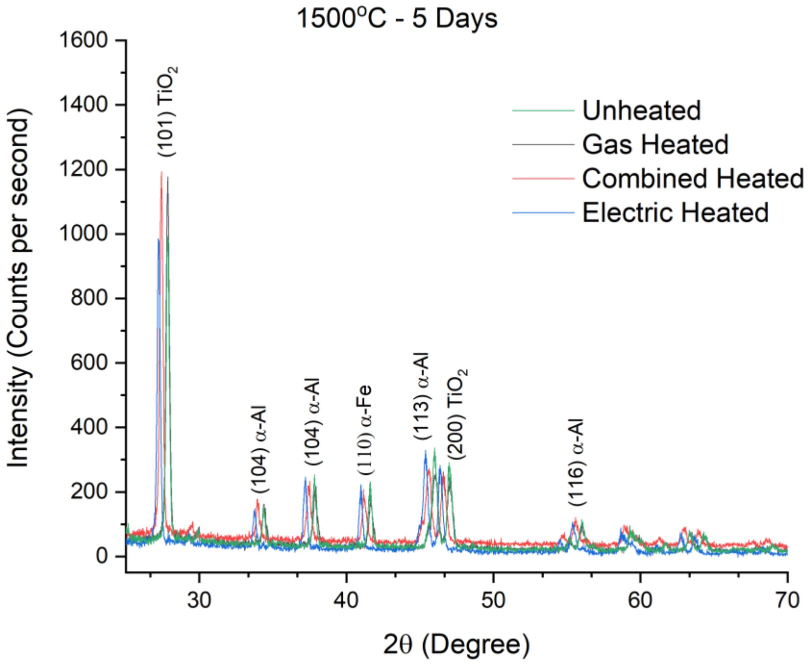

Figure 102: XRD Spectruscopy_G-07_1500ºC 5 Days of soaking time

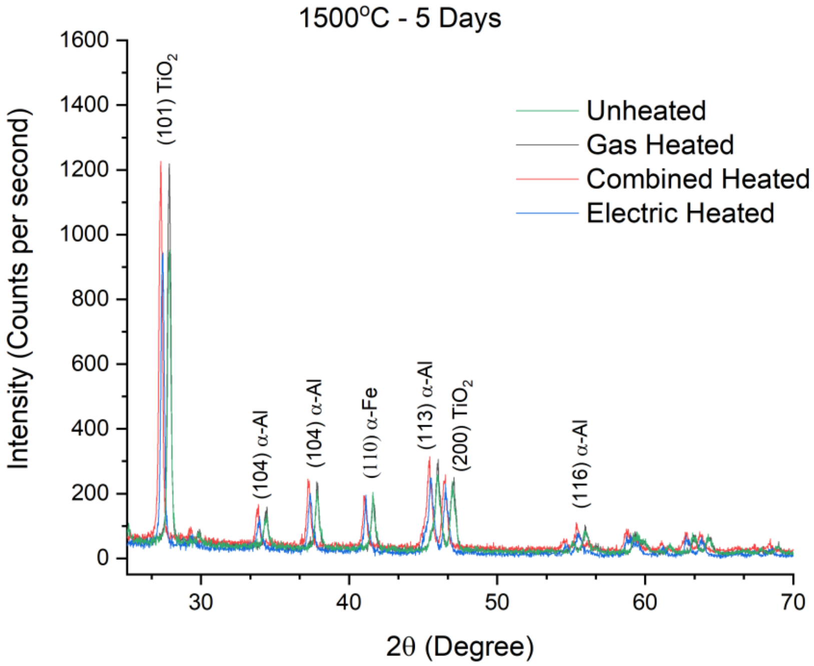

Figure 103: XRD Spectruscopy_G-08_1500ºC 5 Days of soaking time

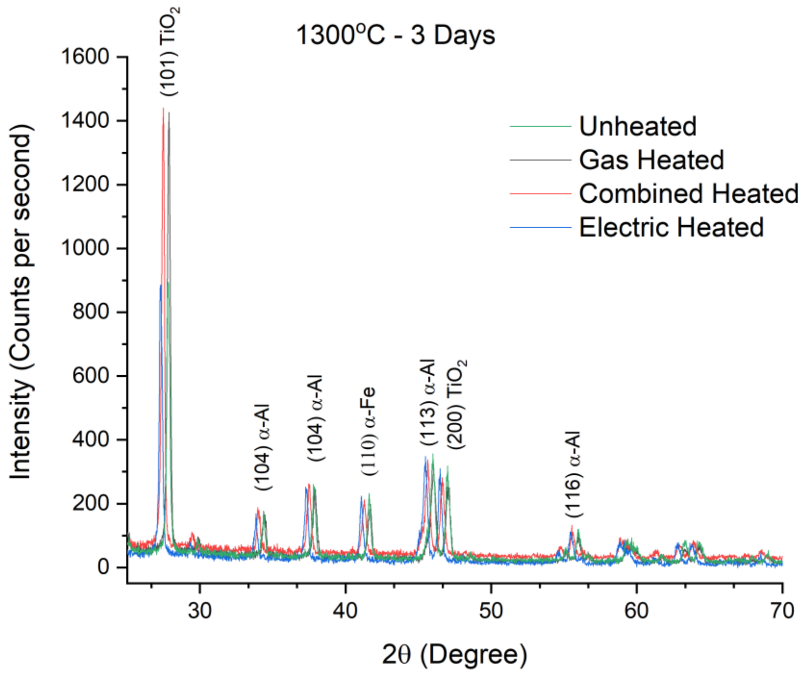

Figure 104: XRD Spectruscopy_G-09_1300ºC 3 Days of soaking time

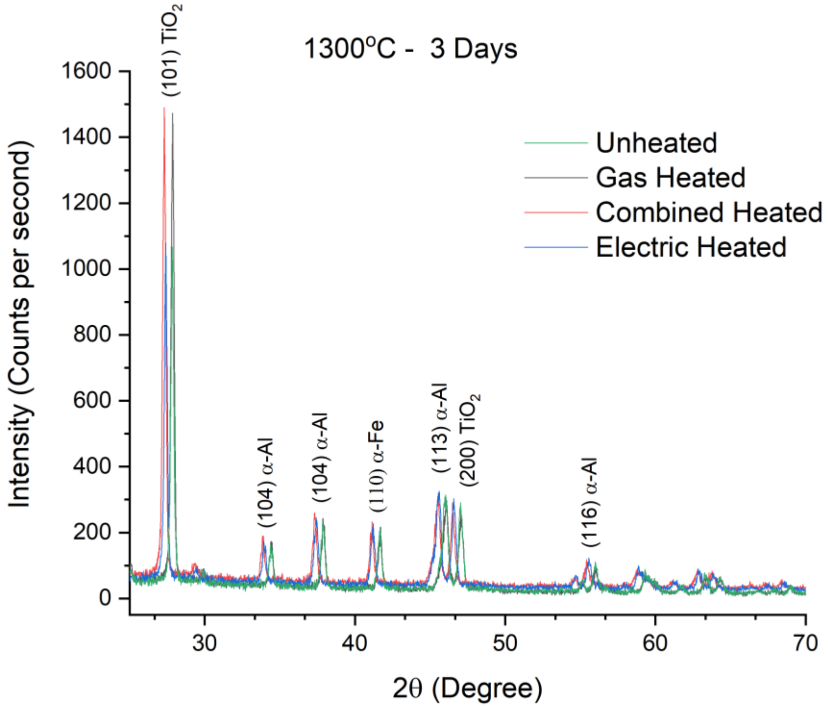

Figure 105: XRD Spectruscopy_G-10_1300ºC 3 Days of soaking time

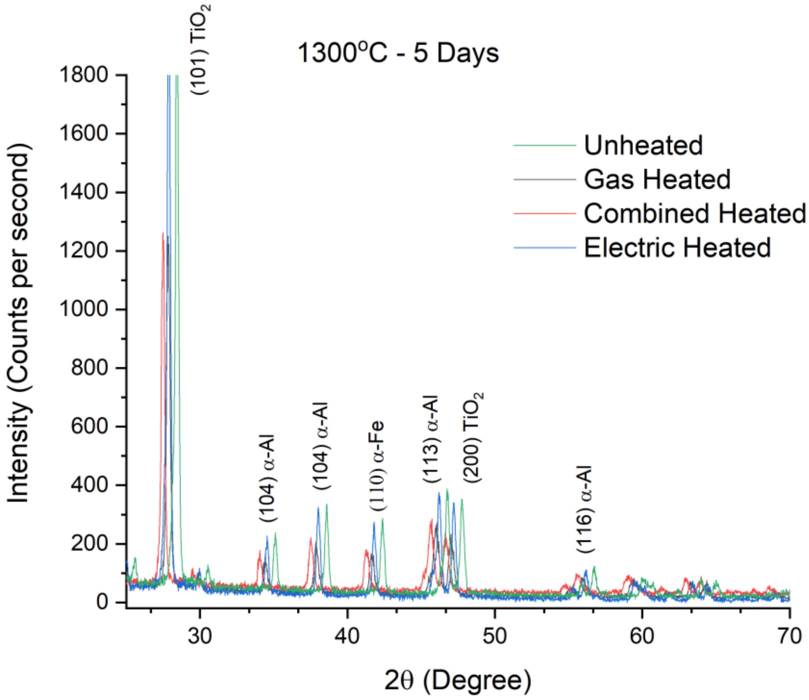

Figure 106: XRD Spectruscopy_G-11_1300ºC 5 Days of soaking time

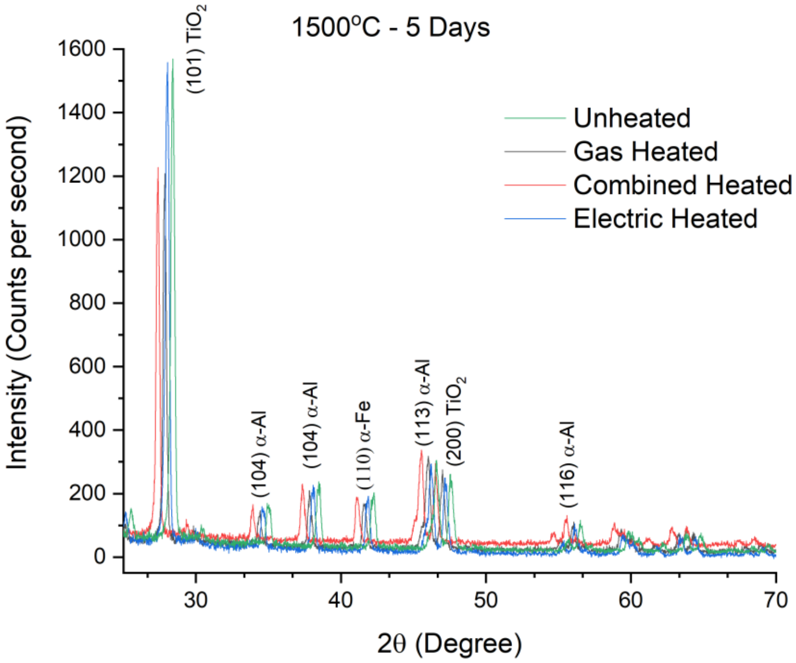

Figure 107: XRD Spectruscopy_G-12_1500ºC 5 Days of soaking time

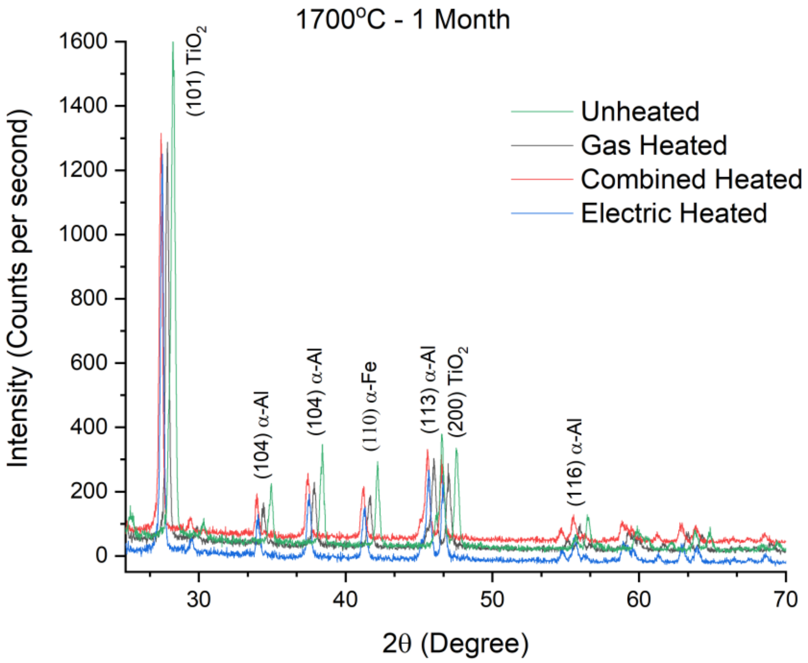

Figure 108: XRD Spectruscopy_G-13_1700ºC 1 month of soaking time

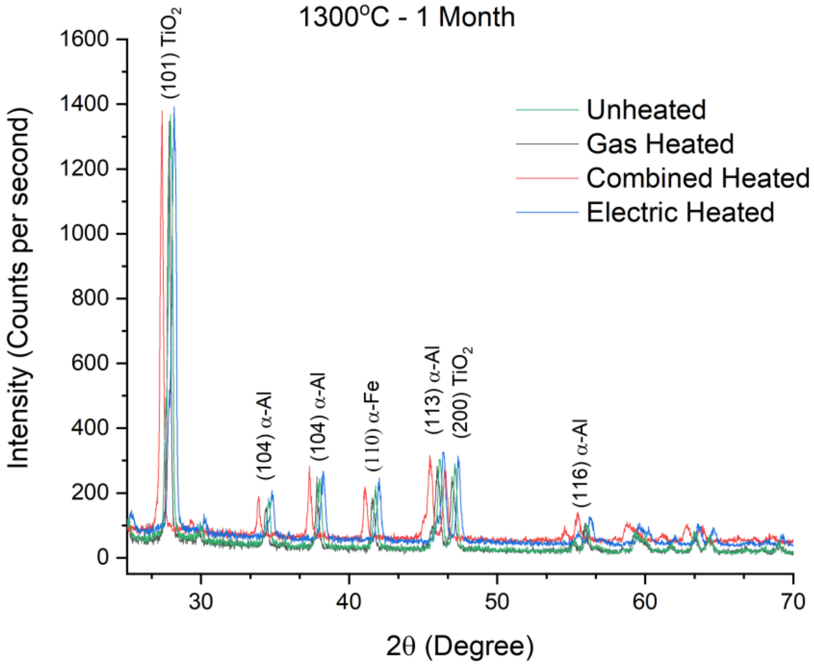

Figure 109: XRD Spectruscopy_G-14_1300ºC 1 month of soaking time

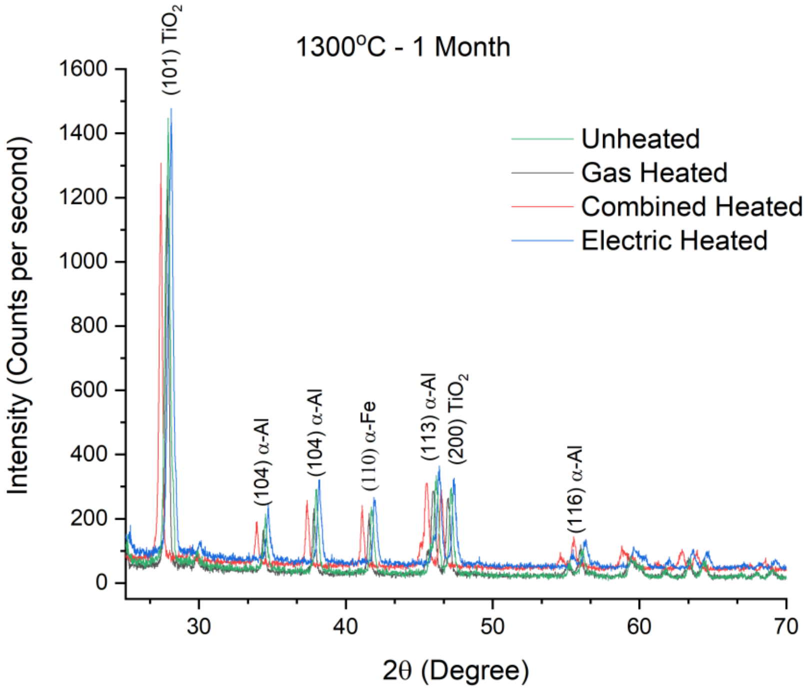

Figure 110: XRD Spectruscopy_G-15_1300ºC 1 month of soaking time

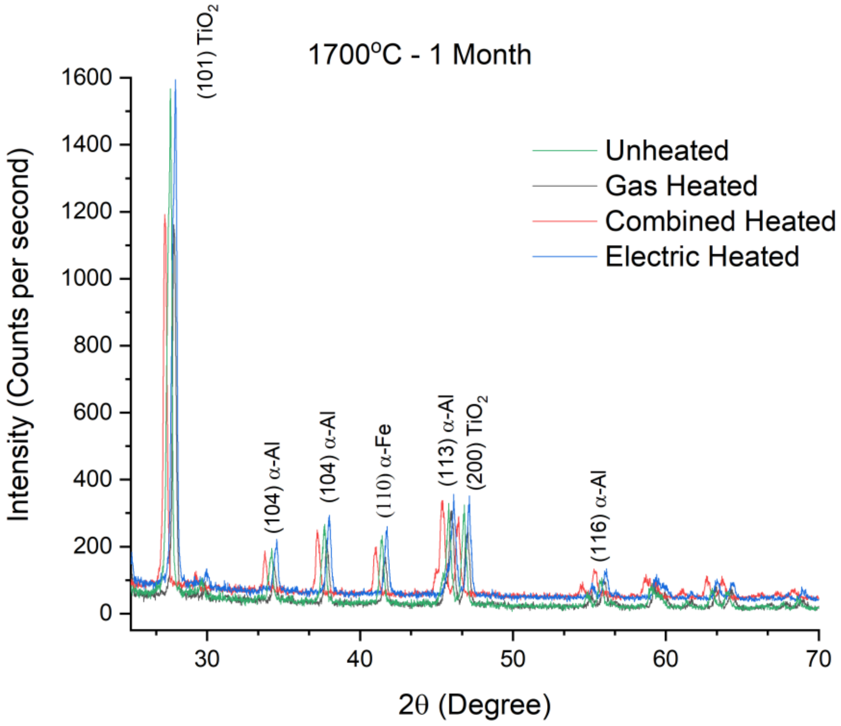

Figure 111: XRD Spectruscopy_G-16_1700ºC 1 month of soaking time

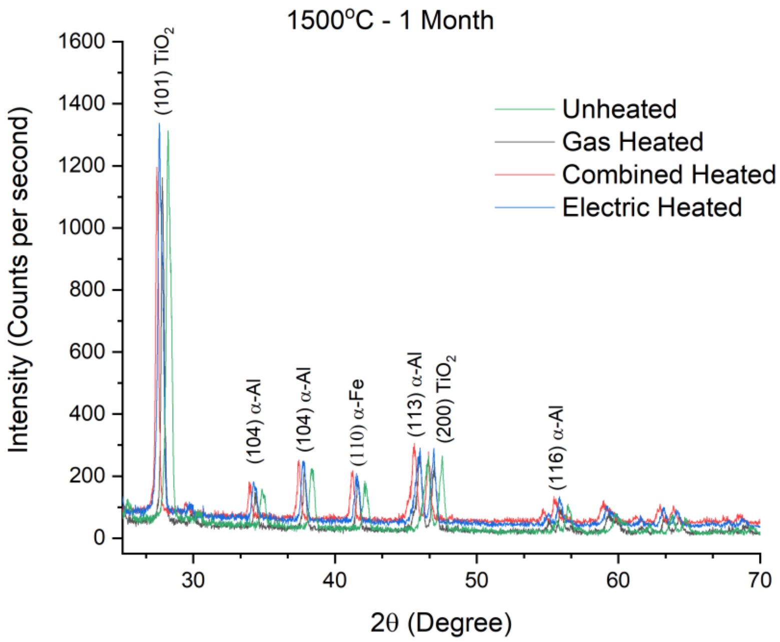

Figure 112: XRD Spectruscopy_G-17_1500ºC 1 month of soaking time

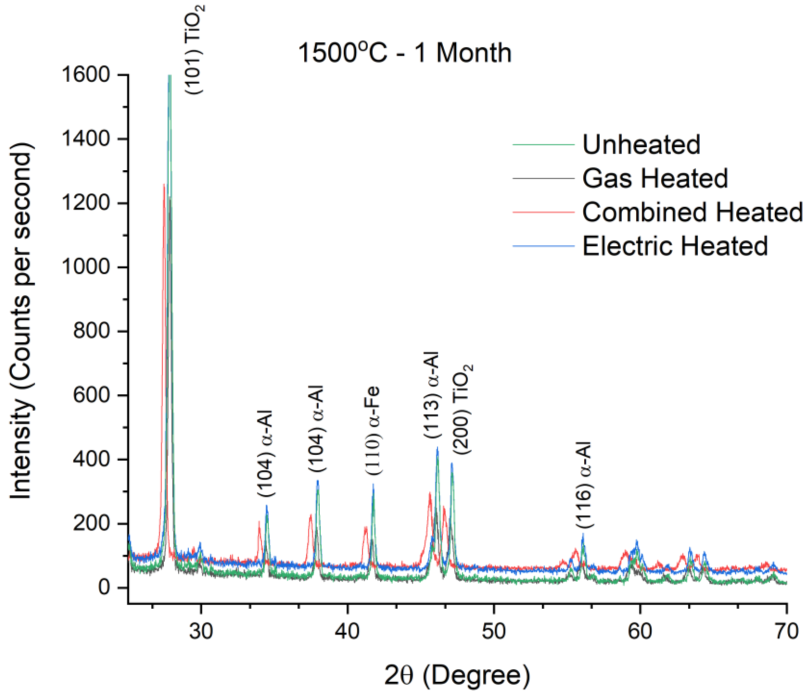

Figure 113: XRD Spectruscopy_G-18_1500ºC 1 month of soaking time

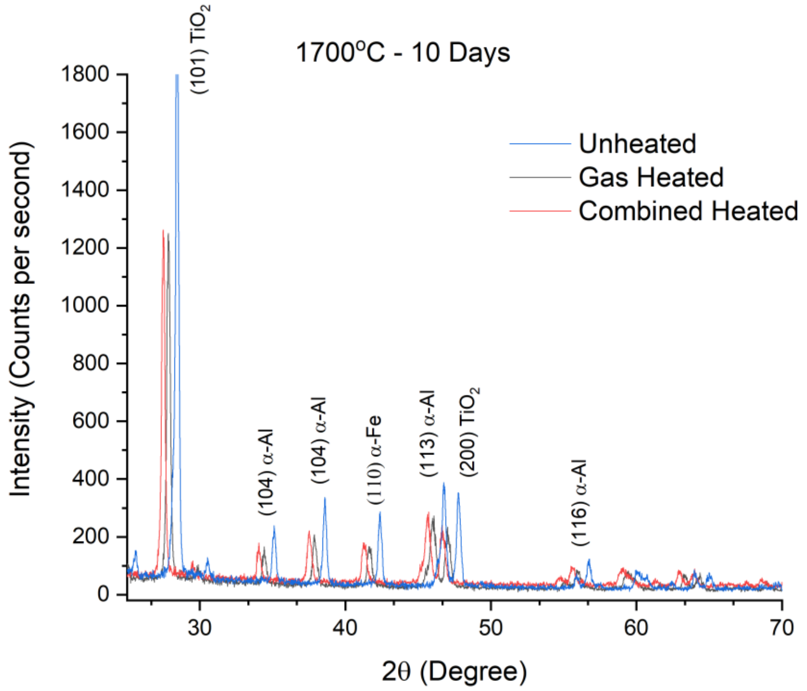

Figure 114: XRD Spectruscopy_G-19_1700ºC 10 days of soaking time

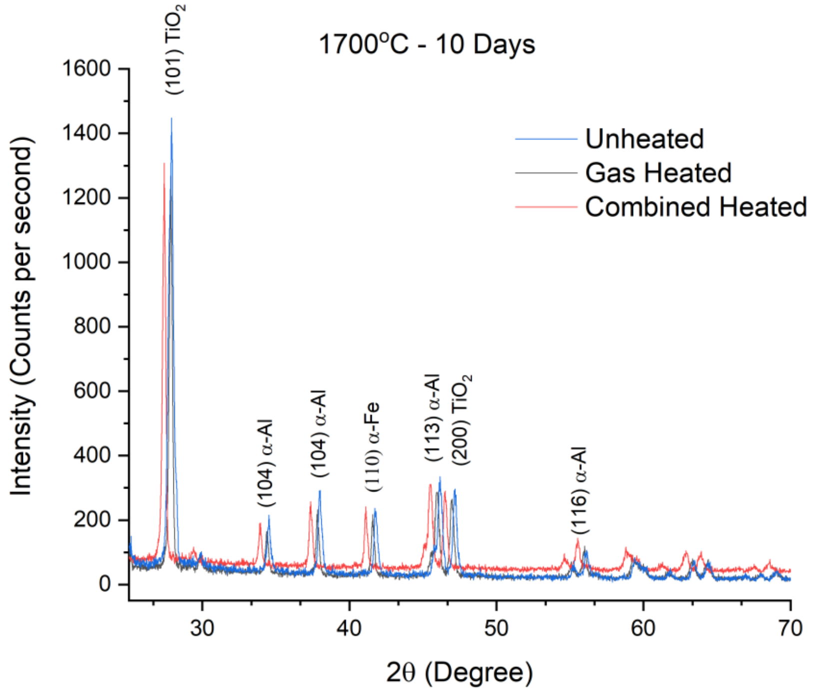

Figure 115: XRD Spectruscopy_G-20_1700ºC 10 days of soaking time

ANNEXURE 04 (D-SPACE CLCULATION FROM XRD DATA)

Table 26: XRD d space vales G_02

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.618	38.150	38.357	37.625	2.389	2.357	2.345	2.389
α Al_2O_3 [2 0 0]	45.891	46.232	45.381	45.871	1.976	1.962	1.997	1.977
α Al_2O_3 [2 2 0]	64.578	64.865	63.722	64.687	1.442	1.436	1.459	1.440
Anatase TiO2 [2 0 0]	47.029	46.934	48.669	47.981	1.931	1.934	1.869	1.895
Anatase TiO2 [1 0 1]	27.882	28.213	28.197	27.848	3.197	3.161	3.162	3.201
α Fe2O3 [1 1 0]	41.743	41.984	41.793	41.933	2.162	2.150	2.160	2.153
α Fe2O3 [3 0 0]	65.678	65.102	65.838	65.289	1.420	1.432	1.417	1.428

Table 27: XRD d space vales G_03

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.625	38.150	38.317	37.625	2.389	2.357	2.347	2.389
α Al_2O_3 [2 0 0]	45.871	46.232	45.781	45.871	1.977	1.962	1.980	1.977
α Al_2O_3 [2 2 0]	64.687	64.865	63.532	64.687	1.440	1.436	1.463	1.440
Anatase TiO2 [2 0 0]	47.981	46.934	47.819	47.981	1.895	1.934	1.901	1.895
Anatase TiO2 [1 0 1]	27.848	28.213	27.397	27.848	3.201	3.161	3.253	3.201
α Fe2O3 [1 1 0]	41.933	41.984	41.633	41.933	2.153	2.150	2.168	2.153
α Fe2O3 [3 0 0]	65.289	65.102	65.938	65.289	1.428	1.432	1.416	1.428

Table 158: XRD d space vales G_04

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	38.117	37.825	37.917	38.150	2.371	2.377	2.371	2.377
α Al_2O_3 [2 0 0]	45.381	45.781	45.981	46.232	1.972	1.980	1.972	1.980
α Al_2O_3 [2 2 0]	63.982	64.547	64.300	64.865	1.448	1.443	1.448	1.443
Anatase TiO2 [2 0 0]	47.979	47.261	47.029	46.934	1.931	1.922	1.931	1.922
Anatase TiO2 [1 0 1]	27.997	27.698	27.893	28.213	3.196	3.218	3.196	3.218
α Fe2O3 [1 1 0]	41.973	41.473	41.633	41.984	2.168	2.176	2.168	2.176
α Fe2O3 [3 0 0]	65.398	65.589	65.300	65.102	1.428	1.422	1.428	1.422

Table 169: XRD d space vales G_05

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.583	37.050	38.117	37.515	2.391	2.424	2.359	2.395
α Al_2O_3 [2 0 0]	45.971	46.532	45.381	45.931	1.973	1.950	1.997	1.974
α Al_2O_3 [2 2 0]	64.563	64.465	63.982	64.767	1.442	1.444	1.454	1.438
Anatase TiO2 [2 0 0]	47.559	47.134	47.979	47.931	1.910	1.927	1.895	1.896
Anatase TiO2 [1 0 1]	27.393	28.463	27.597	27.558	3.253	3.133	3.230	3.234
α Fe2O3 [1 1 0]	41.933	41.834	41.373	41.833	2.153	2.158	2.181	2.158
α Fe2O3 [3 0 0]	65.877	65.432	65.398	65.929	1.417	1.425	1.426	1.416

Table 3017: XRD d space vales G_06

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.150	38.117	37.825	2.371	2.357	2.359	2.377
α Al_2O_3 [2 0 0]	45.981	46.232	45.381	45.781	1.972	1.962	1.997	1.980
α Al_2O_3 [2 2 0]	64.300	64.865	63.982	64.547	1.448	1.436	1.454	1.443
Anatase TiO2 [2 0 0]	47.029	46.934	47.979	47.261	1.931	1.934	1.895	1.922
Anatase TiO2 [1 0 1]	27.893	28.213	27.997	27.698	3.196	3.161	3.184	3.218
α Fe2O3 [1 1 0]	41.633	41.984	41.973	41.473	2.168	2.150	2.151	2.176
α Fe2O3 [3 0 0]	65.300	65.102	65.398	65.589	1.428	1.432	1.426	1.422

Table 31: XRD d space vales G_07

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.873	38.455	38.217	37.925	2.374	2.339	2.353	2.371
α Al_2O_3 [2 0 0]	45.981	46.232	45.164	45.781	1.972	1.962	2.006	1.980
α Al_2O_3 [2 2 0]	64.235	64.865	63.378	64.745	1.449	1.436	1.466	1.439
Anatase TiO2 [2 0 0]	47.934	46.421	47.589	47.231	1.896	1.955	1.909	1.923
Anatase TiO2 [1 0 1]	27.325	28.333	27.785	27.456	3.261	3.147	3.208	3.246
α Fe2O3 [1 1 0]	41.678	41.594	41.673	41.563	2.165	2.170	2.166	2.171
α Fe2O3 [3 0 0]	65.238	65.102	65.788	65.669	1.429	1.432	1.418	1.421

Table 32: XRD d space vales G_08

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.150	38.117	37.825	2.371	2.357	2.359	2.377
α Al_2O_3 [2 0 0]	45.981	46.232	45.381	45.781	1.972	1.962	1.997	1.980
α Al_2O_3 [2 2 0]	64.300	64.865	63.982	64.547	1.448	1.436	1.454	1.443
Anatase TiO2 [2 0 0]	47.029	46.934	47.979	47.261	1.931	1.934	1.895	1.922
Anatase TiO2 [1 0 1]	27.893	28.213	27.997	27.698	3.196	3.161	3.184	3.218
α Fe2O3 [1 1 0]	41.633	41.984	41.973	41.473	2.168	2.150	2.151	2.176
α Fe2O3 [3 0 0]	65.300	65.102	65.398	65.589	1.428	1.432	1.426	1.422

Table 33: XRD d space vales G_09

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.764	38.437	37.935	2.371	2.321	2.340	2.370
α Al_2O_3 [2 0 0]	45.642	46.864	45.763	45.721	1.986	1.937	1.981	1.983
α Al_2O_3 [2 2 0]	64.305	64.567	63.243	64.557	1.447	1.442	1.469	1.442
Anatase TiO2 [2 0 0]	47.987	46.754	47.543	47.518	1.894	1.941	1.911	1.912
Anatase TiO2 [1 0 1]	27.365	28.623	27.958	27.853	3.257	3.116	3.189	3.201
α Fe2O3 [1 1 0]	41.633	41.984	41.853	41.343	2.168	2.150	2.157	2.182
α Fe2O3 [3 0 0]	65.467	65.542	65.386	65.549	1.425	1.423	1.426	1.423

Table 184: XRD d space vales G_10

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.837	38.543	38.347	37.556	2.376	2.334	2.345	2.393
α Al_2O_3 [2 0 0]	45.741	46.243	45.641	45.134	1.982	1.962	1.986	2.007
α Al_2O_3 [2 2 0]	64.653	64.856	63.742	64.467	1.441	1.436	1.459	1.444
Anatase TiO2 [2 0 0]	47.239	46.432	47.945	47.613	1.923	1.954	1.896	1.908
Anatase TiO2 [1 0 1]	27.933	28.321	27.756	27.438	3.192	3.149	3.212	3.248
α Fe2O3 [1 1 0]	41.356	41.468	41.633	41.323	2.181	2.176	2.168	2.183
α Fe2O3 [3 0 0]	65.438	65.124	65.643	65.984	1.425	1.431	1.421	1.415

Table 35: XRD d space vales G_11

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.647	38.532	38.527	37.345	2.387	2.335	2.335	2.406
α Al_2O_3 [2 0 0]	45.741	46.532	45.431	45.418	1.982	1.950	1.995	1.995
α Al_2O_3 [2 2 0]	64.329	64.835	63.512	64.743	1.447	1.437	1.464	1.439
Anatase TiO2 [2 0 0]	47.902	46.534	47.989	47.367	1.897	1.950	1.894	1.918
Anatase TiO2 [1 0 1]	27.834	28.153	27.947	27.568	3.203	3.167	3.190	3.233
α Fe2O3 [1 1 0]	41.323	41.634	41.713	41.341	2.183	2.168	2.164	2.182
α Fe2O3 [3 0 0]	65.364	65.573	65.735	65.726	1.427	1.423	1.419	1.420

Table 36: XRD d space vales G_12

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.817	38.543	38.367	37.855	2.377	2.334	2.344	2.375
α Al_2O_3 [2 0 0]	45.881	46.562	45.741	45.281	1.976	1.949	1.982	2.001
α Al_2O_3 [2 2 0]	64.134	64.865	63.982	64.547	1.451	1.436	1.454	1.443
Anatase TiO2 [2 0 0]	47.453	46.364	47.249	47.361	1.914	1.957	1.922	1.918
Anatase TiO2 [1 0 1]	27.213	28.273	27.967	27.658	3.274	3.154	3.188	3.223
α Fe2O3 [1 1 0]	41.345	41.834	41.753	41.712	2.182	2.158	2.162	2.164
α Fe2O3 [3 0 0]	65.309	65.162	65.378	65.569	1.428	1.430	1.426	1.423

Table 37: XRD d space vales G_13

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.947	38.563	38.762	37.823	2.369	2.333	2.321	2.377
α Al_2O_3 [2 0 0]	45.281	46.352	45.851	45.211	2.001	1.957	1.977	2.004
α Al_2O_3 [2 2 0]	64.397	64.135	63.782	64.587	1.446	1.451	1.458	1.442
Anatase TiO2 [2 0 0]	47.159	46.744	47.739	47.631	1.926	1.942	1.904	1.908
Anatase TiO2 [1 0 1]	27.943	28.563	27.734	27.348	3.190	3.123	3.214	3.258
α Fe2O3 [1 1 0]	41.343	41.624	41.713	41.273	2.182	2.168	2.164	2.186
α Fe2O3 [3 0 0]	65.354	65.638	65.358	65.839	1.427	1.421	1.427	1.417

Table 38: XRD d space vales G_14

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.916	38.150	38.117	37.825	2.371	2.357	2.359	2.377
α Al_2O_3 [2 0 0]	45.941	46.562	45.317	45.831	1.974	1.949	2.000	1.978
α Al_2O_3 [2 2 0]	64.256	64.456	63.832	64.467	1.448	1.444	1.457	1.444
Anatase TiO2 [2 0 0]	47.269	46.344	47.729	47.631	1.921	1.958	1.904	1.908
Anatase TiO2 [1 0 1]	27.623	28.183	27.457	27.238	3.227	3.164	3.246	3.271
α Fe2O3 [1 1 0]	41.723	41.445	41.313	41.233	2.163	2.177	2.184	2.188
α Fe2O3 [3 0 0]	65.383	65.522	65.528	65.934	1.426	1.423	1.423	1.416

Table 39: XRD d space vales G_15

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.715	38.734	37.825	2.371	2.324	2.323	2.377
α Al_2O_3 [2 0 0]	45.981	46.362	45.363	45.781	1.972	1.957	1.998	1.980
α Al_2O_3 [2 2 0]	64.300	64.585	63.279	64.547	1.448	1.442	1.468	1.443
Anatase TiO2 [2 0 0]	47.349	46.354	47.719	47.261	1.918	1.957	1.904	1.922
Anatase TiO2 [1 0 1]	27.263	28.273	27.937	27.368	3.268	3.154	3.191	3.256
α Fe2O3 [1 1 0]	41.383	41.834	41.345	41.443	2.180	2.158	2.182	2.177
α Fe2O3 [3 0 0]	65.182	65.132	65.458	65.359	1.430	1.431	1.425	1.427

Table 40: XRD d space vales G_16

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.817	38.451	38.347	37.225	2.377	2.339	2.345	2.413
α Al_2O_3 [2 0 0]	45.471	46.832	45.851	45.531	1.993	1.938	1.977	1.991
α Al_2O_3 [2 2 0]	64.373	64.853	63.382	64.147	1.446	1.437	1.466	1.451
Anatase TiO2 [2 0 0]	47.249	46.384	47.729	47.651	1.922	1.956	1.904	1.907
Anatase TiO2 [1 0 1]	27.923	28.363	27.732	27.248	3.193	3.144	3.214	3.270
α Fe2O3 [1 1 0]	41.633	41.473	41.753	41.345	2.168	2.176	2.162	2.182
α Fe2O3 [3 0 0]	65.647	65.245	65.568	65.349	1.421	1.429	1.423	1.427

Table 41: XRD d space vales G_17

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.347	38.587	38.745	37.565	2.406	2.331	2.322	2.392
α Al_2O_3 [2 0 0]	45.981	46.532	45.273	45.731	1.972	1.950	2.001	1.982
α Al_2O_3 [2 2 0]	64.452	64.435	63.452	64.437	1.445	1.445	1.465	1.445
Anatase TiO2 [2 0 0]	47.459	46.344	47.219	47.261	1.914	1.958	1.923	1.922
Anatase TiO2 [1 0 1]	27.943	28.523	27.762	27.238	3.190	3.127	3.211	3.271
α Fe2O3 [1 1 0]	41.273	41.884	41.863	41.473	2.186	2.155	2.156	2.176
α Fe2O3 [3 0 0]	65.237	65.652	65.338	65.269	1.429	1.421	1.427	1.428

Table 42: XRD d space vales G_18

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.917	38.150	38.117	37.825	2.371	2.357	2.359	2.377
α Al_2O_3 [2 0 0]	45.581	46.542	45.641	45.931	1.989	1.950	1.986	1.974
α Al_2O_3 [2 2 0]	64.275	64.542	63.922	64.457	1.448	1.443	1.455	1.444
Anatase TiO2 [2 0 0]	47.529	46.478	47.943	47.741	1.912	1.952	1.896	1.904
Anatase TiO2 [1 0 1]	27.723	28.321	27.827	27.548	3.215	3.149	3.203	3.235
α Fe2O3 [1 1 0]	41.553	41.644	41.513	41.273	2.172	2.167	2.174	2.186
α Fe2O3 [3 0 0]	65.732	65.432	65.758	65.319	1.419	1.425	1.419	1.427

Table 43: XRD d space vales G_19

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.567	38.512	38.237	37.255	2.392	2.336	2.352	2.412
α Al_2O_3 [2 0 0]	45.831	46.452	45.211	45.381	1.978	1.953	2.004	1.997
α Al_2O_3 [2 2 0]	64.356	64.235	63.342	64.457	1.446	1.449	1.467	1.444
Anatase TiO2 [2 0 0]	47.529	46.834	47.379	47.731	1.912	1.938	1.917	1.904
Anatase TiO2 [1 0 1]	27.623	28.453	27.927	27.538	3.227	3.134	3.192	3.236
α Fe2O3 [1 1 0]	41.423	41.214	41.233	41.873	2.178	2.189	2.188	2.156
α Fe2O3 [3 0 0]	65.310	65.172	65.568	65.629	1.428	1.430	1.423	1.421

Table 19: XRD d space vales G_20

Miller Indices [h k l]	Degree-UH	Degree-GH	Degree-EH	Degree-CH	d-UH	d-GH	d-EH	d-CH
α Al_2O_3 [1 1 1]	37.827	38.327	38.347	37.375	2.376	2.347	2.345	2.404
α Al_2O_3 [2 0 0]	45.562	46.752	45.531	45.651	1.989	1.941	1.991	1.986
α Al_2O_3 [2 2 0]	64.254	64.325	63.232	64.347	1.448	1.447	1.469	1.447
Anatase TiO2 [2 0 0]	47.569	46.214	47.279	47.251	1.910	1.963	1.921	1.922
Anatase TiO2 [1 0 1]	27.313	28.543	27.921	27.438	3.263	3.125	3.193	3.248
α Fe2O3 [1 1 0]	41.423	41.124	41.633	41.723	2.178	2.193	2.168	2.163
α Fe2O3 [3 0 0]	65.456	65.172	65.658	65.349	1.425	1.430	1.421	1.427