

APPLICATION OF SILICON CARBIDE CRUCIBLE FOR GEMSTONE HEAT TREATMENT IN MICROWAVE OVEN

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ABSTRACT

This research was developed to reduce cost of gemstone heat treatment, defined as a common process to improve a quality of gemstones, for local gem burners by using an interaction of a dielectric material in a microwave oven which can be applied as alternative method to use instead of an electric and a gases furnace. The objectives of the study were (1) to examine the trend of the relationship between times, temperature, and power (2) to find out the best composition between SiC and heat-transfer mediums. After the result was formulated, a research prototype was created by remodeling the crucibles with SiC and the heat-transfer mediums, then heated the system using the microwave oven. Based on the findings of this investigation it was concluded that temperatures can hit the peak at 840°C for oxidation and 1000°C for reduction which is proved by the colour enhancement of zircon. The final model based on this study can be practically used for burn reddish brown zircon (collected from Ratanakiri, Cambodia) to becomes sky blue (reduction) and colorless (oxidation).

Keywords: Gemstones, Heat treatment, Microwave, Silicon Carbide, Dielectric, Zircon

Introduction

Heat treatment is the most common and acceptable process for improving a quality of gemstones in an international gemstone industry. This process is used in order to enhance the color, increase the clarity, and step up the value of gemstones into the higher level. The fundamental principle of the gemstones heat treatment process is to heat gemstones in a specific temperature to create the partial recrystallization of gemstone structure (Wanthanachaisaeng, 2014) or to induce

oxidation ion of an element inside a gemstone; the changing of oxidation number in some elements affects the color of gemstones (Emmett et al., 2003; Fritsch & Rossman, 1987). Nowadays, the heat treatment process has developed; in terms of higher maximum temperature of the machine, and more accurate temperature and atmosphere controlling, to get the highest quality of gemstones enhancement. The development of the process was started from a stove, diesel oil, LPG gas burner, and then the most popular way at this moment, electrical stove which is able to control heating duration and temperature most easily and stably. Moreover, the electrical stove can switch an atmosphere inside the stove between oxidation and reduction which significantly affect the color of gemstones.

The interaction between silicon carbide (SiC) and microwave frequency for producing heat has been interested by many experts (O'Dwyer, 1973; Trew, 1998; Raju, 2003). In 2016, Swain contributed this interaction into a gem and jewelry industry for enhancing the quality of natural ruby (Swain *et al.*, 2016). This publication inspired the researchers to simplify the heat treatment machine from the electrical stove to a household microwave oven by using silicon carbide and crucible as a heat generator.

Methods

Since the size of dielectric materials affects the efficiency of heat-generating interaction (El-Razek *et al.*, 2014), two types of silicon carbide; including grain-size SiC and fine-powder SiC, was experimented. The powder-type SiC was mixed alumina with binder glue and alumina powder to set as a paste (1 SiC: 1.5 binder glue: 1 alumina powder) and painted around on the top edge of crucibles with 1 cm-wide (Fig. 1). The crucible was heated in a conventional furnace to 150 °C for 120 minutes to evaporate the binder and set the paste as a solid layer. Then, the thickness of the SiC powder-glue layer was measured by using a Vernier caliper. All the samples were superimposed by a bigger crucible, and heated the system in a 2.4 GHz household microwave oven (Electrolux-EMM2016W) which was covered the glass plate by ceramic fiber to protect the parts of microwave from thermal radiation. The microwave oven was used in variety of time and electric power, including 5, 10, 15, 20, 25, 30 and 35 minutes, and 100, 400, 600, 800 Watts and defrost mode. After the samples were heated, their cap was opened and a temperature inside the system was measured by using infrared thermometer (GM1650 BENETECH).

The grain-type crucible was prepared by fulfilling gap between two crucibles with grain SiC (740 micron) (Fig.2) by fixing a total quantity of SiC on 16 g. However, the grain-type silicon carbide still needed to find out more information in details, such as the most effective size, then compared the result with this experiment.

The efficiency, in terms of heat generating, of grain-type SiC was developed by mixing heat

transfer mediums, including quartz sand, and carbon powder for oxidation and reduction atmosphere respectively, and grain-type SiC totaling 16 g. This study adjusted the ratios between the mediums and SiC (1:3, 1:5, 1:7 for quartz sand and 1:1, 1:3, 1:5, 1:7, 0:1 for carbon powder). After finding the satisfied proportion for both types of heat-transfer mediums, the temperature result was measured in the same way as previously mentioned in powder-type SiC crucible. The proportion was adapted to create a prototype model and practically tested by doing heat treatment with reddish brown zircon collected from Ratanakiri, Cambodia which theoretically turns from red to colorless when it is heated at 400 °C in oxidation condition, and turns to blue when it is heated at 1000°C in reduction condition (Zeug et al., 2018).

Finally, the unheated and heated zircons were analyzed by Diamond View™, UV-Vis-NIR spectrometer (PerkinElmer model Lambda 950) and FTIR spectrometer (Thermo-Nicolet 6700). Diamond View™ that were developed by the De Beers Diamond Trading Co. (DTC) (Breeding & Shigley, 2009). It is equipped with a UV source at about 220 nm (Devouard & Notari, 2009). Ultraviolet-Visible-Near infrared absorption spectra were obtained in transmittance mode taken from 250 – 1200 nm with sampling interval of 3 nm and scan speed of 441 nm per minute. The transmission band of near infrared to mid infrared spectra (400 – 7500 cm^{-1}) were collected with a resolution of 4 cm^{-1} and 18 scans. These results were illustrated to confirm the practice of this protocol by indicating the differences of color and infrared absorbance between unheated gemstone and heated gemstone.

Results and Discussions

1. powder-type SiC

The amount and mixing composition of SiC, quartz sand and graphite were investigated to evaluate the result temperature of the crucible in the microwave oven. Fig.3 illustrates the different thicknesses of the SiC on the crucible (Fig. 1) which is created by varying the quantity of SiC in the mixture paste before heated the sample in a furnace. There is a clear data that the volume 1.00 g will create the thickest layer. However, the data from Fig.4 can be clearly noticed that the result temperatures between 0.66 g and 1.00 g are much closed to each other. The result meant that the most efficient ratio, in the aspect of economy, is 0.66 g and the temperature can rise up to 600°C.

2. grain-type silicon carbide

The grain-type SiC was also applied in this experiment (Fig 2) to compare the heating temperature to the powder-type SiC. The result of induced temperature as in Fig.5 illustrates the comparison between grain-type and powder-type SiC in the same total weight (0.66 g) and it is cleared by the graph that powder-type SiC have more efficient to work as heat generator. However, it was due to the fact that grain type is importantly cheaper, the grain-type SiC is more effective in terms of industrious using. Thus, the latter was considered to be experimented in a larger quantity. Fig.6

shows the comparison between a larger number of grain-type SiC (16 g) and 0.66 SiC powder and it can be easily seen that 16 g of grain-type SiC can reach to the higher temperature which is 700 °C.

3. heat-transfer mediums

Although 16 g of grain-type SiC crucible can rise the temperature higher than powder-type SiC crucible, the result (700°C) is still unsatisfied since it is not be able to enhance the color of precious gemstones as zircon which requires 1000 °C. In order to increase heat generating efficiency, the researchers mixed heat transfer mediums with the SiC grains. Putting in the mediums significantly affect the result since not only temperatures are increased but the heat transfer mediums can be used as an environment controlling agent which is quartz sand for oxidation and carbon powder for reduction.

3.1 Oxidation environment

The result temperatures from the ratios of SiC and quartz sand are compared in the Fig. 7. It is readily apparent that 1 sand : 5 SiC is the best condition compared to the others. The ratio 1:5 are chosen and measured result temperatures in each different time and power. The Fig. 8 demonstrates the result temperatures of the ratio 1:5 which can be concluded that the highest temperature from this model is 800 °C

3.2 Reduction environment

Since the carbon powder also has a dielectric property as SiC (Liu et al., 2010), the ratios between carbon powder and SiC are separated in more details, which is 1:0 1:1 1:3 1:5 1:7, and the results are illustrated by Fig 9 and referred from Fig 9, 1:3 is chosen to do the measurement in the same way as an oxidation experiment. Fig.10 demonstrate the fact that the highest temperature of this model can reach to 1000 °C.

4. Gemstone heat treatment

The model is made from crucible with the heat generator which is considered as the best condition, 1:5 for sand and 1:3 for carbon, then test it by heating reddish brown zircon collected from Ratanakiri, Cambodia. Fig.11 and Fig.12 demonstrate clear results of color changing after heat treatment. In oxidation environment, after heat for 30 minutes with power 800 watt and average temperature 800 °C, the zircon will turn to colorless crystal. On the other hand, to turn the reddish brown zircon to blue color, temperature need to be rise higher and maintain longer time in reduction environment so the zircon is heated 60 minutes in average temperature 1000 °C before turn to blue zircon.

5. Diamond View™

Diamond View™ was applied in this experiment to observe the luminescence of samples by the high energy ultraviolet source at about 220 nm. The luminescence of color zoning has been

detected in the zircon samples. The figure 12 and 13 indicated that the temperature generated by the SiC model does not high enough to induce structural transformation of zircon, as it can be seen from the existing of visible zoning luminescence in the samples. Referring to the Smith and Balmer, 2009 and Zeug et al, 2018, the most effective temperature to enhance blue colour of Ratanakiri zircon is 900-1000 °C and this enhancement would lead to the disappearance of growth zoning (Zeug et al., 2018; Smith & Balmer, 2009). However, the specify temperature still questioned, as some publications claimed that maximum blue color would appear after 900 °C then fader (Thongcham et al., 2010), some offered that it would reach after 1100 °C (Laithummanoon & Wongkokua, 2013), Thus, it was readily apparent that, in this study, the zircons did not reach the structural transformation temperature, so it might need longer duration (more than an hour) or increase the power of microwave oven.

6. UV-VIS-NIR spectrophotometer

The absorption spectrum of unheated, oxidative heat-treated, reductive heat-treated zircons (Ratanakiri, Cambodia) were reported in Figure 13. It was readily apparent that the unheated gemstone shows higher absorbance in overall region. The unheated zircon spectrum exhibited as a dramatic downward absorption pattern from 300 nm to 600 nm with small couple of peaks in the middle, including at wavelength 480 nm and 520 nm. The high absorbance in the violet to yellow range (400-600 nm) and the releasing of wavelength in red region (600-700 nm) originate the brownish red colour in Ratanakiri zircon. The result of zircons which heated to 700 °C with the oxidative SiC crucible model demonstrated in the Figure 14 and 15. The data showed the more rapidly decrease of absorbance curve from 300 nm to 400 nm compared to the pattern of untreated zircon. The drop of overall absorbance curve after heat significantly affect the gemstone to be colorless. Figure 15 highlighted more on the details of the data. The small peaks of 480 and 525 nm in the heated zircons data lead to slightly more color absorption, compare to the 600 nm region. Thus, after the oxidative heat treatment process, no region in the range of visible light (400-700 nm wavelength) was significantly absorbed, especially the low absorption in yellow region. Consequently, the processed zircons appeared as a colorless gemstone with a very weak yellow tint. Turning to consider the reductive heat treatment data, the comparison of unheated and reductive heated at 900°C was provided in Figure 16. It is noticeable that the absorbance region (about 480 nm) in untreated data generally reduced from the pre-treatment, therefore the color of zircon became lighter. Moreover, there was the appearance of an absorbance peak at 653 nm in Figure 17 and 18. These changes effectuated the color of zircons from reddish brown colour (releasing 600-700 nm wavelength) to slightly blue colour (releasing in most of the light spectrum but release slightly less in red region (500-700 nm)).

7. FTIR

The results of FTIR analyzing from pre-heated and heated in both environment; oxidation and reduction, provided in this study to confirm that the SiC model was practical to use as an implement for gemstone heat treatment. The unique indication of heated Ratanakiri zircon is a disappearance of 4072 and 4262 cm^{-1} FTIR peaks (Siriaucharanon, 2016). The data on figure 19 and 20 showed the vanishing of the couple peak after heat treating via the SiC model in the both environments. This confirmed that this protocol can be practically used as an alternative process for heat treating process.



Figure 1 Model of crucibles for powder-type silicon carbide experiment.



Figure 2 Model of crucibles for the grain-type silicon carbide experiment.

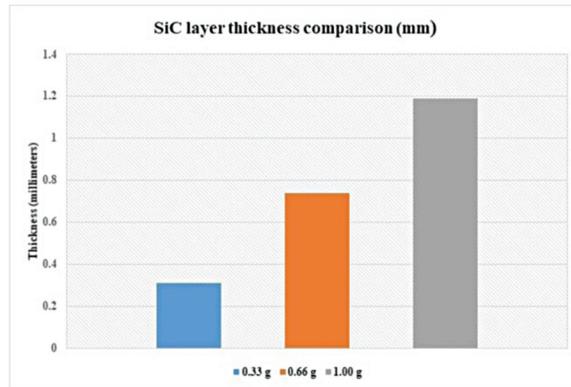


Figure 3 The comparison of the thickness of SiC powder layer.

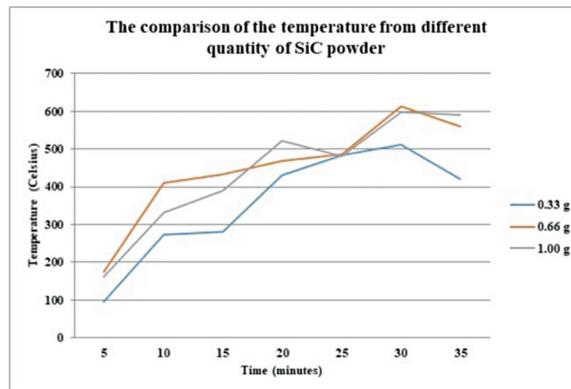


Figure 4 The comparison of the temperature from different quantity of SiC powder.

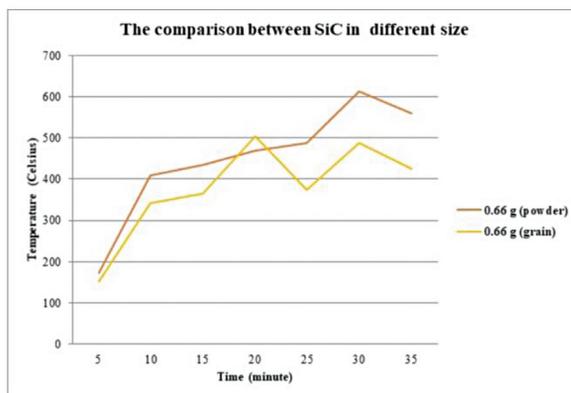


Figure 5 The comparison of the temperature from grain-type and powder-type silicon carbide in the same quantity.

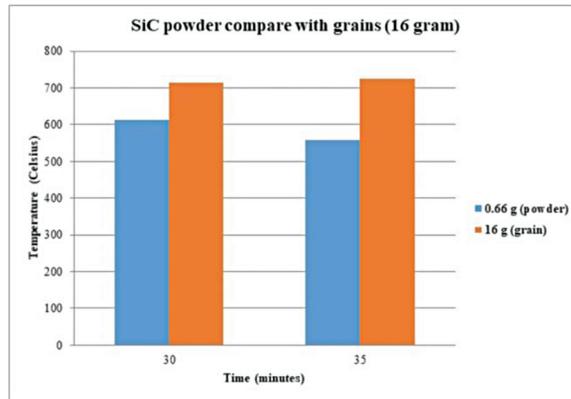


Figure 6 The comparison of the temperature from 16 g of grain-type silicon carbide and 0.66 silicon carbide powder.

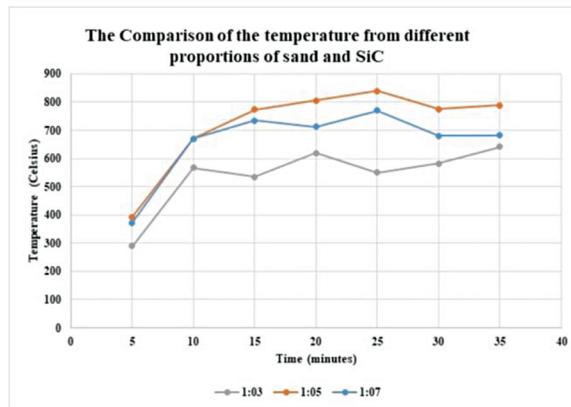


Figure 7 The comparison of the temperature from different proportions of sand and SiC.

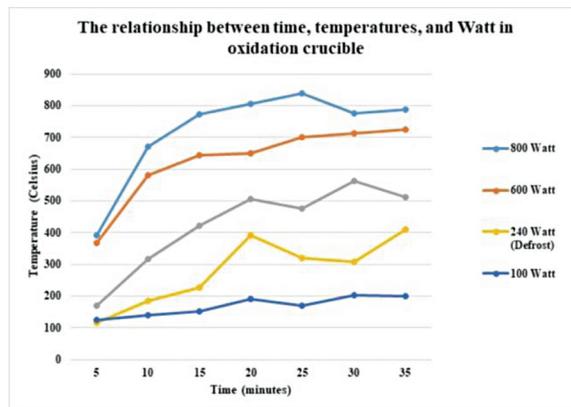


Figure 8 The relationship between time, temperature, and Watt in SiC crucible under oxidizing atmosphere.

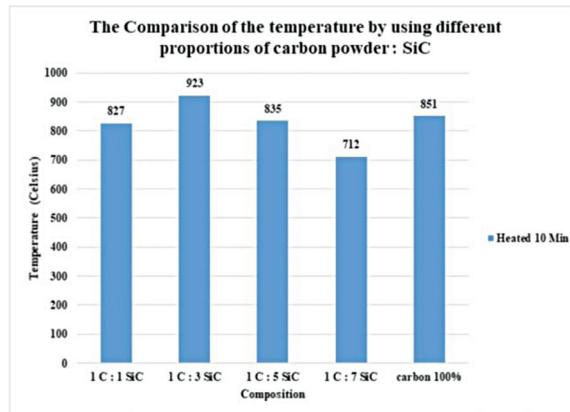


Figure 9 The Comparison of the temperature by using different proportions of carbon powder: Silicon Carbide.

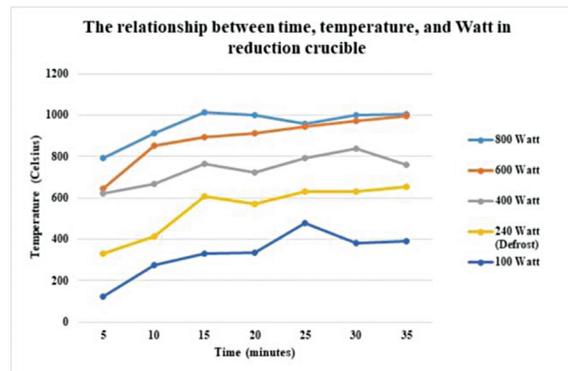


Figure 10 The relationship between time, temperature, and Watt in crucible under reducing atmosphere.



Figure 11 The color changing of reddish brown zircon from Ratanakiri, Cambodia between before (left) and after (right) heat treated by the SiC crucible model with oxidation environment for 60 minutes with power 800 watts, average temperature 700°C.



Figure 12 The color changing of reddish brown zircon from Ratanakiri, Cambodia between before (left) and after (right) heat treated in the SiC crucible model with reduction environment for 60 minutes with power 800 watts, average temperature 900 °C.

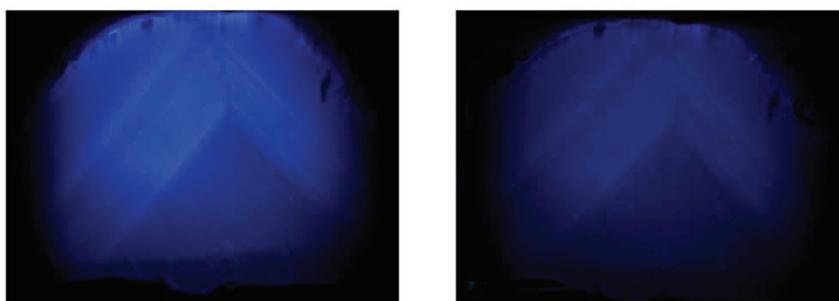


Figure 13 The existing of growth zoning luminescence of the zircon under UV between before (left) and after (right) heat treated by the SiC crucible model.

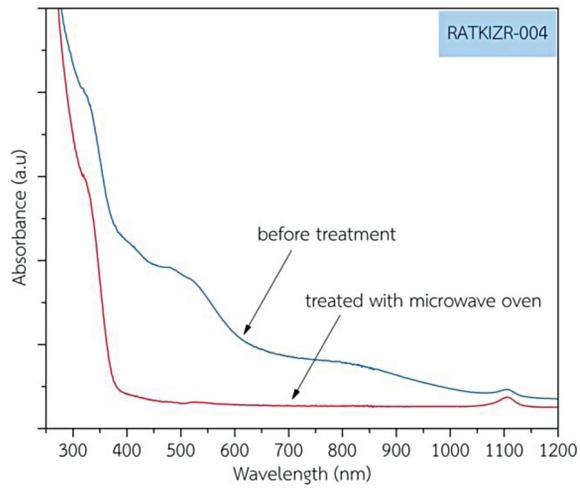


Figure 14 The difference between UV-Vis-NIR absorbance between before and after oxidizing atmosphere heat treatment (700 °C) in the microwave oven.

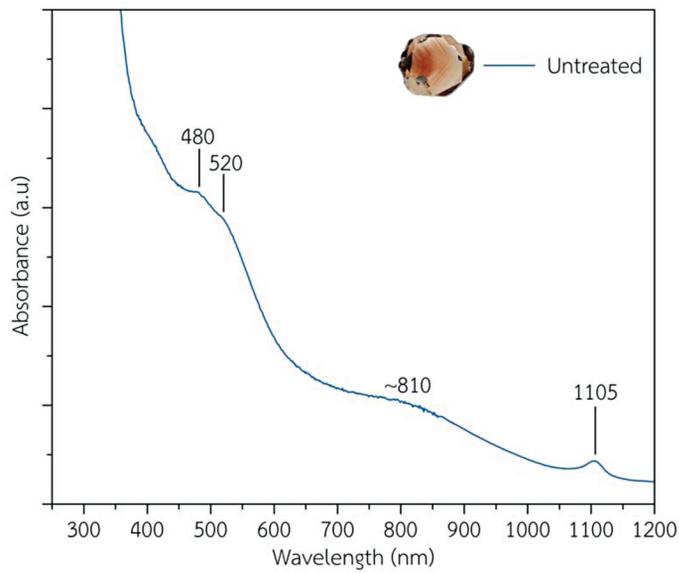


Figure 15 The UV-VIS-NIR absorbance of the unheated reddish brown zircon.

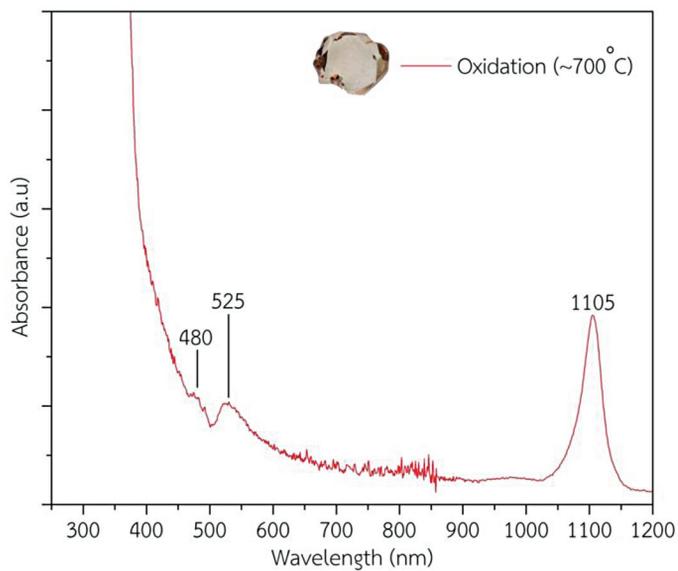


Figure 16 The UV-VIS-NIR absorbance of the heated reddish brown zircon at 700 °C in oxidizing atmosphere for 1 hour.

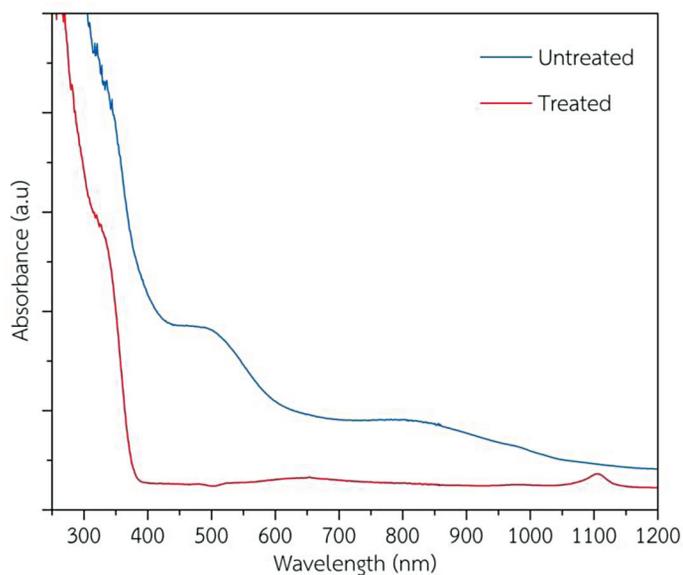


Figure 17 The difference between UV-Vis-NIR absorbance between before and after heat treatment (900 °C) under reducing atmosphere in the microwave oven.

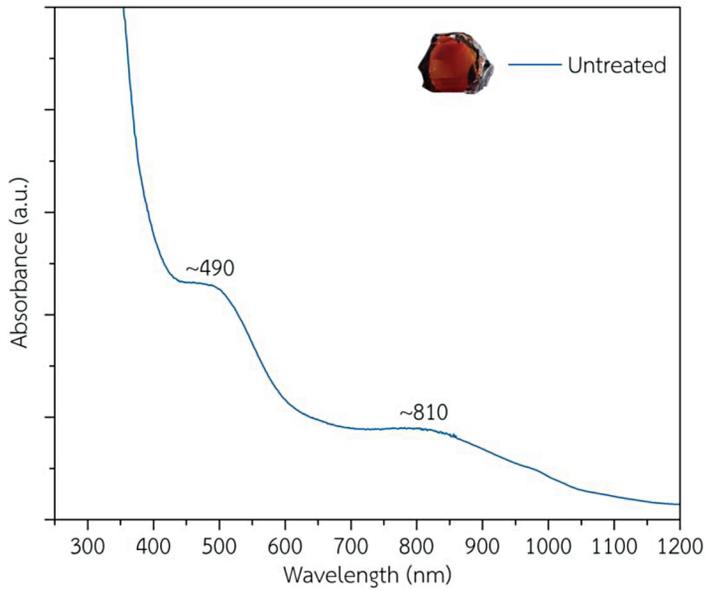


Figure 18 The UV-VIS-NIR absorbance of the unheated reddish brown zircon.

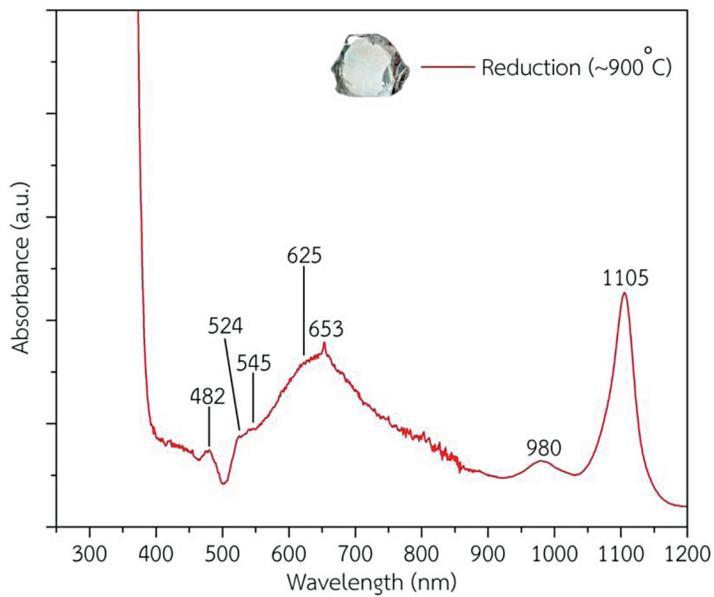


Figure 19 The UV-VIS-NIR absorbance of the heated reddish brown zircon at 900 °C under reducing atmosphere for 1 hour.

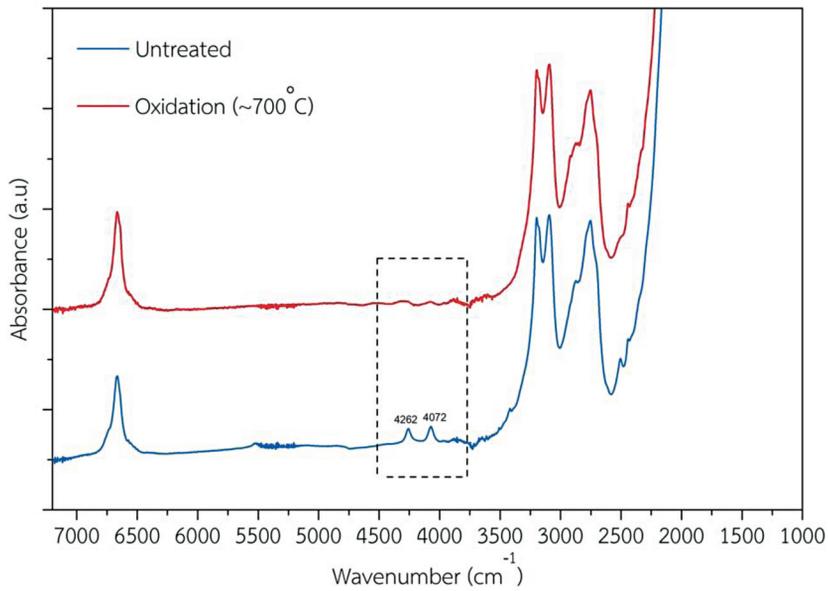


Figure 20 The comparison of FTIR result between unheated and heated zircon under oxidizing atmosphere.

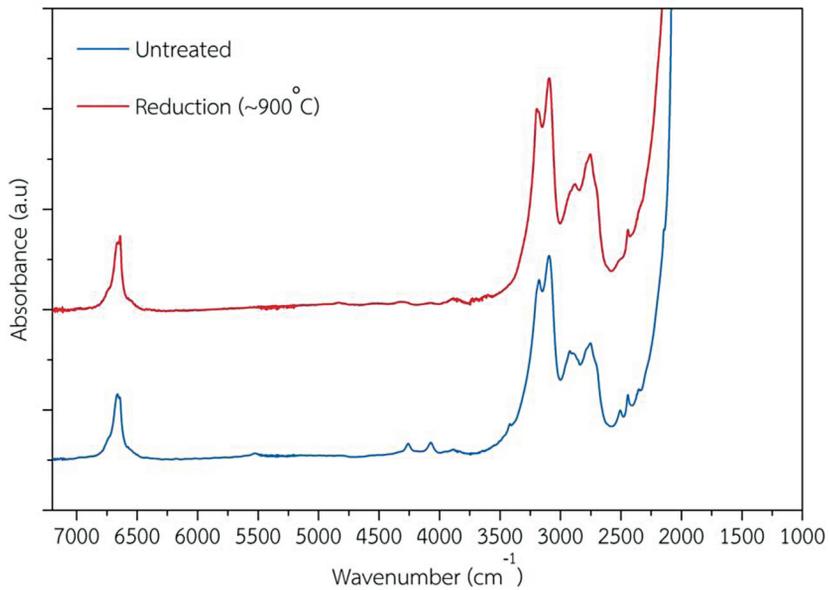


Figure 21 The comparison of FTIR result between unheated and heated zircon under reducing atmosphere.

Conclusions

The results obtained from this study can be practically used for heat treating gemstones both oxidizing and reducing atmosphere such as reddish brown zircon from Ratanakiri, Cambodia or used for other process that require not too high temperature as sintering silver clay. Moreover, this result indicated a possibility to use home microwave oven to treat the gemstone instead of electric furnace.

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