Colour Development of *Geuda* Stones after the Gas-Fired and Electrically Operated Furnace Heat Treatments

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Abstract
Geuda is a low-quality variety of corundum which can be converted into blue sapphire by heat treatment. Colour of the blue sapphire is mainly due to the presence of Iron (Fe) and Titanium (Ti) and their adjacent order in the lattice structure. The process of colouring is called Intervalence charge transfer, where an electron moves from one transition element to an another and the process absorb part of white light resulting in a blue colour. This study identified UV visible spectroscope absorptions behaviours of Geuda before and after gas-fired heat treatment using "Lakmini" furnace and electrically operated Lenton EHF 17/3 furnace. 6 Samples were randomly collected from Ratnapura, Niwithigala, Lunugala and Ambalangoda gemstone markets. Maximum temperature in Lakmini furnace was 1750°C with soaking time of 30 minutes under reduced environmental condition inside the furnace. Lenton EHF 17/3 was used with 1700 °C temperature and three different soaking times (three days, one week, one month). The optical absorption spectra were obtained using multiskan go microplate spectrophotometer through with SkanIt 4.1 software. Data were analysed using OriginPro 2018 software. A peak height difference was obtained at around 560-600nm between gas heated and combined heated (electric furnace heat treatment after gas furnace heat treatment) samples at maximum temperature with increased soaking times. This was maily due to the formation of $[FeTi]^{6+}$ complex where the ate of formation of $[FeTi]^{6+}$ was high with prolonged soaking. Therefore, results confirmed that the presence of both Iron (Fe) and Titanium (Ti) is required to produce the desired blue colour in heat treated Geuda stones.
Keywords: *Geuda heat treatment, Intervalence charge transfer,UV visible spectroscopy,*

1. Introduction

Sri Lanka has been famous from time immemorial for the great variety and abundance of gem minerals of extremely high quality and uniqueness, earned it the name 'Ratna Deepa' meaning Gem Island. From the Earth's greatest concentration of gems, about 75 varieties are found within the country's land area *(Dissanayakeet al.,* 2000). Gem mining has been practised for centuries in Sri Lanka and nearly 25% of the land mass has found to be gem bearings (Dissanayake & Rupasinghe, 1995).

Geuda is one of the varieties of corundum that is found in Sri Lanka abundantly. It is translucent to opaque variety of 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 bluish, yellowish or reddish colour. This particular variety had no commercial value before the 1970s but became a much sought-after gem with the influx of Thai gem traders. About 50-60% of corundum species of gems are thought to be of Geuda variety. Over the last few decades, quality enhancement methods for the *Geuda* were carried out and heat treatment has become more prominent over other methods of treatment.

At present, Sri Lankan gem industry commonly adapts gas-fired furnaces for heat treating *Geuda*, to obtain the desired colour in the finished gems, yet recently introduced electric furnaces have also shown their potential. It is widely believed that, gas furnaces are superior to electric ones in achieving the desired colour, yet no proper evaluation has been done in this regard. This study investigates the colour enhancement potential of heat treated *Geuda* when, gas and electric furnaces are used individually and in combination, under varying soaking times and heat regimes.

2. Experiment

Samples for this study were collected from Ratnapura, Niwithigala, Lunugala and Ambalangoda gemstone markets, to get representative samples from each locality. Six *Geuda* stone samples were thus selected for the research and each *Geuda* stone was cut into three identical pieces to compare the colour changes after each treatment. The 'Lakmini' furnace was used as the gas furnace and maximum temperature applied was 1750°C with a soaking time of 30 minutes under reduced environmental condition inside the gas furnace. Lenton EHF 17/3 was used as the electric furnace where the maximum temperature inside the furnace was set to 1700°C and three different soaking times (three days, one week and one month) were used to treat samples.

The optical absorption spectra were obtained for unheated (reference) samples, gas heated samples and combined heated (electric furnace heat treatment after gas furnace heat treatment) samples, using Multiskan™ GO Microplate Spectro-photometer (Thermo Scientific) with SkanIt 4.1 software. Data Obtained were analysed using OriginPro 2018 software.

3. Results and Discussion

Colour of blue in sapphire is mainly due to the presence of Titanium (Ti) and Iron (Fe). The process of colouring is called "Intervalence Charge Transfer", which means the motion of an electron from one transition metal to other (Nassau, 1997) The above process absorbs some part of the white light energy and produces a blue colour (Ileperuma, 1993).

According to Nassau, (1997), in Al_2O_3 structure, aluminium can be replaced by both iron and titanium .Iron can be present as Fe^{2+}or as $Fe^{3+}$and normally titanium present asTi^{4+}. If both Fe^{2+} and Ti^{4+} are located in an adjacent way, orbits of these irons overlap with each other since the distance between Fe^{2+} and Ti^{4+} are fairly small (2.65). This configuration makes possible for an electron to pass from one ion to 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 the earlier arrangement (2.79Å). Due to that, the overlapping amount is less and energy difference also less than 2.11 eV . Resulting absorption spectra produces a bluish–green dichroism in blue sapphire . A significant visual colour change was obtained in the samples heat treated in either gas fired or electric furnaces or in combination (Fig.1). The intensity of the blue colour, thus the absorption spectra, varied according to the different soaking times tested. There was no significant alteration in the absorption spectra between gas furnace heated and combined heat-treated samples with three days of soaking (Fig.2). However, with one week soaking, a significant change in absorption spectrum was obtained, between 550 nm - 650 nm, for combined heat-treated samples when compared to gas heat treated samples (Fig.3).

A similar behavior in the absorption spectrum was observed for heat treated samples with a soaking time of one month at 550 nm - 650 nm range, where the absorption peak was significantly higher for combine heat treated samples over gas heat treated samples (Fig.4). With prolonged soaking times, the absorbance spectra between 550 nm - 650 nm significantly increased for samples subjected to combined heat treatment. With combine heat treatment, the augmentation of blue colour inside the stone, corresponded to the increase in soaking time when the maximum oven temperature was set to 1700°C.

Apart from the major shift in absorption spectra between 550 nm - 650 nm, two minor peaks were observed for heat treated samples between 388 nm and 450 nm (Fig.5). Presence of these peaks have also been reported previously by Karl *et al*., (1983); Perera ,(1993); and Schmetzer and Peretti, (1999) and indicate the presence of Fe^{3+} in Geuda stones. The broad absorption obtained after 550 nm (Fig.1, 2, 3, 4 & 5) was mainly due to the establishment of $[FeTi]^{6+}$ complex, a fact also established in the previous reports (Ediriweera and

Perera, 1989; Perera, 1993; Spinolo *et al*., 2009). The enhancement in blue colour generation obtained with heat treated Geuda stones (Fig. 1, c, f & i) is mainly due to this formation of $[FeTi]^{6+}$ complex. The best colour enhancement was achieved with combined heat treatment at 1700°C with 30 days of soaking (Fig.1,i).

Figure 1: Colour changes of Geuda stones with different temperatures and soaking times. **a.** Unheated stone, **b.** Gas heat treatment (1750°C). **c.** Combined heat treatment (Electric Heat treatment after gas heat treatment) (3 Days of Soaking time and maximum temp of 1700°C) **d**. Unheated stone, **e.** Gas heat treatment (1750ºC). **f.** Combined heat treatment (Electric Heat treatment after gas heat treatment) (1 Week of Soaking time and maximum temp of 1700ºC). **g.** Unheated. **h.** Gas heat treatment (1750ºC). **i.** Combined heat treatment (Electric Heat treatment after gas heat treatment) (1 month of Soaking time and maximum temp of 1700ºC)

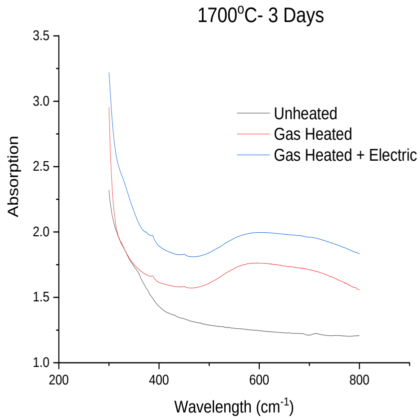

Figure 2: UV visible absorption spectrum for three days of soaking time under 1700°C

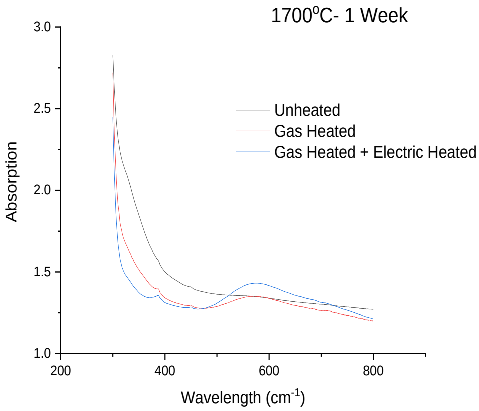

Figure 3: UV visible absorption spectrum for one week of soaking time under 1700°C

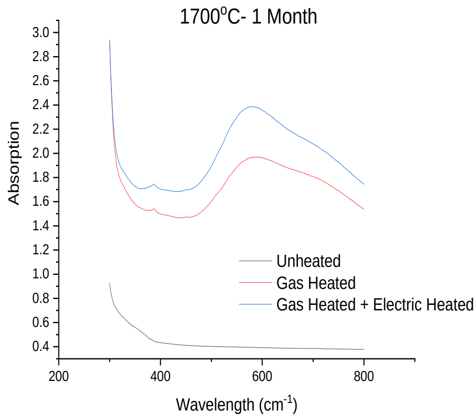

Figure 4: UV Visible absorption spectrum for one month of soaking time under 1700°C

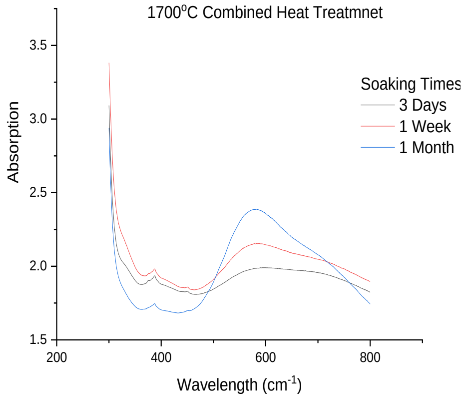

Figure 5: UV Visible absorption spectrum for combined heat treatment (different soaking times under 1700°C

4. Conclusions

Heat treatment of *Geuda* either with gas or electric furnace significantly enhanced the augmentation of blue colour inside the stone. Increase of soaking time while keeping a constant furnace temperature of 1700°C, influenced the rate of formation of $[FeTi]^{6+}$ complex in the stone resulting in a significant colour enhancement. The best colour enhancement was achieved with combined heat treatment at 1700°C with 30 days soaking.

References

Dissanayake., Chandra and Rupasinghe, M. (1995). Classification of gem deposits of Sri Lanka. *Geologie en Mijnbouw*, 74(January), pp. 79–88.

Dissanayake, C., Chandrajith, R. and Tobschall, H. (2000) The geology, mineralogy and rare element geochemistry of the gem deposits of Sri Lanka. *Bulletin of the Geological Society of Finland*, 72(1–2), pp. 5–20. doi: 10.17741/bgsf/72.1-2.001.

Ediriweera, R. and Perera, S. (1989) Heat treatment of Geuda stones - spectral investigation. *Journal of Gemmology*, 21(7), pp. 403–410.

Ileperuma, O. (1993) Chemistry of Geuda Heat Treatment. *National Symposium on Geuda Heat Treatment*, pp. 99–104.

Karl, S., Bosshart, G. and Hanni, H. A. (1983) Naturally coloured and treated yellow and orange-brown sapphires. *The Journal of Gemmology*, XVIII(7), pp. 607–622.

Nassau, K. (1997) *Color of Science, Art and Technology*. 1st Editi. Edited by Nassau, K.. North Holland.

Perera, I. (1993) Identification of Treatable Geuda by Spectral Investigations, *National Symposium on Geuda Heat Treatment*, pp. 89–98.

Schmetzer, K. and Peretti, A. (1999) Some Diagnostic Features of Russian Hydrothermal Synthetic Rubies and Sapphires. *Gems & Gemology*, 35(1), pp.17–28. doi: 10.5741/GEMS.35.1.17.

Spinolo, G. *et al.* (2009). Absorption and emission spectroscopy in natural and synthetic corundum, *EGU general Assembly*, 11(2008).