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REDDISH-BROWN ZIRCONS OF SRI LANKA: A DETAILED STUDY AND DEVELOPMENT OF A NEW TECHNIQUE FOR YELLOW TO GOLDEN YELLOW COLOUR ENHANCEMENT

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ABSTRACT

Sri Lanka is famous for various types of gem minerals. Among these minerals, gem-quality zircon is found in both primary and secondary deposits. The main objective of the research was to study the physical, chemical, and spectroscopic features of reddish-brown zircons (RBZ) of Sri Lanka and to develop a methodology of heat treatment for RBZ of Sri Lanka for colour enhancement. Five randomly selected RBZ samples were selected for this study. All samples were translucent, highly fractured, sub-adamantine, and with euhedral to subhedral crystal form. Samples were analysed with EDXRF, UV-Vis Spectrophotometer, and FTIR methods. The UV-Vis absorption spectrum indicates the cause of colour is due to structural defect colour center by radiation damage from radioactive elements such as U and Th. FTIR spectroscopy indicates that the RBZ of Sri Lanka has gone through a metamictization process. Further FWHM of Raman spectroscopy confirms that RBZ of Sri Lanka belongs to the Intermediate-type. This is also confirmed by the specific gravity of the stones. And more importantly, they were not detectably radioactive which encourages embedding into jewellery. Being the most abundant chemical substitution is Hf, while all the RBZ samples contained a low amount of REE and radioactive elements. Additionally, the ratio of Th: U was consistent with a magmatic origin. Hence, our results confirm that heat treatment under either oxidizing or reducing conditions in an electric furnace produces a yellow to golden yellow colour at around 500- 600 °C with a soaking period of fewer than 90 minutes.

Keywords: *Zircon, Colour, Radioactive, Metamictization, Heat treatment*

1. INTRODUCTION

Sri Lanka is famous for various types of gem minerals. Among these gem minerals, zircon is found in both primary and secondary deposits. Zircon is found in a range of colours varying from colourless, yellow, red, orange, brown, green, and blue (Webster, 1994). Among different colour varieties of zircons, colourless, golden brown (yellow), and sky-blue colours are the most important in jewellery and show the best advantage; the adamantine lustre of zircon and has a higher demand compared to reddish-brown zircons (Abewardana & Malaviarachchi, 2018). In nature, the greyish brown and reddish-browns were the most common colours (Schumann, 1977). Nevertheless, colour changes can be made on zircon through the heat treatment process to acquire certain desired colours (Rossman, 2011).

A common empirical formula of zircon ($ZrSiO_4$) shows some of the range of substitution in (Zr1–y, REEy)(SiO4)1–x(OH)4x–y (Vương & Hương, 2015). Zircon also shares a habit with the uranium mineral coffinite $U(SiO_4)1-x(OH)_{4x}$ and thorium mineral thorite, (Th, U) SiO_4. The radiation from radioactive elements can affect the specific gravity, unit cell dimension, and optical properties of zircon (Holland & Gottfried, 1955). The trace and rare earth element compositions and radiation damage contribute to the color of zircon. For instance, red zircon has radiation-induced color centres in which Nb^{4+} substitutes for Zr^{4+}. Blue zircon is attributed to the presence of U^{4+} (Vương & Hương, 2015).

The zircons are classified into three types based on their level of radiation damage. They are High-type, Intermediate-type, and Low-type. High-type is highly crystalline structures. The structure is completely destroyed to the level of amorphous state in Low-type zircon, whereas the Intermediate-type consists of nearly regular lattices (Yada et al., 1981).

Reddish-brown zircons (RBZ) are common in gem gravels of Sri Lanka. Although, traditional heat treatment methods are employed for colour development of RBZ, yet such techniques have few disadvantages. More importantly, the colour can reverse back to its original hue with time and the treatments are time and energy-consuming. Therefore, developing low-cost and more effective treatment techniques to improve the quality of low-grade zircon to a more demanding colour is one of the important considerations in the gem and jewellery industry. Hence, the main aim of this work is to investigate the physical, chemical, and spectroscopic features of RBZ of Sri Lanka and to develop a feasible methodology to enhance RBZ through heat treatment processes.

2. MATERIALS AND METHODS

RBZs with purplish tint were collected from Kolonna, one of the main gem fields in Sri Lanka for the heat treatment. In this area, zircons are found mainly in primary deposits. The sample collection procedure was type D according to the GIA sample collection manual(Vertriest et al., 2019). Randomly selected samples were heated with an electric muffle furnace (Therm-Craft electric chamber furnace) at different temperatures, soaking time, and reducing agents to find the optimum condition. The optimum condition was selected by the least temperature and soaking period for the finest colour change. Several trials were performed to distinguish the exact temperature to produce yellow to golden yellow zircons from RBZ. Trials were performed at a temperature between 120 °C to 800 °C with different soaking times with both reducing and oxidizing conditions. Some raw and treated samples were then subjected to physical, chemical, and spectroscopic investigations after soaking in aqua regia for 24 hours. Samples were analyzed by EDXRF (Rigaku NEXCG), UV-Vis Spectrophotometer (Jasco V-760), Raman spectrophotometer (GemmoRaman), and FTIR (GemmoFTIR). In addition, specific gravity and the radioactivity of samples were determined by hydrostatic balance (RADWAG) and Geiger counter (GMC-320+) respectively.

3. RESULTS AND DISCUSSION

The raw untreated samples collected from Kolonna region were mainly dark reddish -brown,mostly translucent. Most stones were highly fractured with euhedral to subhedral form (Fig. 1)

Fig. 1: *Tetragonal prisms with distorted termination habit of Kolonna reddish brown zircon*

3.1 Physical, Chemical, and Spectroscopic Features

According to hydrostatic specific gravity (SG) measurements, most of the raw RBZ ranged in between 4.10 to 4.60 confirming that Sri Lanka RBZ belongs to the Intermediate-type (Table 1). Radioactivity of the samples was between 15 - 40 cpm. Since the count is less than 50 cpm, stones are a safe mineral and hence can be used in jewellery.

Table 1 *Table of Zircon Type with Specific Gravity*

Specific Gravity	Zircon Type
<4.1	Low
4.1-4.6	Intermediate
>4.6	High

The mass percentage of elements of RBZ is shown in Table 2. The most abundant chemical substitution was Hf, which varied from 1.03% to 1.33 %. The total rare earth element contents were 0.023%- 0.466% while the Th and U were varying from 0.071 to 0.1603 %. The Th: U ratio was greater than 0.2 for all samples, which is typical for zircon of magmatic origin (Huong et al., 2017).

The typical dominant peaks and bands of the Raman spectrum at 1008, 975, 437, 392, 355, 225, 214, and 202 cm^{-1} were observed in raw samples (Fig. 2). The bands in the 450 – 350 $cm^{–1}$ range and around 1000 $cm^{–1}$ is due to internal (intra-tetrahedral) vibrations of SiO_4 tetrahedral. Special attention was paid to the band of 230 - 200 cm^{-1} which represents the intense external lattice (inter-tetrahedral) vibrations (Nasdalal, 1995). The three peaks in the band range have broadened and shifted to form a single broad band at 200 cm^{-1}, confirming the medium to a high degree of metamictization. But the samples were not completely metamict since the 230 – 200 cm^{-1} band is not completely absent.

Further, the degree of metamictization can be studied with the vibrational peak at 1008 cm^{-1} of the Raman spectrum. The High-type zircon shows a full width at half maximum (FWHM) value of less than 5 cm^{-1} for this peak, whereas this has a greater than 30 cm^{-1} value for Low-type. The Intermediate-type has to be between 5 to 30 cm^{-1} (Huong et al., 2017).

The FWHM values of Vietnamese and Ratanakiri RBZ are in the range of 2–3 cm^{-1} (Wittwer et al., 2013) showing that they are well crystallized whereas the calculated value of Sri Lankan RBZ was 20cm^{-1}. This further confirms the Sri Lankan RBZ has been subjected to a considerable amount of metamictization. Accordingly, the Sri Lankan RBZ can be categorized as an Intermediate-type. Typical strong bands of FTIR spectrum at 2334, 2501, 2761, 2856, 2918, and 3196 cm^{-1} were found in raw RBZ from Sri Lanka (Fig. 3). Some were strong while others were not. A vague absorption band related to Si-O at 1400 - 200 cm^{-1} is also found.

Table 2: *Table of RBZ samples with few elemental mass percentages*

	Zn R A	Zn R B	Zn R C	Zn R D	Average
Zr	74.8	57.1	64.4	73.5	67.45
Si	21.7	31.3	27.5	22.8	26.15
Hf	1.33	1.15	1.03	1.18	1.1425
U	0.0697	0.129	0.0595	0.0707	0.087
Th	0.0199	0.0313	0.0182	0.0250	0.02485
Tb	0.0109	0.186	0.0039	0.197	0.096725

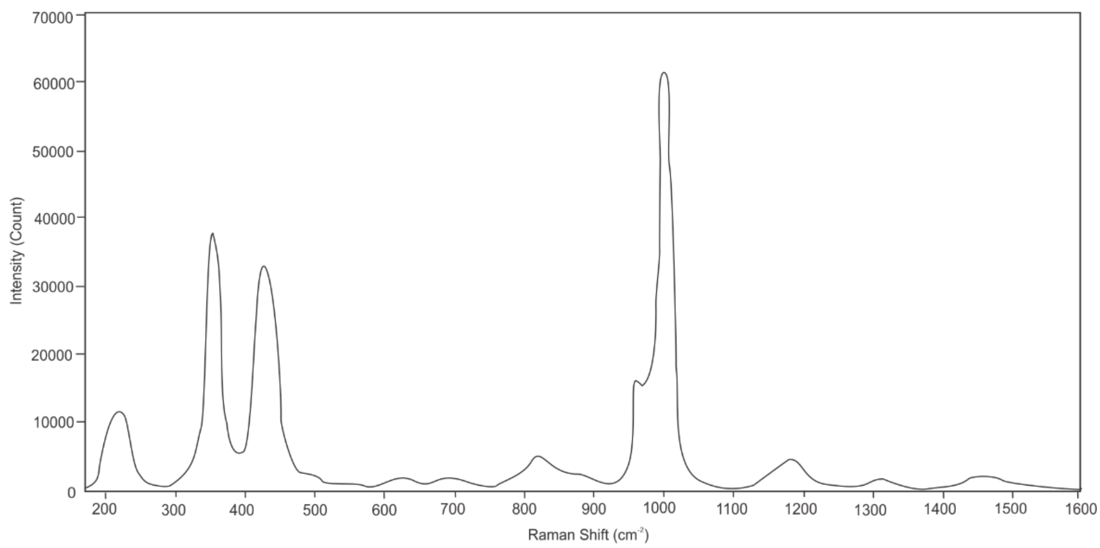

Fig. 2: *Raman spectrum of reddish-brown zircon of Sri Lanka*

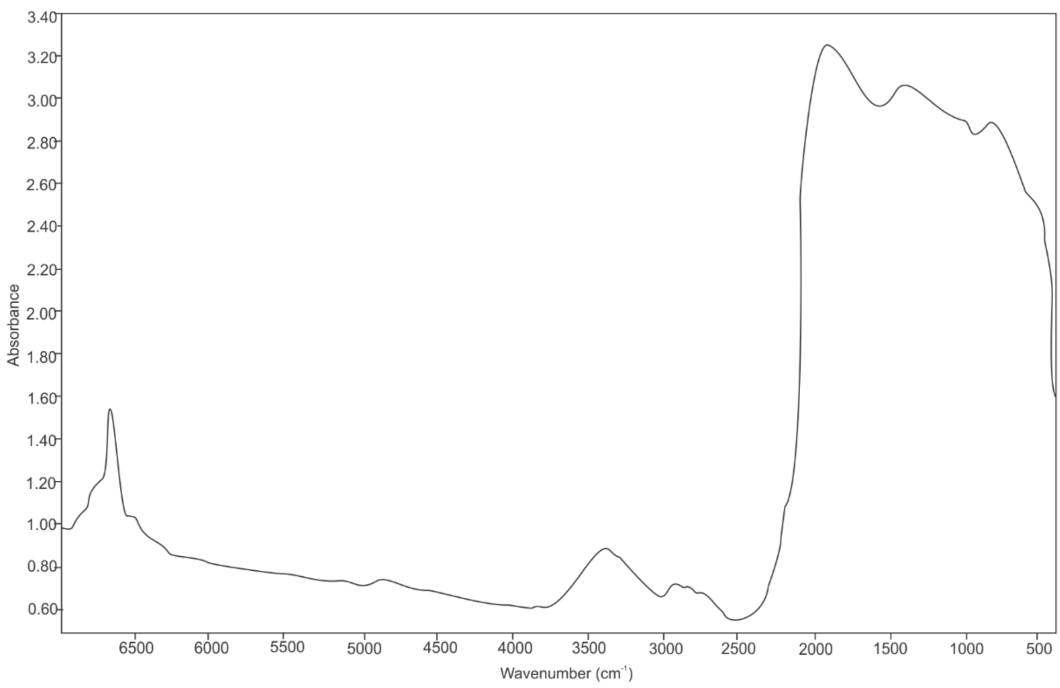

Fig. 3: *FTIR spectrum of reddish-brown zircon of Sri Lanka*

The band at 3800 and 3400 cm^{-1} which corresponds to hydrous components were observed. A sharp single band has been observed in this region which also confirms the significant degree of metamictization. This band is very strong compared to the Vietnamese RBZ spectrum.

UV-Vis-NIR absorption spectra for the untreated rough RBZ samples are shown in Fig. 4. The spectra of all five reddish-brown categories showed an increase in absorption toward the UV region. This gives the brown component of the colour (Vương & Hương, 2015). The broad absorption band in the UV region with an absorption "tail" extending into the visible region can be considered as a result of colour center, which is the cause of the formation of the above colour.

The radiation from radioactive elements such as U and Th may have caused the defect in the crystal structure. This can be recognized by the shoulder at around 600 nm of the absorption spectrum (Vương & Hương, 2015). Whereas this shoulder is observed at around 500 nm in both Vietnamese and Cambodian RBZs (Zeug et al., 2018). This can be also considered as a factor of identification of the crystalline zircon from metamictized zircon.

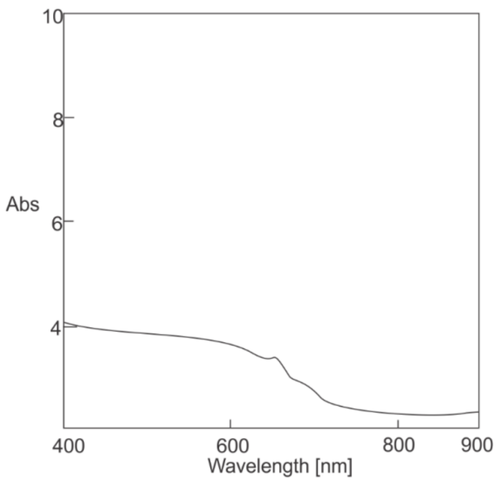

Fig. 4: *Visible spectrum of reddish-brown zircon of Sri Lanka*

A sharp peak at 652 nm and 689 nm were observed in untreated rough RBZ samples which attribute the trace amount of uranium as U^{4+} (Vương & Hương, 2015). Meantime the peak of 652 nm is attributed to the Tb^{3+} ion (Laithummanoon & Wongkokua, 2013).

Similar absorption patterns have been reported for reddish brown and brownish red zircon from other localities, including Ratanakiri (Cambodia), Central Highlands of Vietnam, and Muling (China)(Huong et al., 2017; Chen et al., 2011).

3.2 Development of possible Heat Treatment conditions for Reddish Brown Zircons of Sri Lanka

Several heat-treatment trials were performed between 120 °C to 800 °C. Around 500 °C - 600 °C with less than 90 minutes soaking period with either oxidizing or reducing condition is known to be the optimum condition to produce yellow and golden yellow colour for RBZ of Sri Lanka.

More than 90% of RBZ of Sri Lanka becomes lighter coloured with heat treatment under oxidizing or reducing conditions. Fig. 5 shows the RBZ before heat treatment (left corner) and a series of heat-treated stones between golden yellow to yellow colours. The intensity of the yellow saturation depends on the red component of the initial stone. The treated stones were stable and did not revert to their original appearance when exposed to light.

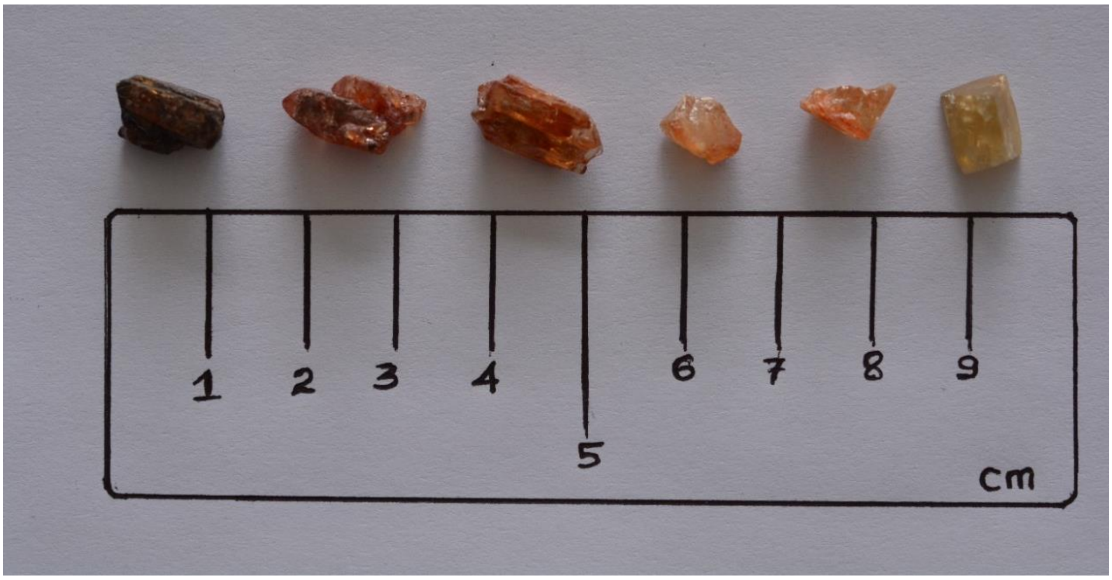

Fig. 5: *Reddish brown zircon before heat treatment and range of colours produced after heat treatment*

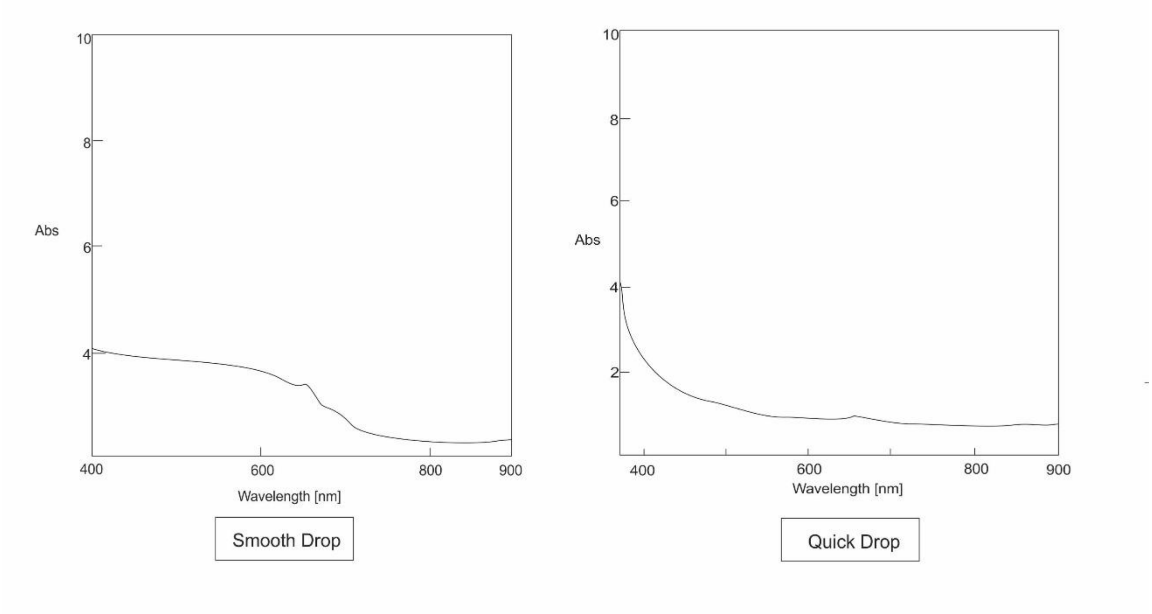

Fig. 6: *Visible spectrum of reddish-brown zircon and heat-treated yellow zircon*

3.3 Unheated Reddish-Brown Zircon Vs. Heat-treated Yellow Zircon

UV-Vis spectroscopy of heat-treated yellow to golden yellow zircons showed a quick drop in absorption around 400nm whereas unheated RBZ has a smooth flow in spectrum with a tail (Fig. 6). This may be due to the absence of brown components in the heat-treated yellow to golden yellow zircon. But the peaks at 652 nm and 689 nm which account for U remain the same in both unheated and heated samples.

A quick drop is observed in yellow to golden yellow zircon while a smooth drop is observed in raw RBZ which accounts for the colour change of the stone. There are no significant changes observed in the level of metamictization even after heat treatment.

4. CONCLUSIONS

The primary deposit of the Kolonna region consists of low to good gem quality reddish-brown zircons (RBZ). The most abundant chemical substitution was Hf, while all the RBZ samples contained a low amount of REE and radioactive elements. Also, the ratio of Th: U was consistent with a magmatic origin. Raman and FTIR spectroscopy indicate that the RBZ of Sri Lanka is of the Intermediate-type which has gone through a metamictization process. This is also confirmed by the specific gravity of the stones. And more importantly, they were not detectably radioactive which encourages embedding into jewellery. The UV-Vis absorption spectrum indicates the cause of colour is due to structural defect by radiation damage from radioactive elements such as U and Th. Heat treatment under either oxidizing or reducing conditions on an electric furnace produces a yellow to golden yellow colour at around 500 °C - 600 °C with a soaking period of less than 90 minutes. The difference in colour of RBZ and heat-treated yellow to golden zircon were distinguished using the UV-Vis spectrum by a smooth and quick drop respectively. Hence, these results help to understand the internal structure of zircon and have contributed towards the development of a precise heat treatment methodology adding extra value to the RBZ of Sri Lanka.

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