Effect of heat treatment on color of natural zircon

ผลกระทบของการเผาอบต่อการเปลี่ยนสีของเซอร์คอนธรรมชาติ

ฐิติมา ไหลธรรมนูญ[1]* และ วิวัฒน์ วงศ์ก่อเกื้อ[2]

บทคัดย่อ

งานวิจัยนี้ศึกษาผลกระทบของการเผาอบเซอร์คอนที่มีต่อตัวอย่างเซอร์คอนธรรมชาติ ตัวอย่างเซอร์คอนสีน้ำตาลแดง จากรัตนบุรี ประเทศกัมพูชา ได้ถูกนำมาเผาอบทั้งในบรรยากาศแบบมีออกซิเจนและแบบไม่มีออกซิเจน อุณหภูมิในการเผาอบตั้งแต่ 600-1100°C เพิ่มครั้งละ 100°C เป็นเวลา 3 ชั่วโมงในแต่ละอุณหภูมิ ผลกระทบต่อสีของตัวอย่างเซอร์คอนถูกนำมาวิเคราะห์ โดยใช้เครื่องสเปกโทรมิเตอร์ UV-Vis, FTIR และ EPR การวิเคราะห์ทำทั้งก่อนและหลังการเผาอบในแต่ละอุณหภูมิ เซอร์คอนเกือบไร้สีภายใต้การเผาอบในบรรยากาศที่มีออกซิเจนที่อุณหภูมิ 900°C เกิดจากการตกผลึกใหม่ของตัวอย่าง สีน้ำเงินของเซอร์คอนภายใต้การเผาอบในบรรยากาศที่ไม่มีออกซิเจนที่อุณหภูมิ 1100°C สอดคล้องกับการเปลี่ยนจาก Tb^{4+} ไปเป็น Tb^{3+} ของสัญญาณอีพีอาร์

คำสำคัญ: การเผาอบ เซอร์คอน ฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี ยูวี–วิสิเบิลสเปกโทรสโกปี อีพีอาร์

1 นักศึกษา ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์

2 อาจารย์ ภาควิชาฟิสิกส์ คณะวิทยาศาสตร์ มหาวิทยาลัยเกษตรศาสตร์

* ผู้นิพนธ์ประสานงาน โทรศัพท์ 08-0277-5340 อีเมล: nimmanorade@hotmail.com

รับเมื่อ 11 ธันวาคม 2555 ตอบรับเมื่อ 26 มีนาคม 2556

Effect of Heat Treatment on Color of Natural Zircon

Thitima Laithummanoon[1]* and Wiwat Wongkokua[2]

Abstract

This research investigated the effect of heat treatment on natural zircon samples. The reddish-brown zircon samples from Ratanakiri, Cambodia were annealed in both oxidizing and reducing atmosphere. The annealing temperatures were 600-1100°C with 100°C increment for 3 hr at each temperature. The effect on color of the zircon samples was analyzed by using UV-Vis, FTIR and EPR spectrometers. The analyses were carried out before and after for comparison. The near colorless property of zircon under oxidizing atmosphere annealing at 900°C was caused by the recrystallized samples. The blue color of zircon under reduced atmosphere annealing at 1100°C corresponded to the changing of Tb^{4+} to Tb^{3+} EPR signal.

Keywords: Annealing, Zircon, FTIR, UV-Vis, EPR

1 Student, Department of Physics, Faculty of Science, Kasetsart University.
2 Lecturer, Department of Physics, Faculty of Science, Kasetsart University.
* Corresponding Author, Tel. 08-0277-5340, E-mail: nimmanorade@hotmail.com

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1. Introduction

Thailand is globally reputed for its gems and jewelry business and its leadership in heat treatment technology of gemstones. There are many heat treatment specialists producing colorful and unique styles in gems.

The conventional heat treatment can enhance the gem's physical appearance without causing outside substance diffusion. The heating can rearrange the atomic elements inside the gem crystal into better order. Some native defects can also be removed by the annealing. The optical effect of heat treatment can result in brightness and vivid color changes.

Zircon is an economic gem. The most popular source of reddish-brown color zircon is from Ratanakiri, Cambodia [1]. The reddish-brown color is caused by the metamic process [2]. However, the most popular color of zircon is blue color, which can be only produced by heat treatments of the reddish-brown color zircon. The annealing recipe was invented by a Thai burner [3].

Heat treatment of zircon can be done by various techniques to produce different colors such as green-blue color by flowing argon gas during the annealing, yellow color by oxidizing atmosphere at 900°C at 6-hr soaking time [4] and blue color by covering with activated carbon at 1000°C at 2-hr soaking time [5] and at 900°C at 6-hr soaking time [6].

In this study, we investigated the causes of color changes from the reddish-brown color zircon by heat treatments under both oxidizing and reducing atmospheres. The main objective was to understand the origin of blue color in zircon produced by the heat treatment under reducing atmosphere by comparing to the near colorless zircon produced by the heat treatment under oxidizing atmosphere. Some spectroscopic techniques such as Ultraviolet Visible spectroscopy (UV-Vis), Fourier Transform Infrared spectroscopy (FTIR) and Electron Paramagnetic Resonance (EPR) were carried out to monitor some changes of defects or trace elements.

2. Materials and Methods

Twenty reddish-brown zircon samples were collected from Ratanakiri, Cambodia. Heat treatment on the samples was carried out under either oxidizing or reducing atmospheres using an electric furnace. In case of oxidizing atmosphere, half of the zircon samples were put into a crucible without any cover to allow air exposure during the annealing. In case of reducing atmosphere, the other half of the zircon samples were covered by graphite powders in a lidded crucible to prevent them from being exposed to ambient air. The annealing temperatures were 600-1100°C with 100°C increments at 3-hr soaking time for each temperature.

The UV-Vis, FTIR, and EPR spectroscopic techniques were employed to investigate the effects of heat treatment before and after each step of annealing. The EPR is a highly sensitive method to measure paramagnetic elements in materials. Some defects in zircon do exhibit paramagnetic property. Normally, unpaired electrons are localized at defect sites due to the wide energy band gap of zircon. The EPR spectrum can provided the link between the paramagnetic defect and the causes of color. The microwave frequency of the EPR system was 9.75 GHz.

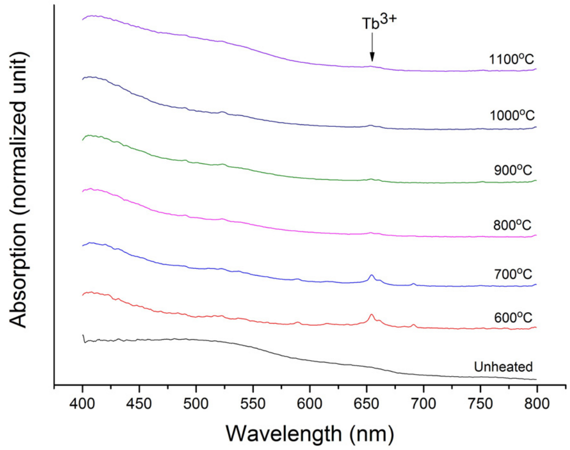
3. Results and Discussion

The native reddish-brown zircons are shown in Figure 1. The color change of the zircon samples after annealing in the oxidizing and reducing atmosphere are shown in Table 1.

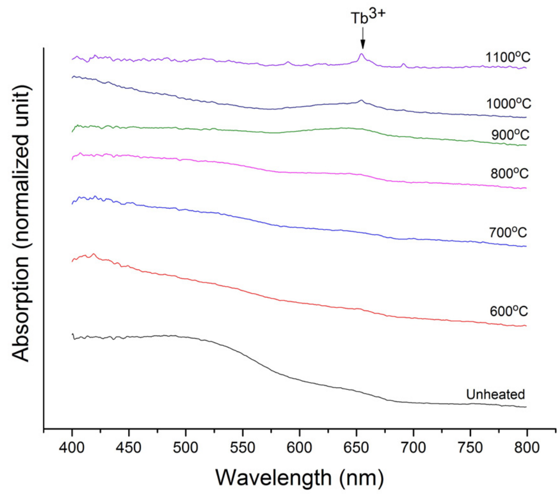
Figure 1 Reddish-brown color zircon samples from Ratanakiri, Cambodia.

Table 1 Comparison of zircon colors after heat treatments at various temperatures

Temperature (°C)	Oxidizing atmosphere	Reducing atmosphere
600		
700		
800		
900		
1000		
1100		



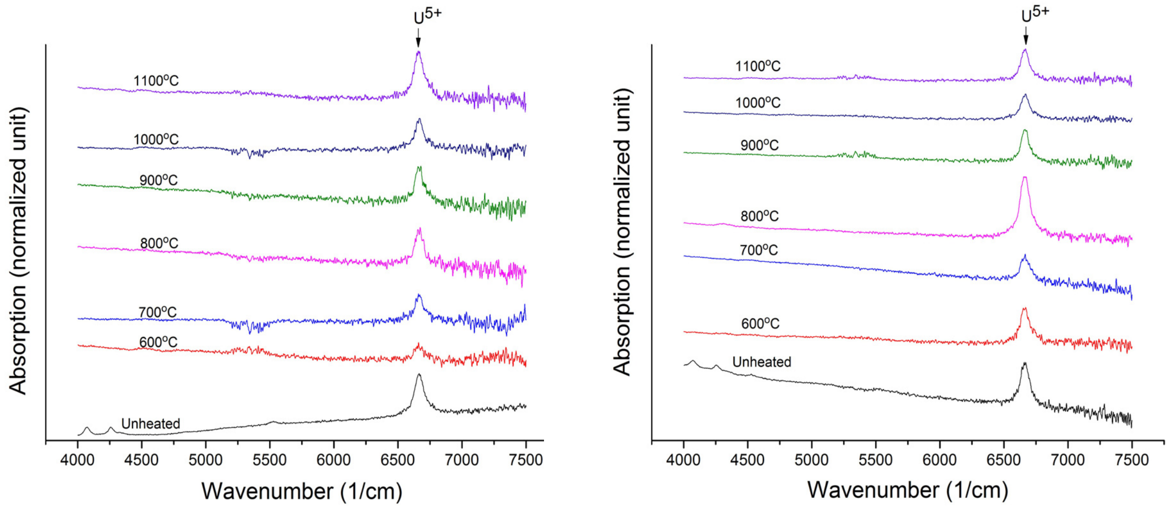
(a)



(b)

Figure 2 UV-Vis spectra of zircon samples before and after heat treatment in (a) oxidizing and (b) reducing atmosphere.

The UV-Vis spectra showed the decreasing of reddish-brown color absorption band at 400-600 nm after annealing in both oxidizing and reducing atmosphere as shown in Figure 2. The most suitable annealing temperature to obtain near colorless zircon was at 900°C for oxidizing atmosphere annealing noticed by the decreasing of absorption band at



(a) (b)

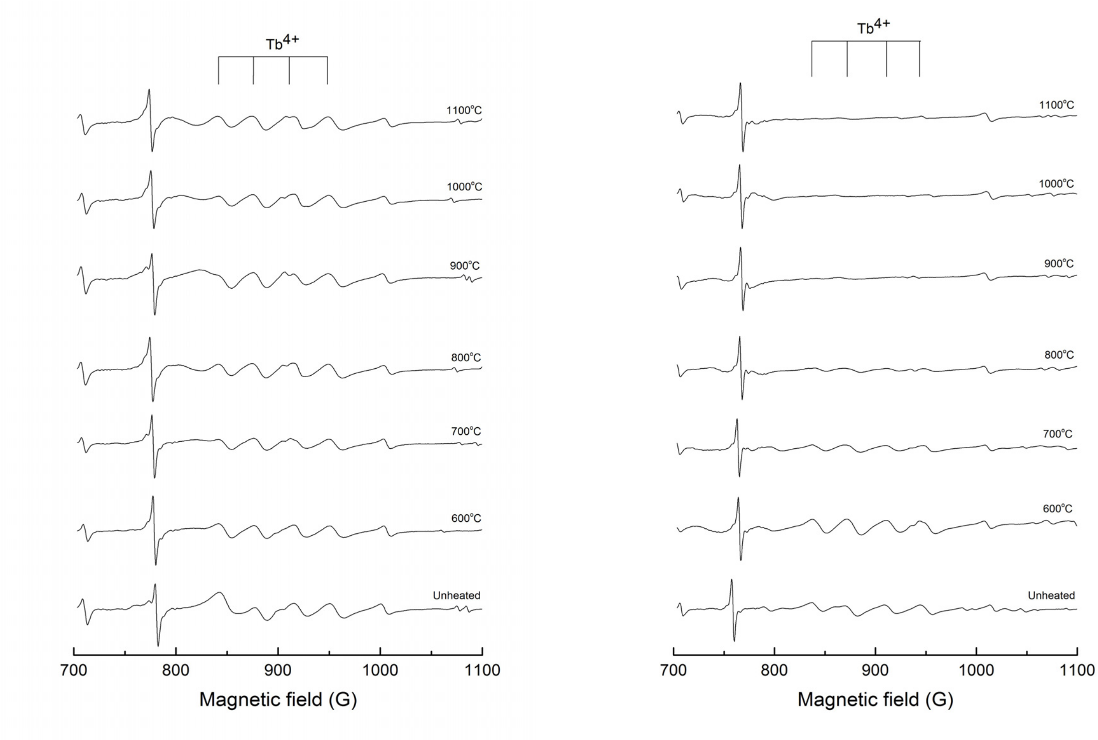
Figure 3 FTIR spectra of zircon samples before and after heat treatments in (a) oxidizing and (b) reducing atmospheres.

around 650 nm. The most suitable temperature to obtain blue zircon was at 1100°C in reducing atmosphere noticed by the increasing of absorption band at around 650 nm.

The origin of yellow tint is caused by Tb^{4+} impurity [7]. We measured Tb impurity in zircon using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) resulting about 2-6 ppm on average. When annealing in oxidizing and reducing atmosphere, zircon crystal could be re-crystallized [8] and plastic deformation was reduced resulting in the decrease of reddish-brown color. However, the yellow tint did not completely disappear due to the native content of Tb^{3+} ions. In the latter case, Tb^{4+} changes to Tb^{3+} by receiving an electron from graphite powders. The intensity of blue color depends on the amount of native Tb^{4+} to be changed to Tb^{3+}.

There was no significant change to U^{5+} peak at 6668 cm^{-1} [9] in FTIR spectra from annealing zircon samples in both oxidizing and reducing atmosphere as shown in Figure 3. The U defect was not influence to the colour change of the annealing zircon as previously proposed [10]. In Figure 4, EPR spectra of zircon samples annealed in the oxidizing atmosphere showed no changes with changing temperatures while annealing in the reducing atmosphere showed decreasing of Tb^{4+} band intensities at magnetic field 800-1100 G. The Tb^{4+} ions obtained electrons from graphite powders and changed to Tb^{3+} ions as already mentioned.

The colorless of zircon caused by the recrystallization of the crystal by annealing in the oxidizing atmosphere at 900°C. The blue color of zircon caused by changing of Tb^{4+} to Tb^{3+} by annealing in the reducing atmosphere at 1100°C. The difference of the color change processes resulted in the difference of the color changing temperatures.



(a) (b)

Figure 4 EPR spectra of zircon samples before and after heat treatments in (a) oxidizing and (b) reducing atmosphere.

4. Conclusion

We applied solid-state spectroscopic techniques, such as, UV-Vis, FTIR, and EPR to study the effect of heat treatment on zircon samples. The zircon samples turned colorless by annealing in oxidation atmosphere at 900°C while blue color zircon were obtained when annealed in reducing atmosphere at 1100°C. The Tb^{3+} peak reduced to minimum at 900°C in Figure 2(a) and increased to maximum at 1100°C in Figure 2(b). The blue color of zircon corresponded to the changing of Tb^{4+} to Tb^{3+} by obtained an electron as monitored by EPR spectroscopy. The source of additional electron donated by the nearly free electron of the covering graphite powder used when annealed in the reducing atmosphere.

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