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# The Effect of Heat Treatment and $CO_2$ Atmosphere on Color Changing in Zircon

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**Abstract**

The purpose of this research was to investigate the effects of heat treatment under $CO_2$ atmosphere on colors and properties of zircon. The zircon was heated at the temperatures of 800, 900, 1000, 1100, 1200 and 1300°C for 6 hours under $CO_2$ atmosphere. The CIE $L^*$ $a^*$ $b^*$ color index of unheated and after heat-treatment in $CO_2$ atmosphere were calculated from transmittance which was measured by UV/VIS spectrophotometer. The major compositions (in oxide form) of Zircon are $ZrO_2$ and $SiO_2$ and similar results were obtained within the range of experimental heat treatment. The XRD patterns showed crystallographic parameters as tetragonal of the space group $I4_1/amd$, and almost constant within the range of experimental heat treatment. The optimized condition was at the temperature of 900 °C for 6 hours. The color changed from dark brown to greenish blue with more clarity in the zircon crystal.


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*Keywords:* zircon; heat treatment; color changing; $CO_2$ atmosphere

## 1. Introduction

Thailand's gem and jewelry industry is widely considered one of the greatest potential markets in the world. This has created a continuous link to other industries. Currently, the Thai gems and jewelry industry is encountering trade obstacles and high competition. These include the deficiency of local raw materials; the rapid growth of the gem and jewelry industry in competing countries with lower labor costs; the development of products such as color which the jewelry trading is required. The important problems troubling the gemologists and the gem dealers are how to improve or enhance the quality of gem such as its color and brilliance [1,2].

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Heat treatment is the important method to color enhancement of gemstones. Each type of gemstone has different conditions of heat treatment. The improvement of color in gemstones depends on the atmosphere in the heating part of the furnace. Dark brown zircon which was heated under oxidizing atmosphere became yellowish brown or colorless, while heated under reducing atmosphere became light blue [3-6]. The most valuable colors which are rarely found in nature therefore an optimum heat treatment condition of zircon are the problem to be systematically examined. The purpose of this work is to enhance color and properties of natural zircon in $CO_2$ atmosphere at optimum temperature.

## 2. Experimental

Natural zircon samples from Cambodia were selected and randomized separately into 7 groups to study. The samples were cleaned up using $H_2SO_4$ and distilled water to remove impurities on their surfaces. The heat treatments were conducted at the setting temperatures of 800, 900, 1000, 1100, 1200 and 1300 °C under $CO_2$ atmosphere using electric furnace. Each group of samples were heated to the setting temperature and maintained at that temperature for 6 hours, then allowed to cool back to room temperature. Samples from both before and after heat treatment step were selected to determine chemical compositions and optical properties. Energy Dispersive X-ray Fluorescence (EDXRF; Panalytical; Minipal-4) was used to examine the chemical compositions of the samples. X-Ray Diffractometer (XRD; Bruker AXS; D8) was used to determine crystal structure of the samples. Each samples were ground into fine powder using alumina mortar, the XRD patterns were measured as a function of the angle (2θ) from 15° - 85° with the step of 0.02° per second. UV/VIS spectrophotometer (Varian; Cary-50) was employed to measure their transmittance within the range of 400 to 700 nm. The CIE L*a*b* color index of unheated and heated treatment under $CO_2$ atmosphere were also calculated from the transmission spectra.

## 3. Results and Discussions

The samples of untreated zircon from Cambodia display dark brown color, as shown in Fig 1. After heat treatment under $CO_2$ atmosphere, the clarity of natural zircon increased when increasing heating temperature from 800 to 1000°C. The significant blue color was observed at the temperature of 900 °C for 6 hours, while at higher temperature the zircon exhibited cloudy within the crystal.


Fig. 1. Visual appearances of Cambodia zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures for 6 hours

The results from EDXRF showed that $ZrO_2$ and $SiO_2$ were the major chemical compositions in zircon crystals, as shown in Table 1.

From Table 1, it was found that the chemical compositions of zircon before and after heat treatment are approximately the same. The majority chemical compositions in zircon samples were $ZrO_2$ (61.962%) and $SiO_2$ (29.624%) while the minorities were MgO (2.494%), $Al_2O_3$ (1.246%), CaO (2.722%), $Cr_2O_3$ (0.100%), $Fe_2O_3$ (0.097%), $Co_3O_4$ (0.015%), NiO (0.020%), $Y_2O_3$ (0.078%), and BaO (0.090%). Crystal structure of natural

zircon before and after heat treatment under $CO_2$ atmosphere at various heating temperatures was achieved using XRD.

Table 1. Chemical compositions in oxide form of natural zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures for 6 hours

| Temp. (°C) | Chemical Compositions | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **MgO** | **$Al_2O_3$** | **$SiO_2$** | **CaO** | **$Cr_2O_3$** | **$Fe_2O_3$** | **$Co_3O_4$** | **NiO** | **$Y_2O_3$** | **$ZrO_2$** | **BaO** |
| unheated | 2.145 | 1.056 | 29.318 | 1.459 | 0.225 | 0.101 | 0.016 | 0.023 | 0.098 | 65.383 | 0.097 |
| 800 | 0.783 | 1.167 | 31.404 | 0.646 | 0.286 | 0.099 | 0.017 | 0.027 | 0.078 | 65.232 | 0.070 |
| 900 | 4.300 | 1.899 | 26.538 | 3.369 | 0.040 | 0.049 | 0.011 | 0.019 | 0.069 | 53.606 | 0.154 |
| 1000 | 1.701 | 0.997 | 28.494 | 3.257 | 0.039 | 0.073 | 0.013 | 0.011 | 0.087 | 65.226 | 0.055 |
| 1100 | 1.682 | 0.787 | 31.065 | 2.049 | 0.022 | 0.063 | 0.020 | 0.013 | 0.077 | 64.135 | 0.044 |
| 1200 | 4.346 | 1.087 | 30.081 | 5.015 | 0.006 | 0.191 | 0.015 | 0.024 | 0.064 | 58.953 | 0.111 |
| 1300 | 2.499 | 1.728 | 30.471 | 3.255 | 0.078 | 0.100 | 0.014 | 0.026 | 0.076 | 61.203 | 0.098 |
| average | 2.494 | 1.246 | 29.624 | 2.722 | 0.100 | 0.097 | 0.015 | 0.020 | 0.078 | 61.962 | 0.090 |

Fig. 2. illustrates a typical XRD pattern of natural zircon which matches with JCPDS file number ICDD 060266. The peak positions corresponding to the Bragg diffractions showing the same XRD pattern which is slightly differ only in the peak intensities. From XRD patterns, unit cell parameters of zircon lattice can be calculated, as shown in Table 2.

Table 2. establishes crystallographic parameters obtained from XRD patterns, from the table, the relations between lattice parameters (*c/a* ratio), which were showed tatragonality of the lattice, are approximately the same. The crystalline phase of zircon is almost constant within the range of experimental heat treatment. The crystalline phase is still tetragonal of the space group $I4_1/amd$.

Table 2. Lattice parameter of natural zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures for 6 hours

| Temperature (°C) | Unit cell parameters | | |
|---|---|---|---|
| | *a* | *b* | *c/a* |
| unheated | 6.6030 | 5.9795 | 0.9055 |
| 800 | 6.6033 | 5.9777 | 0.9052 |
| 900 | 6.6034 | 5.9781 | 0.9057 |
| 1000 | 6.6042 | 5.9789 | 0.9054 |
| 1100 | 6.6035 | 5.9813 | 0.9056 |
| 1200 | 6.6030 | 5.9784 | 0.9053 |
| 1300 | 6.6035 | 5.9789 | 0.9058 |

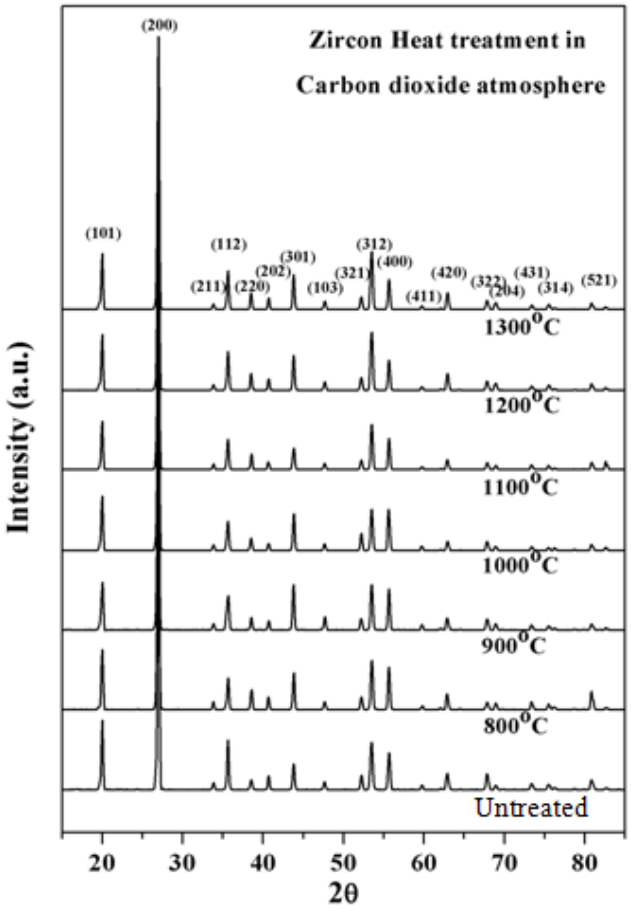


Fig. 2. XRD patterns of natural zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures for 6 hours

UV/VIS spectrophotometer was used to investigate optical properties of natural zircon, after measured in the range of 400 to 700 nm, the data from transmittance spectra of each samples were calculated into CIE L* a* b* color index. Table 3 exhibits data of CIE L* a* b* color index of zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures, the data was then plot in 2 dimensional CIE L* a* b* color index as in Fig. 3. From these results, natural zircon heated at 800 °C under $CO_2$ atmosphere is brighter than heat treated the zircon at 900 °C but the color was not appropriate for jewelry trading, so the optimized condition for color changing in zircon was at the temperature of 900 °C for 6 hours. The color was changed from dark brown to greenish blue with more clarity in the zircon crystal.

Table 3. CIE L* a* b* color index of natural zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures

| Temperature (°C) | CIE L* a* b* color index | | |
|---|---|---|---|
| | L* | a* | b* |
| unheated | 16.046 | 3.4005 | 7.0644 |
| 800 | 28.8054 | 0.2176 | 2.3793 |
| 900 | 21.5511 | -0.1845 | -0.3489 |
| 1000 | 0.357 | 0.5693 | 0.7995 |
| 1100 | 5.8806 | 0.7255 | 2.0508 |
| 1200 | 1.9249 | 1.1707 | 2.4619 |
| 1300 | 2.1161 | 0.5084 | 1.132 |

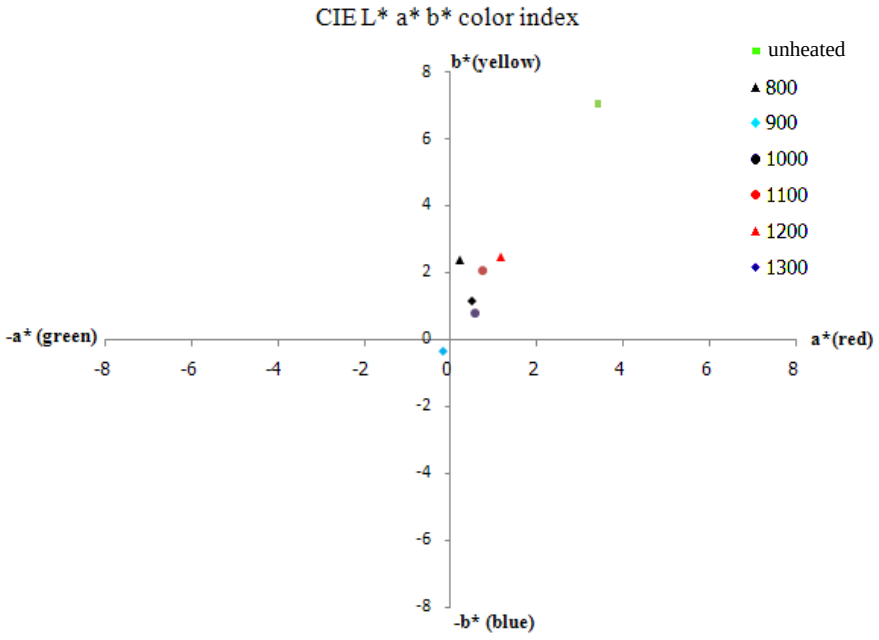


Fig. 3. CIE L* a* b* color index of natural zircon before and after heat treatment under $CO_2$ atmosphere at various temperatures for 6 hours

## 4. Conclusion

The effects of heat treatment on color and clarity of natural zircon were investigated. Natural zircon was heated at the temperatures of 800, 900, 1000, 1100, 1200 and 1300°C for 6 hours in $CO_2$ atmosphere. Chemical compositions were measured using EDXRF, with no significant changing in major compositions between unheated and heated samples. From XRD patterns, unheated and heated zircon showed same tetragonal phase with had space group of $I4_1/amd$. The transmittance within the range of 400 to 700 nm of unheated and heated zircon samples were measured by UV/VIS spectrophotometer. The CIE L* a* b* color index of the samples in $CO_2$ atmosphere were calculated. It was found that, the optimized condition was at the temperature of 900 °C for

6 hours under $CO_2$ atmosphere. The color was changed from dark brown to greenish blue with more clarity in the zircon crystal.

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