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The change of crystal field of Gd^{3+} in natural zircon with heat treatment in oxidizing and reducing atmospheres monitored by ESR spectroscopy

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Abstract

Color appearance in gemstones occurred as the consequences of several factors such as impurity ions, color center or inclusions within gemstones. Variety colors of zircon found in nature, but there is no research showing the clear causes of the color appearance. The main objective of this research is to involving the ESR spectra of the gadolinium ion (Gd3+) impurity ions of in natural zircon crystal to the color of zircon. The Zeeman interaction of impurity ions effect produces the crystal field and weak hyperfine interaction. All of the interactions were calculated by a computer program. In addition, the symmetry of impurity ion site can be seen with the relation between the resonance magnetic field positions and the applied magnetic field directions in the ESR spectra. The variation in the crystal field parameters of heat-treated zircon at different atmospheres was found related to the change in the color of zircon.

Keywords**:** *crystal field, ESR spectroscopy, ESR spectra, gadolinium ion, Gd3+, natural zircon*

1. Introduction

Zircon is a unique gemstone because it is distinguished by its specific gravity and refraction (Mungchamnankit, & Limsuwan, 2007; Mungchamnankit, Limsuwan, Thongcham, & Meejoo, 2008). Zircon has been popular in Thailand. Colorless zircon is well known for its characteristics including: flashes and brilliance of multicolor light, close to the properties of diamond. The sources are often associated with corundum and good quality zircons can be found in Thailand and Cambodia. Heat treatment is an important method to improve the color of gems. Each gemstone has different heat treatment conditions and depends on the atmosphere in the heating part of the furnace (Achiwawanich, Brack, James & Liesegang, 2006). Dark brown zircon heated under an oxidizing atmosphere, its color turn to yellowish brown or colorless, while heating under a reducing atmosphere its color turn to light blue (Winotai, Saiseng, & Sudyoadsuk, 2001; Mungchamnankit, Limsuwan, & Winotai, 2006; Kittiauchawal, Mungchamnankit, Sujinnapram, Kaewkhao, & Limsuwan, 2012).

In 2006, we began to study the impurity ions in zircon, using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and electron spin resonance (ESR) spectroscopy (Mungchamnankit et al., 2006; Mungchamnankit & Limsuwan, 2007; Mungchamnankit, Limsuwan, Winotai & Meejoo, 2007). The ESR study of the impurity ions such as Gd^{3+} in the natural zircon crystal in these researches (Grimes, Wooden, Cheadle, & John, 2015; Nikolaev et al., 2016) were dedicated to explain color changing in crystal of the natural gemstones in the presence of the impurity ions. In the following year, experiments were carried out by heat treating of zircons at 900 ^{o}C in oxygen and argon atmosphere and their related crystal field parameters were calculated. Heat treating experiment had been found to affect the second degree crystal field parameter (B_2^0). The gadolinium ion experiences a large axial crystalline electric field generated from its surrounding oxygen ions within the zircon lattice (Mungchamnankit & Limsuwan, 2007). From 2012 to 2014, more was learnt on the effect of CO_2 atmosphere on color changing in zircon and that the optimized condition

for heat-treating zircon was found 900 ^{o}C for 6 hours. The treated zircons color was changed from dark brown to greenish blue with more clarity in the zircon crystal (Mungchamnankit, Ruengsri, Angnanon, Srisittipokakun, & Kaewkhao, 2013). The crystal filed parameters were at the time was not calculated.

According to our previous works, heat-treated zircon in the oxidizing and reducing atmospheres produced two different shades. In oxidizing atmosphere, zircon color turns from dark brown to light yellowish brown. While in a reducing atmosphere heat treated zircon color changes to greenish blue and yellowish blue. But there appears no research to clearly explain the causes of the color changing phenomena.

2. Objectives

In this research, the change of Gd^{3+} crystal field in zircon after heat treating in the oxidizing and reducing atmospheres was studied and calculated from ESR spectra and explained in relation to the color changing in zircon crystals.

3. Materials and methods

The zircon crystal samples obtained from Cambodia were surface cleaned using H_2SO_4 and solvent to remove all stains and other impurities. The samples with a known c-axis having dimension of about 2×2×5 mm^3 were separated into two groups. The first group was subjected to heat at 900 ^{o}C in oxygen atmosphere while the second group was heated in CO_2 reducing atmosphere at 900 ^{o}C. ESR measurements were performed on both groups of samples at room temperature (298 K) in the microwave range of X-band (~9.86 GHz) at the usual 100 kHz field modulation by a Bruker E500 CW ESR spectrometer. The sample was mounted on a quartz sample holder rotatable about its axis. The ESR spectra were measured in two orientations; with the c-axis [001] parallel and perpendicular to the applied magnetic field. The magnetic field strength was varied from 0 to 650 mT. The data were recorded at every 15^{o} of the rotation angle, about c-axis (ϕ) and the rotation angle (θ) about x or y-axis from 0 to 180^{o}. The measurement planes are shown in Figure 1. The variations of the magnetic field strength with positions of the rotation angles ϕ and θ were observed in order to confirm the impurity ion site symmetry in the zircon crystal. The spin Hamiltonian parameters and energy level diagrams were calculated from ESR spectra.

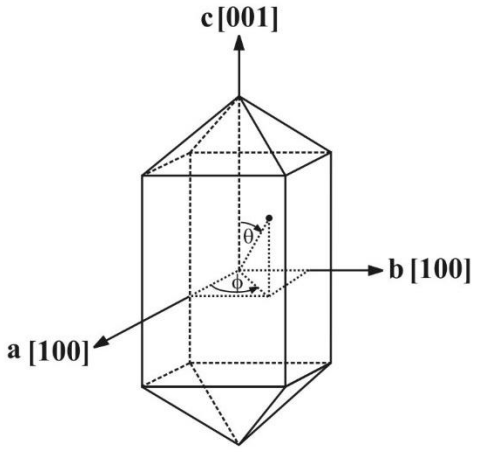

Figure 1 Indicates the rotation angle (θ) and the angle about c-axis (ϕ) for ESR spectra acquiring (Mungchamnankit, Limsuwan, Thongcham, & Meejoo, 2008)

4. Results and discussion

The ESR spectra of zircons before and after heat treatment in oxygen and CO_2 atmosphere were observed in X-band with the applied magnetic fields parallel to the c-axis [001] at room temperature (298 K) are shown in Figures 2 and 3; respectively. Seven peaks of resonance absorption belong to Zeeman interaction were observed due to a present of the Gd^{3+} trace in the natural zircon. Since the electron configuration of Gd^{3+} is $[Xe]4f^7$, hence the spin quantum number is S = 7/2 and the ground state is $^8S_{7/2}$. The state $^8S_{7/2}$ splits into 2S+1 = 8 states, then the seven allowed transitions according to the selection rule, $\Delta M_S = \pm 1$, are obtained (Mungchamnankit, Limsuwan, Thongcham, & Meejoo, 2008; Kittiauchawal et al., 2012). The ESR spectra can be described by a spin Hamiltonian incorporating with Zeeman interaction, hyperfine structure and crystal field operators (Abraham, Clark, Finch, Reynolds, & Zeldes, 1969; Tennant, Claridge, Walsby, & Lees, 2004; Reynolds, Boatner, Finch, Chatelain, & Abraham, 1972) and given by equation:

$$H = \boldsymbol{\beta}\cdot\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B} + B_2^0O_2^0 + B_4^0O_4^0 + B_4^4O_4^4 + B_6^0O_6^0 + B_6^4O_6^4 \quad (1)$$

The first term corresponds to the Zeeman interaction arises from the interaction between electron spin angular momentum and external magnetic field where **β**, **S**, **g** and **B** are the Bohr magneton, the spin operators, gyromagnetic tensor and magnetic field, respectively. The second term is the crystal field term which arises from the crystal field potential generated from the surroundings of the paramagnetic ion in zircon. This term depends on the local symmetry of paramagnetic ion site and the electronic configuration of ion. The sum of the spin angular momentum operators called Stevens' operators or the equivalent operators ($B_2^0, B_4^0, B_4^4, B_6^0$ and B_6^4) with their coefficients ($O_2^0, O_4^0, O_4^4, O_6^0$ and O_6^4) are the crystal field parameters.

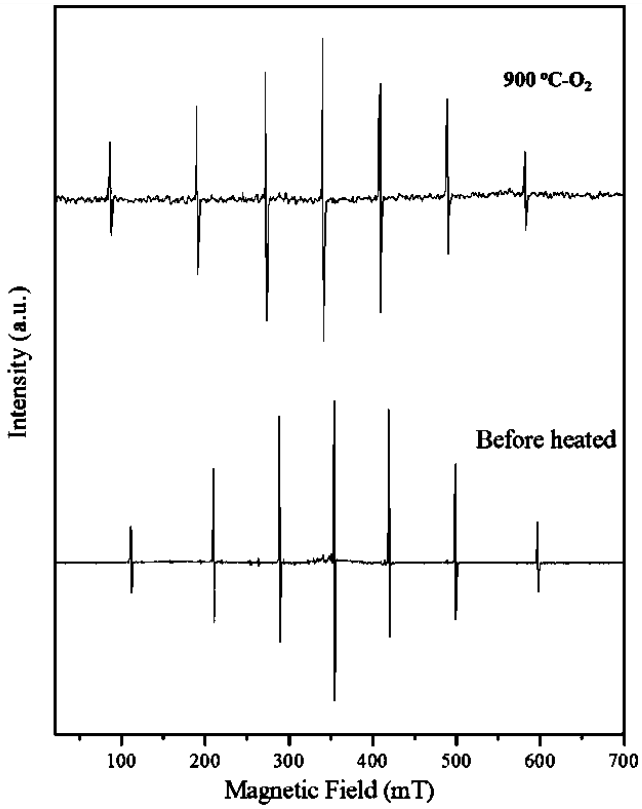

Figure 2 Shows zircon ESR spectra before and after heated at 900°C in oxygen atmosphere with the applied magnetic field parallel to the c-axis

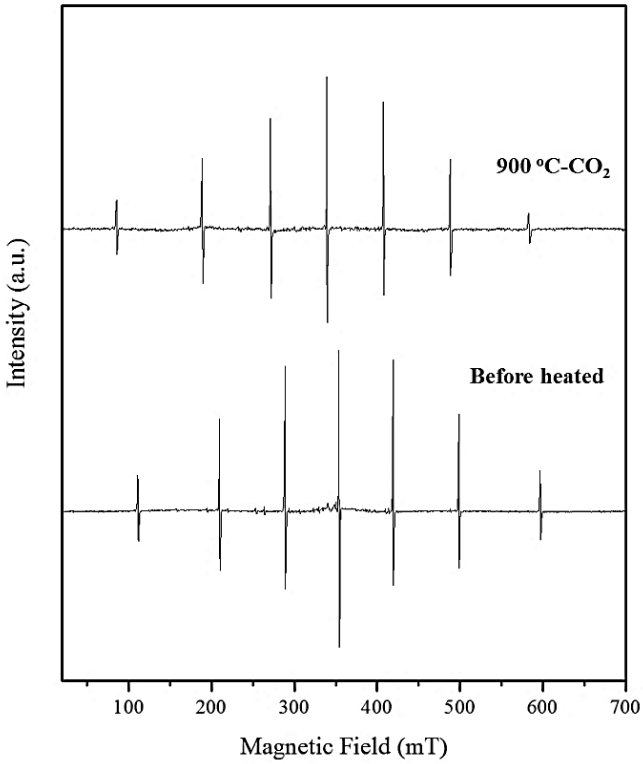

Figure 3 Shows zircon ESR spectra before and after heated at 900°C in CO_2 atmosphere with the applied magnetic field parallel to the c-axis.

The parameters in Eq. (1) were calculated from the resonance magnetic field positions in the ESR spectra and the obtained parameters are given in Table 1. The principal spin Hamiltonian parameters B_k^q were determined by measuring the magnetic field positions of the ESR spectra measured with the applied magnetic fields both parallel and perpendicular to the c-axis.

Table 1 Spin Hamiltonian parameters of Gd^{3+} in zircon before and after heat treatment at 900°C in both oxygen and CO_2 atmospheres

Parameters	O_2 atmosphere		CO_2 atmosphere	
	Before heated	After heated	Before heated	After heated
$g_{xx} = g_{yy}$	1.9914	1.9912	1.9914	1.9910
g_{zz}	1.9919	1.9920	1.9919	1.9918
B_2^0	376.45	373.24	369.73	378.56
B_4^0	7.02	7.80	8.05	7.92
B_4^4	78.29	76.91	76.01	78.64
B_6^0	0.65	0.75	0.68	0.59
B_6^4	0.12	0.12	0.12	0.12

The constant g_{zz}, B_2^0, B_4^0 and B_6^0 could be accurately determined by perturbation theory when the magnetic field is parallel to the c-axis (agreed with de Biasi & Grillo, 2015; Fuks, Typeka, Berkowski, Głowacki, & Tomaszewicz, 2018). The off-diagonal matrix elements O_4^4 and O_6^4 are considerably smaller than the diagonal ones for sufficiently high resonance frequency. Since the

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corresponding spin Hamiltonian parameters B_4^4 and B_6^4 are usually small, the contributions arising from these terms can be neglected for the orientation **B**‖c. By using the parameters shown in Table 1, the energy level diagrams can be simulated (EPR-NMR program) and the results for unheated zircon are presented in Figure 4. It was found that the transition energies between the two simulated energy levels of Zeeman splitting line are nearly the same as the absorbed microwave energy obtained from the ESR experiments.

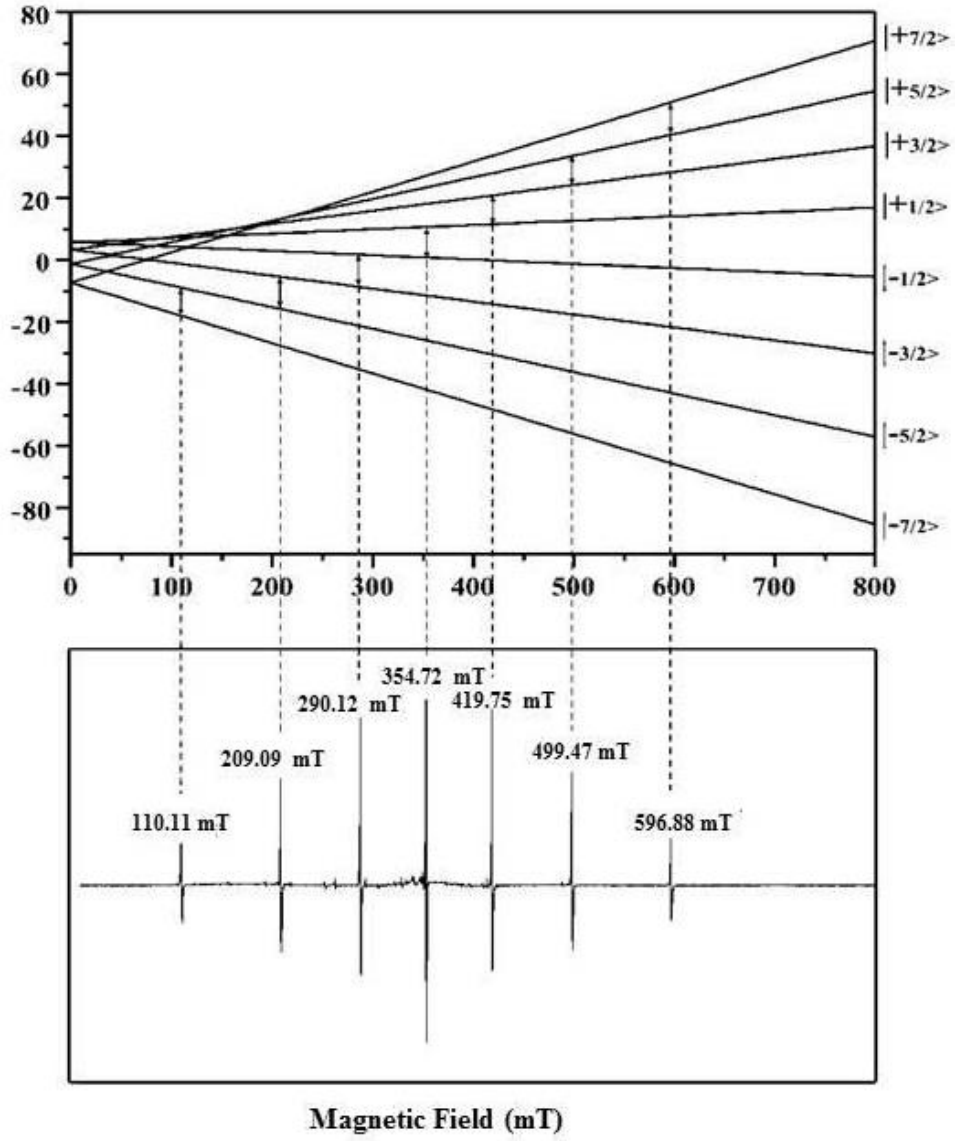

Figure 4 Energy levels diagram of Gd^{3+} in unheated zircon with magnetic field applied parallel to the c-axis (above), and the transitions were corresponding well to the peaks measured with ESR spectra (below)

In the same way, the seven allowed transitions ($\Delta M_S = \pm 1$) occur at the magnetic field positions or responding by the following first order expressions (Rappaz, Boatner, & Abraham, 1980).

$$\begin{aligned}
\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2} : \mathbf{B} &= \frac{1}{g\beta}\left[h\nu \pm \left(-6B_2^0 - 20B_4^0 - 6B_6^0\right)\right] \\
\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2} : \mathbf{B} &= \frac{1}{g\beta}\left[h\nu \pm \left(-4B_2^0 + 10B_4^0 + 14B_6^0\right)\right] \\
\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2} : \mathbf{B} &= \frac{1}{g\beta}\left[h\nu \pm \left(-4B_2^0 + 10B_4^0 + 14B_6^0\right)\right] \\
+\frac{1}{2} \leftrightarrow -\frac{1}{2} : \mathbf{B} &= \frac{h\nu}{g\beta}
\end{aligned} \qquad (2)$$

ν is the microwave frequency. The ground state energy level Gd^{3+} in the natural zircon splits into four doublets; denoted by $|\pm 7/2\rangle$, $|\pm 5/2\rangle$, $|\pm 3/2\rangle$, and $|\pm 1/2\rangle$, due to crystal field or zero field splitting. Applying the magnetic field to the zircon, the magnitude of splitting becomes larger due to Zeeman interaction. However, the transition energies calculated by Eq. (2) were only for the magnetic field parallel and perpendicular to zircon crystal. When the crystals were rotated (Fuks et al., 2018), some peaks of ESR spectra could not be observed due to overlapping of the energy levels. So, it is necessary to calculate and simulate the energy levels of Gd^{3+} in zircon by using the computer program.

The Zeeman interaction, the weak hyperfine interaction, and the crystal field interaction due to the environments of the impurity ions were calculated from the ESR results. Particularly, the changes in the crystal field parameters of heat-treated zircon under different atmospheres were investigated and these they were related to the color change of zircon.

5. Conclusion

The effect of heat treatment on ESR spectra of zircon crystals were studied in both oxygen and CO_2 atmospheres with the direction of magnetic field applied parallel and perpendicular to the *c*-axis [001]. The microwave energy absorptions due to the transitions between the spin states of impurity ions (Gd^{3+}, S = 7/2 in the natural zircon crystal were investigated. These were confirmed by the clearly resolved fine structure of the gadolinium ion.

The second degree crystal field parameter (B_2^0) is much larger than the other crystal field parameters. This result reveals that the gadolinium ion is in the presence of a large axial crystalline electric field of generated from tetragonal symmetry of the surrounding oxygen ions within the zircon lattice. This generating the ESR spectra with the applied magnetic field direction. The change of the crystal field parameters of heat-treated zircon under different atmospheres were clearly related to the change in color of zircon.

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