The Effect of Heat Treatment on Crystal Structure in Zircon Monitored by ESR and XRD

T. Kittiauchawala, A. Mungchamnankit*, S. Sujinnapram, J. Kaewkhao, P. Limsuwane

*Faculty of Science and Technology, Thaksin University, Lopburi, 15000, Thailand
Department of Physics, Faculty of Science, Rangsit University, Pathumthani, 12000, Thailand
Department of Physics, Faculty of Liberal Arts and Science, Kasetsart University, Nakhon Pathom 73140, Thailand
Center of Excellence in Glass Technology and Materials Science, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
Thailand Center of Excellence in Physics, CHE, Ministry of Education, Bangkok 10400, Thailand
Department of Physics, King Mongkut’s University of Technology Thonburi Bangkok, 10140, Thailand

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Abstract

X-band ESR spectra of zircon before and after heat treatment under oxygen rich atmosphere were measured with directions of the magnetic field applied in parallel and perpendicular to c-axis [001]. Seven peaks of Zeeman interaction were generated from the microwave energy absorptions due to the transitions between the spin states of natural impurity, gadolinium ions (Gd³⁺, S = 7/2). Angular variation of peak positions reflects that the symmetry surrounding of Gd³⁺ is D₂d, signifying the replacement of Zr⁴⁺ by Gd³⁺ in the lattice. From XRD patterns, the unheated and after heated zircon are the same phase i.e. tetragonal phase of the space group I₄₁/amd. The Rietveld refinement method was employed for derivation of the bond distance and bond angles of zirconium, silicon and oxygen atoms.

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1. Introductions

Zircon (ZrSiO₄) has attracted in the field of material science and has been extensively studied to the range of physical properties [1]. For jewelry trading, zircon is unique among gemstones because of the
remarkable range observed in its specific gravity and its refractivity [2]. The crystal structure of zircon may not always be perfect due to the impurity ions such as rare earth ions. In chemical composition, zircon is comparatively simple, being a zirconium silicate, corresponding to the formula ZrSiO$_4$, but it invariably contains small of impurity ions, rare earth ions and several other transition ions. ZrSiO$_4$ comprises an arrangement of SiO$_4$ tetrahedrons and ZrO$_8$ dodecahedron. ZrSiO$_4$ has a tetragonal body-centered Bravias lattice with 12 atoms in the unit cell (Fig. 1). The space group is I4$_1$/amd ($D^{19}_{4h}$) and the unit cell contains four SiO$_4$ and four ZrO$_8$ groups. The SiO$_4$ groups are distorted tetrahedral elongated along a twofold c-axis (crystallographic axis) and their symmetry is D$_{2d}$ [3].

Fig. 1. Portion of the zircon unit cell showing interconnection of SiO$_4$ tetrahedral and ZrO$_8$ dodecahedron along the 4 axis [3].

The eight oxygen atoms co-ordinate to a zirconium atom have the geometry of a triangular dodecahedron. Four of them are arranged according to a distorted tetrahedron elongated along a twofold c-axis. The other four oxygen atoms are disposed according to a distorted tetrahedron compressed along the same c-axis and rotated by 90° with respect to previous one. The overall symmetry of ZrO$_8$ group is also D$_{2d}$ [3].

Electron Spin Resonance (ESR) was used for investigating the detailed physical properties of paramagnetic defects. Actually the magnetic resonance can be employed in different experimental techniques but ESR is the most prominent technique. In the case of impurity ions carry greater charge than the host ion they replace, the electrostatic attractive force acting on the impurity ions by the nearest neighboring O$^{2-}$ ions becomes larger than that on the replaced host ion [4]. The objective of this research is dedicated to the ESR study of the impurity ions (i.e. Gd$^{3+}$) in the natural zircon crystal before and after heat treatment because the presence of the impurity ions in the crystal usually causes the color in crystal. The ESR spectra of Gd$^{3+}$ ions in a zircon crystal were investigated at various rotation angles before and after the heat treatment at 900°C in oxygen atmosphere. The obtained ESR spectra were least-square fit by using a numerical diagonalization of the spin Hamiltonian matrix and the spin Hamiltonian parameters were calculated. In the addition, the Rietveld refinement were used to determine the crystal structure before and after heat treatment obtained from XRD data.
2. Experimental

For ESR measurement, natural zircons used in this study were obtained from Cambodia. They were cleaned thoroughly with acid and solvent to removed stain and other impurities on its surface. A zircon crystal sample of dimension about 2×2×5 mm³ and known c-axis were selected for ESR measurements. A zircon sample before and after heat treatment in oxygen atmosphere was used for ESR measurements at room temperature (293 K) in the microwave range of X-band (~9.86 GHz) with the usual 100 kHz field modulation on a Bruker ELEXYS E500 CW ESR spectrometer. The sample was mounted on a quartz sample holder in which it could be rotated about its axis. The rotation angles are shown in Fig. 2.

![Fig 2. The rotation angles θ and φ](image)

The ESR spectra were measured with the c-axis [001] parallel and perpendicular to the applied magnetic field. The magnetic field was varied from 0 to 650 mT. The ESR spectra were recorded every 15° of the rotation angle, φ about c-axis and the rotation angle, θ about x or y-axis from 0 to 180°. The variations of the resonance magnetic field positions as a function of the rotation angles θ and φ were observed to confirm the impurity ion site symmetry in the crystal sample. The ESR spectra, then, were used to calculate the spin Hamiltonian parameters and the energy level diagrams were determined.

For XRD measurement, the two groups of zircon were pulverized manually yielding into very fine powder using an alumina mortar. After that, the pulverized samples were detected any change in crystal structure untreated and treated samples in different atmosphere by XRD. The X-ray diffraction patterns will be collected using Bruker X-ray diffractometer model D8 Advance with CuKα1 (1.54060 Å) and CuKα2 (1.54439 Å) radiation at 40 kV/40 mA controlled by DiffracPlus software. The intensity of X-ray powder pattern was measured as a function of the diffraction angle (2θ) from 18°-70° with the step of 0.02° per second. The obtained XRD diffraction patterns were refined by the Rietveld method using the Fullprof program to obtain the crystallographic parameters.
3. Results and Discussions

The first derivative spectra of zircon before and after heat treatment in oxygen atmosphere were observed in X-band (~9.86 GHz) when the applied magnetic fields are parallel and perpendicular to the \(c\)-axis [001] at room temperature (298 K) as shown in Fig. 3-4.

Seven resonance absorption peaks of Zeeman interaction are obtained due to a trace of the Gd\(^{3+}\) present in the natural zircon. We can explain the occurrence of the ESR spectra as follow. Since the electron configuration of Gd\(^{3+}\) is \([\text{Xe}]4f^7\), hence the spin quantum number, \(S = 7/2\) and the ground state of Gd\(^{3+}\) 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.

The ESR spectra can be described by a spin Hamiltonian incorporating with Zeeman interaction, hyperfine structure and crystal field operators [5-7] is given by equation

\[
H = H_{\text{Zeeman}} + H_{HF} + H_{CF}
\]

The first term corresponds to the Zeeman interaction arises from the interaction between electron spin angular momentum and external magnetic field. The Zeeman term is given by equation
\[ H_{\text{Zeeman}} = \beta S \cdot g \cdot B = \beta \begin{bmatrix} S_x & S_y & S_z \end{bmatrix} \cdot \begin{bmatrix} \tilde{g}_{xx} & \tilde{g}_{xy} & \tilde{g}_{xz} \\ \tilde{g}_{yx} & \tilde{g}_{yy} & \tilde{g}_{yz} \\ \tilde{g}_{zx} & \tilde{g}_{zy} & \tilde{g}_{zz} \end{bmatrix} \cdot \begin{bmatrix} B_x \\ B_y \\ B_z \end{bmatrix} \] (2)

where \( \beta, B, g \) and \( S \) are the Bohr magneton, magnetic field, gyromagnetic tensor, the spin operators \( S_x, S_y \) and \( S_z \), respectively.

The second term is the hyperfine interaction term arises from the interaction between the electron spin and nuclear spin. The hyperfine term is written in the form

\[ H_{\text{HF}} = S \cdot A \cdot I \] (3)

where \( S \) and \( I \) are the electron spin vector operator and nuclear spin operator, respectively, whereas \( A \) is hyperfine coupling tensor.

The third term is the crystal field term 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. It is the sum of spin angular momentum operators called Stevens’ operators or the equivalent operators \((O^0_2, O^4_4, O^6_6, O^0_4, O^0_6)\) with their coefficients \((B^0_2, B^0_4, B^4_4, B^0_6, B^4_6)\) as the crystal field parameters. The crystal field Hamiltonian is usually written in the spherical-tensor notation as the following relation

\[ H_{\text{CF}} = B^0_2 O^0_2 + B^0_4 O^4_4 + B^4_4 O^4_4 + B^0_6 O^0_6 + B^4_6 O^4_6 \] (4)

Therefore, the spin Hamiltonian can be written in the form

\[ H = \beta S \cdot g \cdot B + S \cdot A \cdot I + B^0_2 O^0_2 + B^0_4 O^4_4 + B^4_4 O^4_4 + B^0_6 O^0_6 + B^4_6 O^4_6 \] (5)

However, the hyperfine term is small compared with the Zeeman term so that it can be neglected. Then, the spin Hamiltonian in equation (5) becomes

\[ H = \beta S \cdot g \cdot B + B^0_2 O^0_2 + B^0_4 O^4_4 + B^4_4 O^4_4 + B^0_6 O^0_6 + B^4_6 O^4_6 \] (6)

The parameters in Eq. (6) were calculated from the resonance magnetic field positions in the ESR spectra and the obtained parameters are shown in Table 1. The principal spin Hamiltonian parameters \( B^k_4 \) shown in Table 1, were determined by measuring the magnetic field positions of the ESR spectra both the applied magnetic fields parallel and perpendicular to the c-axis. The constant \( g_{zz}, B^0_2, B^0_4 \) and \( B^4_6 \) could be accurately determined by perturbation theory when the magnetic field is parallel to the c-axis [5, 6]. The resonance absorption magnetic field positions at \( \theta = 0^\circ \) and \( 180^\circ \) are exactly the same for all two cases of zircon, before heated and after heat treatment in oxygen atmosphere, it reflects that the crystal field symmetry of the surroundings around Gd^{3+} or the point-symmetry at the Zr^{4+} site is D_{2d} [3, 5]
Table 1. Spin Hamiltonian parameters of Gd$^{3+}$ in zircon before heated and after heat treatment in oxygen atmosphere

| Parameters | Before heat treatment in oxygen atmosphere | After heat treatment zircon in oxygen atmosphere |
|------------|------------------------------------------|-----------------------------------------------|
| $g_{xx} = g_{yy}$ | 1.9915 | 1.9911 |
| $B_{0z}$ | 1.9919 | 1.9918 |
| $B_{0z}^2$ | 378.72 | 371.98 |
| $B_{0z}^4$ | 8.13 | 7.58 |
| $B_{0z}^6$ | 74.82 | 77.15 |
| $B_{0z}^8$ | 0.96 | 0.84 |
| $B_{0z}^{10}$ | 0.15 | 0.15 |

The obtain x-ray powder diffraction patterns of zircon, before heated and after heat treatment in the oxygen atmosphere are shown in Fig. 5.

![X-ray diffraction patterns](image)

Fig. 5. Powder x-ray diffraction (XRD) patterns of zircon (ZrSiO$_4$): before heat treatment, after heat treatment in oxygen atmosphere at 900°C for 6 hours.

Table 2. Crystallographic parameters obtained from the XRD patterns of untreated zircon and heat-treated zircon in the oxygen atmosphere

| Crystallographic parameter | Untreated zircon | Heat-treated zircon in oxygen atmosphere |
|----------------------------|------------------|------------------------------------------|
| Space group | $I4_1/amd$ | $I4_1/amd$ |
| Crystal structure | Tetragonal: $\alpha=\beta=\gamma=90^\circ$ | Tetragonal: $\alpha=\beta=\gamma=90^\circ$ |
| $a$ (Å) | 6.6017 | 6.6040 |
| $b$ (Å) | 6.6017 | 6.6040 |
| $c$ (Å) | 5.9778 | 5.9795 |
| $c/a$ | 0.9055 | 0.9054 |
| $V$ (Å$^3$) | 260.5257 | 260.7792 |
| Atom: Fractional atomic coordinates | | Fractional atomic coordinates |
| $Z$ | (0, 3/4, 1/8) | (0, 3/4, 1/8) |
| Si | (0, 3/4, 5/8) | (0, 3/4, 5/8) |
| O | (0, $y$, z); $y = 0.0665(13)$, $z = 0.2054(15)$ | (0, $y$, z); $y = 0.0563(66)$, $z = 0.2024(58)$ |
The crystalline phase of zircon is characterized more precisely by the Rietveld refinements of the obtained powder x-ray diffraction data using FULLPROF 2007 program with the least-squares fitting procedure. The backgrounds of all obtained patterns are quite smooth to be properly defined by the polynomial functions. The pattern profile is well refined with the pseudo-Voigt function. The good initial structural model for this refinement is taken from the previously reported zircon-structure compounds [7]. The refined crystallographic parameters of untreated zircon and heat-treated zircon in the oxygen atmosphere are also summarized in Table 2. The unit cell parameters on the Table 2 show that the relations between the lattice parameters \((a\) and \(c\)) , the \(c/a\) ratio defined as a tetragonality is almost constant. The change of parameter \(a\) is almost proportional to the change of parameter \(c\) in zircon lattice. The crystalline phase of zircon is unchanged within the range of experimental heat treatment. The crystalline phase is still the tetragonal phase.

The important structural data such as the interatomic distances and the bond angles of zircon structure before and after the heat treatment are calculated from XRD data analysis and are also summarized in Table 3.

### Table 3. Selected interatomic distances and bond angles of untreated zircon and heat-treated zircon in the oxygen atmosphere

| Parameter                  | Untreated zircon | Heat-treated zircon in oxygen atmosphere |
|----------------------------|------------------|-----------------------------------------|
| Interatomic distance       |                  |                                         |
| Zr-O(1) (Å)                | 2.317            | 2.338                                   |
| Zr-O(2) (Å)                | 2.144            | 2.078                                   |
| Si-O (Å)                   | 1.580            | 1.643                                   |
| Bond angles                |                  |                                         |
| O-Si-O(1) (degree)         | 114.32           | 113.24                                  |
| O-SO(2) (degree)           | 100.15           | 102.18                                  |

To consider the correlation between the results from the previous section of the ESR investigation and those from this section of the XRD analysis, it is necessary to recognize that, in the part of ESR analysis, the crystalline electric field (or the crystal-field potential) affecting on the \(\text{Gd}^{3+}\) replaced at \(\text{Zr}^{4+}\) site in zircon due to the surrounding ions (i.e., oxygen ions) becomes lower at heat treatment in oxygen atmosphere. This mentioned crystal-field effect can be evidently related to the changes in the zircon structure detected from XRD data.

### 4. Conclusions

Electron spin resonance spectroscopy is the one of the most sensitive, site-specific techniques for investigating the local environment of paramagnetic impurities (or centers) in crystalline materials. In the present case, the crystalline electric field splitting of the \(^{8}S_{7/2}\) ground state of \(\text{Gd}^{3+}\) is highly sensitive probe of the environment and experiment. As for the second degree crystal field parameter (\(B_2^0\)), it is much larger than the other crystal field parameters and slightly change after heat treatment. This result reveals that the gadolinium ion is in the presence of a large axial crystalline electric field generated from its surrounding oxygen ions within the zircon lattice. Then, the heat treatment has effect on the nearest neighboring \(\text{O}^{2-}\) ions of \(\text{Gd}^{3+}\) which replace the \(\text{Zr}^{4+}\) site.

The correlation between the results from ESR investigation and the XRD analysis, it is necessary to recognize that, in the part of ESR analysis, the crystalline electric field (or the crystal-field potential) affecting on the \(\text{Gd}^{3+}\) replaced at \(\text{Zr}^{4+}\) site in zircon due to the surrounding ions (i.e., oxygen ions) becomes lower at heat treatment in oxygen atmosphere. This mentioned crystal-field effect can be evidently related to the changes in the zircon structure detected from XRD data. These results reveal that the crystal field parameter becomes lower when the bond distances becomes longer.
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