# Alternative approaches used to assess structural changes of natural zircon caused by heat treatment

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## ARTICLE INFO

## ABSTRACT

It is known that large changes in the crystal structure of zircon ($ZrSiO_4$) can be assessed through the linewidth of the characteristic Raman mode ($\Delta v_3$) at 1008 cm$^{-1}$. However, the use of $\Delta v_3$ to assess small changes caused by heat treatment at temperatures below its decomposition temperature of ~1670 °C is difficult. The present work points out that the combination of X-ray diffraction (XRD) analyses, and photoluminescence (PL) and Raman (RS) measurements with different excitation wavelengths is an effective approach to solve the above problem. In this context, we have selected natural zircon containing some rare-earth (RE) impurities, and then studied the changes in its crystal structure caused by heat treatment at temperatures $T_{an}$=400–1600 °C. XRD analyses reveal that small modifications of the unit-cell parameters occur as $T_{an} > 600$ °C. Taking the intensity ratios of the $v_3$ mode to RE-related emissions ($Iv_3/I_{RE}$) or the PL intensity ratios between RE-related emissions into consideration, the similar results in good agreement with the XRD analyses are also found. We believe that the small structural changes are related to the migration and redistribution of defects and impurities, and re-crystallization of zircon. This could be further confirmed though the relation between paramagnetic and ferromagnetic signals when $T_{an}$ changes.

## 1. Introduction

Zirconium silicate occurs in nature as zircon with the chemical formula of $ZrSiO_4$, where Zr is partially substituted by Hf (1−4 wt%) and actinides of U and Th [1]. Depending on geographical location, a large variety of transition and rare-earth (RE) metal cations with very small amounts can also be present in zircon [2]. The existence of U and Th causes radioactive decay and various structure transformations (such as the loss of translational symmetry, generation of point defects, formation of metastable phases, and metamictization) [3–5]. Particularly, due to the structural resilience versus high radiation doses over significant time-scales, zircon has been suggested as a promising material for age dating of igneous rocks, and a long-term storage of nuclear wastes [3,4,6]. Apart from these behaviors, zircon has been proven to be a hard material, with hardness ranging from 6.5 to 7.5. With low-thermal expansion and conductivity, high resistance to thermal shock, good corrosion resistance, and highly chemical stability, it is also widely used in the ceramic, foundry, and refractory industries [2,7,8].

Previous studies pointed out that the crystal structure of natural $ZrSiO_4$ is very stable versus thermal processes up to about 1700 °C [1,9]. While large structural changes usually caused by high irradiation doses, geological processes, or applied high pressures can be assessed effectively through the linewidth of the characteristic Raman mode ($\Delta v_3$) at 1008 cm$^{-1}$ [5,10], the assessment of small structural changes induced by heat treatment at temperatures below zircon's decomposition temperature of ~1670 °C based on $\Delta v_3$ is impossible. The seeking of other suitable approaches is thus necessary to solve this issue. Additionally, it comes to our attention that the correlation between the crystal structure and the optical and magnetic properties versus heat treatment of zircon was not taken into account.

This work bases on sensitive probes of X-ray diffraction (XRD), photoluminescence (PL) and Raman spectroscopy, and vibrating sample magnetometer to solve the above problems. The XRD analyses indicate that small modifications of the unit-cell parameters occur as $T_{an} > 600$ °C. Taking into account for the intensity ratios of the $v_3$ mode to RE-related emissions ($Iv_3/I_{RE}$), or the PL intensity ratios between RE-related emissions, the results in good agreement with the XRD

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analyses are also found. We think that the small structural changes caused by heat treatment are due to the migration and redistribution of defects and impurities, and/or re-crystallization. This would be additionally confirmed though the relation between the paramagnetic (PM) and ferromagnetic (FM) behaviors.

## 2. Experimental details

A natural zircon fragment with uniform reddish-brown color collected from a mine in Central Highlands of Vietnam was used for this study. The as-received sample was then cut into small pieces. One part was polished its surface for analyzing chemical components based on electron micro-probe analyses (EMPA), using a JEOL JXA-8900RL microscope equipped with wavelength dispersive spectroscopy, and on a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS). Results of chemical-composition analysis revealed a fairly homogeneous distribution of elements in zircon, which is constituted of $ZrO_2$ (65.811 wt%), $SiO_2$ (32.342 wt%) and $HfO_2$ (1.08 wt%). Other elements such as Th (84.54 ppm) and U (100.9 ppm), Nd (0.64 ppm), Dy (33.78 ppm), Er (55.31 ppm), Tm (11.57 ppm), and several transition metals were also traced. Remaining zircon parts were used to anneal in air for 12 h at temperatures ($T_{an}$) in the range 400–1600 °C. After annealing, the crystal structure of final products was checked by an X-ray diffractometer (Rigaku, MiniFlex), working with a Cu-$K_\alpha$ radiation source ($\lambda$=1.5406 Å) and fixed scanning steps of 0.01°. Their PL and Raman scattering (RS) spectra were studied by using Acton-SpectraPro fluorescence (750-Triplet Grating Monochromator) and XPLORA-Plus Horiba micro-Raman spectrometers, which worked with excitation wavelengths ($\lambda_{exc.}$) of 355, 532, and 785 nm. Magnetization versus magnetic-field measurements were performed on a vibrating sample magnetometer (VSM, LakeShore 736). All measurements were carried out at room temperature.

## 3. Results and discussion

Concerning heat treatment, we found that natural color of zircon (reddish brown) is paled soon after annealing at 400 °C. Particularly, it becomes colorless as $T_{an}$=1600 °C. The crystal structure of these samples was then checked by an X-ray diffractometer. Fig. 1(a) shows an XRD pattern of the unheated sample in the angle range $20° \leq 2\theta \leq 70°$. The results of structural analyses based on the Rietveld technique (used the FullProf Suite program) reveal the best fit between the experimental and calculated patterns (with $\chi^2 \approx 4\%$), and this sample to be single phase in a tetragonal structure (the $I41/amd$ space group), with the lattice constants $a=b$=6.6045(3) Å and $c$=5.9783(3) Å, and the unit-cell volume $V$=260.769(9) Å³. Fitting the experimental data is also shown in Fig. 1(a). The coordinates of Zr, Si and O atoms, inter-atomic lengths and bond angles obtained from the refinement are listed in Table 1. For the structure of zircon, it consists of chains of [SiO₄] tetrahedra and [ZrO₈] polyhedra, Fig. 1(b). There are one Si-O bond length (×4) 1.624(1) Å, and two independent Zr-O bonds (×4) of lengths 2.116(4) Å and 2.270(2) Å. For [SiO₄] tetrahedra, there are two different bond angles with O-Si-O(1)=115.93(6)° and O-Si-O(2) =97.20(6)°. Small differences among refinement results are usually ascribed to minor metamictization existing in natural zircons and/or problems related to extinction [4]. Notably, an accurate identification of the Hf site in $ZrSiO_4$ based on Rietveld refinement for normal XRD patterns is impossible because of very mirror structural and electronic differences between Zr and Hf.

In Fig. 2, it shows the XRD patterns of the heated samples. The feature of the patterns is quite the same as that of the unheated sample, consisting of the sharp and strong-intensity peaks from tetragonal $ZrSiO_4$. Having performed the Rietveld refinement for these data (within $\chi^2$=4–6%), we determined the values of the unit-cell parameters $a$, $c$, and $V$, as graphed in Fig. 3. Their changes at temperatures $T_{an} > 600$ °C are very small (about 0.1–0.2%), which are ascribed to the
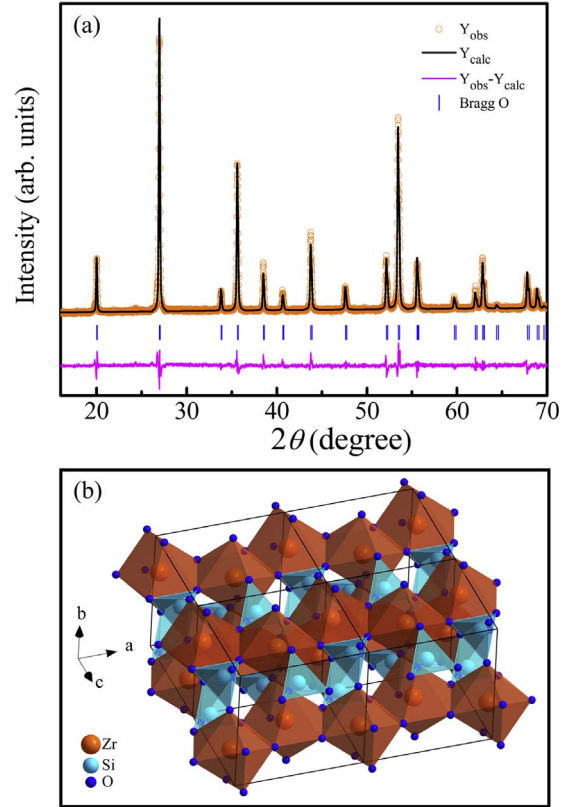


**Fig. 1.** (a) XRD pattern and Rietveld refinement (carried out for the $I41/amd$ structure) for the unheated sample, where $Y_{obs}$ and $Y_{calc}$ are the Bragg peak positions of the observed and calculated patterns, respectively, and the difference between $Y_{obs}$ and $Y_{calc}$ data ($Y_{obs}-Y_{calc}$) is shown at the bottom. (b) The crystal structure of $ZrSiO_4$ is formed from the chains of alternating edge-sharing [ZrO₈] polyhedra and [SiO₄] tetrahedra.

migration and redistribution of defects and impurities, and/or the re-crystallization of aperiodic/amorphous state (this state is generated from metamictization) when natural zircon is subjected to the annealing. The results indicate that the crystal structure of zircon is very stable, even at high temperatures up to 1600 °C. This is understandable because the dissociation of $ZrSiO_4$ usually takes place above 1670 °C [1,9].

In addition to the structural check based on XRD, we have studied the RS spectra of the samples. The feature of phonon-vibration modes can give more information about local structures of zircons. For this purpose, we recorded RS spectra at different positions on the samples. The data obtained from these positions were averaged to release the final data. As mentioned above that zircon belongs to the $I41/amd$ space group, its vibration spectrum thus consists of 36 modes, occurring with $\Gamma=2A_{1g}+4B_{1g}+5E_g+A_{2g}+B_{1u}+A_{1u}+2B_{2u}+4A_{2u}+5E_u$ [11]. Among these, the first four terms ($2A_{1g}+4B_{1g}+B_{2g}+5E_g$) characterize 12 Raman-active modes, and the $A_{2u}$ and $E_u$ modes are active in the infrared (i.e., acoustic and IR-activated modes) [1,4,5]. Its has

**Table 1**
The atomic coordinates and isotropic displacement parameters of $I41/amd$ tetragonal $ZrSiO_4$ (the unheated sample) at room temperature.

| Atom | Site | x | y | x |
|------|------|---|---|---|
| Zr | 4a | 0 | 3/4 | 1/8 |
| Si | 4b | 0 | 3/4 | 5/8 |
| O | 16h | 0 | 0.0656(2) | 0.1954(3) |
| Si-O [×4]*=1.624(1) Å | | O-Si-O(1)=115.93(6)° | | |
| Zr-O [×4]=2.116(4) Å | | O-Si-O(2)=97.20(6)° | | |
| Zr-O [×4]=2.270(2) Å | | | | |

* Square-bracketed numbers are bond multiplicities.