Raman spectroscopy of synthetic zircon: Effects of chemical composition

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Abstract Raman spectra of zircon show a distinctive pattern according to the amount of stored radiation damage. Nasdala et al. (2001) demonstrated that a linear relationship exists between the full width at half-maximum (FWHM) of the $\nu 3(\text{SiO}_4)$ band, observed at \(\sim 1000 \text{ cm}^{-1}\), and the alpha fluence calculated from the uranium content, thorium content and the zircon age. Their finding could lead to a new microspectroscopic method to determine zircon ages. This study examines the effect of chemical composition on Raman spectra by the analysis of synthetic zircons that were doped with elements using Li-Mo flux. Zircons were found to be able to incorporate high concentrations of group 3 elements (including lanthanides and actinides) while elements belonging to other groups were less incorporated. The FWHM of the group 3 doped zircon $\nu 3(\text{SiO}_4)$ band showed a linear relationship with concentration, clearly indicating that the FWHM is a function of chemical composition as well as of radiation damage. However, a very high concentration of group 3 elements is required to influence these Raman spectra (e.g., more than $\sim 5,000 \text{ ppm}$).

1 Introduction

Zircon is an important accessory mineral in Earth Sciences because of its high radionuclide concentration. To understand histories of terrestrial materials, zircons have been analyzed using various dating techniques such as U-Pb, Pb/Pb, fission-track, U-Th and U,Th-He methods. A geochronological method that still needs to be developed will
utilize alpha-damage (including alpha-recoil damage) of the zircon crystal through the
decay chain of U or Th (Gogan and Wagner, 2000). Spectroscopic methods such as
X-ray diffraction (e.g., Murakami et al., 1991) and infrared spectroscopy (Deliens et
al., 1977, Zhang et al., 2000a) are successful in qualitatively estimating the degree
of metamictization, which is caused by the accumulation of radiometric damage and
the resulting crystal disorder. Raman spectroscopy has also been used to estimate the
degree of metamictization (e.g., Pidgeon et al., 2007) and these authors’ methodology
showed potential for quantitative determinations (Zhang, et al., 2000ab, Nasdala et al.,
1995, 2001). Nasdala et al. (2001) found a linear relationship between the full width
at half-maximum (FWHM) of the ν3(SiO4) band, observed at ∼1000 cm⁻¹, and the
alpha fluence calculated from uranium and thorium concentrations as well as estimated
ages. Raman spectra, however, reflect the nearest environment of vibrating bonds and
thus incorporation of chemical impurities might affect Raman signals (Geisler et al.,
2005). Here, we examine effects of chemistry by investigating synthetic zircons that
were doped with various elements.

2 Samples and analyses

Zircons were synthesized using Li-Mo flux (Chase and Osmer, 1966). A mixture of
ZrO₂ (3 mol%), Li₂SiO₃ (3 mol%), Li₂MoO₄ (10 mol%), MoO₃ (83.2 mol%) and the
doping element (oxide, 0.8 mol%) was heated at 1250°C for 2.5 hours and afterwards
cooled at a rate of 10°C/h to synthesize zircon crystals. Doping elements used for each
synthesis experiment are listed in Table 1. Experimental details and resultant products
have been described in Shinno (1987). Synthetic zircon crystals >∼1 mm in diameter
were used for Raman spectroscopy and chemical analyses.

Raman spectra were measured with a FT-Raman SPECTRUM 2000R (PerkinElmer Inc.)
at the Wakasa Wan Energy Research Center, Fukui, Japan. Crystals were attached
to the target area with adhesive tape. The laser energy was 70 mW. The slit width
(an instrumental resolution) was 2.00 cm⁻¹ and data were acquired every 0.5 cm⁻¹.
Spectra between 950 and 1050 cm⁻¹ were used to calculate the FWHM and are shown
in Fig. 1. Resultant FWHM values are listed in Table 1.

Chemical compositions were measured by Laser Ablation - Inductively Coupled
Plasma - Mass Spectrometry (LA-ICP-MS) using an Agilent 7500 instrument equipped
with a Microlas Excimer laser ablation system at Kanazawa University, Japan (Ishida
et al. 2004; Morishita et al. 2005). After obtaining Raman spectra, crystals were
mounted in epoxy resin and ground to expose their internal surface. Doped elements
and hafnium were measured along with the ²⁹Si internal standard and calibrated with
the NIST610 external standard (Pearce et al., 1997, Longerich et al., 1996). Because
of expected chemical heterogeneity, three or four spots were analyzed for each grain
Figure 1: Raman spectra of synthetic zircons after doping with all studied elements.
Raman spectroscopy of synthetic zircon: Effects of chemical composition

<table>
<thead>
<tr>
<th>doped element</th>
<th>Group of element</th>
<th>atomic number</th>
<th>FWHM (cm(^{-1}))</th>
<th>concentration of doped element (ppm)</th>
<th>Hf concentration (ppm)</th>
<th>Sc concentration (ppm)</th>
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<tbody>
<tr>
<td>B</td>
<td>13</td>
<td>5</td>
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<td>8400±400</td>
<td>210±7</td>
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<tr>
<td>Sc</td>
<td>3</td>
<td>21</td>
<td>2.8</td>
<td>6360</td>
<td>8300</td>
<td>6360</td>
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<tr>
<td>Mn</td>
<td>7</td>
<td>25</td>
<td>2.8</td>
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<td>Co</td>
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<td>0.38±0.02</td>
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<td>320±1</td>
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<tr>
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<td>33</td>
<td>2.1</td>
<td>640</td>
<td>24.39</td>
<td>210</td>
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<tr>
<td>Sr</td>
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<td>0.07±0.01</td>
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</tbody>
</table>

FWHM: A full width at half-maximum (FWHM) of ν3(SiO\(_4\)) band (Nasdala et al., 2001). Error represents ±\(σ\).

Table 1: Results of Raman FWHM measurements and chemical analyses.

except for the few grains that had a small exposed area. The detailed measurement procedure is described elsewhere (Jarvis and Williams, 1993; Hasebe et al., 2004; 2009). The error range was estimated based on variations in spot analyses or estimated to be as large as \(\sim 5\%\) for grains that underwent a single spot analysis through repeated analyses of the NIST612 glass (Hasebe et al., 2009). Results are shown in Table 1.

### 3 Results

Concentrations of doped elements are plotted against their group numbers from the periodic table (Table 1 and Fig. 2). Even though the reagent was prepared to include the same amount (mol\%) of target element for each synthesizing experiment, Group 3 elements show high concentrations of up to \(\sim 3.5\,\text{wt}\%\) while other groups show low concentrations of up to 640 ppm (\(\mu\text{g/g}\)). Concentrations of hafnium and scandium are high for most samples probably because of incorporation from the original reagent (Table 1). Figure 3 shows no systematic relationship between the amount of hafnium and scandium and the doped elements. This may suggest that incorporated hafnium and scandium do not originate from doping elements reagents but from other reagents such as ZrO\(_2\). The resultant degree of incorporation of elements during synthesizing process is similar to the situation found in natural zircon, namely the HREE (Ho, Yb, and Lu in this study) is enriched relative to LREE (Ce and Nd). Therefore, substitution process
proposed for natural zircons (Hoskin and Shaltegger, 2003) should control the process and resultant chemical concentration. The elements with ionic radii matched by the Zr$^{4+}$ (smaller-radii HREE) are incorporated more than elements with the larger LREE. In natural environment where a variety of elements are available, substitution of multiple elements to retain charge balance is also an important process to explain the resultant chemistry, though it is not the case for synthetic zircons analyzed here.

When concentrations of doped elements are plotted against the FWHM (Fig. 4a), a linear relationship is found while the concentration of hafnium shows no significant relationship with the FWHM (Fig. 4b). This result indicates that the FWHM is a function of the chemical composition as well as of
radiation damage or the amorphous state (Zhang, et al., 2000ab, Nasdala et al., 1995, 2001). A very high concentration of group 3 elements influences Raman spectra (e.g., more than \( \sim 5,000 \text{ppm} \)). However, such high concentrations are rarely observed in natural zircons so that as far as we deal with natural zircons we still have a possibility to develop radiation damage dating using Raman spectroscopy.

![Diagram](image)

Figure 4: (a) Doped element concentrations that show a linear relationship with the FWHM. (b) The hafnium concentration plotted against the FWHM with no significant relationship. Error bars represent \( \pm \sigma \). Circles are for group 3 elements and triangles for others.
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References


