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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 $\nu 3(SiO_4)$ band, observed at $\sim$1000 cm^{-1}, and the alpha fluence calculated from the uranium content, thorium content and the zircon age. Their finding could lead to a new micro-spectroscopic 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 $\nu 3(SiO_4)$ 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$5,000ppm).

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 $\nu 3(SiO_4)$ band, observed at $\sim$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 ZrO_2 (3 mol%), Li_2SiO_3 (3 mol%), Li_2MoO_4 (10 mol%), MoO_3 (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 $>\sim$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 ^{29}Si 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

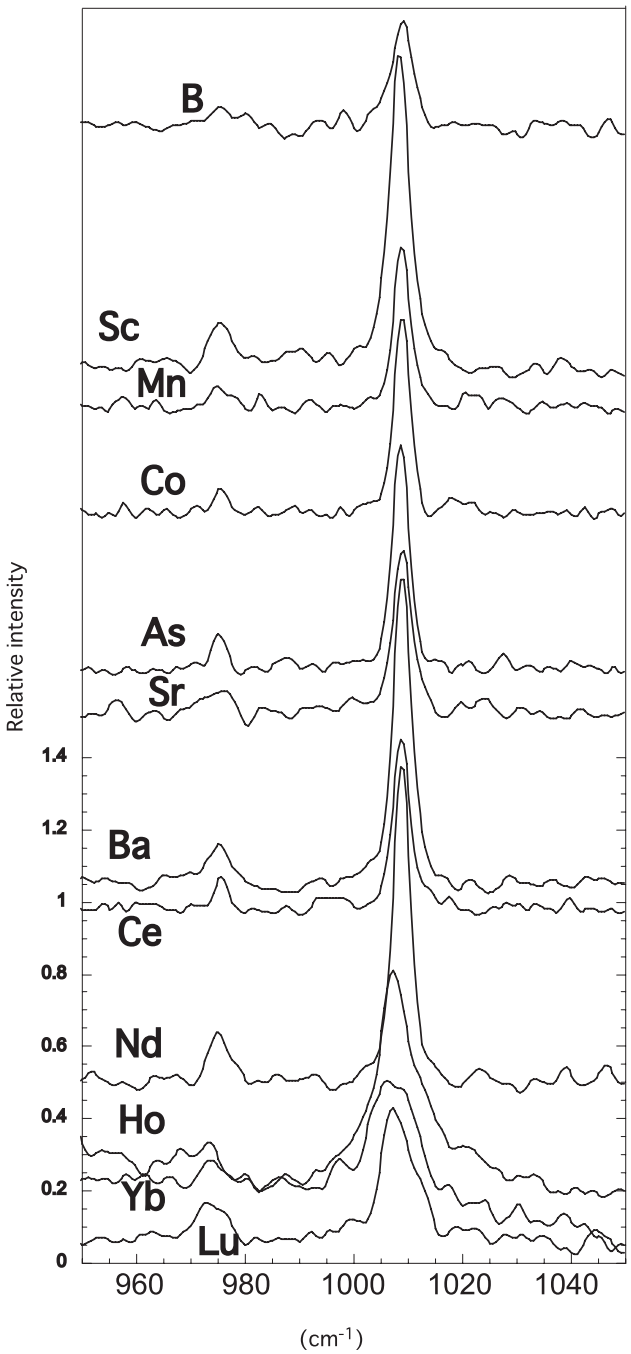

Figure 1: Raman spectra of synthetic zircons after doping with all studied elements.

doped element	Group of element	atomic number	FWHM (cm^{-1})	concentration of doped element (ppm)	Hf concentration (ppm)	Sc concentration (ppm)
B	13	5	4.1	407±95	8400±400	210±7
Sc	3	21	2.8	6360	8530	6360
Mn	7	25	2.8	0.70±0.12	6190±90	350±4
Co	9	27	2.8	0.38±0.02	5960±30	320±1
As	15	33	2.1	640	24.39	210
Sr	2	38	2.8	0.07±0.01	8180±100	320±4
Ba	2	56	2.8	0.01	6750	200
Ce	3	58	2.1	ND	5900±30	340±3
Nd	3	60	2.8	22±2.5	6880±350	320±5
Ho	3	67	6.4	9600	6820	190
Yb	3	70	9.6	33200±2200	6830±460	280±20
Lu	3	71	5.9	17000±2400	7.6±2.0	190±33
U	3	92	3.3	680±150	5700±190	300±20

FWHM: A full width at half-maximum (FWHM) of $\nu 3(SiO_4)$ band (Nasdala *et al.*, 2001). Error represents $\pm\sigma$.

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 wt% while other groups show low concentrations of up to 640 ppm (μg/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

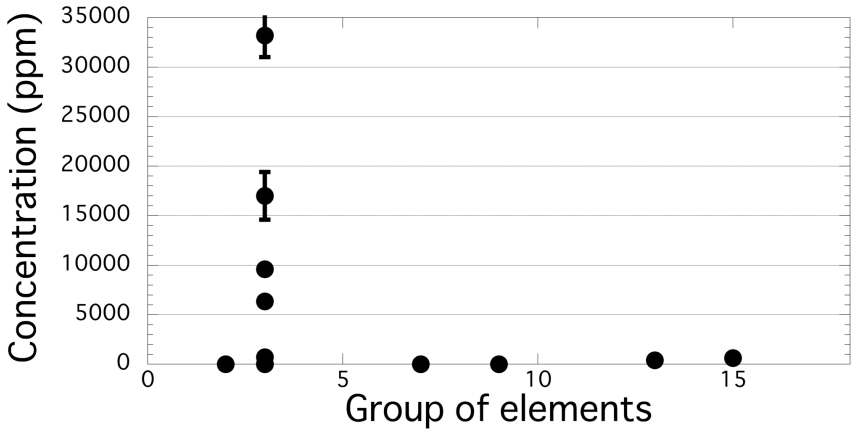

Figure 2: Concentrations of doped elements plotted against their periodic table group.

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

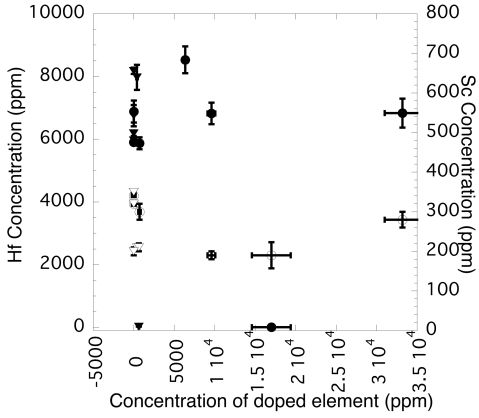

Figure 3: Hafnium and scandium concentrations plotted against concentrations of doped elements. Error bars represent $\pm\sigma$. Solid symbols represent hafnium and open symbols represent scandium data. Circles are for group 3 elements and triangles for others.

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 ∼5,000ppm). 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.

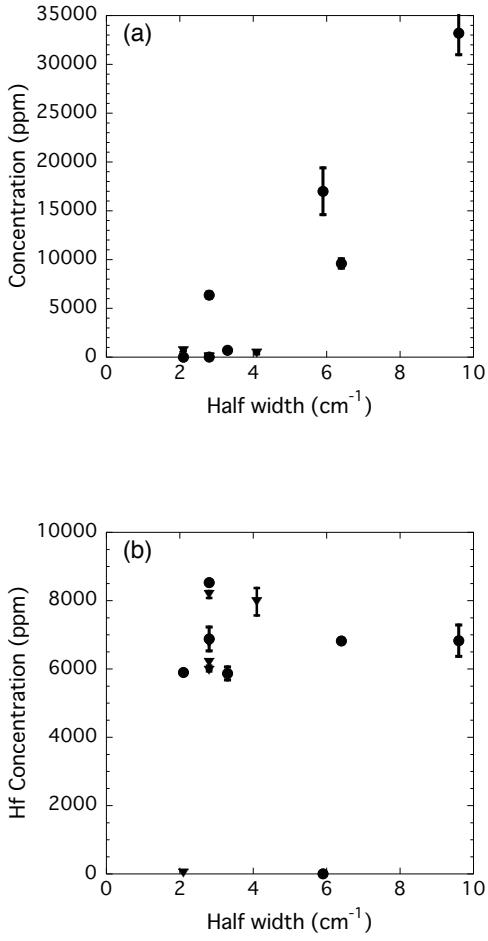

Figure 4: (a) Doped element concentrations that show a linear relationship with the FWHM. (b) The hafnium concentration plotted against the FWHM with no significant relationship. Error bars represent $\pm\sigma$. Circles are for group 3 elements and triangles for others.

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References

Chase, A.B., and Osmer, J.A. (1966) Growth and Preferential Doping of Zircon and Thorite. Journal of Electrochemical Society **113**, 198-199.

Deliens, M., Delhal, J., and Tarte, P. (1977) Metamictization and U-Pb systematics: a study by infrared absorption spectrometry of Precambrian zircons. Earth and Planetary Science Letters **33**, 331-344.

Geisler, T., Burakov, B.E., Zirlin, V., Nikolaeva, L., and P?ml, P. (2005) A Raman spectroscopic study of high-uranium zircon from the Chernobyl "lava". European Journal of Mineralogy **17**, 883-894.

Gogen, K., and Wagner, G.A. (2000) Alpha-recoil track dating of Quaternary volcanics. Chemical Geology Isotope Geoscience Section **166**, 127-137.

Hasebe, N., Barbarand, J., Jarvis, K., Carter, A., and Hurford, A.J. (2004) Apatite fission-track chronometry using laser ablation ICP-MS. Chem. Geol. **207**, 135-145.

Hasebe, N., Carter, A., Hurford, A.J., and Arai, S. (2009) The effect of chemical etching on LA-ICP-MS analysis in determining uranium concentration for fission-track chronometry. Geological Society Special Publication **324**, 37-46.

Hoskin, P.W., and Shaltegger, U. (2003) The composition of zircon and igneous and metamorphic petrogenesis, Reviews in Mineralogy and Geochemistry **53**, 27 - 62.

Ishida, Y., Morishita, T., Arai, S., and Shirasaka, M. (2004) Simultaneous in-situ multi-element analysis of minerals on thing section using LA-ICP-MS. The Science Report of Kanazawa University **48**, 31-42.

Jarvis, K.E., and Williams, J.G. (1993) Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): a rapid technique for the direct, quantitative determination of major, trace and rare-earth elements in geological samples. Chemical Geology **106**, 251-262.

Longerich, H.P., Jackson, S.E., and Gunther, D. (1996) Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. J Anal. Atom. Spectrom. **11**, 899-904.

Morishita, T., Ishida, Y., Arai, S., and Shirasaka, M. (2005) Determination of multiple trace element compositions in thin ($< 30\ \mu$m) layers of NIST SRM 614 and 616 using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Geostandards and Geoanalytical Research **29**, 107-122.

Murakami, T., Chakoumakos, B.C., Ewing, R.C., Lumpkin, G.R., and Weber, W.J. (1991) Alpha-decay event damage in zircon. Am. Mineral. **76**, 1510-1532.

Nasdala, L., Irmer, G., and Wolf, D. (1995) The degree of metamictization in zircon: a Raman spectroscopic study. European Journal of Mineralogy **7**, 471-418.

Nasdala, L., Wenzel, M., Vvra, G., Irmer, G., Wenzel, T., and Kober, B. (2001) Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage. Contributions to Mineralogy and Petrology **141**, 125-144.

Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., and Chenery, S.P. (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards Newsletter **21**, 115-144.

Pidgeon, R.T., Nemchin, A.A., van Bronswijk, W., Geisler, T., Meyer, C., Compston, W., and Williams, I.S. (2007) Complex history of a zircon aggregate from lunar breccia 73235. Geochimica et Cosmochimica Acta **71**, 1370-1381.

Shinno, I. (1987) Color and photo-luminescence of rare earth element-doped zircon. Mineralogical Journal **13**, 239-253.

Zhang, M., Salje, E.K.H., Ewing, R.C., Farnan, I., Rios, S., Schlüter, J., and Leggo, P.J. (2000a) Alpha-decay damage and recrystallization in zircon: evidence for an intermediate state from infrared spectroscopy. Journal of Physics: Condensed Matter **12**, 5189-5199.

Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark, A.M., and Leroux, H. (2000b) Metamictization of zircon: Raman spectroscopic study. Journal of Physics: Condensed Matter **12**, 1915-1925.