

Interpretation of Raman spectra of the zircon–hafnon solid solution

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Abstract: Zircon (ZrSiO_4), hafnon (HfSiO_4) and five intermediate compositions were synthesized from a Pb silicate melt. The resulting crystals were 20–300 μm in size and displayed sector and growth zoning. Raman spectra were acquired at locations in the sample for which preceding electron microprobe (EMP) analyses revealed sufficient compositional homogeneity. The dataset documents shifts of Raman bands with changing composition. In this study, bands that have previously not been reported were found for the intermediate compositions and for pure hafnon, in particular at wavenumbers less than 200 cm^{-1} . For these external modes, the dataset provides new insight into the compositional dependence of their frequencies. Density-functional theory calculations support the observations and are used for a detailed interpretation of the spectra. The pitfalls of the EMP analysis along the zircon–hafnon join are highlighted.

Key-words: zircon, hafnon, solid solution, Raman spectroscopy, synthesis, density-functional theory, hafnium analysis.

Introduction

Zircon is an accessory mineral occurring in a variety of rock types. Its ability to incorporate a large number of minor and trace elements and its durability in most geological processes are further reasons why zircon is one of the most frequently studied minerals in geosciences, in particular to characterize the conditions and age of rock formation.

Zircon (ZrSiO_4) is a tetragonal nesosilicate crystallizing in the $I 4_1/a m d$ space group. It is composed of chains of ZrO_8 triangular dodecahedra that are interconnected by SiO_4 tetrahedra (Speer, 1982). Low field strength as well as high field strength trace elements may substitute on both polyhedral sites of the crystal structure (Finch & Hanchar, 2003).

Raman spectra of zircon have been the subject of intense research since the 60s of the last century (*e.g.* Griffith, 1969; Dawson *et al.*, 1971; Nicola & Rutt, 1974; Syme *et al.*, 1977; Schmidt *et al.*, 2013). Dawson *et al.* (1971) predicted 12 Raman active modes and their symmetries through group-theory and symmetry analysis. Seven of them are internal modes caused by vibrations within the SiO_4 tetrahedron: one ν_1 (symmetric stretching, A_{1g}), two ν_2 (symmetric bending, A_{1g} and B_{2g}), two ν_3 (antisymmetric stretching, B_{1g} and E_g), and two ν_4 (antisymmetric bending,

B_{1g} and E_g). In addition, there are five external or lattice modes caused by vibrations between Zr^{4+} and the SiO_4 tetrahedron: one rotational mode of the SiO_4 tetrahedron (E_g) and four translational modes ($2 B_{1g} + 2 E_g$).

Zircon forms a complete solid solution with hafnon (HfSiO_4 , Hfn), which crystallizes in the same structure as zircon (Speer & Cooper, 1982). As the cation Zr^{4+} (0.84 Å) is a little larger than Hf^{4+} (0.83 Å, 8-fold coordination, Shannon, 1976), the lattice parameters a and c are decreasing from zircon to hafnon (Ramakrishnan *et al.*, 1969). Wavenumbers and line width of Raman bands of zircon–hafnon solid solutions change with composition due to changes in bond angles and lengths as well as the change of the average mass of the cation at the dodecahedral position. Because of shortening of the Si–O bonds (1.63 in zircon vs. 1.62 Å in hafnon, Finger, 1974; Speer & Cooper, 1982), the frequencies of the SiO_4 -internal modes increase with increasing Hf content. Despite the amount of research already done on this topic, the assignment of most bands to individual modes is still a matter of discussion. Only for the three internal bands at 438, 974 and 1008 cm^{-1} there is general agreement on which modes they are generated from (Nasdala *et al.*, 2003). The assignment of a band to a mode may be supported by observation of changes in the Raman spectra with

isostructural substitution of an atom by one of the same charge but different atomic mass and ionic radius, *e.g.* Si^{4+} by Ge^{4+} or Zr^{4+} by Hf^{4+} (Nasdala *et al.*, 2004). For the zircon structure, Hoskin & Rodgers (1996) conducted such a Raman spectroscopic study on the zircon–hafnion solid solution. Another powerful approach is the mode assignment based on predictions from *ab initio* simulations (*e.g.* Jahn & Kowalski, 2014), which for crystals are usually performed in the framework of density-functional theory (*e.g.* Lazzeri & Mauri, 2003; Veithen *et al.*, 2005). Here, we combine Raman spectroscopy and *ab initio* simulations to resolve the remaining questions about band assignment for the end-members and to re-investigate the changes with composition in the Raman spectra of the zircon–hafnion solid solution.

In its type localities, pegmatites in the Zambézia Province, Mozambique, hafnion can have near end-member composition with an X_{Hafnion} of 0.972 (Correia Neves *et al.*, 1974), but hafnion is generally very rare in nature and samples are difficult to acquire. Furthermore, the solid-solution series is not well covered by natural samples of suitable quality. This is not only because nearly all natural samples are close to the ZrSiO_4 end-member but also because they display variable metamictization, which has a large effect on wavenumbers and line widths of the Raman bands (*e.g.*, Nasdala *et al.*, 2003). In this work, we therefore synthesized zircon, hafnion and five intermediate compositions. The aim was to grow sufficiently large and homogeneous crystals for Raman spectroscopy. The homogeneity and composition was examined by electron-microprobe (EMP) analysis to be able to correlate composition and spectral parameters. Simulations were performed for zircon, hafnion, and one intermediate composition. With these new results, we generally confirm the earlier work by Hoskin & Rodgers (1996) but provide a more detailed view on the dependence of the Raman spectra on the Hf-content of zircon.

Experimental and analytical methods

Synthesis

Zircon, hafnion and five intermediate compositions were synthesized using a method proposed by Watson *et al.* (1997). The crystals were grown from a Pb silicate melt at ambient pressure. Figure 1A shows the design of the capsule used in the experiments. Powders of PbO (99.999 % purity) and SiO_2 (99.99 % purity) with a mass ratio of 7:3 were mixed in a mortar and blended with about 8 wt% ZrO_2 (99.9 % purity) or the molar equivalent of HfO_2 (99.95 % purity) or the ZrO_2 – HfO_2 intermediate composition. Table 1 shows the mass proportions that were used in the experiments. Platinum capsules with a diameter of 6.4 mm were loaded with 300 mg of the mixtures. The welded capsules were heated and annealed following the time–temperature path shown in Fig. 1B. After keeping the capsules for 1 hour at 1430°C, they were cooled at a rate of 1°C/h to 1330°C and then quenched in water.

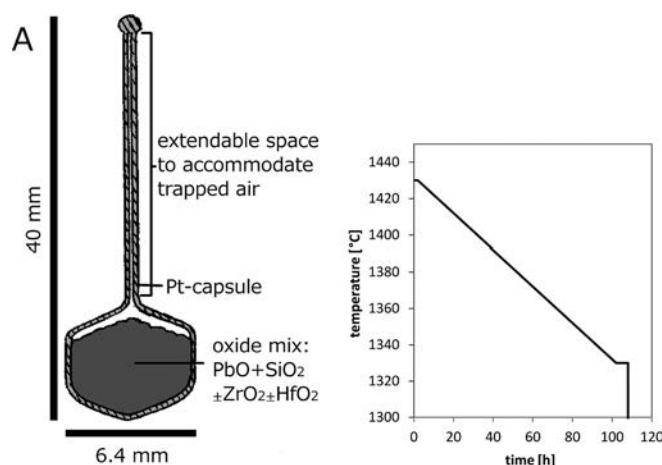


Fig. 1. Experimental procedure for the synthesis of zircon, hafnion, and five intermediate compositions. (a) Schematic sketch of the capsules used for the synthesis. (b) Temperature–time path of the syntheses.

Table 1. Weight proportions (and total mass, m_{tot}) of oxides used for the synthesis of the zircon–hafnion series.

Sample	1	2	3	4	5	6	7
$n_{\text{Zr}}: n_{\text{Hf}}$	1: 0	5: 1	2: 1	1: 1	1: 2	1: 5	0: 1
PbO wt%	64.4	63.9	63.3	63.1	62.7	61.8	58.2
SiO_2 wt%	27.5	27.4	27.3	26.6	26.3	26.3	25.5
ZrO_2 wt%	8.1	6.5	5.1	3.8	2.6	1.2	—
HfO_2 wt%	—	2.2	4.6	6.5	8.5	10.7	16.3
m_{tot} [mg]	307.6	309.9	312.9	317.5	321.8	322.1	651.6

Sample preparation

The zircon or hafnion crystals were separated from the Pb-silicate glass by dissolving the latter in 40 % hydrofluoric acid and filtering. The filter cake was cooked in 1 M hydrochloric acid leaving only zircon or hafnion crystals in the filter. The crystals were mounted in araldite epoxy and polished to $\frac{1}{4}$ μm . The samples were coated with carbon for investigation with the electron microprobe. For Raman spectroscopy, the carbon coating was removed by polishing.

Electron microprobe

The EMP of the GFZ Potsdam (JEOL HYPERPROBE JXA-8500F) was used for examination of crystal shape and size, chemical homogeneity, zoning, inclusions, and for detailed chemical analysis. Zircon was used as standard for Zr and Si, galena as standard for Pb and hafnium oxide as standard for Hf (standardization A). A second standardization using hafnion as a standard of Hf and Si, galena as standard for Pb and zircon as standard for Zr was used to improve the analytical results (standardization B).

The EMP was used in back-scattered electron (BSE) imaging mode to check for zoning and inclusions.

Quantitative chemical analyses were performed by wavelength-dispersive X-ray spectroscopy (WDX) with a focused beam at 15 kV accelerating potential, a sample current of 50 nA and a beam diameter of 40 to 50 nm. Emitted $K\alpha$ X-rays of Si and $L\alpha$ X-rays of Zr were collected using TAP (thallium acid phthalate) crystals and 30 s peak measurement time. The $L\alpha$ X-rays of Hf were collected using a LIF (lithium fluoride) crystal and $K\alpha$ X-rays of Pb using a PET (pentaerythritol) crystal with 40 s peak measurement time.

An analytical problem occurred for the matrix correction and standardization of the WDX measurements, which is likely caused by the large density difference between zircon ($\rho = 4.65 \text{ g cm}^{-3}$) and hafnon ($\rho = 6.97 \text{ g cm}^{-3}$). The applied ZAF matrix correction corrects the fluorescence intensity for the effect of atomic number Z , absorption A , and (secondary) fluorescence F . In theory, the density has to be known for a full matrix correction of the measured fluorescence intensity. In practice, the standardization procedure yields reliable results if standard and sample have similar densities. In the ZAF procedure, there are several positions where density has a substantial influence. There is an influence on the Z -correction, but the impact on the final result should be negligible, because the two components of the Z correction – stopping power and backscatter correction – compensate for each other (Reed, 1996). The A -correction depends on density and the mass absorption, which itself is dependent on the atomic mass, the absorption cross-section, and the mass fraction of the elements in a given compound. While the absorption cross sections are well known, the ZAF matrix correction does not take into account the real densities of standard and unknown sample.

With standardization A (HfO_2 as reference for Hf and ZrSiO_4 for Zr and Si), the Hf concentrations were underestimated, while the Si concentrations were overestimated with increasing Hf concentrations. With standardization B (HfSiO_4 as reference for Hf and Si), the Zr concentrations were overestimated whereas the Si concentrations were underestimated with decreasing Hf concentrations. Microprobe measurements of Correia Neves *et al.* (1974) of two natural hafnon crystals display similar apparent non-stoichiometry. In order to test the influence of the zircon composition on the absorption of the fluorescence yield of the elements analyzed here, we calculated the transmission of the $K\alpha$ X-rays of Si and the $L\alpha$ X-rays of Zr and Hf along the zircon–hafnon solid solution for a sample thickness of 1 μm . The densities used were calculated by linear combination of the densities of zircon and hafnon given above. The calculations were done on basis of the DABAX database using the program XOP2.3 (Rio & Dejus, 2004) and the results are shown in Fig. 2. The transmission of the $L\alpha$ X-rays of Hf changes only little with composition, but the transmissions of $L\alpha$ X-rays of Zr and $K\alpha$ X-rays of Si decrease drastically from zircon to hafnon.

The best solution for this problem would be to change the density used by the matrix correction procedure and

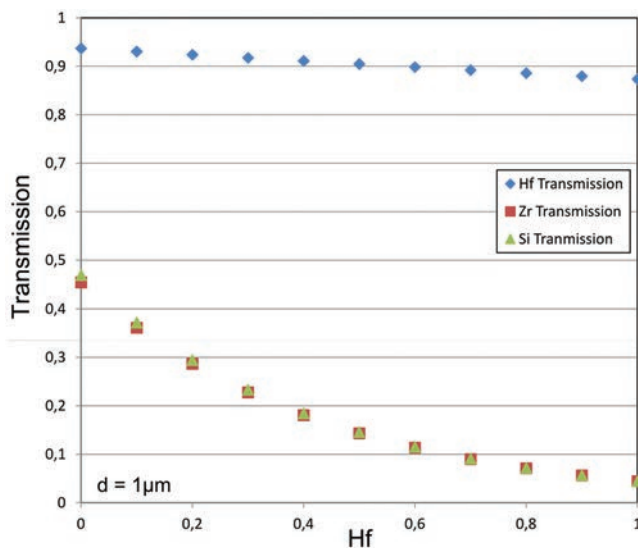


Fig. 2. Calculated transmission for Hf and Zr $L\alpha$ X-ray emission and for Si $K\alpha$ X-ray emission as a function of Hf content modeled for a zircon–hafnon solid solution. The data were calculated on the basis of the DABAX database using the program XOP2.3 (Rio & Dejus, 2004) for a thickness d of 1 μm , which is in the order of the approximate excitation volume for the EMPA. (online version in colour)

adjust it to the real densities of specimen and standard. Another approach would be the use of several standards along the zircon–hafnon solid solution, so that the density effect would cancel out. Because both approaches could not be used, we corrected the data of standardisation B. We assumed the Hf concentrations to be correct (due to the negligible effect on fluorescence absorption) and the Si concentration to be stoichiometric (one Si per four O). The difference of stoichiometric to measured Si concentration was subtracted from the Zr concentration. This procedure resulted in a stoichiometric composition of the samples.

Raman spectroscopy

All samples were analyzed with a HORIBA Jobin Yvon LabRAM HR800 VIS at the GFZ Potsdam. The Raman spectrometer has a focal length of 800 mm and is equipped with a CCD detector (2048×512 pixel) and an Olympus BXFM microscope with motorized XYZ-stage. Measurements were done with an excitation wavelength of 532 nm provided by a Laser Quantum Torus 532 DPSS laser, a grating of 1800 lines/mm, and using $50\times$ objectives. The spectra were recorded in two wavenumber segments, $149\text{--}681 \text{ cm}^{-1}$ (samples 1 and 2) or $128\text{--}662 \text{ cm}^{-1}$ (samples 3–7) and $666\text{--}1164 \text{ cm}^{-1}$. All samples were measured at 21°C . The recorded wavenumbers of the Raman spectra were calibrated by simultaneous acquisition of Ne atomic emission lines from a neon lamp. Because Raman spectroscopy was done

after the EMP measurements, it was possible to record Raman spectra of single crystals of sufficient size and homogeneity at positions of known composition. This permitted direct correlation of crystal composition and Raman spectra. All measurements were done at a second crystal orientation rotated by 90° from the first one to ensure sufficient signal from Raman bands with pronounced orientation dependence of their intensity. In summary, eight spectra were recorded at each spot, *i.e.* in two different orientations with two wavenumber segments, each with and without simultaneous acquisition of Ne atomic emission lines. The spectra without Ne lines were used in the figures and used to distinguish low intensity Ne emission lines from Raman bands. The accuracy in the reported wavenumber is ± 0.1 to $\pm 0.2 \text{ cm}^{-1}$ for peak positions that can be fitted with a standard error of less than 0.1 cm^{-1} . The spectral resolution is about 1 cm^{-1} as determined from the full width at half maximum of the recorded neon lines.

The spectra were analyzed with the program PeakFit v4.11 by SYSTAT Software Inc. A linear function was used for background correction. The neon emission lines were fitted with a symmetric Gauss-Lorentz function, and the Raman bands from the zircon and hafnion samples were fitted using the asymmetric Pearson-VII model. Note that the asymmetric peak function does not imply that the Raman bands had an asymmetric shape. It was only selected because of the slightly better fits compared to a symmetric function, but the difference in the obtained wavenumbers was normally less than 0.1 cm^{-1} , *i.e.* within experimental error.

Ab initio calculation of Raman spectra

Theoretical Raman spectra were computed in the framework of density-functional perturbation theory (DFPT) using the ABINIT software package (Gonze *et al.*, 2009). For the electronic structure calculations, the Kohn-Sham orbitals were expanded in a planewave basis set up to a cutoff energy of 1900 eV. Calculations were performed in the local density approximation (LDA) of the exchange-correlation functional and Troullier-Martins-type pseudopotentials were employed. The reciprocal space was sampled by using a $4 \times 4 \times 4$ Monkhorst-Pack grid (Monkhorst & Pack, 1976) and calculations were restricted to the center of the Brillouin zone. The primitive cell of the zircon and hafnion crystal structure contains 12 atoms (2 Zr/Hf, 2 Si and 8 O).

In a first step, the atomic positions and cell parameters were optimized to minimize the total energy of both zircon and hafnion crystals at zero pressure and temperature (which resembles ambient conditions). The resulting lattice parameters are $a = 6.518 \text{ Å}$, $c = 5.860 \text{ Å}$ for zircon and $a = 6.494 \text{ Å}$, $c = 5.860 \text{ Å}$ for hafnion. These values are up to 2 % smaller than corresponding experimental data, *cf.* $a = 6.607 \text{ Å}$, $c = 5.982 \text{ Å}$ for zircon (Robinson *et al.*, 1971) and $a = 6.573 \text{ Å}$, $c = 5.963 \text{ Å}$ for hafnion (Speer & Cooper, 1982). The underestimation of the cell lengths is typical of LDA calculations. In a second set of

calculations, the unit-cell volumes of the two end-member compositions were fixed to the experimental values during the optimization of the structural parameters. The DFT-optimized lattice parameters for these conditions are $a = 6.649$, $c = 5.928 \text{ Å}$ for zircon and $a = 6.597$, $c = 5.918 \text{ Å}$ for hafnion.

The *ab initio* calculation of spectra for intermediate compositions is computationally quite challenging, as it involves simulations of large super-cells in order to simulate realistic compositions. Here, we restricted our investigations of compositional effects on the calculated spectra replacing one of the two Zr atoms in the primitive cell by Hf. This results in an ordered structure that has a lower symmetry, *i.e.* $I-4m2$ instead of $I4_1/a m d$. The spectrum of such a hypothetical crystal allows evaluation if special modes appear that might refer to *e.g.* direct Hf–Zr neighbor interactions. Structure optimization of this intermediate structure at zero pressure leads to lattice constants $a = 6.506 \text{ Å}$ and $c = 5.860 \text{ Å}$.

Starting from the optimized structures, phonon frequencies were derived from the dynamical matrix that was computed in the harmonic approximation. The Raman tensors were computed analytically as the third-order derivative of the energy with respect to the electric field and to atomic displacements (Veithen *et al.*, 2005).

Results

Crystal morphology and chemical composition

The synthetic single crystals are generally euhedral and range in size from 20 to 300 μm . The zircon and hafnion end-member syntheses display only Pb-silicate glass inclusions. These inclusions are also observed in crystals of intermediate compositions (Fig. 3) which may

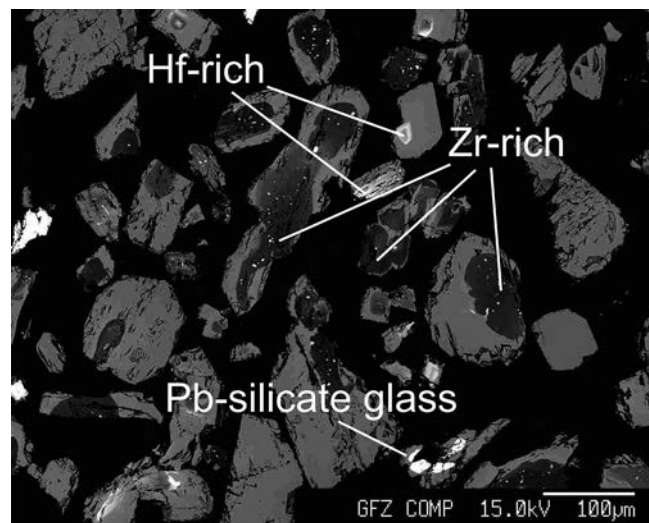


Fig. 3. Backscattered-electron (BSE) image of typical crystals of the intermediate compositions in sample 2. The brighter areas are rich in Hf, the dark areas are Zr-rich and the brightest areas are Pb-silicate glass inclusions.

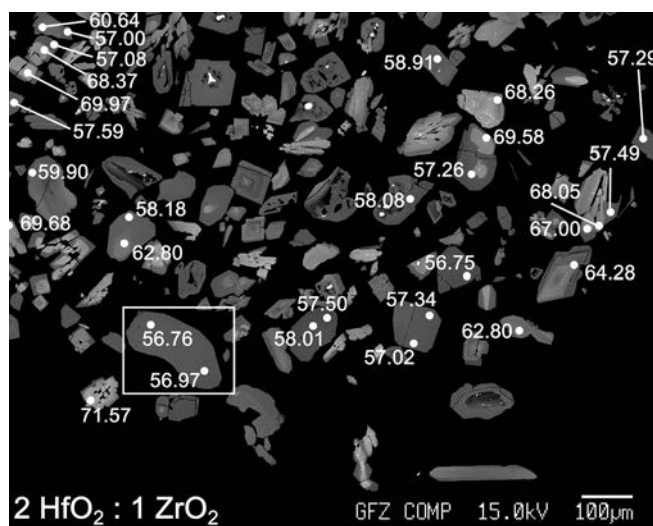


Fig. 4. BSE image of sample 5 with a $\text{HfO}_2\text{:ZrO}_2$ ratio of 2:1 in the oxide mix. The annotations indicate the HfO_2 content in wt%. The crystal highlighted by the frame is one example for a sufficiently homogeneous area to be used for Raman analysis.

additionally exhibit sector or growth zoning in the Zr- and Hf-content (Fig. 4). Interestingly, growth-zoned crystals with Hf-rich rim as well as with Hf-rich core can be found in the same sample (Fig. 4), so that no clear growth sequence in terms of composition is deducible.

The results of the quantitative WDX analysis are given in the Supplementary Material (linked to this article on the GSW website of the journal and freely available at <http://eurjmin.geoscienceworld.org/>), reporting both the original values of standardization B as well as the corrected values. The differences in composition within one sample of intermediate composition are striking. The measured HfO_2 -content in sample 2 ranges from 4.45 to 44.61 wt%, in sample 3 from 1.94 to 71.59 wt%, in sample 4 from 46.66 to 72.17 wt%, in sample 5 from 56.75 to 71.57 wt%, and in sample 6 from 53.05 to 75.67 wt%. Still, there are crystals in each sample that are homogeneous in BSE-images and are thus suitable for Raman spectroscopic investigations.

The temperature (T)–time (t) path during synthesis is likely the reason for the inhomogeneity observed. The path used here for all seven compositions followed that of the synthesis of zircon by Watson *et al.* (1997). However, that T – t -path would have to be adjusted because the liquidus temperature changes with the Zr/Hf ratio of the solid solution. Ideally, the crystallization temperature should be about 50 K below the liquidus temperature in order to grow large homogeneous crystals. This requires knowledge of liquidus temperature and composition of the coexisting phases for the whole solid-solution series. However, a full evaluation of the phase diagram of the solid-solution series was beyond the scope and the time frame of this study.

Raman spectroscopy

Selected Raman spectra of crystals with different compositions of the zircon–hafnon solid solution are shown in Figs 5 and 6 for the wavenumber range from 875 to 1075 cm^{-1} and in Figs 7 and 8 in the range from about 130 to about 670 cm^{-1} . Most Raman bands were observed along the whole solid-solution series. The evolution of Raman wavenumbers as function of composition is shown in Fig. 9 and compared to the data of Hoskin & Rodgers (1996). The wavenumbers are compiled in Table 2.

Eleven bands were observed in the spectra of pure zircon. Following the band assignments by Hoskin & Rodgers (1996) and Nasdala *et al.* (2003), these include the more intense bands at 1008 cm^{-1} ($\nu_3(\text{SiO}_4)$, B_{1g}), 974 cm^{-1} ($\nu_1(\text{SiO}_4)$, A_{1g}), 438 cm^{-1} ($\nu_2(\text{SiO}_4)$, A_{1g}), and 356 cm^{-1} (E_g), the less intense bands at 224 cm^{-1} (E_g), 213 cm^{-1} (B_{1g}), and 201 cm^{-1} (E_g), as well as the weak bands at 640 cm^{-1} ($\nu_4(\text{SiO}_4)$, B_{1g}), 547 cm^{-1} ($\nu_4(\text{SiO}_4)$, E_g), 393 cm^{-1} (B_{1g}), and 265 cm^{-1} ($\nu_2(\text{SiO}_4)$, B_{2g}). The band at 925 cm^{-1} ($\nu_3(\text{SiO}_4)$, E_g) could not be observed for the zircon end-member but appears for the compositions $\text{Hfn}_{0.19}$ to $\text{Hfn}_{0.20}$ and $\text{Hfn}_{0.51}$ to $\text{Hfn}_{0.99}$ (band assignment after Syme *et al.*, 1977).

The bands that are generally assigned to internal modes, *i.e.* at 1008 cm^{-1} , 974 cm^{-1} , 925 cm^{-1} , 640 cm^{-1} , 438 cm^{-1} , and 265 cm^{-1} for the zircon end-member, clearly shift to higher wavenumbers with increasing Hf content. Only the band at 547 cm^{-1} remains nearly constant over the whole range of the zircon–hafnon solid solution (Fig. 9). The most intense band shifts from zircon to hafnon from 1008 cm^{-1} to 1021 cm^{-1} by $0.134\text{ cm}^{-1}/\text{mol}\%$ Hfn. The width of this band is lowest for the zircon end-member with 2.5 cm^{-1} , shows higher values up to 3.3 cm^{-1} for solid solutions, and is about 3.1 cm^{-1} for the hafnon end-member (Table 2). Unlike the behavior of the band positions, the change in the line width with composition is nonlinear, with the highest values reached close to $\text{Hfn}_{0.5}$. The ν_1 (A_{1g}) band shifts from zircon to hafnon from 974 cm^{-1} to 985 cm^{-1} by $0.108\text{ cm}^{-1}/\text{mol}\%$ Hfn. The weaker ν_3 (E_g) band shifts from 926 cm^{-1} at $\text{Hfn}_{0.19}$ to 935 cm^{-1} at the hafnon end-member by $0.118\text{ cm}^{-1}/\text{mol}\%$ Hfn. The ν_4 (B_{1g}) band shifts from zircon to hafnon from 640 cm^{-1} to 647 cm^{-1} by $0.078\text{ cm}^{-1}/\text{mol}\%$ Hfn. A doublet is observed at $\text{Hfn}_{0.41}$ and higher Hf-contents, where the second peak has an almost constant wavenumber of 638 to 639 cm^{-1} , called ν_{638} . The ν_2 (A_{1g}) band shifts from zircon to hafnon from 438 cm^{-1} to 448 cm^{-1} by $0.105\text{ cm}^{-1}/\text{mol}\%$ Hfn, while the ν_2 (B_{2g}) band shifts from zircon to hafnon from 265 cm^{-1} to 268 cm^{-1} by $0.031\text{ cm}^{-1}/\text{mol}\%$ Hfn.

All other bands related to external modes show decreasing wavenumbers with increasing Hf contents. The $E_g(\text{I})$ band decreases from 356 cm^{-1} for end-member zircon to 350 cm^{-1} for end-member hafnon by $0.065\text{ cm}^{-1}/\text{mol}\%$ Hfn. The bands $E_g(\text{III})$, $B_{1g}(\text{II})$, and $E_g(\text{II})$ are located at 224 cm^{-1} , 213 cm^{-1} , and 201 cm^{-1} for the zircon end-member. The positions of these bands are difficult to determine in the spectra of the

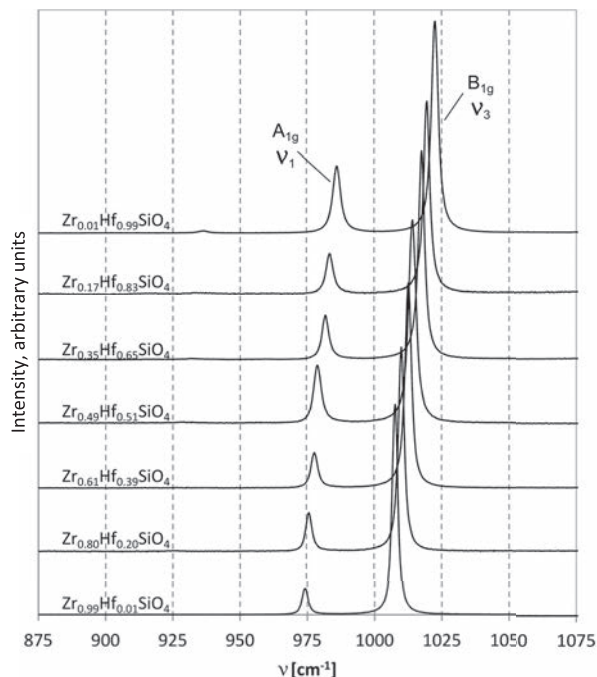


Fig. 5. Raman spectra in the wavenumber range 875–1075 cm^{-1} of the measured points 1 (sample 1), 66 (sample 2), 17 (sample 3), 106 (sample 4), 167 (sample 5), 141 (sample 6), and 113 (sample 7).

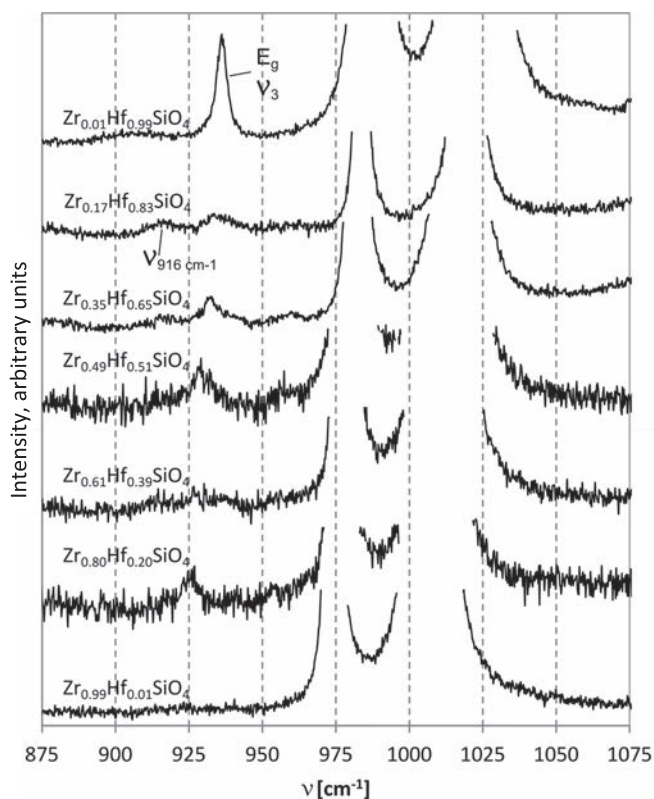


Fig. 6. Enlarged view of the Raman spectra in Fig. 5 displaying the low-intensity bands.

intermediate compositions. In the spectra of $\text{Hf}_{0.19}$ and $\text{Hf}_{0.20}$, all three bands are clearly distinguishable, although they are slightly overlapping and their

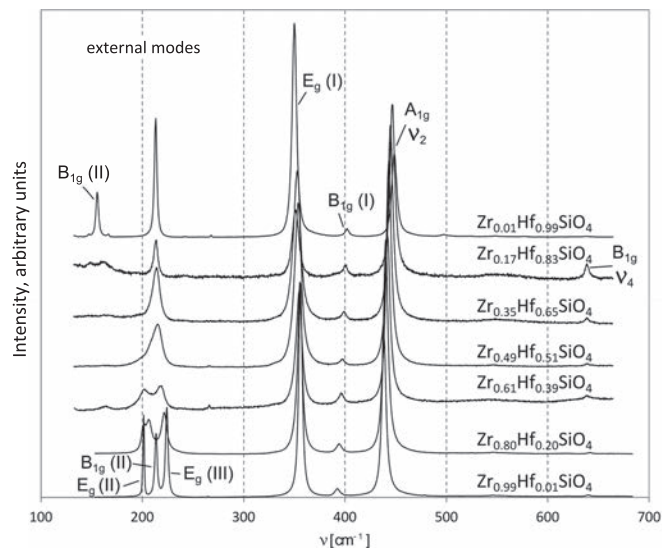


Fig. 7. Raman spectra in the wavenumber range 128–681 cm^{-1} of the measured points 1 (sample 1), 66 (sample 2), 17 (sample 3), 106 (sample 4), 167 (sample 5), 141 (sample 6), and 113 (sample 7).

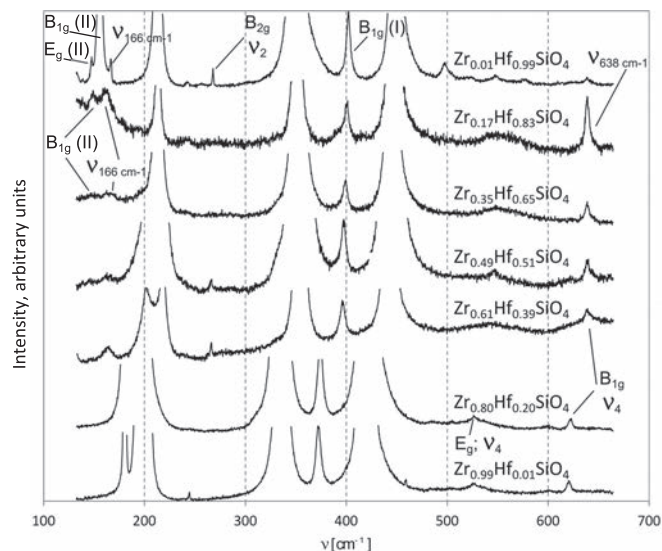


Fig. 8. Enlarged view of the Raman spectra in Fig. 7 displaying the low-intensity bands.

wavenumbers are lower than those of the zircon end-member (see Fig. 6). In the spectra of $\text{Hf}_{0.39}$ to $\text{Hf}_{0.67}$, the bands overlap strongly, but width and asymmetry indicate that there is more than one band. In the spectra of $\text{Hf}_{0.82}$ to $\text{Hf}_{0.99}$, only one band is observed in the range between 190 and 225 cm^{-1} , *i.e.* at 213 cm^{-1} . This variation between the samples could be caused by an overlap of the three bands combined with a decrease of intensity of the $\text{B}_{1g}(\text{II})$ and $\text{E}_g(\text{II})$ bands with increasing Hf content. Based on the fits of the bands $\text{E}_g(\text{III})$, $\text{B}_{1g}(\text{II})$, and $\text{E}_g(\text{II})$ in the range 190–225 cm^{-1} across the whole series, the $\text{E}_g(\text{III})$ band shifts from zircon to hafnon from 224 cm^{-1} to 213 cm^{-1} by $-0.121 \text{ cm}^{-1}/$

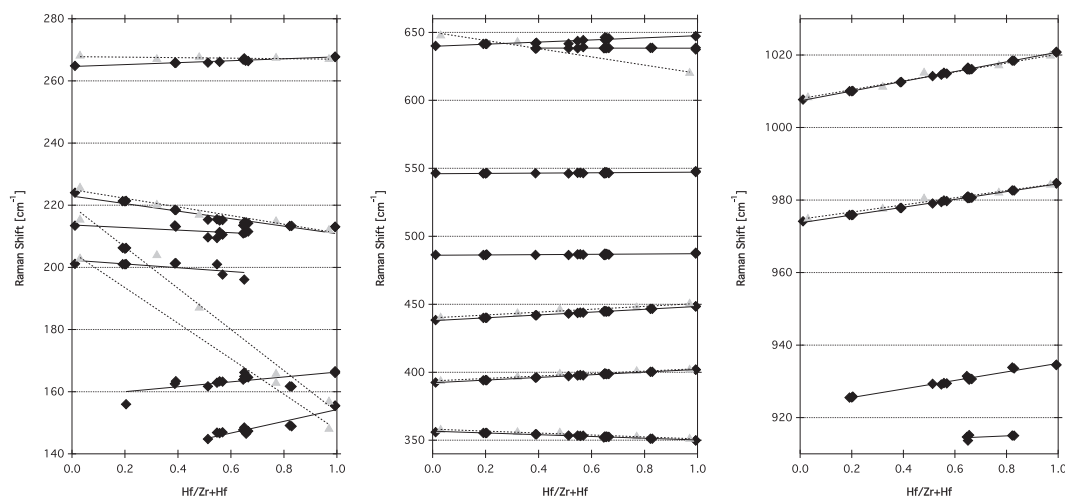


Fig. 9. Position of the Raman bands as a function of the Hf content at the analysed spots; the regression lines were fitted to the measured band positions as a function of crystal composition. Black diamonds and the line drawn through are data of this work. Gray triangles and dashed lines are data of Hoskin & Rodgers (1996), for comparison.

mol% Hfn. The $B_{1g}(II)$ band shifts from zircon to $Hfn_{0.65}$ from 213 cm^{-1} to 211 cm^{-1} by $-0.042\text{ cm}^{-1}/\text{mol\% Hfn}$. For $Hfn_{0.2}$, there is a band at 206 cm^{-1} , which falls off the compositional trend of the $B_{1g}(II)$ band. The $E_g(II)$ band decreases from zircon to $Hfn_{0.65}$ from 201 cm^{-1} to 196 cm^{-1} by -5 cm^{-1} and is not observed at higher Hf contents.

Bands at $147\text{--}155$ and at $156\text{--}166\text{ cm}^{-1}$ were observed in spectra of all samples except for the zircon end-member. One band was observed in $Hfn_{0.51}$ to $Hfn_{0.99}$. It shifts from 147 cm^{-1} to 155 cm^{-1} , and is most intense in the hafnon end-member. In the latter, there is an additional band at 147 cm^{-1} . The other band appears in the samples $Hfn_{0.20}$ to $Hfn_{0.99}$ with a shift from 156 cm^{-1} to 166 cm^{-1} and is least intense in pure hafnon. Bands at 155 and 147 cm^{-1} in hafnon were also described by Nicola & Rutt (1974) and Hoskin & Rodgers (1996) and assigned to the $B_{1g}(II)$ and $E_g(II)$ external modes in hafnon, respectively. The band that varies from 156 to 166 cm^{-1} , named ν_{166} after the position in hafnon, has not been reported, yet. Interestingly, the spectrum of hafnon shown by Nicola & Rutt (1974) shows a broad band in that frequency region, which was not discussed by the authors. There is no indication for a band at this frequency in the spectrum shown by Hoskin & Rodgers (1996). The ν_{166} band is best resolved for the hafnon end-member and traceable in the solid solution.

In addition to the bands described above, some further bands were observed in some samples. In the following they are named ν_{638} , and ν_{915} using their position in the spectra of the hafnon end-member. The band ν_{915} was only observed in the spectra of $Hfn_{0.65}$ to $Hfn_{0.83}$ next to the ν_3 (E_g) band. Similarly, ν_{638} was only observed next to the ν_4 (B_{1g}) band in the spectra of $Hfn_{0.39}$ to $Hfn_{0.99}$. The ν_{915} and ν_{638} bands do not shift significantly with Hf content. Due to their low intensity and large width as well as their insensitivity to composition it seems likely that

these bands are related to background or minor compositional artefacts.

Ab initio simulated Raman spectra

Theoretical Raman spectra of zircon and hafnon end-members are shown in Fig. 10a in comparison to experimental spectra. All Raman-active modes from the calculations can be assigned to bands in the experimental spectra (see Table 2), which confirms the assignment of the major modes made above. Also, the relative intensities of the theoretical spectra are in reasonable agreement with experiment (see Fig. 10a). Predicted band positions simulated at 0 GPa differ by up to 50 cm^{-1} from those of the corresponding experimental spectra. For the spectra, calculated at the experimental density, the difference is smaller (up to 20 cm^{-1}) for bands with frequencies lower than 700 cm^{-1} , whereas the positions of the bands at frequencies higher than 900 cm^{-1} differs by up to 40 cm^{-1} . The observed differences are mainly due to the approximations of DFT-LDA calculations. For both simulations, the extent of the shift depends on the mode and is different for hafnon and zircon, as documented in Table 2. The effect of composition on the calculated wavenumbers is detailed in Fig. 10b for spectra simulated at 0 GPa. For example, the shift of the internal ν_3 (SiO_4) B_{1g} mode from zircon to hafnon is 9 cm^{-1} , but 13.4 cm^{-1} in the experiment. The ν_2 (SiO_4) A_{1g} mode shifts by about 2 cm^{-1} in comparison to an experimental shift of 10.5 cm^{-1} . The $E_g(I)$ mode shifts by about -20 cm^{-1} . In the experiment, this mode also shifts, but only by -6.5 cm^{-1} . For spectra simulated for experimental volumes, the shifts are different, *i.e.* 19 cm^{-1} for ν_3 (SiO_4), 5 cm^{-1} for ν_2 (SiO_4) and 0 cm^{-1} for $E_g(I)$ mode. The differences between the two simulations highlight the fact the

Table 2. Position of Raman bands in cm^{-1} . The uncertainty in frequency is $0.1\text{--}0.2\text{ cm}^{-1}$, uncertainty in composition is 1 %rel. The bands are labeled after Nasdala *et al.* (2003) and Hoskin & Rodgers (1996). Exceptions are the bands labeled as $\nu_{\text{Xcm-1}}$, which are not mentioned in these publications. Labels containing Roman numerals are external modes, labels containing $\nu_2(\text{SiO}_4)$ are internal modes (after Hoskin & Rodgers, 1996). The regression lines for the compositional dependence of the band positions are defined by the gradient m and the intercept n . Only full width at half maximum of the most intense external and internal bands ($E_g(\text{I})$ and $B_{1g}(\nu_2(\text{SiO}_4))$) are shown in the columns FWHM. DFT refers to the theoretical spectra simulated at 0 GPa, DFTex refers to theoretical spectra simulated at experimental density. *For the ordered structure of $\text{ZrHfSi}_2\text{O}_8$ there are additional Raman-active modes above 295 cm^{-1} due to symmetry reduction (space group $I\text{--}4m2$). ⁺See text for band assignment.

Phonon		$E_g(\text{II})^+$	$B_{1g}(\text{II})^+$	ν_{166}^+	$E_g(\text{II})$	$B_{1g}(\text{II})$	$E_g(\text{III})$	B_{2g}^*	$E_g(\text{I})$	$E_g(\text{I})$	$B_{1g}(\text{I})$
Sample	No.	Hf	Hf		Zr	Zr		$\nu_2(\text{SiO}_4)$			FWHM
1	1	—	—	—	201.1	213.4	224.0	264.8	356.0	4.11	392.5
2	65	—	—	—	201.0	206.3	221.3	—	355.4	5.36	394.1
2	66	—	—	156.0	201.1	206.3	221.4	—	355.4	5.34	394.2
2	67	—	—	—	201.0	206.0	221.3	—	355.3	5.41	394.2
3	16	—	—	162.5	201.3	213.5	218.5	265.8	354.4	7.12	396.0
3	17	—	—	163.4	201.4	213.1	218.5	265.8	354.4	7.11	396.2
4	100	—	146.7	163.3	—	211.4	215.1	266.2	353.2	8.31	398.0
4	104	—	147.0	163.3	197.7	210.6	215.3	—	353.4	8.17	397.8
4	105	—	146.9	162.9	201.0	209.5	215.5	—	353.5	8.18	397.7
4	106	—	144.8	161.7	—	209.7	215.4	265.9	353.5	8.12	397.1
5	157	—	148.5	164.9	196.1	211.3	214.5	267.3	352.8	8.42	399.2
5	158	—	147.5	164.6	—	211.2	214.2	266.5	352.5	8.38	398.8
5	165	—	146.5	164.8	—	211.7	214.4	—	352.8	8.34	398.7
5	166	—	147.3	164.6	—	211.5	214.2	266.4	352.5	8.37	398.8
5	167	—	147.4	166.2	—	211.2	214.3	—	352.5	8.31	398.9
5	168	—	147.7	163.9	—	210.9	213.5	266.9	352.1	8.52	398.5
6	140	—	149.1	161.7	—	—	213.3	—	351.2	7.84	400.4
6	141	—	148.9	161.7	—	—	213.4	—	351.2	7.83	400.3
7	113	147.4	155.6	166.6	—	—	213.1	267.8	349.9	5.25	402.0
7	114	147.3	155.4	166.1	—	—	213.1	267.7	349.9	5.24	401.9
			18.9(9)	7.9(6)	−6.1(8)	4.2(8)	−12.1(4)	3.1(6)	−6.5(4)		9.8(4)
			135.4(6)	158.5(4)	202.3(3)	213.7(4)	223.0(3)	264.7(4)	356.7(3)		392.3(3)
DFT	0.0	—	—	—	200.6	230.7	241.9	252.7	413.1		429.4
DFT*	0.5	—	—	—	190.3	196.4	223.8	254.7	402.2		429.5
DFT	1.0	172.5	168.5	—	203.4	216.8	219.2	256.8	393.8		428.1
DFTex	0.0	—	—	—	—	—	242.1	266.0	346.7		404.1
DFTex	1.0	167.2	158.9	—	—	—	226.5	267.7	346.8		408.7

Phonon	A _{lg}		E _g	B _{lg}		E _g		A _{lg}	B _{lg}		B _{lg} ν ₃ (SiO ₄)	
Sample	No.	X _{Hf}	ν ₂ (SiO ₄)	E _g	ν ₄ (SiO ₄)	ν ₃ (SiO ₄)	ν ₆₃₈	ν ₄ (SiO ₄)	ν ₃ (SiO ₄)	ν ₁ (SiO ₄)	ν ₃ (SiO ₄)	FWHM
1	1	0.01	438.4	546.5	—	—	—	640.1	—	974.1	1007.7	2.49
2	65	0.19	440.0	546.3	—	—	—	641.5	—	975.9	1010.1	2.60
2	66	0.20	440.1	546.6	—	—	—	641.5	—	975.9	1010.1	2.62
2	67	0.20	440.1	546.3	—	—	—	641.6	—	975.9	1010.0	2.62
3	16	0.39	441.9	546.4	638.1	—	—	642.0	—	977.8	1012.5	3.07
3	17	0.39	442.0	—	638.3	—	—	642.4	—	977.8	1012.6	2.86
4	100	0.56	444.0	546.8	—	—	—	—	—	979.9	1015.1	3.10
4	104	0.57	443.9	546.5	639.2	—	—	644.3	—	979.7	1014.9	3.07
4	105	0.55	443.6	546.7	638.3	—	—	643.7	—	979.5	1014.6	3.14
4	106	0.51	443.1	546.3	638.4	—	—	641.7	—	979.1	1014.2	3.34
5	157	0.65	445.1	547.3	638.6	—	—	644.5	—	981.0	1016.5	2.96
5	158	0.66	444.7	546.6	638.4	—	—	644.7	915.2	980.7	1016.1	2.89
5	165	0.66	444.7	547.1	638.6	—	—	645.8	—	980.6	1016.0	2.89
5	166	0.67	444.8	546.6	638.5	—	—	645.7	—	980.6	1016.1	2.90
5	167	0.65	444.8	546.2	638.5	—	—	646.4	913.7	980.5	1016.0	2.78
5	168	0.65	444.8	546.4	638.4	—	—	—	914.7	980.8	1016.2	3.11
6	140	0.82	446.7	—	638.7	—	—	—	915.1	982.7	1018.5	2.57
6	141	0.83	446.7	—	638.6	—	—	—	915.0	982.6	1018.5	2.77
7	113	0.99	448.6	547.3	638.7	—	—	647.2	—	984.7	1020.9	3.12
7	114	0.99	448.4	547.9	637.4	—	—	—	—	984.6	1020.7	3.13
		<i>m</i> [cm ⁻¹ /X _{Hf}]	10.5(4)	1.2(5)	7.8(5)	—	—	—	—	10.8(4)	13.4(4)	
		<i>n</i> [cm ⁻¹]	438.0(3)	546.1(3)	638.6(5)	—	—	639.8(3)	—	973.7(3)	1007.4(3)	
DFT		0.0	480.3	551.0	—	—	—	670.0	—	994.4	1040.7	
DFT*		0.5	481.4	550.3	—	—	—	672.2	—	998.5	1044.9	
DFT		1.0	482.6	549.8	—	—	—	674.3	—	1002.7	1049.3	
DFTex		0.0	458.6	540.2	—	—	—	638.4	—	927.18	969.2	
DFTex		1.0	463.4	541.7	—	—	—	648.1	—	946.6	988.7	

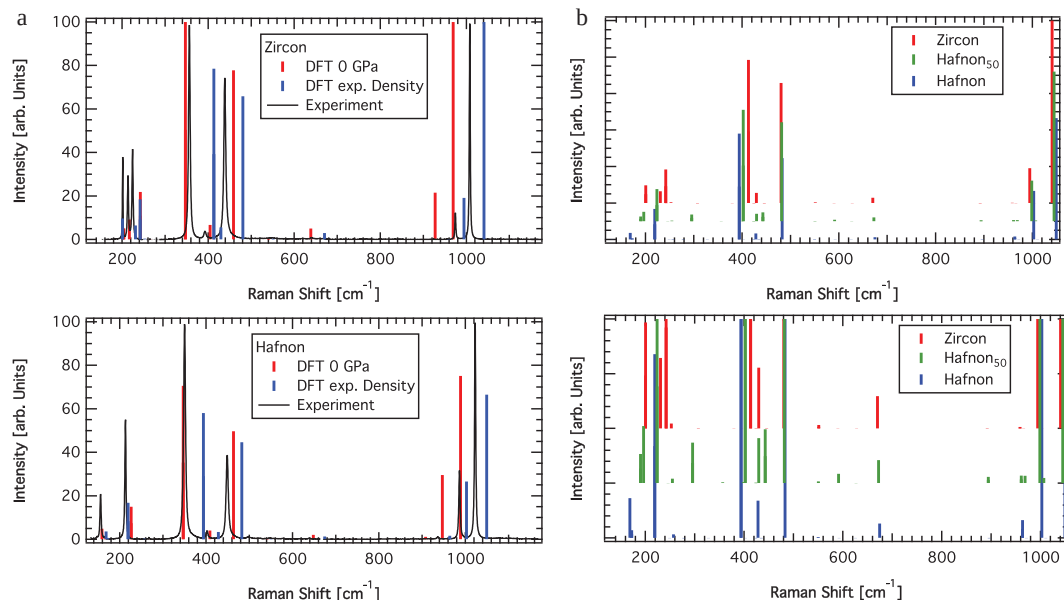


Fig. 10. (a) Comparison between experimental spectra of zircon and hafnon end-member compositions and theoretical spectra from DFT calculations as indicated. For both compositions, different spectra were computed for a structure optimized at 0 GPa and for another structure optimized using the experimental density at ambient conditions as a constraint. (b) Variation of theoretical Raman spectra as a function of composition. Data shown were simulated at 0 GPa. The intermediate spectrum for Hf_n_{0.5} was derived for a hypothetical ordered structure, where one of the two Zr atoms in the tetragonal unit cell was replaced by Hf. The lower graphs show a zoom of the upper ones, magnifying the low-intensity bands. (online version in colour)

results are highly sensitive to details of the computations.

The two end-members show 16 vibrational modes in the calculations that are not Raman-active, whereas in the hypothetical solid solution all but two external modes (at 127 and 245 cm⁻¹) have finite Raman intensity. Particular enhancement is observed for modes at 969 cm⁻¹, at 894 cm⁻¹, 591 cm⁻¹, 443 cm⁻¹ and 296 cm⁻¹. None of these additional modes is observed in the experimental spectra.

Discussion

We successfully synthesized a suite of hafnon–zircon solid solutions with more than five intermediate compositions. Although the synthesis of compositionally homogeneous batches was not successful, single crystals within a batch are homogeneous enough to perform Raman micro-spectroscopic spot measurements. The detailed analysis of the high-quality spectra along the join confirms the observations and assignments made by previous authors (Dawson *et al.*, 1971; Nicola & Rutt, 1974; Syme *et al.*, 1977; Hoskin & Rodgers, 1996), however, with a considerably higher number of compositions. Particularly for external lattice modes, this dataset provides new insight into the variations of these modes with composition, which will be discussed in more detail below.

The complementary *ab initio* simulations of theoretical Raman spectra support the mode assignments for the end-member compositions. However, computation of spectra

for intermediate compositions is challenging (and beyond the scope of this study) due to the large simulation cells needed to model a solid solution. The Raman spectrum computed for a hypothetical ordered crystal with half of the Zr atoms replaced by Hf shows an increase in the number of Raman-active bands due to the lower symmetry imposed by an ordered arrangement of Hf and Zr. As these additional Raman-active bands are not found in the experimental spectra, such an ordered phase of Hf_n_{0.5} can be excluded. This also means that there is no indication for vibrational modes due to nearest-neighbor Hf–Zr interactions in the solid-solution series. This result is consistent with DFT simulations of NMR spectra for the zircon–hafnon solid solution (Cota *et al.*, 2013).

Internal Raman modes

An increase in the Hf content leads to an increase of the average cation mass at the dodecahedral site and thus to shifts in the frequency of the Raman-active modes including the internal modes of the SiO₄ tetrahedra. The observations on the internal modes as described above are quite similar to those by Hoskin & Rodgers (1996), except for the ν_4 (B_{1g}) band. Hoskin & Rodgers (1996) reported a strong decrease in the wavenumber of this band from about 640 cm⁻¹ in zircon to 620 cm⁻¹ in Hf_n_{0.99}. Based on this, they concluded that this band was either overlain by another band or not produced by an internal mode. In our study, the ν_4 (B_{1g}) band at 640 cm⁻¹ shows a gradual positive shift to 647 cm⁻¹, and a band at 620 cm⁻¹ was not observed at all. We only

observed a small and broad band at 638 cm^{-1} , which is not sensitive to composition. Our observation on the band at 640 cm^{-1} supports the interpretation by Syme *et al.* (1977) and Kolesov *et al.* (2001) of this band as ν_4 (SiO_4) (antisymmetric bending). The *ab initio* Raman spectra confirm the band shift to higher wavenumbers from 670 to 674 cm^{-1} at 0 GPa or from 638 to 648 cm^{-1} at the experimental density. Further, the displacement vectors of this mode are consistent with the ν_4 (SiO_4) mode assignment.

External Raman modes

For the bands of the external modes, there is considerable disagreement in the literature regarding the band assignments. The $B_{1g}(\text{I})$ band shifts from zircon to hafnon from 393 cm^{-1} to 402 cm^{-1} by $0.09\text{ cm}^{-1}/\text{mol}\%$ Hfn. The width of this band shows a clear compositional trend with an increase from 4.1 cm^{-1} for $\text{Hfn}_{0.01}$ to 8.5 cm^{-1} for $\text{Hfn}_{0.65}$, which reflects increasing structural disorder or mass disorder on the A site. At higher Hf contents, the width decreases again to 5.24 cm^{-1} for $\text{Hfn}_{0.99}$. Some authors (Syme *et al.*, 1977; Hoskin & Rodgers, 1996; Kolesov *et al.*, 2001) interpret this band as external translational mode B_{1g} . The experimental data presented here across the zircon–hafnon series would also be consistent with the interpretation as internal antisymmetric bending ν_4 (Dawson *et al.*, 1971; Nicola & Rutt, 1974) due to the similarity to the variations in the band parameters of other internal modes with composition. The $B_{1g}(\text{I})$ mode from the *ab initio* calculations with a

wavenumber of $428\text{--}429\text{ cm}^{-1}$ (0 GPa) or $404\text{--}408\text{ cm}^{-1}$ (experimental density) is almost independent on composition (Table 2). Its displacement vector reveals clearly the external translational character of this mode. Unfortunately, the underlying mechanism for the increasing wavenumber of this mode along the solid-solution series in the experimental spectra remains unexplained here.

Next, we discuss the assignment and nature of the lowest-frequency external modes $E_g(\text{II})$, $E_g(\text{III})$ and $B_{1g}(\text{II})$. Syme *et al.* (1977) and Hoskin & Rodgers (1996) assigned the lattice mode $E_g(\text{III})$ with the smallest shift across the compositional series as being largely rotational in character. The $B_{1g}(\text{II})$ and $E_g(\text{II})$ bands were considered by Syme *et al.* (1977) to be restricted to cations only and related to translational modes (Hoskin & Rodgers, 1996). Therefore, a strong difference in the frequency is observed between the zircon and hafnon end-members. That is, $B_{1g}(\text{II})$ is at 213 cm^{-1} in zircon and 155 cm^{-1} in hafnon. Our simulations confirm these two assignments with respect to symmetry of the Raman tensor and relative Raman intensities (Fig. 10a). The displacement vectors show that the $B_{1g}(\text{II})$ modes of the end-members are almost entirely translational whereas the $E_g(\text{III})$ modes have a strong rotational character (Fig. 11). The $E_g(\text{II})$ mode of the theoretical Raman spectrum is the lowest-wavenumber mode in zircon (201 cm^{-1} at 0 GPa and 203 cm^{-1} at experimental volume) but has a higher wavenumber ($173\text{ cm}^{-1}/167\text{ cm}^{-1}$) than the $B_{1g}(\text{II})$ mode ($169\text{ cm}^{-1}/159\text{ cm}^{-1}$) in hafnon. If the sequence of bands with increasing wavenumbers is correctly predicted by the calculations, the assignment of the $E_g(\text{II})$

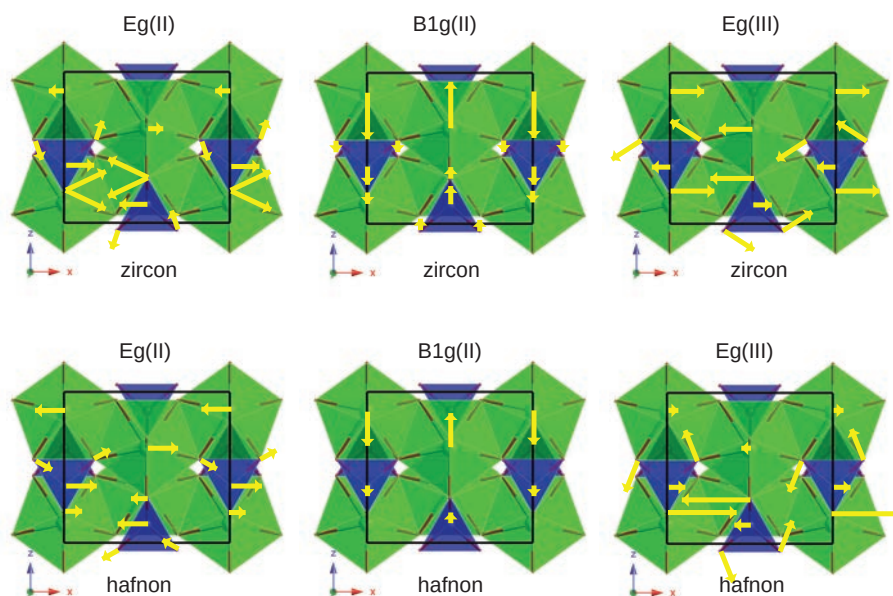


Fig. 11. XZ projections of the displacement vectors of the three external modes $E_g(\text{II})$, $B_{1g}(\text{II})$ and $E_g(\text{III})$ obtained from the *ab initio* simulations. The $B_{1g}(\text{II})$ mode is purely translational, whereas the E_g modes of zircon have both translational and rotational components. For hafnon, $E_g(\text{II})$ is predominantly translational and $E_g(\text{III})$ rotational. (online version in colour)

band of hafnon will have to be revised. While Nicola & Rutt (1974) and Hoskin & Rodgers (1996) assigned the $E_g(\text{II})$ mode to the 147 cm^{-1} band, an alternative assignment would be the 166 cm^{-1} band. From our measurements on the solid-solution samples, it becomes obvious that for the $B_{1g}(\text{II})$ and $E_g(\text{II})$ modes the bands can be sub-divided into those related to Zr–Zr lattice modes (213 to 211 cm^{-1} , 201 to 196 cm^{-1}) and those related to Hf–Hf modes (155 to 147 cm^{-1} , 147 cm^{-1} or 166 to 156 cm^{-1}). Particularly in compositions close to $\text{Hfn}_{0.5}$, both sets of bands can be observed in the same spectrum. Still, the frequency of each set is affected by the bulk composition. From our experimental observations we have no clear indication for modes related to direct Hf–Zr interactions. According to the *ab initio* simulations, such interactions should show up in additional modes.

In conclusion, we have shown that our series of relatively closely spaced samples along the zircon–hafnon solid-solution series provides a more detailed picture of and new insight into the compositional influence on the vibrational spectra. Particularly, the co-existence of Zr–Zr and Hf–Hf external modes in intermediate composition was not documented before. This information can be helpful in studies on order–disorder in solid solutions.

In order to provide a thorough characterization of structural as well as thermodynamic mixing properties along the zircon–hafnon solid-solution series, it would be desirable to develop an experimental protocol to synthesize homogeneous bulk crystals at various Zr/Hf ratios. These properties are important for an understanding of fractionation processes of Zr and Hf, or high-field-strength elements in general, during fluid–rock or melt–rock interactions involving minerals of the zircon–hafnon series.

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