

## Raman spectroscopic study of zircon to high pressure and temperature

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The four most intense Raman bands of zircon at wavenumbers  $>300\text{ cm}^{-1}$  have been assigned to internal vibrations of the  $\text{SiO}_4$  tetrahedra. Specific assignments include  $\nu_3(\text{SiO}_4)$  (antisymmetric stretching) to the band at  $1008\text{ cm}^{-1}$ ,  $\nu_1(\text{SiO}_4)$  (symmetric stretching) to the band at  $974\text{ cm}^{-1}$ ,  $\nu_2(\text{SiO}_4)$  (symmetric bending) to the band at  $439\text{ cm}^{-1}$ , and  $\nu_4(\text{SiO}_4)$  (antisymmetric bending) or an external lattice mode to the band at  $356\text{ cm}^{-1}$  (Nasdala et al., 2003). The effect of pressure ( $P$ ) on the frequency of these bands (and on the linewidth of  $\nu_3(\text{SiO}_4)$ ) has previously been characterized at  $\sim 300\text{ K}$  for fully crystalline and radiation-damaged zircon (Knittle and Williams 1993, Nasdala et al. 2008). This has not been studied at elevated temperatures ( $T$ ). Here, we determine the frequency and the linewidth of these Raman bands for fully crystalline synthetic zircon ( $\text{ZrSiO}_4$  endmember composition) as functions of  $P$  and  $T$  to  $6.6\text{ GPa}$  and  $950\text{ }^\circ\text{C}$  using a HORIBA LabRAM HR800 Raman microprobe (unpolarized spectra, backscattering geometry, gratings  $1800\text{ lines/mm}$ , excitation by  $488\text{ nm}$  line of  $\text{Ar}^+$  laser) and diamond-anvil cells or a Linkam TS1000 heating stage.

At  $0.1\text{ MPa}$ , the  $\nu_2(\text{SiO}_4)$  band displays by far the largest increase in linewidth with  $T$  (from  $\sim 5\text{ cm}^{-1}$  at  $22\text{ }^\circ\text{C}$  to  $\sim 24\text{ cm}^{-1}$  at  $900\text{ }^\circ\text{C}$ ), while those for  $\nu_3(\text{SiO}_4)$  and  $\nu_1(\text{SiO}_4)$  are moderate (from  $\sim 2\text{ cm}^{-1}$  at  $22\text{ }^\circ\text{C}$  to  $\sim 13$  or  $12\text{ cm}^{-1}$  at  $900\text{ }^\circ\text{C}$ ). The  $\nu_3(\text{SiO}_4)$  band shows the largest wavenumber decrease with  $T$  ( $\sim -0.038\text{ cm}^{-1}/\text{K}$ ). The  $\partial\nu/\partial T$  slopes of the other bands are  $\sim -0.023\text{ cm}^{-1}/\text{K}$  for  $\nu_1(\text{SiO}_4)$ ,  $\sim -0.017\text{ cm}^{-1}/\text{K}$  for  $\nu_2(\text{SiO}_4)$ , and  $\sim -0.019\text{ cm}^{-1}/\text{K}$  for the  $356\text{ cm}^{-1}$  band. The isothermal change in wavenumber with  $P$  is nearly constant for the studied Raman bands. At  $23\text{ }^\circ\text{C}$ , the obtained  $\partial\nu/\partial P$  slope of the  $\nu_3(\text{SiO}_4)$  band to  $6.6\text{ GPa}$  is  $5.68\text{ cm}^{-1}/\text{GPa}$ , and  $5.75\text{ cm}^{-1}/\text{GPa}$  to  $2.5\text{ GPa}$ . This slope does not significantly change with  $T$ , as determined for the  $700$  and  $600\text{ }^\circ\text{C}$  isotherms ( $\partial\nu/\partial P \sim 5.9\text{ cm}^{-1}/\text{GPa}$ ) and along the  $500\text{ }^\circ\text{C}$  isotherm ( $\partial\nu/\partial P \sim 6.1\text{ cm}^{-1}/\text{GPa}$ ). At  $23\text{ }^\circ\text{C}$ , the  $\partial\nu/\partial P$  slopes to  $6.6\text{ GPa}$  of the other bands are  $5.15\text{ cm}^{-1}/\text{GPa}$  for  $\nu_1(\text{SiO}_4)$ ,  $1.45\text{ cm}^{-1}/\text{GPa}$  for  $\nu_2(\text{SiO}_4)$ , and  $4.55\text{ cm}^{-1}/\text{GPa}$  for the  $356\text{ cm}^{-1}$  band, and are not significantly different for isotherms at higher  $T$ . A general tendency of slight (often nonsignificant) decreases in the linewidths of the studied Raman bands with pressure was observed at  $23\text{ }^\circ\text{C}$  to  $6.6\text{ GPa}$ , and along other isotherms to  $700\text{ }^\circ\text{C}$  to  $P$  of  $1.3\text{ GPa}$ .

Because of its fairly large and temperature-independent shift with  $P$  ( $\partial\nu/\partial P \sim 5.8\text{ cm}^{-1}/\text{GPa}$ ), the frequency of the  $\nu_3(\text{SiO}_4)$  ( $\sim 1008\text{ cm}^{-1}$ ) Raman band of fully crystalline synthetic zircon can be used as a pressure sensor for experiments using optical cells at high  $P$  and  $T$ . This is of particular advantage in situations where other phases cannot be used as pressure sensors because of phase transitions or high solubility. However, the actual sample temperature should be well known for accurate determination of  $P$  using this sensor because of the temperature sensitivity of the frequency, which is described by the equation  $\nu(\text{cm}^{-1}) = 7.26 \cdot 10^{-9} \cdot T(^\circ\text{C})^3 - 1.58 \cdot 10^{-5} \cdot T(^\circ\text{C})^2 - 2.893 \cdot 10^{-2} \cdot T(^\circ\text{C}) + 1008.64$  ( $22 \leq T(^\circ\text{C}) \leq 950$ ).

### References:

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Knittle E., Williams Q. (1993), *American Mineralogist*, 78, 245-252.  
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