Raman spectra for estimation of the Fe^{3+} content in clinozoisite-epidote series

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Providing a tool for fast estimation of the Fe^{3+} content in $Ca_2(Al, Fe^{3+})_3Si_3O_{12}(OH)$-epidotes Raman spectroscopy was applied to 33 analytical areas from 15 natural specimens with 0.22-1.13 Fe^{3+} atoms per formula unit (apfu). The Raman spectra were collected from the areas where the chemical compositions were independently determined by wavelength-dispersive electron microprobe analysis (WD-EPMA). Both the OH-stretching region (3215–3615 cm^{-1}) and the spectral range generated by the framework vibrations (15–1215 cm^{-1}) have been analyzed. Similar to the IR spectra, the Raman peaks in the OH-stretching region shift toward higher wavenumbers with increasing Fe^{3+} in epidotes. However, the quantification of Fe^{3+} based on OH-stretching Raman peaks should be hindered by the multicomponent overlapping, peak broadening, and significant intensity variations with the crystal orientation. In the framework vibration region, the position of four peaks (near 250, 570, 600, and 1090 cm^{-1}), in particular, linearly varies with increasing Fe^{3+} content. However, the peak near 250 cm^{-1} attributed to MO_6 vibrations is not always well-resolved due to the orientational dependence. On the other hand, the peaks near 570, 600, and 1090 cm^{-1} arise from Si_2O_7 vibrational modes and although their intensities also vary with the crystal orientation, all three signals are well resolved in a random orientation. Among the three peaks, the 570 cm^{-1} peak is the sharpest (peak width < 10 cm^{-1}) and is easily recognized as a separate peak. Thus, we propose to use the position of this peak as a highly reliable parameter to estimate the Fe^{3+} content, via the linear trend given as w570 = 577.1(3)-12.7(4)x, where w = wavenumber (cm^{-1}), and x = Fe^{3+} content (apfu), with accuracy ±0.04 Fe^{3+} apfu. The relations determined based on the 600 and 1090 cm^{-1}-peak positions can be used complementarily for Fe^{3+} estimation: w600 = 611.6(2)-13.8(4)x and w1090 = 1098.8(3)-13.5(5)x.

Keywords: Raman spectroscopy, Epidote, Clinozoisite, Fe content