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Temperature dependence of Raman shifts and line widths for Q^0 and Q^2 crystals of silicates, phosphates, and sulfates

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Abstract

The temperature dependence of Raman shifts and line widths (full-width at half maxima or FWHM) for the A_1 symmetric stretch of TO_4 (T = Si, P, S) have been analyzed for nine alkali and alkaline earth silicates, phosphates, and sulfates. In crystalline silicates, the Q^0 and Q^2 species Raman shifts decrease with temperature, whereas FWHM increase. The strikingly similar behavior of Q^0 and Q^2 in silicates and Q^0 in phosphates makes it possible to estimate to within ±4 cm^{-1} Raman shifts up to ~1000 K. Similarly systematic increases in FWHM with temperature can be estimated to within ±5 cm^{-1} up to ~1400 K. The type of element centering TO_4 (i.e., Si, P, or S) has no appreciable effect on the temperature dependence of Raman shifts or line widths; the local environment of the Q^0 and Q^2 tetrahedra is the primary determinant of the temperature dependence. The type of cation in the first coordination sphere of the tetrahedron may have a secondary effect by affecting Heisenberg lifetimes of Raman virtual states.

Previous theoretical considerations have been modified to include the effect of the Heisenberg (or natural) lifetime on Raman FWHM. This contribution is required to explain the anomalous FWHM of Li_2SiO_3 relative to the FWHM of isostructural Na_2SiO_3 and the large Li_2SO_4 and Li_3PO_4 FWHM (relative to Ba and Sr phosphates). The theoretically based expressions dictate a necessary, simple relationship among temperature, Raman shift, and FWHM. The relationship is developed and it allows, with one measurement of Raman shift and FWHM (e.g., measured at 298 K), prediction of Raman shifts and FWHM of Q^0 and Q^2 crystals to within 5 cm^{-1} up to ~1500 K. The properties of the TO_4 moiety (T = Si, P, S) are mostly responsible for the striking regularity of Raman shifts and FWHM, although alkali and alkaline earth cations affect to varying extent Heisenberg lifetimes, hence FWHM.

Keywords: Raman shifts in crystals, Raman line widths in crystals, temperature dependence of Raman shifts, temperature dependence of Raman line widths