

Temperature dependence of Raman shifts and line widths for Q⁰ and Q² 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 A₁ symmetric stretch of TO₄ (T = Si, P, S) have been analyzed for nine alkali and alkaline earth silicates, phosphates, and sulfates. In crystalline silicates, the Q⁰ and Q² species Raman shifts decrease with temperature, whereas FWHM increase. The strikingly similar behavior of Q⁰ and Q² in silicates and Q⁰ 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 TO₄ (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 Q⁰ and Q² 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 Li₂SiO₃ relative to the FWHM of isostructural Na₂SiO₃ and the large Li₂SO₄ and Li₃PO₄ 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 Q⁰ and Q² crystals to within 5 cm⁻¹ up to ~ 1500 K. The properties of the TO₄ 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