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 Li₂PO₄ 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

INTRODUCTION

The Raman spectra of crystals in the region 800–1200 cm⁻¹ (i.e., the A₁ TO₄ symmetric stretching mode) commonly display a prominent, narrow Lorentzian peak with a well-defined position at room temperature. The best documented data on crystalline silicate Raman shifts and line widths are provided by Richet et al. (1996, 1998), who present data for Li₂SiO₃, Na₂SiO₃, CaSiO₃, and Ca₀.₃Mg₀.₇SiO₃ metasilicate crystals from 298 K to their melting points. These crystals have different structures but all consist of Si tetrahedra where each Si center is bonded to two bridging oxygen atoms (BO or Si-O-Si) and two non-bridging oxygen atoms (NBO or e.g., Si-O-Na). These are referred to as Q² species (Q indicates a Si center and the superscript indicates the number of BO atoms per tetrahedron). In addition, numerous papers provide reasonably well-characterized data (in graphical form) on Raman shifts and line widths for crystals containing Q⁰ species, including silicates, phosphates, and sulfates (Cazzanelli and Frech 1984; Popovic et al. 2003; Kolesev and Geiger 2004; Zhai et al. 2011, 2014). These data have been inspected and where feasible Raman shifts and line widths have been evaluated. After studying the data we arrive at two major questions concerning the spectra of crystals. First, do Raman shifts and FWHM of the Q species describe similar trends as a function of temperature or do they describe unique trends in temperature, each trend being dependent on crystal structure and composition? Second, can the temperature dependence of the Raman shifts and FWHM be explained using existing theories? Our goals are to answer these questions. There has been no comprehensive study relating these two temperature-dependent spectral properties for silicates, phosphates or sulfates and few on other materials (e.g., Klemens 1966; Liu et al. 2000). Our most important observation is that the temperature dependence of Raman shifts and FWHM predicted from theory is observed for experimental data. Moreover, Raman shifts or FWHM can be reasonably estimated at high temperature provided the temperature dependence of the other is known.

Richet et al. (1996, 1998) demonstrated that the Raman line widths and peak shapes change within the premelting regions of the Q² crystals Na₂SiO₃, Li₂SiO₃, and CaSiO₃, and Nesbitt et al. (2017a) interpreted the changes in these spectra to result from