Raman and infrared spectroscopic indications for a temperature-induced phase transition in norsethite, $BaMg(CO_3)_2$

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In course of investigations of the temperature- and pressure-dependent behaviour of norsethite, $BaMg(CO_3)_2$, suspected structural changes related to the ambiguous symmetry of the crystal structure at ambient conditions (as indicated by split atom positions / disorder in previous work of Effenberger and Zemann, 1985) were also studied by vibrational spectroscopy. Thus, in a first step, Raman and infrared (IR) spectra were acquired at variable temperatures, i.e., –191 to +200 °C (Raman), and +22 to +300 °C (IR), using a commercial heating/cooling stage.

Synthetic norsethite from Lippmann (1968) was available for the spectroscopic investigations. Whereas single-crystals with a maximum size of approximately 50 × 50 × 100 μm^3 were preferred for confocal micro-Raman experiments; KBr-diluted and pressed powder pellets were chosen as IR samples. Unpolarised spectra were acquired in the Raman shift / wavenumber range of 40 to 1800 cm^{-1} (Raman) and 550 to 4000 cm^{-1} (IR). Thus, the fundamental stretching (ν_1, ν_3) and bending (ν_2, ν_4) vibrations of the carbonate group (~ 700 to 1450 cm^{-1}) as well as combination and overtone modes (>1450 cm^{-1}) and lattice modes (<400 cm^{-1}) could be obtained (Böttcher et al., 1997).

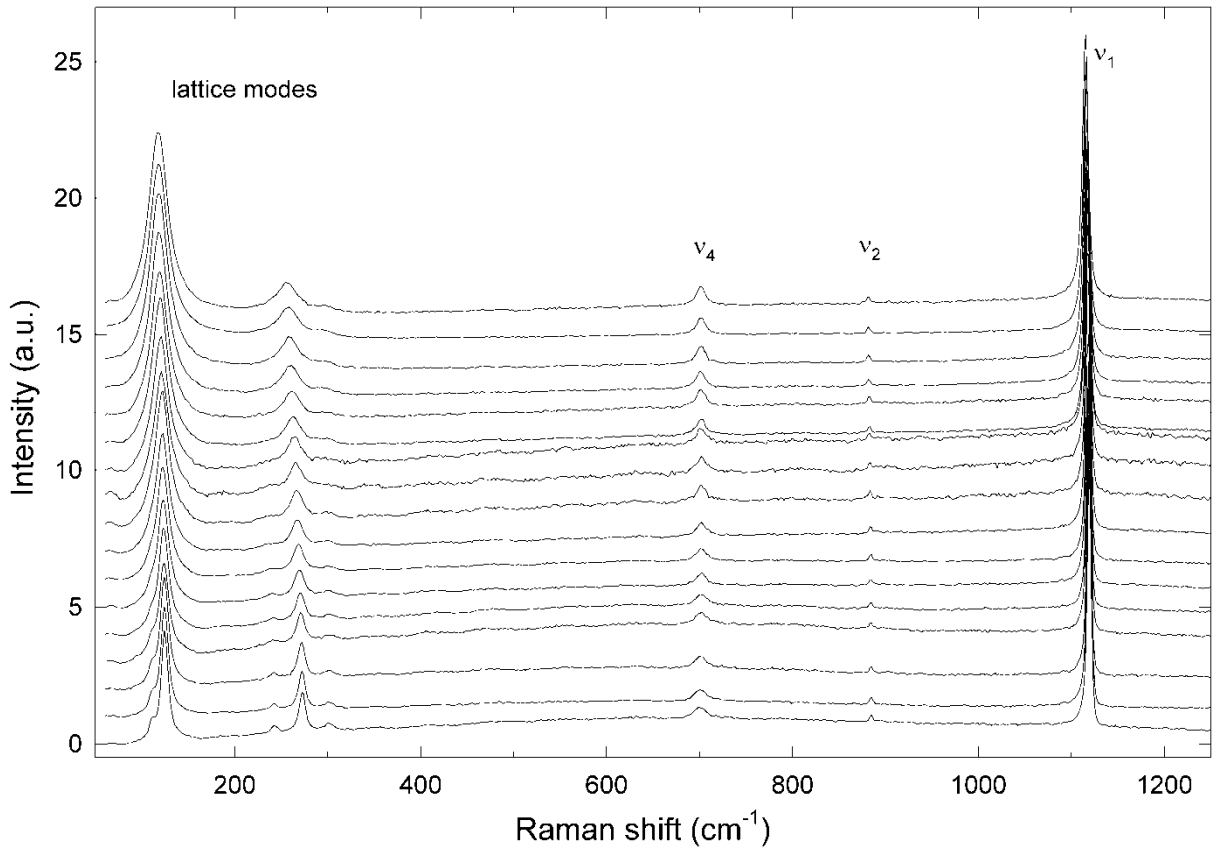

Fig. 1. *Raman spectra of norsethite (offset) from -191 °C (bottom) to 200 °C (top).*

Figure 1 shows the evolution of Raman spectra from low to high temperatures. The spectra appear identical at a first glance, and even closer inspection does not reveal a discontinuous evolution of bands, neither in position nor in band width. The same result is obtained from equivalent plots of IR spectra. Therefore, to reveal faint changes in spectral parameters with temperature, peak fitting techniques were applied (program PeakFit 4.01, Gauss-Lorentz functions, $R^2 > 0.99$ in most cases).

Whereas changes of band parameters, i.e. position and full width at half maximum (FWHM), were continuous or even linear in many cases, a number of bands showed a peculiar change close to 100 °C, which is definitely beyond any level of uncertainty. Figure 2 gives two examples of the non-linear evolution of band parameters with temperature.

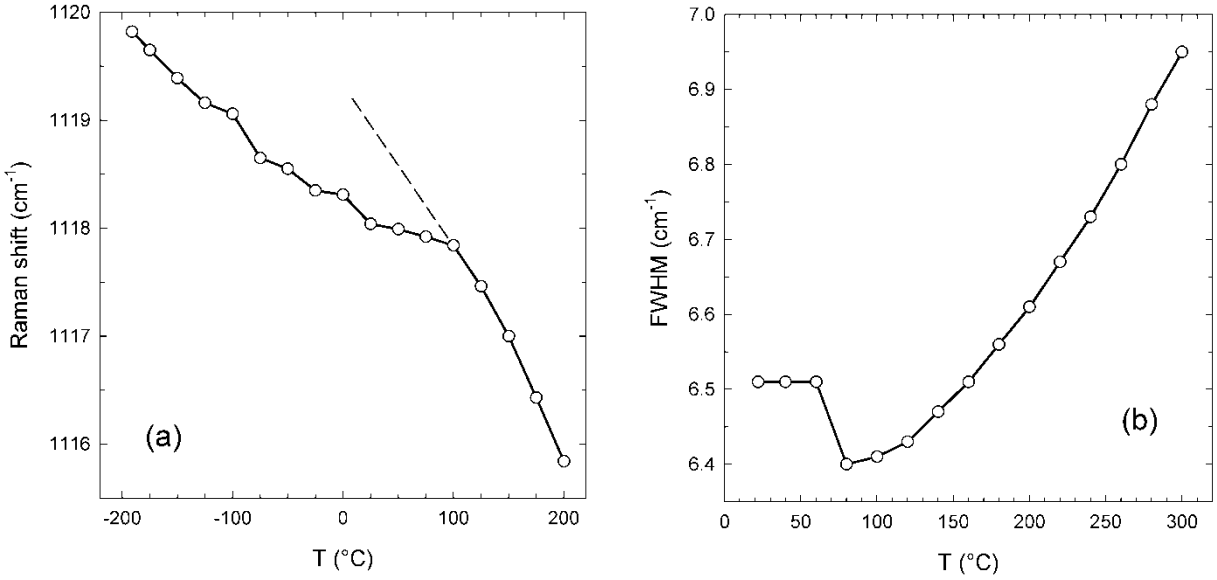

Fig. 2. *Non-linear evolution of spectral band parameters of norsethite with temperature. (**a**) Position of the CO_3 symmetric stretching mode ν_1 at ~1120 cm^{-1} in Raman spectra. (**b**) FWHM of the CO_3 out-of-plane bending mode ν_2 at ~880 cm^{-1} in IR spectra.*

Even though the Raman band positions in Fig. 2a are not perfectly smooth at low temperatures, the principal change of the trend at ~ 100 °C is beyond any doubt. The FWHM values of the 880 cm^{-1} IR band in Fig. 2b show an even more dramatic change at ~ 80 °C. The slightly different temperatures may be related e.g. to a different sample treatment (single-crystal vs. KBr powder pellet). Although the observed changes are mostly faint in terms of absolute values, the non-linear evolution of parameters indicates a phase transition in norsethite. Single-crystal X-ray diffraction experiments at different temperatures are in progress to reveal the mechanism of the structural changes.

References:

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