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An infrared investigation of the otavite–magnesite solid solution

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ABSTRACT

The local mixing and ordering behavior of the otavite-magnesite solid solution has been characterized using infrared powder absorption spectroscopy in the spectral region 50–2000 cm^{-1} at room temperature. Lattice modes due to Cd translations (75–200 cm^{-1}) and Mg translations (200–350 cm^{-1}) were both observed in the IR spectra for samples of intermediate composition. Peak positions of Cd translations remain constant as a function of composition, whereas those of Mg translations decrease in wavenumber with increasing otavite content. This suggests that the otavite-magnesite solid solution displays a combination of one-mode and two-mode behavior, most likely due to the large difference in atomic weight between magnesium and cadmium. Vibrational bands relating to the CO_3^{2-} groups in the spectral region 600–900 cm^{-1} vary linearly as a function of composition and are not sensitive to the degree of order. The vibrational band at ~1400–1450 cm^{-1} also varies linearly with composition, but $R\bar{3}$ ordered samples show a marked increase in frequency compared to their $R\bar{3}c$ counterparts. Positive deviations from linearity are observed for the effective line width determined using the autocorrelation method (expressed in terms of Δcorr values) for both lattice modes and bending vibrations of the CO_3^{2-} molecular groups, whereas a linear variation as a function of composition of the Δcorr values of the CO_3^{2-} stretching mode is observed for the 800 °C solid solution. Only in the region 600–900 cm^{-1} is an effect of order observed as a reduction in Δcorr values with respect to the sample with $R\bar{3}c$ symmetry. The difference in Δcorr values between the ordered and disordered samples was used to determine the local order parameter, q, which is consistent with a tricritical order-disorder transition.

Keywords: IR spectroscopy, otavite-magnesite solid solution, autocorrelation, phase transition, carbonates.