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 CO³⁻ 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 R³ ordered samples show a marked increase in frequency compared to their R³c 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 CO³⁻ molecular groups, whereas a linear variation as a function of composition of the Δcorr values of the CO³⁻ 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 R³c 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.

INTRODUCTION

In the last few decades Raman and Infrared (IR) spectroscopy have been used successfully as a primary tool for investigating phase transitions. In particular, Hard Mode Infrared Spectroscopy (HMIS) utilizes phonon energies to determine the evolution of a structure as a function of temperature, pressure or composition (Salje 1992; Salje and Bismayer 1997; Salje et al. 2000; Boffa Ballaran and Carpenter 2003). Line widths of IR spectra have been observed to correlate with local strain fields present in high-symmetry phases. Such strains are reduced in the low-symmetry phase as a result of a phase transition and a subsequent decrease in the linewidth in the low-symmetry phase spectra is observed (Salje 1992; Salje and Bismayer 1997). Analogous changes in line width are also expected in spectra for samples for which the only variable is composition, if strain fields develop during the formation of the solid solution. This appears to be a valid assumption for silicates. Several mineral families have been investigated to date by means of HMIS, and the use of a systematic methodology to collect and analyze IR spectra allowed detailed study of the variation in line width due to cation substitution and ordering across different solid solutions (Atkinson et al. 1999; Boffa Ballaran et al. 1998, 1999, 2001b; Geiger and Grams 2003; Rodehorst et al. 2004; Tarantino et al. 2002; Tarantino et al. 2003). This methodology has also been applied successfully to the study of CaTiO₃-CaFeO₂.₅ and CaTiO₃-SrTiO₃ perovskites (Becerro et al. 2000; Meyer et al. 2002). In this study HMIS is used to quantify the local mixing behavior of a series of samples belonging to the otavite-magnesite solid solution. This join provides an excellent system to test if local strain heterogeneities play an important role in the solid solution formation of carbonates. Frequency shifts and variations in linewidth have been analyzed as a function of composition and degree of order and the results obtained have been compared with the macroscopic mixing and ordering behavior of the same samples, previously characterized by means of X-ray diffraction (Bromiley et al. 2007).

EXPERIMENTAL METHOD

A list of the samples used in this study is reported in Table 1. Synthesis conditions and sample characterization are reported in detail in Bromiley et al. (2007). Pellets were prepared with extreme care to ensure homogeneity of samples with matrix material. Run products were ground by hand for five minutes in an agate pestle and mortar under acetone. The powder to matrix ratio was determined by trial and error to determine the correct dilution for reproducible data. For KBr pellets this was 1 mg sample: 500 mg KBr (for a 200 mg pellet) and for polyethylene (PE) pellets 2.2 mg sample: 110 mg PE (for a 100 mg pellet). Two standard pellets, one of pure PE (100 mg) and one of pure KBr (200 mg) were also prepared. KBr pellets were kept in a drying oven to prevent water being absorbed before spectra were taken. Spectra were collected under vacuum at room temperature using a Bruker 113v FT-IR spectrometer. For the mid-infrared region (MIR, 400–4000 cm⁻¹) a Globar source was used with a KBr beamsplitter and a DTGS detector with a KBr window. For the KBr far-infrared region (FIR, 200–500 cm⁻¹) the Globar source was used with a Ge-coated 6 micrometer Mylar beamsplit-* E-mail: tiziana.boffa-ballaran@uni-bayreuth.de