American Mineralogist, Volume 92, pages 837–843, 2007

An infrared investigation of the otavite–magnesite solid solution

FIONA A. BROMILEY,[1] TIZIANA BOFFA BALLARAN,[1,]* AND MING ZHANG[2]

[1]Bayerisches Geoinstitut, Universitaet Bayreuth, 95440 Bayreuth, Germany
[2]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

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.

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 from 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, 2001a, 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 $CaTiO_3$-$CaFeO_{2.5}$ and $CaTiO_3$-$SrTiO_3$ 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 5 m each 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 beamsplitter and a DTGS detector with a polyethylene window. For the FIR (50–400 cm^{-1} measured using the PE pellets), a mercury lamp source was used with the Ge-coated 6 micrometer Mylar beamsplit-

---

* E-mail: tiziana.boffa-ballaran@uni-bayreuth.de

0003-004X/07/0506–837$05.00/DOI: 10.2138/am.2007.2317

TABLE 1. List of samples used for this study

Samples	X_{Mg}*	Space group
Sample synthesized at 500 °C and 1 GPa for 96 h		
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}$
Samples synthesized at 600 °C and 1 GPa for 3 h		
$CdCO_3$	0.0	$R\bar{3}c$
$Mg_{0.1}Cd_{0.9}CO_3$	0.1	$R\bar{3}c$
$Mg_{0.2}Cd_{0.8}CO_3$	0.2	$R\bar{3}c$
$Mg_{0.3}Cd_{0.7}CO_3$	0.3	$R\bar{3}c$
$Mg_{0.4}Cd_{0.6}CO_3$	0.4	$R\bar{3}$
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}$
$Mg_{0.6}Cd_{0.4}CO_3$	0.6	$R\bar{3}$
$Mg_{0.9}Cd_{0.1}CO_3$	0.9	$R\bar{3}$
$MgCO_3$	1.0	$R\bar{3}$
Samples synthesized at 600 °C and 1 GPa for 19 h		
$Mg_{0.4}Cd_{0.6}CO_3$	0.4	$R\bar{3}$
$Mg_{0.45}Cd_{0.55}CO_3$	0.45	$R\bar{3}$
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}$
$Mg_{0.55}Cd_{0.45}CO_3$	0.55	$R\bar{3}$
$Mg_{0.6}Cd_{0.4}CO_3$	0.6	$R\bar{3}$
Sample synthesized at 600 °C and 1 GPa for 96 h		
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}$
Sample synthesized at 650 °C and 1 GPa for 120 h		
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}$
Samples synthesized at 800 °C and 1 GPa for 1 h		
$CdCO_3$	0.0	$R\bar{3}c$
$Mg_{0.1}Cd_{0.9}CO_3$	0.1	$R\bar{3}c$
$Mg_{0.2}Cd_{0.8}CO_3$	0.2	$R\bar{3}c$
$Mg_{0.3}Cd_{0.7}CO_3$	0.3	$R\bar{3}c$
$Mg_{0.4}Cd_{0.6}CO_3$	0.4	$R\bar{3}c$
$Mg_{0.5}Cd_{0.5}CO_3$	0.5	$R\bar{3}c$
$Mg_{0.6}Cd_{0.4}CO_3$	0.6	$R\bar{3}c$
$Mg_{0.7}Cd_{0.3}CO_3$	0.7	$R\bar{3}c$
$Mg_{0.8}Cd_{0.2}CO_3$	0.8	$R\bar{3}c$
$Mg_{0.9}Cd_{0.1}CO_3$	0.9	$R\bar{3}c$
$MgCO_3$	1.0	$R\bar{3}c$

* Nominal compositions.

ter and DTGS detector with polyethylene window. All measurements taken were averaged over 512 scans with an instrumental resolution of 2 cm^{-1}.

RESULTS

IR powder-absorption spectra

From factor group analysis (White 1974, and reference therein), end-member carbonate minerals with $R\bar{3}c$ symmetry are expected to show 8 IR-active modes, of which three are internal modes of the CO_3^{2-} group, and five are produced from the vibrations of the CO_3^{2-} group interacting with the cations (low frequency lattice modes are also defined as translations of the M cations). Cation ordering in dolomite-type structures and consequent lowering of the symmetry to $R\bar{3}$ leads to modification of the selection rules, so that 10 IR-active modes are permitted: one extra internal mode and one extra lattice mode with respect to the $R\bar{3}c$ structure.

The merged IR spectra of the series of samples synthesized at 800 °C across the solid solution are shown in Figure 1. All eight IR-active modes are present in the IR spectra of the magnesite and otavite end-members. Due to the large separation between the transverse and longitudinal components of the lattice modes, the low energy absorption peaks of these spectra appear as broad bands. The CO_3^{2-} stretching mode (ν_3) at ~1450 cm^{-1} also exhibits a substantial separation which is responsible for the strong broad band usually observed in the IR powder-absorption spectra of carbonates (White 1974). Substantial changes are visible in the lowest wavenumber region as Cd/Mg substitution occurs, whereas only peak shifting is observed for the internal modes of the CO_3^{2-} group.

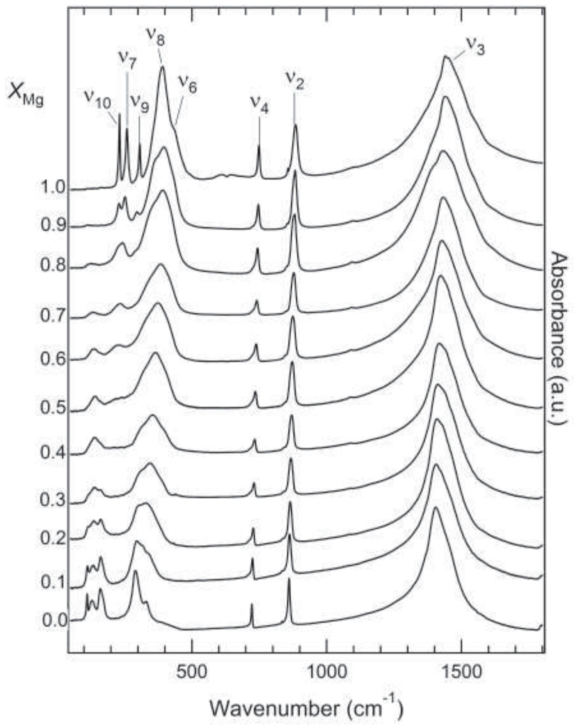

FIGURE 1. Stacked and merged IR powder-absorption spectra collected at room temperature for all samples synthesized at 800 °C and 1 GPa for 1 h. The nomenclature of the eight IR-active modes of the carbonate end-members is taken from White (1974).

IR spectra of samples of composition $Mg_{0.5}Cd_{0.5}CO_3$ with varying degree of order are shown in Figure 2. No major changes appear to be associated with the $R\bar{3} \rightarrow R\bar{3}c$ phase transition. As pointed out by White (1974) the additional IR-active modes of the ordered structure are difficult to measure experimentally and powder IR spectra of ordered and disordered Cd-dolomites appear identical. A detailed analysis of the unmerged spectra is, therefore, required to quantify the small changes in peak position and linewidth due to cation ordering.

Wavenumber shift

The wavenumber variation of the absorption bands in the spectral region 700–1700 cm^{-1} has been obtained using a computer routine (the "Find Peak" routine in the Igor Pro 4.09A software) that identifies peak maxima by analyzing the first and second derivatives of the absorption signals. The peak position of the highest energy absorption band falls somewhere between the transverse and longitudinal frequencies of the ν_3 IR-active mode, and it is not, therefore, an accurate measure of either (Axe and Petit 1966). However, the aim of this paper is to quantify the effect of cation substitution and order on the peak positions and line widths of IR spectra, hence, only relative changes with respect to the end-members are of interest. The wavenumber shifts of the internal modes of the CO_3^{2-} groups (in the range 600–1700 cm^{-1}) are shown in Figures 3a, 3b, and 3c as a function of composition. The shift in band frequency of the vibrational

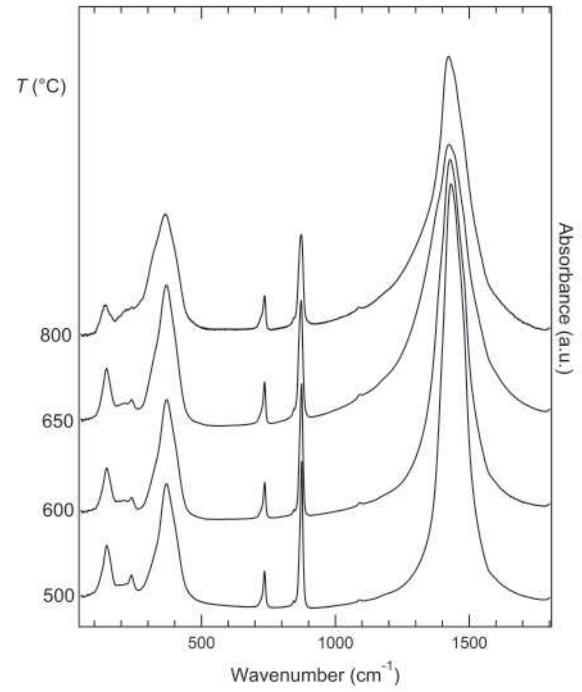

FIGURE 2. Stacked and merged IR spectra for samples of composition $Mg_{0.5}Cd_{0.5}CO_3$ (Cd-dolomite) synthesized at different temperatures. The sample synthesized at 800 °C is completely disordered. All other samples have $R\bar{3}$ symmetry and show some degree of order.

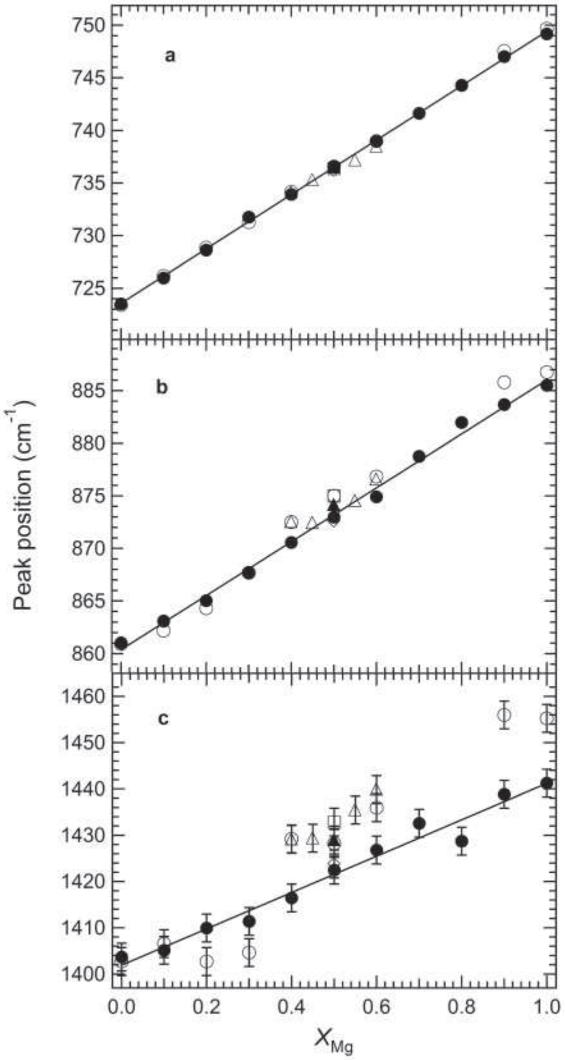

FIGURE 3. Wavenumber shifts as a function of composition of the CO_3^{2-} internal modes. (**a**) ν_4; (**b**) ν_2; (**c**) ν_3. (Note that for the ν_3 band the uncertainties of the peak position are very large). Nomenclature is from White (1974). Symbols: solid circles = 800 °C series; open circles = 600 °C 3 h series; open triangles = 600 °C 19 h series; filled triangles = 600 °C 96 h sample; open square = 500 °C sample; open diamond = 650 °C sample. The solid lines are linear fits through the sets of data from the 800 °C series, given by $\nu_4 = 723.6(1) + 25.8(2)X_{Mg}$; $\nu_2 = 860.4(3) + 25.6(6)X_{Mg}$; and $\nu_3 = 1402(2) + 39(2)X_{Mg}$.

modes ν_2 and ν_4, is linear as a function of composition and does not depend on the degree of order of the Cd-dolomite samples (Figs. 3a and 3b). The vibrational mode ν_3 of the disordered $R\bar{3}c$ carbonates synthesized at 800 °C also shows a linear dependence on composition, however, the samples within the Cd-dolomite stability field ($Mg_{0.4}Cd_{0.6}CO_3$–$Mg_{0.6}Cd_{0.4}CO_3$, $R\bar{3}$ symmetry) appear to have higher band frequencies than their $R\bar{3}c$ counterparts (Fig. 3c), although the uncertainties on these peak positions are quite large due to the broadness of the band. The magnesite and $Mg_{0.9}Cd_{0.1}CO_3$ samples synthesized at 600 °C also show higher band frequency positions with respect to the samples of the same composition synthesized at 800 °C; however, these two samples contain a small amount of brucite (Bromiley et al. 2007) which may affect the results.

The behavior of a solid solution, as observed from IR spectra, can be described in terms of one-mode or two-mode (Hofmeister et al. 1996, and references therein). One-mode behavior may be thought of as continuous shift of the phonon bands of the IR spectra from one end-member to the other. In the case of two-mode behavior, the spectrum of a sample of intermediate composition should be similar to the superposition of the IR spectra of the two end-members. The lattice vibrations ν_6 and ν_8 are due to translational motions of the cations and the CO_3^{2-} groups (White 1974), and appear as a broad absorption band in the spectral range 290–450 cm^{-1} (Fig. 1). The two IR-modes are clearly visible in the end-members spectra (Fig. 1), but the broad band in the spectra of sample of intermediate composition appears to consist of more than two vibrational peaks. This suggests that the otavite–magnesite solid solution exhibits two-mode behavior. As a result, fitting this absorption band is an arbitrary procedure, and hence, peak shift as a function of composition has not been quantified. Two-mode behavior is also observed for the other low energy lattice modes. The IR spectra collected for the 800 °C series in the spectral region 50–340 cm^{-1} are shown in Figure 4. The three lowest energy vibrations (ν_{10}, ν_7, and ν_9) can be assigned to Cd translations and librational motions of the CO_3^{2-} molecule in the region 75–200 cm^{-1} (IR spectrum of otavite) and to Mg translations and librational motions of the CO_3^{2-} molecule in the region 200–350 cm^{-1} (IR spectrum of magnesite) (White 1974). The relative absorbance of these bands changes drastically when one cation is substituted for the other in the solid solution. However, two broad bands, one between 75 and 200 cm^{-1} and the other between 200 and 350 cm^{-1}, are present in the IR spectra of samples of intermediate compositions. These low energy vibrations were analyzed by fitting Lorentzian profiles (Salje and Bismayer 1997) in the attempt to resolve the overlapping peaks. The fits for the end-member spectra are shown in Figures 5a and 5b. To obtain a reasonable fit, four and three Lorentzian profiles have been used for the absorption signals of Cd and Mg translations respectively. The resulting peak positions are shown in Figure 6 as a function of composition for the 800 °C series. The vibrational bands of samples at intermediate compositions are poorly resolved, thus the fitting procedure only gives reliable results up to 30% of one end-member into the other. The energy of the Cd translational modes appears to be almost constant across the solid solution, whereas that of the Mg translational modes is more sensitive to cadmium substitution into the magnesite structure.

Autocorrelation analysis

The autocorrelation function (Salje et al. 2000) has been used to quantify the variation of the effective line width of phonon bands in a given spectral range following a procedure described in previous work (Boffa Ballaran et al. 2001a; Tarantino et al. 2003; Rodehorst et al. 2004; and references therein).

Four different regions were considered for each carbonate IR spectrum; 75–275 cm^{-1}, 275–500 cm^{-1}, 600–900 cm^{-1}, and 1000–1700 cm^{-1}. A linear baseline was subtracted from the recorded absorptions for each region. The boundary at 275 cm^{-1} was chosen for the two lowest energy regions to characterize the response of the Cd and Mg translations and librational motions of the CO_3^{2-} molecules separately from that of the cooperative translations of the cations and the CO_3^{2-} groups between 275 and 500 cm^{-1}. A boundary at 275 cm^{-1} lies between ν_7 and ν_9 in the IR spectra of Mg-rich carbonates, and may, as a first approximation, be considered a background point. Autocorrelation analysis of the whole spectral region (75–500 cm^{-1}), performed on merged IR spectra from both the PE and KBr FIR regions, gives rise to similar results overall. The Δcorr data over the whole region are more scattered, however, but this is most likely due to aberration arising from the merging procedure.

The Δcorr values obtained for all samples are plotted as a function of composition in Figures 7 and 8. The data for the 800 °C series shows a positive deviation from linearity for all spectral regions investigated, except for the one relating to the stretching mode of the CO_3^{2-} groups (Fig. 8b). The curves drawn through the data of the 800 °C series in Figures 7–8 are obtained using an equation similar to the asymmetric expression for the excess properties of subregular solid solution models (Putnis 1992):

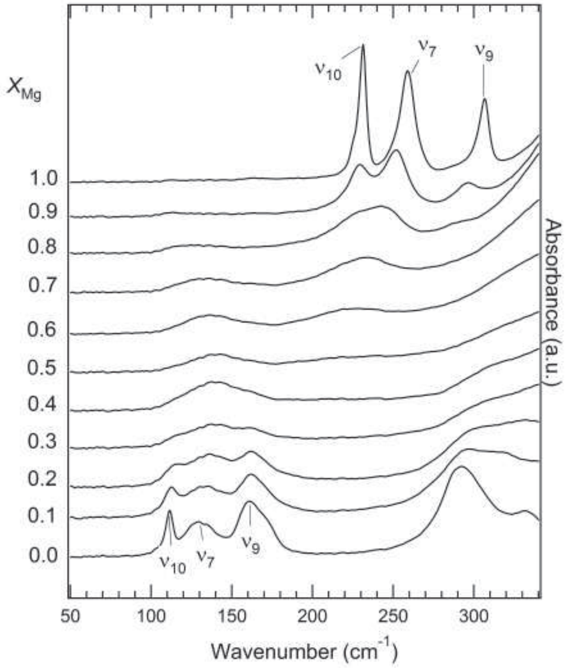

FIGURE 4. Detailed section of the IR spectra for the 800 °C series of samples in the region 50–340 cm^{-1}.

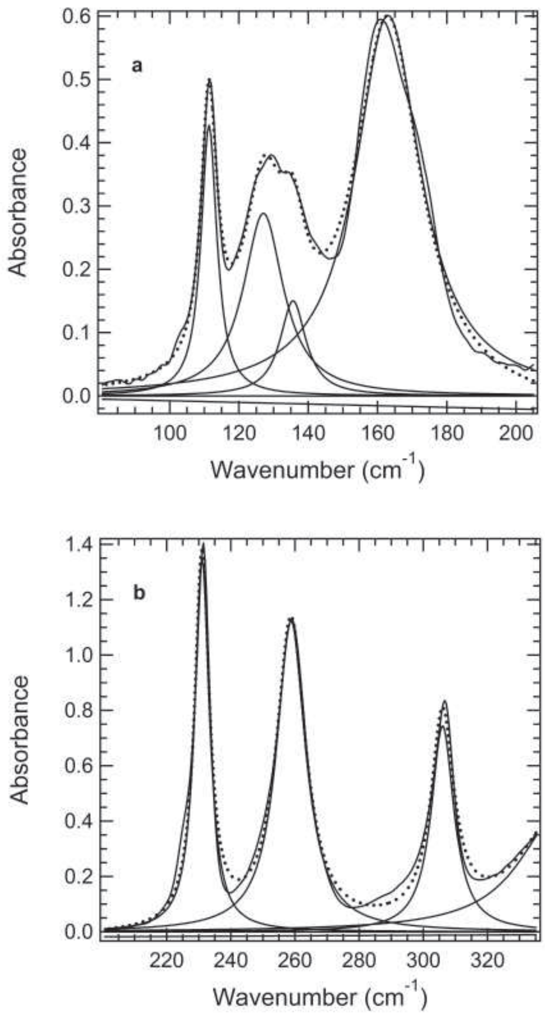

FIGURE 5. Example of Lorentzian fit for the three lowest energy bands of (**a**) otavite end-member and (**b**) magnesite end-member. To obtain a reasonable fit of the observed IR absorbances, four and three Lorentzian profiles have been used for the otavite and the magnesite vibrational bands respectively. Dashed lines show the results of the fitting procedures.

$$\Delta\text{corr} = a_1 + a_2X_{\text{Mg}} + X_{\text{Mg}}X_{\text{Cd}}\,[a_3X_{\text{Cd}} + a_4X_{\text{Mg}}] \qquad (1)$$

where X is the composition expressed as a mole fraction.

The different degree of order of the Cd-dolomite samples has a very small and scattered effect on the linewidth of the vibrational bands at low wavenumbers (Fig. 7), whereas in the region 600–900 cm^{-1} (Fig. 8a) a clearer decrease in bandwidth is observed as a function of the degree of order, at least for the $Cd_{0.5}Mg_{0.5}CO_3$ samples. In the same region (600–900 cm^{-1}), the magnesite sample and sample of composition $Mg_{0.9}Cd_{0.1}CO_3$ synthesized at 600 °C have much smaller Δcorr values than samples of the same composition synthesized at 800 °C. However, these two run products contained a very small amount of brucite (Bromiley et al. 2007), which might have affected the Δcorr values.

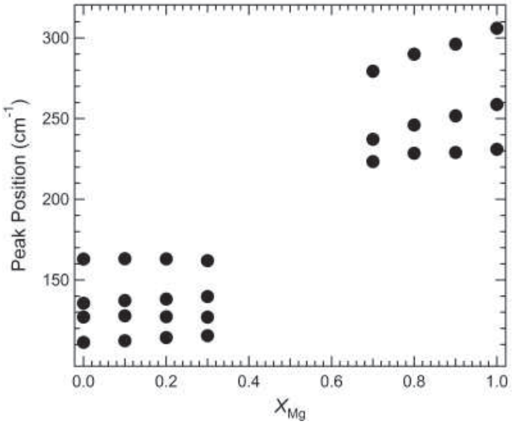

FIGURE 6. Wavenumber shift as a function of composition of the vibrational bands (Cd and Mg translations and librational motions of the CO_3^{2-} molecule) in the region 100–320 cm^{-1} for samples synthesized at 800 °C.

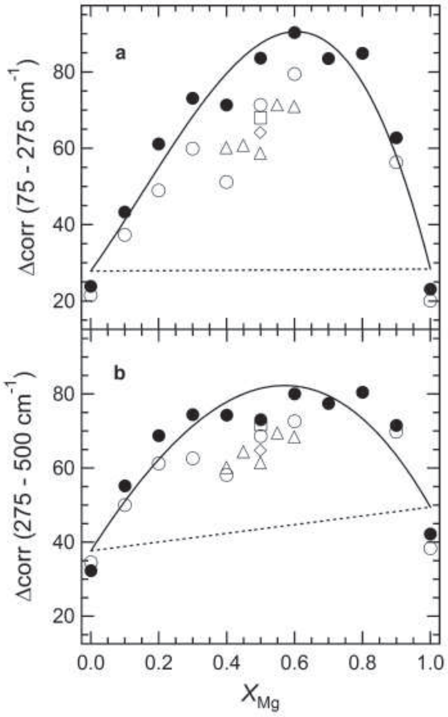

FIGURE 7. Variation, as a function of composition, of the Δcorr values obtained for the IR lattice modes of the otavite-magnesite system (**a**) in the region 75–275 cm^{-1}; and (**b**) in the region 275–500 cm^{-1}. The solid curves are the fits through the data of the 800 °C series according to Equation 1: (**a**) $\Delta\text{corr} = 28(6) + 0(8)X_{\text{Mg}} + X_{\text{Mg}}X_{\text{Cd}}\,[124(4)X_{\text{Cd}} + 350(4)\,X_{\text{Mg}}]$; and (**b**) $\Delta\text{corr} = 38(6) + 12(9)X_{\text{Mg}} + X_{\text{Mg}}X_{\text{Cd}}\,[131(4)X_{\text{Cd}} + 172(4)\,X_{\text{Mg}}]$. Symbols as in Figure 3.

DISCUSSION

The response of the vibrations of the carbonate structure to cation substitution and ordering depends on the spectral region analyzed, with a clear distinction between the behavior of the CO_3^{2-} group internal modes and that of the low energy lattice modes.

Mechanism of solid solution formation

The variation of all vibrational modes of the recorded IR spectra as a function of composition is easy to follow across the otavite-magnesite solid solution, in contrast to the more complicated changes observed in the IR spectra of silicate systems (Boffa Ballaran and Carpenter 2003; Tarantino et al. 2002, 2003). This is most likely due to the rigidity of the CO_3^{2-} molecular groups, which remain almost unchanged across the solid solution. All peak positions analyzed are linear with composition for the 800 °C series (Figs. 3 and 6). Variation of the Δcorr values of the highest energy mode, ν_3, for the $R\overline{3}c$ carbonates synthesized at 800 °C is also linear as a function of composition (Fig. 8b),

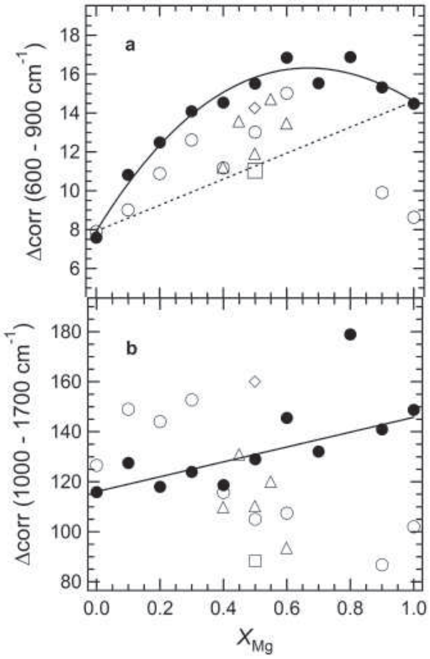

FIGURE 8. Variation, as a function of composition, of the Δcorr values obtained (**a**) for the bending modes of the CO_3^{2-} groups (region 600–900 cm^{-1}); and (**b**) for the stretching mode of the CO_3^{2-} groups (region 1000–1700 cm^{-1}). The solid curves are the fits through the 800 °C series according to Equation 1: (**a**) $\Delta\text{corr} = 7.9(5) + 6.7(8)X_{\text{Mg}} + X_{\text{Mg}}X_{\text{Cd}}\,[20(4)X_{\text{Cd}} + 17(4)\,X_{\text{Mg}}]$; and (**b**) $\Delta\text{corr} = 116(4) + 30(7)X_{\text{Mg}}$. Note that the Δcorr value for the $Cd_{0.2}Mg_{0.8}CO_3$ sample has not been taken into account for the linear fit of the Δcorr values in the region 1000–1700 cm^{-1}. Symbols as in Figure 3.

suggesting that for complete random substitution of cations, the individual CO_3^{2-} groups "see" a homogeneous environment. The data for the 600 °C series and for the ordered carbonates are quite scattered due, perhaps, to the broadness of this vibrational band. The autocorrelation method is, in fact, very sensitive to any small changes in the IR spectra, as may be seen for the $Cd_{0.2}Mg_{0.8}CO_3$ sample synthesized at 800 °C, which shows a small shoulder in the ν_3 mode (Fig. 1), and plots outside the linear trend defined by the other 800 °C samples (Fig. 8b). Non-linearity of the line broadening is observed for all other spectral regions analyzed. This is consistent with the presence of some heterogeneities in the $R\bar{3}c$ samples at intermediate compositions on a length scale of a few unit cells, and with some positive excess enthalpy of mixing for the disordered otavite–magnesite solid solution (Capobianco et al. 1987). The deviation from linearity of the Δcorr values is virtually symmetric for the ν_2, and ν_4 vibrational modes (out-of-plane and in-plane bending of the CO_3^{2-} groups), and asymmetric toward the magnesite end-member for the lattice modes in the spectral regions between 75 and 500 cm^{-1}. Studies of dilute, divalent cation substitution in calcite have shown that the strain, due to the size difference of the substituting atom, is highly localized (Reeder et al. 1999; Lee et al. 2002). However, for the otavite–magnesite system, line broadening of the vibrational bands in the lowest wavenumber region is already observed when 10 mol% of one end-member is substituted into the other (Fig. 7a). This is consistent with the presence of local structural heterogeneities and local strain fields, with dimensions exceeding the distance to neighboring octahedra and on the order of a few unit cells.

One of the main differences between the carbonate system investigated in this study and silicate systems described in previous studies (Boffa Ballaran and Carpenter 2003; Tarantino et al. 2002, 2003) is the behavior of the solid solution at low frequencies. Whereas the silicate systems show one-mode behavior, with a systematic shift in band frequency across the solid solution, the magnesite-otavite system displays a combination of both one- and two-mode behavior (Figs. 4 and 6). This is probably due to the difference in atomic weight between the magnesium and cadmium atoms. Since the difference in atomic weight between magnesium and calcium in the magnesite-calcite solid solution is smaller than that of cadmium and magnesium, an analogy between the mixing behavior of the otavite-magnesite and magnesite-calcite systems is not straightforward.

MECHANISM OF CATION ORDERING

Additional vibrational modes due to cation ordering are not visible in the IR powder-absorption spectra of $R\bar{3}$ carbonates (White 1974). However, some small changes due to the order-disorder phase transformation can be quantified in the existing bands of the Cd-dolomites IR spectra. It appears, therefore, that HMIS could be a useful tool for studying partially ordered dolomite found in sediments, contrary to previous suggestion (White 1974). Ordering of Cd/Mg onto different layers of the carbonate structure mainly affects the vibrational energy of the ν_3 vibrational mode at 1400–1450 cm^{-1} (Fig. 3c), and the line width of the bands in the 600–900 cm^{-1} spectral region (Fig. 8a). Ordering gives rise to an increase in the energy required for the asymmetric stretching of the CO_3^{2-} groups and reduces the broadening of the bending modes of the CO_3^{2-} groups. The differences in band positions (Δν) and in Δcorr values (δΔcorr) between $R\bar{3}$ and $R\bar{3}c$ $Cd_{0.5}Mg_{0.5}CO_3$ samples are linearly dependent and can be used as quantities proportional to the square of the local order parameter, *q* (Salje and Bismayer 1997). $\Delta\nu^2$ and $\delta\Delta corr^2$ scale linearly with temperature (Fig. 9), suggesting that the order–disorder phase transition displays tricritical behavior on a local scale. The transition temperatures obtained from the linear fits through the two sets of data are 656(20) and 684(10) °C, respectively. Given the scatter of the data and the uncertainties, these values of T_c are in agreement with the $T_c = 702 \pm 10$ °C obtained from the variation of the long range order parameter *Q* calculated from site occupancies (Bromiley et al. 2007).

Comparison with silicate solid solutions

Empirical correlations between the "excess" Δcorr and the enthalpy of mixing have been observed for silicate solid solutions (Boffa Ballaran and Carpenter 2003; Tarantino et al. 2002, 2003), with the assumption that the Landau expansion of the form $\Delta H = AQ^2 + BQ^4 + CQ^6 + \ldots$ can be approximated by $\Delta H \propto Q^2$.

Enthalpies of mixing and ordering have been obtained for $CdMg(CO_3)_2$ by Capobianco et al. (1987) from solution calorimetry. As none of our samples are completely ordered, a direct comparison between changes in Δcorr, due to cation ordering, and enthalpy of ordering is not straightforward. However we can scale the "excess" Δcorr, δΔcorr, taken as the deviation from linearity in the lowest wavenumber region for the disordered $CdMg(CO_3)_2$ 800 °C sample, with the enthalpy of mixing reported by Capobianco et al. (1987), normalized with respect to molar volume. We can then compare our results with those obtained for silicate solid solutions. As suggested by Tarantino et al. (2003) the different linear correlations observed for different solid solutions may depend on the size and charge difference of the exchanged cations, and on the capacity of the mineral structure to accommodate them. One may assume that elastically soft materials will relax more easily around substituting atoms, meaning there should be some correlation between the lo-

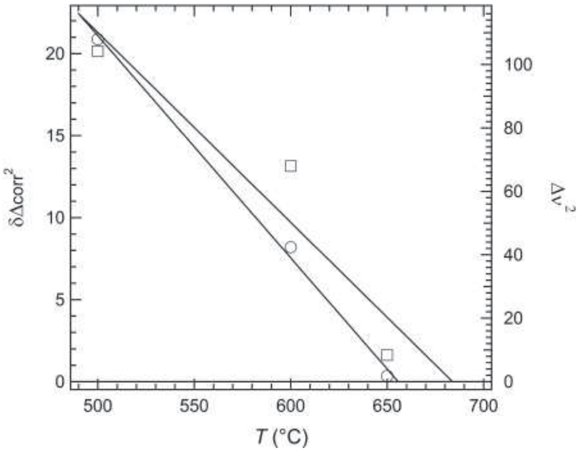

FIGURE 9. Variation of the square of the difference in peak position of ν_3 ($\Delta\nu^2$, right axis, open circles) and of the difference in Δcorr values ($\delta\Delta corr^2$, left axis, open squares) between ordered and disordered $Cd_{0.5}Mg_{0.5}CO_3$ samples as a function of the synthesis temperature. The solid lines are linear fits through the data: $\Delta\nu^2 = 459(43) - 0.7(1)T$ and $\delta\Delta corr^2 = 79(23) - 0.12(4)T$.

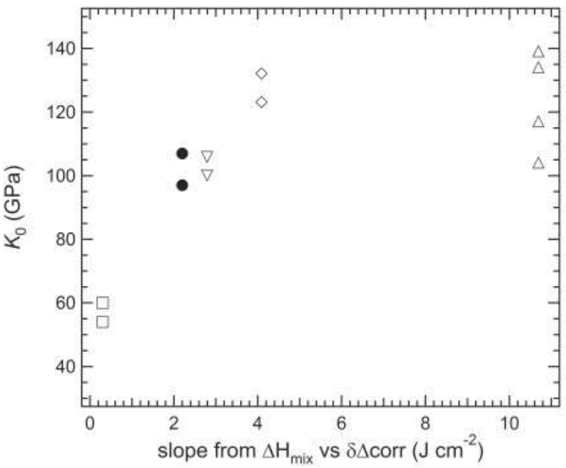

FIGURE 10. Qualitative correlation between the bulk moduli, K_0, and the slopes of the empirical calibrations between enthalpy of mixing and excess Δcorr for different solid solutions. Filled circles: carbonates; this study, K_0 of otavite and magnesite from Zhang and Reeder (1999); open squares: plagioclases Atkinson et al. (1999); Angel (2004); open inverted triangles: orthopyroxenes Tarantino et al. (2002), K_0 of orthoenstatite from Angel and Jackson (2002), and of orthoferrosilite from Hugh-Jones et al. (1997); open diamond: olivines Tarantino et al. (2003), K_0 of forsterite from Kudoh and Takeuchi (1985), and of fayalite from Kudoh and Takeda (1986); open triangles: augite-jadeite Boffa Ballaran et al. (1998), K_0 of omphacite from Pavese et al. (2001) and McCormick et al. (1989); of diopside from Zhang et al. (1997), and of jadeite from Nestola et al. (2006).

cal structural heterogeneities and the elastic properties of a given substance. In Figure 10 we show the correlation between the slope of the empirical calibration between ΔHmix and δΔcorr obtained for our samples and the bulk modulus, K_0 of otavite and magnesite (Zhang and Reeder 1999), compared with other silicate solid solutions (Tarantino et al. 2003). The carbonate data follow the trend defined by the silicate solid solutions. It appears therefore that the empirical correlations between line-broadening, excess enthalpy and elastic properties may hold also for carbonate structures, reinforcing the view that local elastic strain fields could be responsible for a substantial part of the excess enthalpy of mixing.

ACKNOWLEDGMENTS

This work has been financed by the Sofja Kovalevskaja Award to Tiziana Boffa Ballaran. Friedrich Seifert is thanked for his help with the preparation of the manuscript. The authors also thank J. Zemann and an anonymous referee for reviewing the manuscript.

REFERENCES CITED

Angel, R.J. (2004) Equation of state of plagioclase feldspars. Contribution to Mineralogy and Petrology, 146, 506–512.

Angel, R.J. and Jackson, J.M. (2002) Elasticity and equation of state of orthoenstatite, $MgSiO_3$. American Mineralogist, 87, 558–561.

Atkinson, A.J., Carpenter, M.A., and Salje, E.K.H. (1999) Hard mode infrared spectroscopy of plagioclase feldspars. European Journal of Mineralogy, 11, 7–21.

Axe, J.D. and Petit, G.D. (1966) Infrared dielectric dispersion and lattice dynamics of uranium dioxide and thorium dioxide. Physics Reviews, 151, 676–680.

Becerro, A.I., Carpenter, M.A., Boffa Ballaran, T., and Seifert, F. (2000) Hard mode infrared spectroscopy of $CaTiO_3$–$CaFeO_{2.5}$ perovskite. Phase Transitions, 71, 161–172.

Boffa Ballaran, T. and Carpenter, M.A. (2003) Line broadening and enthalpy: Some empirical calibrations of solid solution behaviour from IR spectra. Phase Transitions, 76, 137–154.

Boffa Ballaran, T., Carpenter, M.A., Domeneghetti, M.C., Salje, E.K.H., and Tazzoli, V. (1998) Structural mechanisms of solid solution and cation ordering in augite-jadeite pyroxenes: II. A microscopic perspective. American Mineralogist, 83, 434–443.

Boffa Ballaran, T., Carpenter, M.A., Geiger, C.A., and Koziol, A.M. (1999) Local structural heterogeneity in garnet solid solutions. Physics and Chemistry of Minerals, 26, 554–569.

Boffa Ballaran, T., Carpenter, M.A., and Domeneghetti, M.C. (2001a) Phase transition and mixing behaviour of the cummingtonite–grunerite solid solution. Physics and Chemistry of Minerals, 28, 87–101.

Boffa Ballaran, T., Carpenter, M.A., and Ross, N.L. (2001b) Infrared powder-absorption spectroscopy of Ca-free $P2_1/c$ clinopyroxenes. Mineralogical Magazine, 65, 339–350.

Bromiley, F.A., Boffa Ballaran, T., Langhnhorst, F., and Seifert, F. (2007) Order and miscibility in the otavite–magnesite solid solution. American Mineralogist, 92, 829–836.

Capobianco, C., Burton, B.P., Davidson, P.M., and Navrotsky, A. (1987) Structural and calorimetric studies of order-disorder in $CdMg(CO_3)_2$. Journal of Solid State Chemistry, 71, 214–223.

Geiger, C.A. and Grams, M. (2003) Cordierite IV: structural heterogeneity and energetics of Mg-Fe solid solutions. Contribution to Mineralogy and Petrology, 145, 752–764.

Hofmeister, A.M., Fagan, T.J., Campbell, K.M., and Schaal, R.B. (1996) Single-crystal IR spectroscopy of pyrope-almandine garnets with minor amounts of Mn and Ca. American Mineralogist, 81, 418–428.

Hugh-Jones, D.A., Chopelas, A., and Angel, R.J. (1997) Tetrahedral compression in (Mg,Fe)SiO_3 orthopyroxenes. Physics and Chemistry of Minerals, 24, 301–310.

Kudoh, Y. and Takeda, H. (1986) Single-crystal X-ray diffraction study on the bond compressibility of fayalite, Fe_2SiO_4 and rutile, TiO_2 under high pressure. Physica, 139 and 140B, 333–336.

Kudoh, Y. and Takeuchi, T. (1985) The crystal structure of forsterite Mg_2SiO_4 under high pressure up to 149 kbar. Zeitschrift für Kristallographie, 117, 292–302.

Lee, Y.J., Reeder, R.J., Wenskus, R.W., and Elzinga, E.J. (2002) Structural relaxation in the $MnCO_3$–$CaCO_3$ solid solution: a Mn *K*-edge EXAFS study. Physics and Chemistry of Minerals, 29, 585–594.

McCormick, T.C., Hazen, R.M., and Angel, R.J. (1989) Compressibility of omphacite to 60 kbar: role of vacancies. American Mineralogist, 74, 1287–1292.

Meyer, H.-W., Carpenter, M.A., Becerro, A.I., and Seifert, F. (2002) Hard-mode infrared spectroscopy of perovskites across the $CaTiO_3$–$SrTiO_3$ solid solution. American Mineralogist, 87, 1291–1296.

Nestola, F., Boffa Ballaran, T., Liebske, C., Bruno, M., and Tribaudino, M. (2006) High-pressure behaviour along the jadeite $NaAlSi_2O_6$–aegirine $NaFeSi_2O_6$ solid solution up to 10 GPa. Physics and Chemistry of Minerals, 33, 417–425.

Pavese, A., Diella, V., Levy, D., and Hanfland, M. (2001) Synchrotron X-ray powder diffraction study of natural P2/n-omphacite at high-pressure conditions. Physics and Chemistry of Minerals, 28, 9–16.

Putnis, A. (1992) Introduction to Mineral Sciences. Cambridge University Press, U.K.

Reeder, R.J., Lamble, G.M., and Northrup, P.A. (1999) XAFS study of the coordination and local relaxation around Co^{2+}, Zn^{2+}, Pb^{2+}, and Ba^{2+} trace elements in calcite. American Mineralogist, 84, 1049–1060.

Rodehorst, U., Carpenter, M.A., Boffa Ballaran, T., and Geiger, C.A. (2004) Local structural heterogeneity, mixing behaviour and saturation effects in the grossular–spessartine solid solution. Physics and Chemistry of Minerals, 31, 387–404.

Salje, E.K.H. (1992) Hard mode spectroscopy: Experimental studies of structural phase transitions. Phase Transitions, 37, 83–110.

Salje, E.K.H. and Bismayer, U. (1997) Hard mode spectroscopy: The concept and applications. Phase Transitions, 63, 1–75.

Salje, E.K.H., Carpenter, M.A., Malcherek, T.G.W., and Boffa Ballaran, T. (2000) Autcorrelation analysis of infrared spectra. European Journal of Mineralogy, 12, 503–519.

Tarantino, S.C., Boffa Ballaran, T., Carpenter, M.A., Domeneghetti, M.C., and Tazzoli, V. (2002) Mixing properties of the enstatite-ferrosilite solid solution: II. A microscopic perspective. European Journal of Mineralogy, 14, 537–547.

Tarantino, S.C., Carpenter, M.A., and Domeneghetti, M.C. (2003) Strain and local heterogeneity in the forsterite–fayalite solid solutin. Physics and Chemistry of Minerals, 30, 495–502.

White, W.B. (1974) The carbonate minerals. In V.C. Farmer, Ed. The infrared spectra of minerals, Mineralogical Society, Monograph 4, p. 227–284.

Zhang, J. and Reeder, R.J. (1999) Comparative compressibilities of calcic-structure carbonates: Deviations from empirical relations. American Mineralogist, 84, 861–870.

Zhang, L., Ahsbahs, H., Hafner, S.S., and Kutoglu, A. (1997) Single-crystal compression and crystal structure of clinopyroxene up to 10 GPa. American Mineralogist, 82, 245–258.

MANUSCRIPT RECEIVED MAY 19, 2006
MANUSCRIPT ACCEPTED DECEMBER 22, 2006
MANUSCRIPT HANDLED BY EUGEN LIBOWITZKY