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LETTER

A high-pressure phase transition of calcite-III

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ABSTRACT

We document the presence of a high pressure phase transition in metastable calcite-III using infrared spectroscopy. The post-calcite-III transition initiates at a pressure of 15.5 (±2) GPa, and is completed between 25 and 30 GPa. The transition is particularly apparent in the ν_4-in-plane bending vibration of the carbonate group, in which two new peaks progressively supplant the doublet associated with calcite-III. Additionally, both the ν_3-asymmetric and ν_1-symmetric stretches of the carbonate group in the high-pressure phase occur at substantially lower frequencies than the extrapolated positions of the corresponding calcite-III peaks. The geometry of the carbonate unit within the high-pressure phase is likely closer to trigonal symmetry than in the calcite-III structure, and the C-O bond is probably longer than in the lower pressure calcite-III phase.

INTRODUCTION

The behavior of metastable high-pressure polymorphs of calcite has been a topic of interest since the pioneering work of Bridgman (1939). Although the transition sequence between calcite, calcite-II, and calcite-III has been well documented (Suito et al. 2001; Hess et al. 1991; Liu and Mernagh 1990; Merrill and Bassett 1975; Fong and Nicol 1971; Davis 1964), these transitions occur at pressures below 2.5 GPa, and the stability of calcite-III to high pressures has been controversial. X-ray and Raman results of Suito et al. (2001) demonstrate that calcite-III is metastable to at least 10 GPa at 300K, while Fiquet et al. (1994) reported that calcite-III X-ray reflections were "replaced above 8 GPa by broader peaks," and interpreted these changes as progressive transformations of calcite-III. For comparison, Williams et al. (1992) observed no change in the number of bands in the mid-infrared spectrum of calcite-III to pressures of 32 GPa. To provide additional constraints on the high-pressure metastable polymorphism of calcite, we have measured the infrared spectrum of calcite to pressures of 52 GPa, with considerably smaller pressure steps than the prior infrared study (Williams et al. 1992). We document a shift in bonding characteristics of the calcite-III lattice that initiates at 15.5 (±2) GPa: the change is manifested primarily by the appearance of two new peaks in the ν_4-in-plane bending region that progressively supplant the two in-plane bending bands associated with calcite-III. The number of peaks appears unchanged across the high-pressure transition. Furthermore, we observe the possible onset of a Fermi resonance between the ν_4-in-plane bending vibration and the ν_2-out-of-plane bend at the higher pressures of our measurements.

EXPERIMENTAL TECHNIQUE

Pure $CaCO_3$-calcite (99 + %) was obtained from the Aldrich Chemical Company, Inc., and powdered with KBr and Pt in a 50% calcite, 48.5% KBr, to 1.5% Pt weight ratio in an agate mortar. KBr was chosen for this experiment to serve as both a pressure transmitting medium and an infrared window, and Pt was added for potential laser-heating of the sample (this was not conducted in the present study). The zero-pressure infrared spectrum of the calcite agrees excellently with prior determinations (White 1974).

Pressures in the sample were produced using a Mao-Bell Type diamond anvil cell equipped with 16-sided type IIa diamonds with 350 μm culets. A spring steel gasket was pre-indented by the diamonds and a 120 μm hole was drilled in the center to contain the sample. Ruby grains, ranging in size from 1–5 μm, were spread throughout the sample to measure the pressure during compression and decompression and to map out pressure gradients using the standard ruby fluorescence method (Piermarini et al. 1975). Three to five ruby grains were measured at each pressure. This method yields ± ~7% variation in pressure on compression above ~10 GPa and ±7–10% variation or distribution of pressure on decompression.

Infrared spectra were taken using a Bruker IFS-66V Fourier Transform Infrared (FTIR) Spectrometer equipped with a KBr beamsplitter, a globar mid-infrared source, and a liquid-N_2 cooled MCT detector with 4 cm^{-1} resolution mounted in an evacuated sample chamber. Spectra were taken in 2–5 GPa intervals on compression from 6.0 to 52 GPa.

RESULTS AND DISCUSSION

Compression

Infrared spectra on compression and decompression are shown in Figures 1a and 1b, with corresponding peak positions plotted in Figure 2. The infrared peak assignments associated with the calcite-III phase have been extensively discussed and are well-understood (Weir et al. 1959; Schock and Katz 1968; Cifrulak 1970; Adams and Williams 1980; Williams et al. 1992). The ν_3-asymmetric stretching bands near 1400 cm^{-1} have two well-resolved peaks, and possible shoulders at both high- and low-frequency, and the ν_1-symmetric stretch has a single component between 1100 and 1150 cm^{-1} throughout the pressure range of these measurements. The lower frequency region, between 600 and 900 cm^{-1}, shows more complicated behavior. While the ν_2-out-of-plane bend at ~870 cm^{-1} is essentially constant in frequency throughout these measurements, the ν_4-in-plane bending vibrations undergo a well-resolved change in character between 13.5 and 17.5 GPa. At pressures of 13.5 GPa and below, the in-plane bends are present as two distinct peaks separated by ~70 cm^{-1}. As pressure is increased, four peaks are clearly visible in this region of the spectrum (Figs. 3a and 3b),

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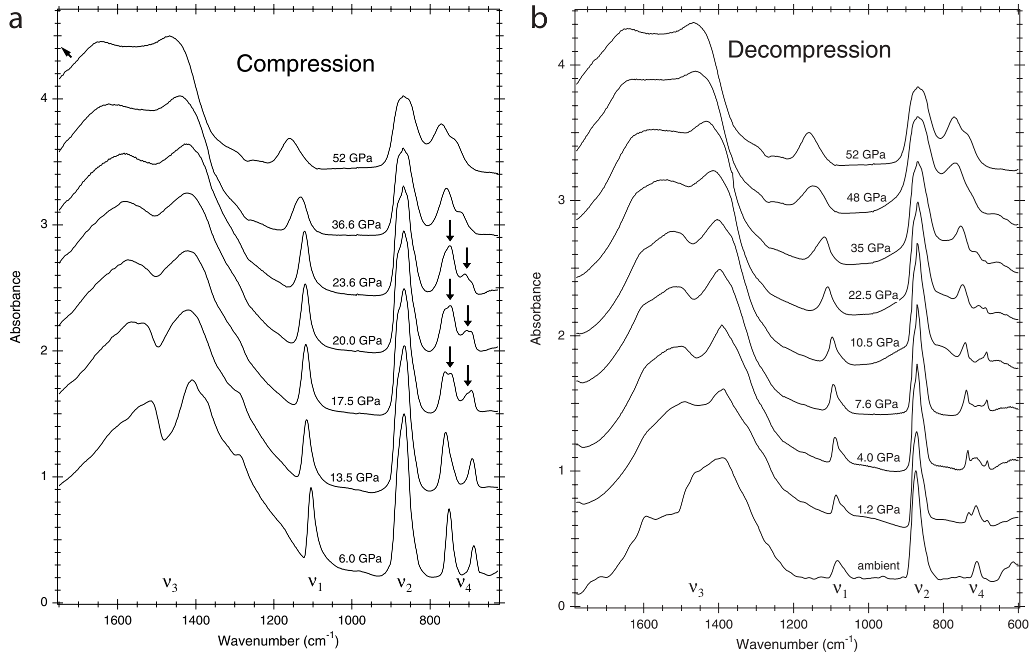

FIGURE 1. (**a**) Representative infrared spectra of $CaCO_3$ on compression. Arrows denote the appearance of new features that progressively grow in amplitude with pressure. Spectra are offset from one another. (**b**) Representative infrared spectra of $CaCO_3$ on decompression; the spectrum at ambient conditions is of a sample removed from the diamond anvil cell.

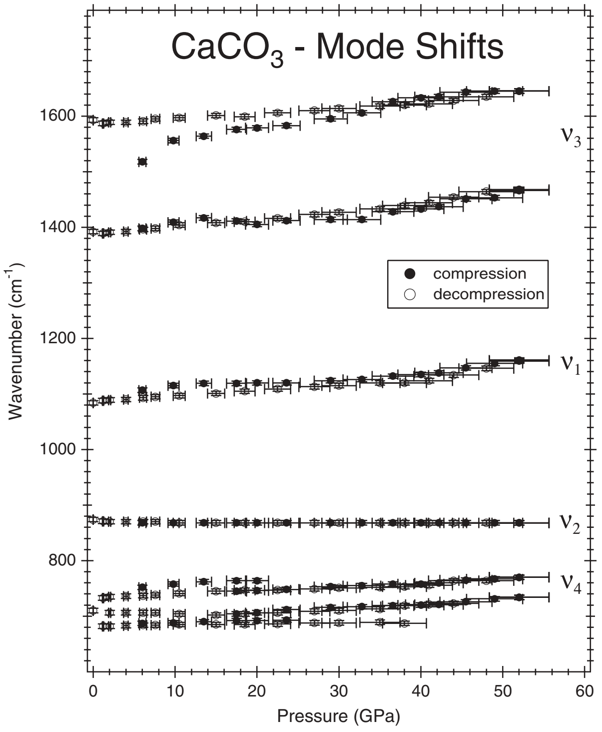

FIGURE 2. Mode shifts of $CaCO_3$ on both compression (closed symbols) and on decompression (open symbols).

with two additional components appearing in between the two lower pressure peaks. These new peaks increase in amplitude, and ultimately supplant the initial doublet: the components of the low pressure doublet progressively decrease in amplitude to pressures near 30 GPa, where only the two more narrowly split peaks are resolvable. The separation between these two new ν_4-in-plane bends is ~40 cm^{-1} (Fig. 3b). Accordingly, it appears that a structural rearrangement gradually occurs between 13.5 and 30 GPa, with the principal manifestation being a shift in the splitting of the ν_4-in-plane bend, indicative of a more trigonal carbonate group. This discrete structural rearrangement is responsible for the initial increase followed by an anomalous higher-pressure decrease in peak splittings between these bands reported by Williams et al. (1992).

More subtle manifestations of the phase transformation are evident in the mode shifts of ν_3 and ν_1 (Fig. 4). For example, both the principal ν_3-asymmetric and ν_1-symmetric stretches (with initial frequencies near 1400 cm^{-1} and 1100 cm^{-1}, respectively) have comparatively rapid shifts below 13.5 GPa, followed by near-zero mode shifts between 13.5 and 30 GPa, followed by a subsequent increase. We attribute these anomalous shifts in slope to the presence of a mixed-phase region between 13.5 and 30 GPa. In the high-pressure phase, the vibrational frequencies of the ν_3-asymmetric and the ν_1-symmetric stretches lie ~50 cm^{-1} and ~30 cm^{-1}, respectively, below the extrapolated peak positions of the low-pressure phase. In contrast, the higher frequency component of the ν_3-asymmetric stretching vibration, with an extrapolated zero pressure frequency near 1520 cm^{-1}, has an extrapolated position in the high-pressure phase that lies ~40 cm^{-1} above that of the corresponding peak in calcite-III. Whether this higher frequency asymmetric stretch is associated with the asymmetric stretch of a different carbonate site, or is instead the longitudinal optic (LO) component of the 1400 cm^{-1} band is unclear (Williams et al. 1992). For comparison, the ν_2-out-of-plane bending peak near 870 cm^{-1} has essentially a zero pressure shift, and no change in its location can be resolved due to this apparent phase transition: this vibration is notoriously insensitive to high pressure polymorphism in carbonates (Adams and Williams 1980; Kraft et al. 1991).

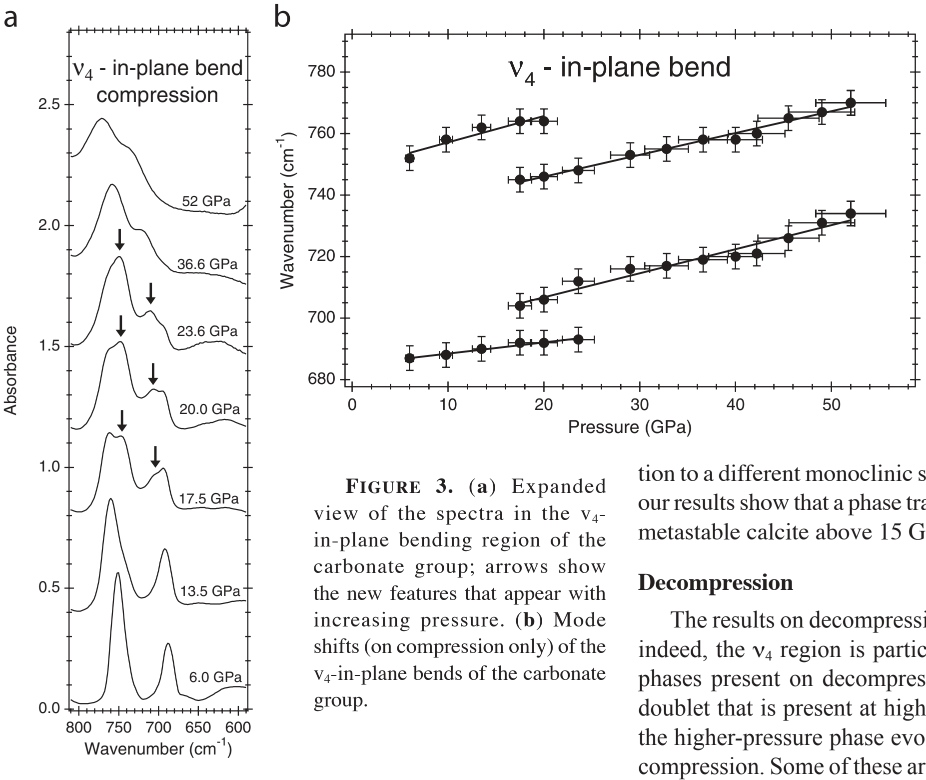

FIGURE 3. (**a**) Expanded view of the spectra in the ν_4-in-plane bending region of the carbonate group; arrows show the new features that appear with increasing pressure. (**b**) Mode shifts (on compression only) of the ν_4-in-plane bends of the carbonate group.

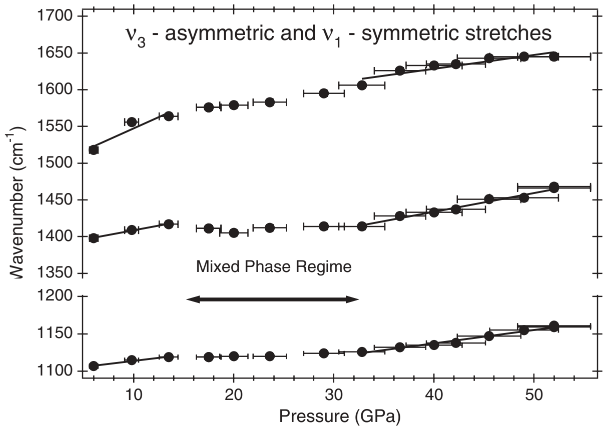

FIGURE 4. Expanded view of the mode shifts of the ν_3-asymmetric and ν_1-symmetric stretches of the carbonate group (on compression only)

The amplitude of the higher frequency peak of the ν_4-in-plane bending vibrations approaches that of the ν_2-out-of-plane bend at the highest pressures of these measurements. We attribute this effect to the onset of a probable Fermi resonance between these two peaks. Such Fermi resonances, in which two peaks of the same symmetry type approach one another and progressively take on each other's characteristics, have been previously proposed to occur within both carbonates and hydroxylated minerals (Duffy et al. 1995; Santillan and Williams 2004). In this instance, the progressive pressure-induced convergence (Fig. 2) between the ν_4-in-plane and ν_2-out-of-plane bends, coupled with the apparent relative increase in amplitude of the higher frequency of the two ν_4-in-plane bends, is entirely consistent with the onset of Fermi resonance between these bands. However, the changes in position of the ν_4 vibrations, coupled with the changes in mode shifts of ν_1 and ν_3, definitively illustrate that a change in structure of $CaCO_3$ has taken place: the presence of the same number of peaks in the high-pressure phase implies at least that the number of formula units within the unit cell (8: Hagiya et al. 2005) is likely the same between the lower and higher pressure phases, and may indicate that calcite-III undergoes a transition to a different monoclinic space group at this pressure. Thus, our results show that a phase transition occurs within compressed metastable calcite above 15 GPa.

Decompression

The results on decompression show considerable hysteresis; indeed, the ν_4 region is particularly diagnostic of the possible phases present on decompression (Fig. 1b). In particular, the doublet that is present at high pressures in both calcite-III and the higher-pressure phase evolves multiple components on decompression. Some of these are likely a consequence of a mixed phase assemblage on decompression; the spectrum at 1.2 GPa on decompression clearly is consistent with a mixture of high- and low-pressure phases. The role of calcite-II, which has often been observed at or near zero pressure in calcite decompressed from high pressures (Biellman et al. 1993; Suito et al. 2001), is unclear, and we cannot preclude its presence within our samples. Our fully decompressed sample is consistent with either strained calcite-I or a calcite-II/calcite-I mixture; the ν_1-symmetric stretch near 1090 cm^{-1} is symmetry-forbidden in calcite, and this peak in our decompressed sample lies close to the location of ν_1 in calcite-II (Adams and Williams 1980).

Constraints on bonding and the high-pressure phase diagram of carbonates

Some constraints on the bonding within the high-pressure phase can be derived from the spectral changes that occur in conjunction with the onset of the high-pressure phase. For example, the decrease in splitting of the ν_4-in-plane bend is indicative of changes in the local geometry of the carbonate group. This splitting is related to the deviation of the carbonate group from its ideal trigonal symmetry (Greenaway et al. 1986); the decrease in splitting is thus indicative of the carbonate groups being closer to trigonal symmetry within the high-pressure phase.

The discontinuous mode shifts of the ν_3-asymmetric and ν_1-symmetric stretches of the carbonate group (Fig. 4) also yield constraints on the bonding within the post-calcite-III structure. The positions of the principal asymmetric and symmetric stretches of the high pressure phase, when extrapolated to low pressure, lie at substantially lower frequency than those of calcite-III. The extrapolated difference is near 50 cm^{-1} for the ν_3-asymmetric stretch, and near 30 cm^{-1} for the ν_1-symmetric stretch (Fig. 4). These lowered frequencies imply that the carbon-oxygen bonds in the high-pressure phase are *weaker* than those within the calcite-III; we believe that the ν_1-symmetric stretch provides a particularly sensitive probe of the C-O bond strength, as the frequency of this vibration is determined by the C-O bond stretching force constant, while the ν_3-asymmetric stretch also is influenced by the ν_4-in-plane bending force constant (White 1974). The possible origins for such a decreased bond strength include: (1) a lengthening of the C-O bond; (2) a shift in the effective charges of the carbon and/or oxygen ions; or (3) a strengthening of the Ca-O bonds. These explanations are not exclusive from one another; for example, stronger Ca-O bonds within the high-pressure phase might both lengthen the C-O bonds and shift their charge distribution. The most straightforward explanation for the shift in the C-O stretching vibrations involves a lengthening of the C-O bonds. The idea that pressure-induced C-O bond lengthening can occur in carbonates has precedence: such behavior has been proposed to occur within magnesite at pressures above 30 GPa (Fiquet et al. 2002; Santillan et al. 2005). In the case of magnesite, this lengthening is likely caused by progressive rotations of the MgO_6 octahedra (Santillan et al. 2005). Similarly, the bond lengthening in the post-calcite-III phase is likely the result of a discontinuous change in the geometry of the calcium octahedra relative to the calcite-III structure (Smyth and Ahrens 1997). The ultimate resolution of the underlying cause of this bond weakening hinges on characterizing the precise structure of the high-pressure phase using x-ray diffraction. However, we note the notorious difficulties with solving the structures of the high-pressure metastable phases of calcite (Davis 1964; Merrill and Bassett 1975; Fiquet et al. 1994; Smyth and Ahrens 1997). The available diffraction patterns of calcite at pressures greater than 7 GPa (Fiquet et al. 1994) were conducted only to pressures (18 GPa) that our data indicate are in a mixed phase region, and show a few broad peaks that are not easily indexed. For comparison, our spectroscopic results provide a demonstration of the existence and pressure range of onset of a high-pressure phase of calcite-III, and provide constraints on the bonding properties of the carbonate unit in this phase.

Finally, we note that our results may have relevance for the behavior of carbonates under shock-loading. It has long been recognized that the volumes of shock-compressed calcite and aragonite closely converge at pressures above 10 GPa (Vizgirda and Ahrens 1982; Tyburczy and Ahrens 1986). This convergence led Tyburczy and Ahrens (1986) to propose that a phase that they named "calcite-VI" may exist above this pressure. The pressure of onset of the shock-observed transition in calcite near 10 GPa may be crystallographically controlled (Ahrens and Gregson 1964). The transformation we observe may be correlated with the lower pressure shock transition: the hysteresis of the transition that we observe implies that it is kinetically impeded at 300 K. It is possible that the higher temperatures of the shock measurements [which are still less than 800 K at 10 GPa: Tyburczy and Ahrens (1986)] may cause this transition to proceed at lower pressures even under the rapid loading, but higher temperatures, associated with the shock experiments. If there is a correlation between the transition we document and the shock transition, then the density of the high pressure phase of calcite-III might lie close to that of aragonite.

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