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RAMAN SPECTROSCOPY AT SIMULTANEOUS HIGH PRESSURE AND TEMPERATURE: PHASE RELATIONS AND LATTICE DYNAMICS OF CaCO_3

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Raman spectra of oriented single crystals of calcite were measured at simultaneous high pressures and temperatures up to 40 kbar and 350 °C. The fluorescence frequency shift of Sm:YAG was utilized for accurate pressure determination at elevated temperature, which exhibits negligible temperature shift in this temperature range. With increasing pressure the calcite- $\text{CaCO}_3(\text{II})$ and $\text{CaCO}_3(\text{II})$ - $\text{CaCO}_3(\text{III})$ transformations are observed at 14.5 and 18.5 kbar, respectively, and $\text{CaCO}_3(\text{III})$ remains the stable phase beyond 40 kbar. At elevated temperature and pressure, the width of the $\text{CaCO}_3(\text{II})$ stability field decreases and, at temperatures greater than 200 °C, $\text{CaCO}_3(\text{III})$ transforms to aragonite. The $\text{CaCO}_3(\text{III})$ -aragonite phase boundary is insensitive to pressure over the 20 to 40 kbar interval. Calcite- $\text{CaCO}_3(\text{II})$ phase transition is first order and reversible, the $\text{CaCO}_3(\text{II})$ - $\text{CaCO}_3(\text{III})$ transition exhibits kinetic irreversibility, and the $\text{CaCO}_3(\text{III})$ -aragonite transition is sluggish and irreversible. Lattice dynamical calculations along Γ to F direction in calcite indicate an unstable phonon mode. The atomic displacements associated with this mode are consistent with those required for a continuous, displacive calcite- $\text{CaCO}_3(\text{II})$ phase transition.

Keywords: Calcium carbonate, Raman spectroscopy, Lattice dynamics.

INTRODUCTION

Many experiments on the phase relations of calcium carbonate have been conducted as a function of pressure or temperature alone and have utilized a single crystal calcite, powdered calcite, and polycrystalline calcite as sample materials. These studies include x-ray diffraction [1,2,3], vibrational spectroscopic studies [4,5,6], acoustic wave velocity [7,8], differential calorimetry [9,10], and elasticity measurements [11]. The few investigations at simultaneous pressure and temperature have employed experimental techniques, such as acoustic wave velocity measurements [12,13,14], that probe macroscopic properties such as density or compressibility. However, the phase boundary determined by a macroscopic technique is questionable if the bulk properties of adjacent phases are similar. Hence a microscopic technique, such as Raman spectroscopy is advantageous for sharp demarcation of the phase boundary.

These issues pertain to the discussion of calcium carbonate phase stability. At high pressure, calcite is observed to transform to metastable phases of $\text{CaCO}_3(\text{II})$ at 14.5 kbar and to $\text{CaCO}_3(\text{III})$ at 18.5 kbar. High pressure vibrational spectroscopic studies are able to identify unequivocally these phase transformations by the sudden appearance or disappearance of lines in the vibrational spectrum [5,6,15]. In contrast, acoustic wave velocity profiles over the same

region reveal a deep, broad attenuation spanning the entire region of $\text{CaCO}_3(\text{II})$ phase stability [7,8,12,13,14] and a small, sharp discontinuity associated with the transformation to $\text{CaCO}_3(\text{III})$ [8]. The pressure at the velocity reaches maximum attenuation has been used as the calcite- $\text{CaCO}_3(\text{II})$ transformation pressure, but because the transformation appears as a broad deflection from approximately 8 to 22 kbar, the pressure at which the transformation occurs is ill defined. The discontinuity at the $\text{CaCO}_3(\text{II})$ - $\text{CaCO}_3(\text{III})$ transformation had not been identified for some time because it was not observed readily in the velocity profile [8]. Although the wave velocity profile measurements can be difficult to interpret, none the less, they have been used to define a curved P-T path for the calcite- $\text{CaCO}_3(\text{II})$ phase boundary at elevated temperature [13,14]. Such a curved phase boundary is unusual for a solid-solid transition and may suggest a change in the nature of the phase transformation mechanism.

In this paper we present the results of a Raman spectroscopic study on oriented single crystal calcite at simultaneous pressures to 40 kbar and temperatures to 350 °C. With increasing pressure, the transformation from calcite to $\text{CaCO}_3(\text{II})$ to $\text{CaCO}_3(\text{III})$ is observed in agreement with previous work [4,5,6]. At room pressure and elevated temperatures to 700 °C, no transformation is observed, again in agreement with earlier work [10,16]. At simultaneous pressure and temperature, an aragonite stability field is identified that had not been recognized previously in the laboratory time frame. Quantitative analysis of the vibrational mode frequency dependence on pressure and temperature is utilized to study the phase transformation mechanism. Finally, lattice dynamical calculations for calcite are carried out in the rigid-molecular-ion-model (RMIM) and a soft mode is identified, which drives the calcite- $\text{CaCO}_3(\text{II})$ transition.

EXPERIMENTAL TECHNIQUE

Raman spectra of four phases of CaCO_3 were collected as a function of simultaneous pressure and temperature using a Raman microprobe (SPEX 1482) mounted to a triple spectrometer (SPEX 1377) and an externally heated Merrill-Bassett [17] diamond anvil cell (DAC). Raman spectra were excited with 75 mW of 488.0 nm excitation focused to a 5 μ spot size using a 36X Ealing reflecting objective. The scattered light was collected by the same objective using a 180 ° backscattering geometry and focused on to the slit of the spectrometer. The dispersed light was detected by a 512 channel intensified, gated diode array (Tracor Northern TN-6133). The diamond anvil cell was placed in a resistively heated copper block furnace. Temperature was regulated and controlled proportionally using a K-type thermocouple inserted between the backing plates of the DAC. Temperature insensitive, pressure-induced fluorescence frequency shift of samarium doped yttrium aluminum garnet (Sm:YAG) was used as the pressure calibrant [18,19]. 100 μ plates of single crystal calcite, oriented normal to c-axis, several 5 to 10 μ chips of Sm:YAG, and methanol:ethanol pressure medium were loaded into a 300 μ cavity in an Inconel 600 gasket. For all experiments, the DAC was pressurized and then heated to the temperature of interest. The DAC was held at temperature for 60 minutes,

then the pressure was measured, prior to collection of the vibrational spectrum. Data acquisition times for vibrational spectra averaged 100 seconds.

RESULTS AND DISCUSSION

Raman spectra acquired at known pressure and temperature allowed definite identification of each phase encountered (Figure 1). The appearance or disappearance of characteristic Raman vibrational modes (Figure 2) were used to locate the phase boundaries in the pressure-temperature space. At room temperature with increasing pressure, the calcite- $\text{CaCO}_3(\text{II})$ and the $\text{CaCO}_3(\text{II})$ - $\text{CaCO}_3(\text{III})$ phase boundaries were encountered at 14.5 and 18.5 kbar, respectively. With decreasing pressure, the $\text{CaCO}_3(\text{III})$ - $\text{CaCO}_3(\text{II})$ transformation is overstepped and $\text{CaCO}_3(\text{III})$ transformed directly to calcite at approximately 14.5 kbar. At elevated temperature, the same phase relationships held; however, at temperatures above 200 °C, the irreversible $\text{CaCO}_3(\text{III})$ -aragonite phase transition was observed. Curvature of the calcite- $\text{CaCO}_3(\text{II})$ phase boundary was not observed in the pressure-temperature region investigated. From high pressure X-ray diffraction studies [3], the calcite- $\text{CaCO}_3(\text{II})$ transition is known to involve the opposing rotation of CO_3^{2-} groups coupled to the displacement of the Ca^{2+} ions off the 3 symmetry axis. The ω_{14} vibrational mode of calcite at 158 cm^{-1} has associated atomic displacements resulting in the rotation of the CO_3^{2-} groups, and thus it may be used to probe the transformation mechanism. At the calcite- $\text{CaCO}_3(\text{II})$ phase boundary, the Raman shift of the ω_{14} mode changes by 6 cm^{-1} discontinuously at room temperature. At elevated temperature, the magnitude of the discontinuity at the phase boundary decreases markedly. This suggests that the transition is becoming second order at elevated temperature, whereas at room temperature it is clearly first order.

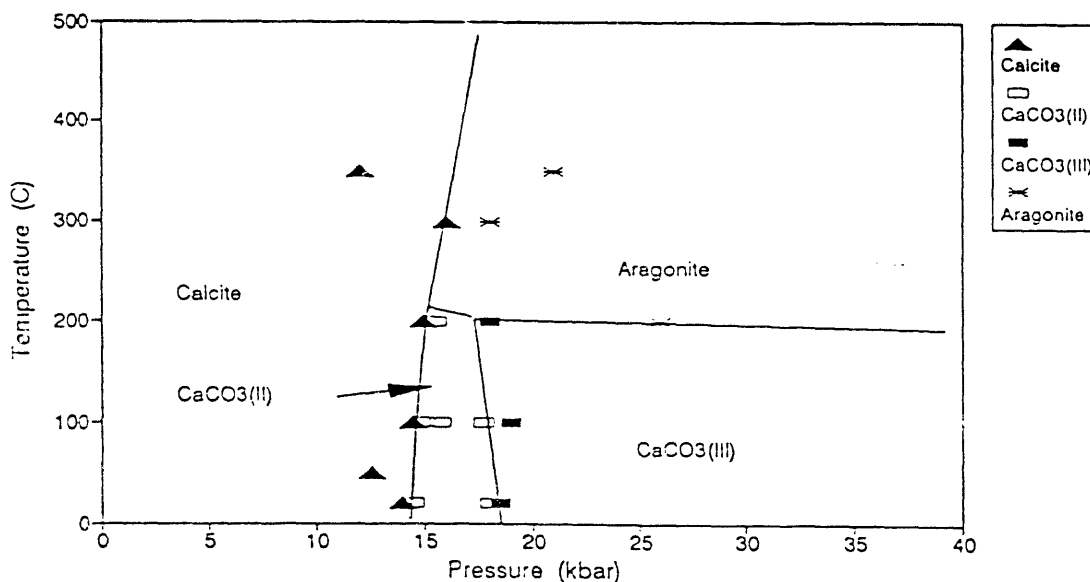


Figure 1. Calcium carbonate phase diagram.

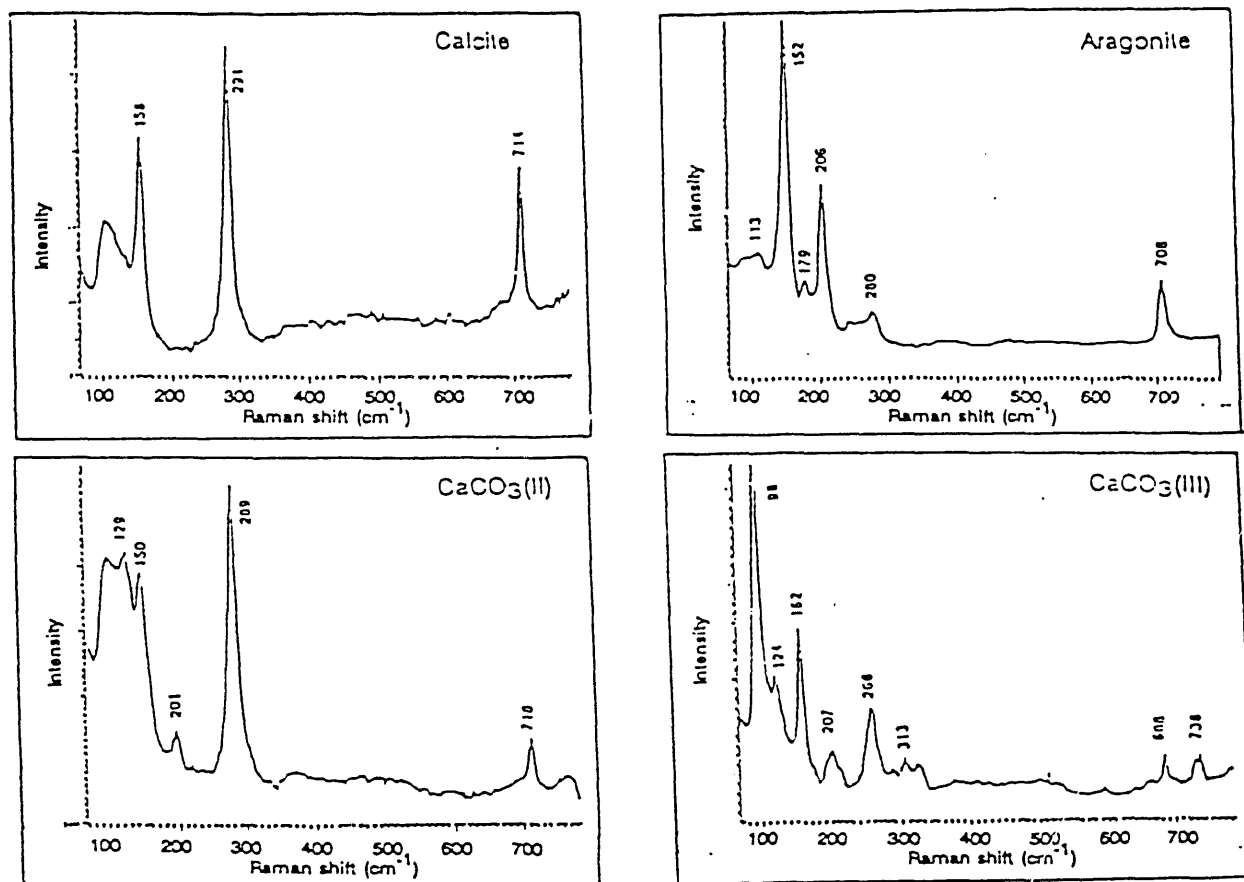


Figure 2. Raman spectra of the CaCO₃ phases encountered.

LATTICE DYNAMICAL CALCULATIONS

An understanding of the structural instability driving the calcite-CaCO₃(II) phase transition requires a knowledge of the phonon dispersion throughout the Brillouin zone [20]. Existing experimental knowledge of phonon dispersion relations for calcite are limited to Raman and infrared vibrational studies that provide information at the zone boundary and inelastic neutron scattering experiments [21] along Γ to Z, a high symmetry direction. However, lattice dynamical models for calcite [21,22], and isomorphous NaNO₃ [23,24], have been developed from which phonon dispersion curves in any direction in the Brillouin zone can be calculated. Of these, the Rigid Molecular Ion Model (RMIM), treats molecular groups such as CO₃²⁻ as a single, rigid body with translational and rotational degrees of freedom that interact with the translational motion of the Ca²⁺ ions. The details of the RMIM approximation are given elsewhere [22,23,25], but the required input for RMIM approximation and the FORTRAN code DISPR [26] includes atomic position, mass, effective ionic charge and radii. Earlier work on calcite using the RMIM [23] were unsuccessful at approximating the inelastic neutron scattering data along Γ to Z direction. However, a new choice of ionic charge (Ca = 1.58, C = 0.82, and O = -0.80) and radii (Ca =

1.80, C = 0.80, and O = 1.35 Å) match the experimental phonon dispersion curves closely [14] and predict physically reasonable elastic constants [11].

In light of the success of RMIM at predicting the phonon dispersion relations along the Γ to Z direction, it is of interest to see if RMIM would predict a lattice instability along the Γ to F direction as predicted from Landau Theory [27,28,29]. The Γ to F direction is a lower symmetry direction lifting the degeneracy of the phonon branches in the Γ to Z direction and many more phonon branches are observed. One branch, F_2^- , begins to decrease in frequency at approximately $\mathbf{q} = (0, 0.3, 0, 3)$ (Figure 3a). The eigenvector for this branch consists of rotation of the CO_3^{2-} group about the z-axis and coupled displacement of the Ca^{2+} ion in the x-direction. The decrease in frequency of the F_2^- branch with this atomic displacement suggests a lattice instability at the F point as predicted from Landau Theory [27,28,29] and is consistent with the displacive mechanism known from high pressure x-ray diffraction experiments [3].

The F point instability allows the calcite- $\text{CaCO}_3(\text{II})$ transition to occur by a continuous, displacive mechanism. For the transition to be second order, the frequency of the F_2^- must attain imaginary value. To test whether the F_2^- take on imaginary values, the lattice constant was contracted from its equilibrium value of 6.361 Å to 6.122 Å to simulate a pressure of 14.5 kbar. The resulting phonon dispersion relations are shown in Figure 3b.

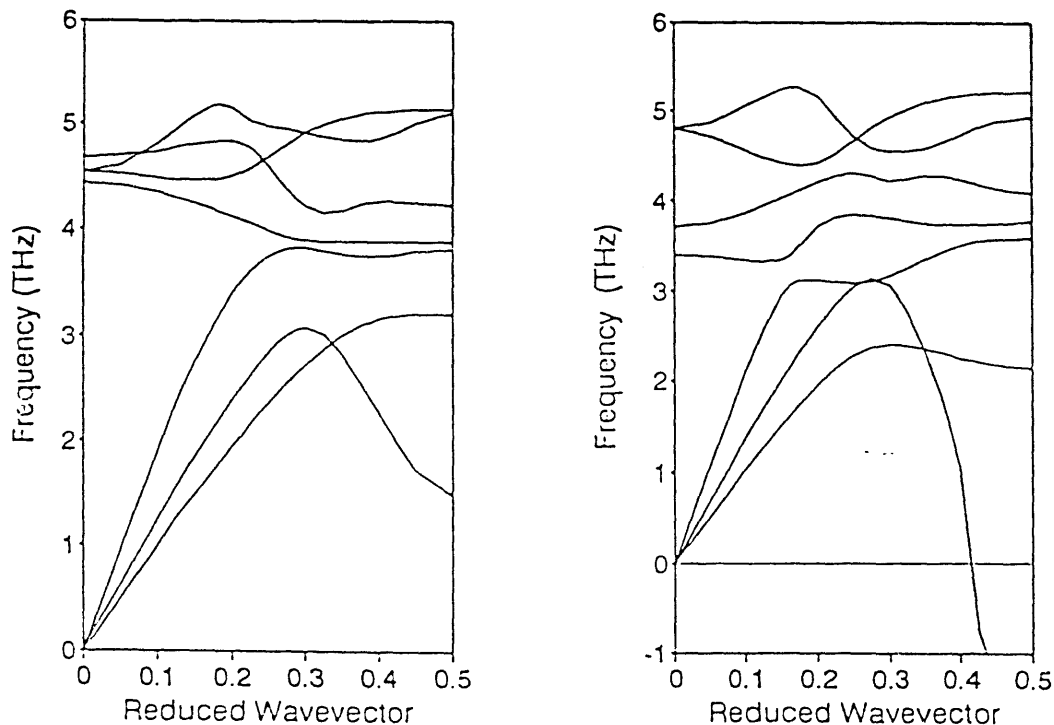


Figure 3. Low frequency phonon branches in the Γ to F direction. The lattice constant is contracted from 6.361 Å in (3a) to 6.122 Å in (3b).

CONCLUSIONS

The characteristic pattern of Raman-active modes allowed certain identification of the calcium carbonate phase present at known pressure and temperature. This technique allowed mapping calcium carbonated phase equilibria using a direct probe of crystalline symmetry. Lattice dynamical investigations, using the RMIM approximation, resulted in calculated phonon dispersion curves in good agreement with experimental values and the existence of a lattice instability that drives the calcite-CaCO₃(II) transition as predicted by Landau Theory.

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