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TRANSFORMATION IN CALCITE

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RAMAN STUDIES OF PRESSURE AND TEMPERATURE INDUCED PHASE TRANSFORMATIONS IN CALCITE

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ABSTRACT

Phase stability in the calcium carbonate system was investigated as a simultaneous function of pressure and temperature up to 40 kbar and several hundred degrees Kelvin using micro-Raman techniques to interrogate samples constrained within a resistively heated diamond anvil cell. Measured spectra allow unequivocal identification of crystalline phases and are used to refine the P,T phase diagram. Calcium carbonate was found to exhibit both reversible and irreversible transformation phenomena among the four known phases which exist under these conditions. Time-dependent Raman intensity variations as the material is perturbed from its equilibrium state allow real-time kinetics measurements to be performed. Evidence suggests that the order of certain observed transformations may be pressure dependent. The utility of Raman spectroscopy to follow transformation phenomena and to estimate fundamental thermophysical properties from the stress dependence of vibrational mode frequencies is demonstrated.

INTRODUCTION

Laser Raman spectroscopy often is used in phase characterization studies owing to the adaptability of the measurement as an *in situ* probe and to the extent of chemical bonding information which can be extracted from measured spectra. Vibrational Raman measurements of materials constrained within diamond anvil cells have been used to establish regions of phase stability and investigate the molecular structure of high density phases. [1,2] Many observed transformations are first order and occur rapidly in time. However, some transformations are *sluggish* suggesting that the transformation mechanism may involve translational or rotational motion of localized structural units which comprise the lattice. Coupling to a lattice excitation becomes possible if the symmetry and direction of the displacement coincide with that of the allowed vibrational mode. Glass transition phenomena in ionic oxide glasses are thought to proceed according to this mechanism. [3] Transformation phenomena in crystalline phases can be described in an analogous manner. Soft mode behavior is evident if the lattice vibration frequency for a particular mode varies monotonically with an applied stress, then becomes inactive in the new phase. [4] Therefore, vibrational spectroscopy becomes an important probe of both the mechanistics and kinetics of transformation phenomena in materials.

The temperature and pressure dependence of phonon frequencies and associated force constants also are used to evaluate anharmonicity in the lattice potential energy from which fundamental thermophysical properties may be estimated. [5,6] The relative change in mode frequency with applied pressure is usually written in terms of the mode Grüneisen parameter, γ , and the relative change in crystal volume over the same pressure interval. The change in frequency with applied pressure then is proportional to the isothermal compressibility. Under conditions of a perfectly harmonic potential energy, no frequency shift with applied pressure would be expected and γ would be zero. Non-zero values of γ signify the degree of anharmonicity associated with a particular normal vibrational mode. The *quasiharmonic* approximation often is used to describe variations in mode frequency as a function of applied temperature. Based on

a simple anharmonic oscillator model, the square of the mode frequency is predicted to vary linearly with temperature. [5] The slope of this curve is used to determine the anharmonic contribution to the potential energy from which the isobaric linear thermal expansion coefficient of a material may be estimated. [5]

Work reported here demonstrates the utility of Raman spectroscopy for unequivocal identification of the equilibrium crystalline phases in calcite (CaCO_3) as it is simultaneously subjected to changes in temperature and pressure. Four principal phases (calcite, $\text{CaCO}_3(\text{II})$, $\text{CaCO}_3(\text{III})$, and aragonite) exist at pressures from 0 - 25 kbar and temperatures between 300 - 600 K. Discontinuities in mode frequency variations throughout P,T space establish phase boundaries and are used to refine the existing phase diagram. [7] Such contours also illustrate trends in mode anharmonicity as a function of these two variables. First order transformation of calcite to the II, III, and aragonite phases has been observed under isothermal conditions with increasing pressure. However, as the pressure is reduced, the III phase transforms directly into calcite, overstepping the CaCO_3 stability field altogether. An irreversible transformation of $\text{CaCO}_3(\text{III})$ to aragonite also occurs. Time-dependent changes in Raman mode intensities characteristic of each phase are used to follow the transformation as the compressed sample is rapidly heated to temperatures between 450 and 650 K. Preliminary results suggest that the rate constant for this transformation is pressure dependent.

EXPERIMENTAL

Raman spectra of the known calcium carbonate phases were recorded at simultaneous elevated pressure and temperature. A Raman microprobe (Spex 1482) fitted with a 20X power objective (0.30 NA) was used to image the laser excitation onto the sample and to collect the scattered light and induced fluorescence from the pressure calibrant. The light was imaged onto the slits of a 0.5 m triple spectrometer (Spex 1877) equipped with 1200 and 600 lines/mm gratings in the dispersive and filter stages respectively. A 512 channel intensified, gated diode array (Tracor Northern TN-6133) detector allowed transient recording of the Raman spectra. The Merrill-Bassett diamond anvil cell constructed from Inconel 718X was located in a resistively-heated copper block furnace. Temperature was regulated by a K-type thermocouple inserted between the backing plates of the diamond anvil cell, and proportionally controlled. The sample consisted of a single calcite crystal oriented normal to the c-axis, 100 to 150 micrometers in diameter and 30 micrometers thick. The sample was placed in a 250 micrometer hole in an Inconel 600 gasket (50 micrometers thick) along with several 5 - 10 micrometer diameter chips of Sm:YAG which served as the pressure sensor. A 4:1 methanol-ethanol mixture also was introduced and was used to maintain hydrostatic conditions in the cell. The pressure-induced fluorescence shift of Sm:YAG was used as an *in situ* pressure probe; measured pressures are known to ± 1.5 kbar. [8] Time resolved Raman spectra were acquired at constant elevated temperature and pressure. Using a laser excitation power of 75 milliwatts (488 nm) measured at the sample, array exposure times averaged 30 seconds. The instrumental resolution was 8 cm^{-1} .

RESULTS AND DISCUSSION

Raman measurements reported here are used to investigate external mode anharmonicity in P,T space, refine phase stability regions for calcite, and explore the transformation kinetics at 26 kbar between the metastable $\text{CaCO}_3(\text{III})$ phase and aragonite. This transformation exhibits an apparent dependence upon applied pressure.

Dependence of Mode Frequency on Applied Stress.

Vibrational frequencies for all Raman active modes in calcite were found to be both temperature and pressure dependent which reflects the presence of anharmonic contributions to the lattice potential energy. A typical frequency variation map is illustrated in **Figure 1** for the ν_{14} mode. This external lattice mode which occurs at 156 cm^{-1} under ambient conditions involves shear-like displacement of planar carbonate groups located in adjacent layers in the crystal. **Figure 1** was constructed from a master

Figure 1. Frequency difference $\{\nu(P, T) - \nu(1 \text{ bar}, 298 \text{ K})\}$ for the ν_{14} mode of calcite as a function of temperature and pressure. Discontinuities in the frequency plot establish phase transformation boundaries; the texture of the frequency surface suggests that thermophysical properties vary among the respective phases. $\{300 \leq T \leq 700 \text{ K}; 0 \leq P \leq 30 \text{ kbar}\}$

equation developed from selected measured Raman frequencies within the indicated P, T space. A number of important features are illustrated. In general, mode frequencies decrease with increasing temperature and increase with increasing pressure. Discontinuities correspond to transformation boundaries between the calcite, $\text{CaCO}_3(\text{II})$, and $\text{CaCO}_3(\text{III})$ phases. The texture of the frequency surface provides information about the mode anharmonicity from which fundamental thermophysical properties can be inferred. For example, at fixed increasing pressure, the slope $(\partial\nu/\partial T)_P$ which can be related to the linear thermal expansivity, [5] is found to increase. Also, at fixed increasing temperature, the slope $(\partial\nu/\partial P)_T$ which can be related to the isothermal compressibility also increases. Plots similar to this one have been constructed for several other phonon modes in calcite and are used to develop the phase diagram discussed in the following section.

Equilibrium Phase Boundaries in Calcite.

Based upon the appearance of the Raman spectrum as a function of temperature and pressure, four distinct crystalline phases and their stability fields have been found. Data was used to construct the phase diagram shown in **Figure 2**. Raman-active modes above 400 cm^{-1} are assigned to internal vibrational modes of the carbonate group and show little variation among the observed phases. However, the phase transformation

Figure 2. Equilibrium phase diagram for calcite with Raman spectra characteristic of the observed crystalline phases.

boundaries between calcite, $\text{CaCO}_3(\text{II})$, and $\text{CaCO}_3(\text{III})$ were identified readily from discontinuities in the $\nu(\text{P}, \text{T})$ plot shown in Figure 1 for the external ν_{14} mode. From x-ray diffraction studies at elevated pressure, the calcite $\rightarrow \text{CaCO}_3(\text{II})$ transformation at 14.5 kbar is known to be displacive and involves the coupled anti-rotation of the carbonate groups and the displacement of the Ca^{+2} ions. [9] At 293 K, the first-order transformation is reversible, exhibiting a 6 cm^{-1} decrease in the external mode frequency and appearance of new features characteristic of the transformed phase. At 475 K, the magnitude of this discontinuity decreases markedly, suggesting that the transformation becomes second-order under these conditions. The change in the order of the transformation also is confirmed by EPR measurements [10], theoretical calculations [11], and lattice dynamical calculations [7].

The structure of $\text{CaCO}_3(\text{III})$ remains unsolved; however, analysis of the number of observed Raman-active modes suggests that the transformation to this phase involves a doubling of the size of the $\text{CaCO}_3(\text{II})$ unit cell. [12] The $\text{CaCO}_3(\text{II}) \rightarrow \text{CaCO}_3(\text{III})$ phase boundary at 18.5 kbar is associated with an 18 cm^{-1} discontinuity of a low frequency $\text{CaCO}_3(\text{II})$ mode, and the appearance of several new modes in this frequency region characteristic of the new phase. This transformation is irreversible. Raman spectra acquired following release of pressure to 14.5 kbar are characteristic of the $\text{CaCO}_3(\text{III})$ phase. Upon further release of pressure, this phase reversibly transforms to calcite.

The $\text{CaCO}_3(\text{III}) \rightarrow$ aragonite transformation is manifested by a gradual loss of intensity of the Raman spectrum characteristic of the $\text{CaCO}_3(\text{III})$ phase and the appearance of weak Raman lines intrinsic to aragonite. Analysis of the pressure-induced Raman shift through the phase transformation boundaries at several temperatures provides insight into the mechanism and reversibility of the transformation. At pressures near 26 kbar, $\text{CaCO}_3(\text{III})$ undergoes a time-dependent transformation to the aragonite phase which depends upon temperature. Time dependent changes in mode intensities are used to follow this transformation and are discussed below.

Kinetics of the $\text{CaCO}_3(\text{III}) \rightarrow$ Aragonite Transformation.

Changes in Raman mode intensities characteristic of the transforming and evolving phases can be used to follow the transformation as a function of time at fixed pressure and temperature. Transient Raman spectra were recorded upon introduction of the pressurized cell into the heated furnace. The cell temperature was found to stabilize within several minutes at which successive Raman spectra could be recorded. The intensity ratio $(I_a / [I_a + 0.33I_c])$ was found to adequately represent the fractional aragonite content of the crystal during the isothermal transformation from the $\text{CaCO}_3(\text{III})$ phase. Here, I_a is the intensity of the 210 cm^{-1} mode intrinsic to the aragonite phase, and I_c is the intensity of the 98 cm^{-1} mode characteristic of $\text{CaCO}_3(\text{III})$. The 0.33 factor in the denominator normalizes the absolute intensities of the two external modes to the internal carbonate mode at 714 cm^{-1} . The logarithmic dependence of this intensity ratio on time shown in Figure 3 suggests that the transformation obeys a first-order rate law. The rate constant determined at 498 K is approximately a factor of four larger than that measured at 473 K from which an activation energy of 105 kJ/mole can be estimated. This value is comparable to that measured for the calcite $\rightarrow$ aragonite transformation (67 kJ/mole) at 17 kbar using thermal analysis techniques. [13] Initial isothermal measurements as a function of pressure indicate that the rate constant for the $\text{CaCO}_3(\text{III}) \rightarrow$ aragonite transformation increases markedly at higher pressures. A pressure-dependent rate constant also has been determined for the calcite $\rightarrow$ aragonite transformation. [14]

Figure 3. Linear dependence of the logarithmic normalized intensity ratio versus time for the $\text{CaCO}_3(\text{III}) \rightarrow$ aragonite phase transformation at 26 kbar. (Here, I3 represents 1/3 the measured Raman intensity of the $\text{CaCO}_3(\text{III})$ phase, and I is the intensity of the aragonite phase.)

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