Pressure response on hydrogen bonds in potassium hydrogen carbonate and sodium hydrogen carbonate

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Pressure responses of hydrogen bonding interactions were compared between potassium hydrogen carbonate (KHCO3) and sodium hydrogen carbonate (NaHCO3). KHCO3 undergoes a pressure-induced structural change at 2.8 GPa and room temperature whereas no phase transition has been found so far for NaHCO3 up to 11 GPa. KHCO3 exhibits a substantial decrease in the O–H···O angle with increasing pressure. This change could be a trigger for the phase transition at 2.8 GPa. By contrast, no significant change in O–H···O angle was observed for NaHCO3 up to 7 GPa. Based on the observations using neutron diffraction, X-ray diffraction and vibrational spectroscopy at high pressure, a possible mechanism for the phase transition of KHCO3 is suggested. In addition, the phase boundary of KHCO3 caused by the pressure-induced transition was determined using in situ Raman spectroscopy at high pressure.

Keywords: Hydrogen bond; High pressure; Neutron diffraction; Phase transition; Hydrogen carbonate; Earth science

INTRODUCTION

The geometry of hydrogen bond, and particularly the competition between H-bond formation and H···H repulsion, bears directly on the mechanism of hydrogen incorporation and the stability of the materials in which the hydrogen is incorporated. Pressure is an excellent variable for the investigation of the competition between H-bond formation and H···H repulsion in isochemical systems. The geometry of the H-bond and the stability of hydrous minerals are of direct relevance to important problems in earth sciences such as the origin of deep-focus earthquakes, deformation of rocks, etc. We have studied hydrogen bonding in ionic solid materials at high pressure and the pressure responses of the structure for layered metal hydroxides and hydrous silicate minerals which can be...
thermodynamically stable in the deep part of the earth [1–4]. Hydrogen bonds in solid material are strengthened with increasing pressure and at further high pressures a repulsion between hydrogen atoms can be a trigger of amorphousization [3]. In our continuing projects on deep earth process, our attention has focused on the pressure-response of materials with strong hydrogen bonds. This is because some new phenomena such as symmetrization of hydrogen bond observed for ice at megabar pressure could be expected at moderately high pressure in materials with strong hydrogen bonding at ambient pressure conditions [5].

We have chosen two hydrogen carbonate (bicarbonate) compounds having strong hydrogen bonding with an O–H···O distance of approximately 2.6 Å: potassium hydrogen carbonate (KHCO₃) and sodium hydrogen carbonate (NaHCO₃). Despite similarity in their chemical formulae, the geometrical arrangements of hydrogen bonds are quite different in these two compounds. KHCO₃ consists of a stacking of dimers formed by the fusion of the two HCO₂⁻ ions through the formation of hydrogen bonds whereas NaHCO₃ has a structure consisting of infinite chains [6]. These different structural arrangements offer the possibility of different pressure responses of the hydrogen bonds. KHCO₃ undergoes a pressure-induced structural change at 2.8 GPa and room temperature [7], whereas no phase transition has been found for NaHCO₃ up to 11 GPa. In addition, even at ambient pressure, a phase transition was reported at 319 K for KHCO₃ [8,9].

Recently, we have observed change in the local structure of hydrogen bonds in KHCO₃ by means of neutron diffraction and vibrational spectroscopy at high pressure [10]. In the present study, we compare the pressure-responses on the hydrogen bond structures between KHCO₃ and NaHCO₃ in order to further our insight into the mechanism of the pressure-induced phase transition in KHCO₃.

**EXPERIMENTAL PROCEDURES**

Time-of-flight neutron-diffraction data were collected on the POLARIS beamline at the UK pulsed-neutron facility, ISIS, at the Rutherford Appleton Laboratory. All measurements were conducted at room temperature. Deuterated powder samples (KDCO₃, NaDCO₃) were loaded into vanadium cans to measure the neutron powder diffraction pattern at ambient pressure. Data at high pressure were collected using the Paris–Edinburgh opposed-anvil cell (P–E cell). We used a new cell assembly that enables the use of 4:1 methanol–ethanol mixtures and achieves hydrostatic pressure up to at least 9 GPa [11]. The pressure generated was estimated from the unit cell volume of the samples and a previously determined equation of state. The data obtained were used for Rietveld structural refinement with the GSAS program [5,12]. The structural model derived from the ambient data was then used as a starting point for the refinement of high-pressure structures. The atomic coordinates and isotropic atomic-displacement parameters of all atoms were refined.

Raman spectra of KHCO₃ at various pressures and temperatures were obtained in order to determine a phase boundary between low-pressure phase and high-pressure phase of KHCO₃ using a diamond anvil cell. The cell was externally cooled or heated with circulated water flow. Pressure was measured by the standard ruby fluorescence technique and temperature was determined from the emf of a W–Re thermocouple attached on the diamond anvil. A 4:1 methanol/ethanol pressure medium was used for measurements at high pressure. The incident light was 514.5 nm line of Ar⁺ laser and the power at the sample surface was approximately 5 mW and individual spectra were obtained with an exposure of 100 s.
RESULTS AND DISCUSSION

The unit cell parameters and atomic coordinates obtained by means of Rietveld structural refinement method allows discussion of the pressure response of bond lengths and bond angles, particularly those relevant to the hydrogen bonding. As shown in Fig. 1, KDCO$_3$ exhibits a substantial decrease in O–D···O angle with increasing pressure and this change results in the distortion of hydrogen bonding structure and could be a trigger for the phase transition at 2.8 GPa [10]. Since the crystal structure of the high-pressure phase of KDCO$_3$ has not yet been solved, the data on the pressure dependence of the O–D···O angle is limited to 2.8 GPa. By contrast, the present results on the crystal structure of NaDCO$_3$ have shown that the O–D···O angle of hydrogen bonds in NaDCO$_3$ did not significantly decrease with increasing pressure up to 7 GPa (Fig. 1). This observation suggests that the local structure surrounding the hydrogen atoms did not exhibit significant change and that the hydrogen bonding structure is preserved with increasing pressure for NaDCO$_3$. At present, no pressure-induced phase transition has been observed for NaHCO$_3$ (NaDCO$_3$) up to at least 11.7 GPa from observations of Raman spectra and X-ray diffraction at high pressure and room temperature. The absence of pressure-induced phase transition for NaHCO$_3$ is attributed to the robust structure of hydrogen bonds at high pressure. The differences in pressure response in NaHCO$_3$ and KHCO$_3$ may be attributed to the difference in the hydrogen bonding structures: a dimer structure for KHCO$_3$ and polymer structure for NaDCO$_3$.

At ambient pressure, intense Raman bands are observed at 1037, 678 and 637 cm$^{-1}$ due to the combination of C=O(1) stretch and C–O(3) stretch, the combination of in-plane bending of O(2)–C–O(3), and stretching of C–O(2) and in-plane bending of C=O(1), respectively. By plotting the frequencies of these modes versus pressure, a clear discontinuity can be observed at the phase transition in the case of KHCO$_3$ [10]. In this study, the phase relationship between the high-pressure phase and low-pressure phase was determined by detecting the discontinuity in the pressure-dependence of the Raman frequencies (see Fig. 2). At constant pressure load, temperature was controlled by flowing hot or cold water through the metal tubings around the diamond anvil cell. The stability fields of the low-pressure phase (closed symbol) and high-pressure phase (open symbol) of KHCO$_3$ were determined by

![Figure 1](image_url)
Raman spectroscopy. The phase boundary between the two phases was drawn as a straight line although some ambiguities exist at the phase boundary presumably as a consequence of hysteresis at the phase transition. The phase boundary determined here was almost horizontal in the pressure–temperature dimension suggesting that $dP/dT = \Delta H/T \Delta V < 0$.

On the basis of these data, we would like to propose a possible structure model for the pressure-induced phase transition of KDCO$_3$. In general, pressure-induced structural changes for ionic compounds (AX) results in transformation to an isostructural phase of BX where B has smaller ionic radius than that of A. Since the ionic radius of K is much larger than that of Na, it is possible that a high-pressure form of KDCO$_3$ is isostructural with ambient-pressure phase of NaDCO$_3$. In deed, we can build the NaDCO$_3$-type structure from the KDCO$_3$ structure by small sliding of structural blocks as shown in Fig. 3. In this model, we assume that the block slips along the $b$ axis for the distance of 0.5$b$. The evidence, a phase boundary between a low pressure and a high-pressure phase of KDCO$_3$ is almost independent on temperature, may support such a martenstic transformation mechanism. Furthermore, it is noteworthy that this slip can be accompanied by the change in the hydrogen bonding structure from the dimer arrangement into the infinite chain arrangement. The next steps in this project will concentrate on testing the above hypothesis for the high-pressure form of KDCO$_3$ using both powder and single crystal diffraction data collected at high pressure.

**CONCLUSIONS**

X-ray, neutron and vibrational spectroscopic measurements confirmed the occurrence of reversible pressure-induced phase transition of KHCO$_3$ at 2.8 GPa and room temperature. In contrast, no pressure-induced phase transition has been found for NaHCO$_3$ up to 11 GPa. Significant decrease in the O–D···O angle was observed for KDCO$_3$ with increasing pressure up to the phase transition point, whereas no significant decrease in the O–D···O angle was observed for NaDCO$_3$. Phase boundary between the high- and low-pressure phases determined by Raman spectroscopic observations revealed that the temperature dependence...
of transition pressure is almost constant with increasing temperature within the observed temperature range (270–350 K).

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REFERENCES


