Single crystal X-ray diffraction study on high-pressure phase of KHCO$_3$

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Summary
The monoclinic and triclinic high-pressure phases of KHCO$_3$ were identified for the first time by in-situ high-pressure single crystal X-ray analysis. These monoclinic and triclinic lattices are different from three previously identified phases, I-III. We propose that the monoclinic and triclinic variants be called phase IV and V, respectively. The two lattices are superimposed along $a^*$ with $a_{IV} = 2 \times a_{V}$, i.e., the $bc$ plane is common in both lattices in real space. The space group of phase IV is $P2_1/b11$ with unit cell parameters of $a = 10.024(3)$ Å, $b = 6.912(5)$ Å, $c = 4.1868(11)$ Å, $\alpha = 115.92(4)^\circ$, and $V = 260.9(2)$ Å$^3$. The crystal structure of phase IV, without hydrogen site, was refined.

Introduction
Because of great interest in the dynamic nature of proton transfer, the H bond in potassium hydrogen carbonate KHCO$_3$ has been studied using a variety of techniques including X-ray and neutron diffraction. In earlier work Thomas et al. (1974a,b) showed that the H bond associated with O...O = 2.59 Å is moderately strong and that the protons occupy two possible sites in the H bond in the rough proportions 4:1. In the IR and Raman spectra, the OH stretching vibration is a broad band between 1800 cm$^{-1}$ and 3500cm$^{-1}$ (Novak et al., 1963; Lucazeau and Noval, 1973). A quasi-symmetric double minimum potential for the proton-stretching mode was proposed to explain the spectroscopic results (Fillaux, 1983). A detailed inelastic neutron-scattering study (Ikeda et al., 2002) concluded that anharmonicity plays a major role and that proton dynamics cannot be represented with normal coordinates within the harmonic force-field approximation. Pressure is as an attractive tool for understanding the proton dynamics, because in principle the O...O distance associated with the H-bond would be decreased with decreasing volume, allowing the anharmonicity to be continuously tuned.

At atmospheric pressure, KHCO$_3$ undergoes an antiferrodistortive phase transition of an order-disorder type between phase I (high-temperature phase, space group: $C2/m$) and phase II (low-temperature phase, space group: $P2_1/a$) at 318K (Kashida and Yamamoto, 1990). Two (HCO$_3^-$) groups in the crystal are bonded by two H-bonds, and form (HCO$_3^-$)$_2$ dimers. These dimers have two stable rotational angles around the $c$ axis and are disordered in phase I and ordered with an antiphase configuration in phase II.

Recently, new polymorphs of KHCO$_3$ were reported (Takasaka et al., 2002; Nagai et al., 2002; Kagi et al., 2003). One transition, promoted by shear stress, results in phase III. Although the crystal structure of phase III is not confirmed by X-ray or neutron diffraction methods, it is assigned to a ferrodistortive phase having an in-phase configuration of dimers by Brillouin scattering (Takasaka et al., 2002). The other transition is to an unassigned
phase discovered at high-pressure by powder X-ray diffraction study (Nagai et al., 2002). This high-pressure phase results from a reversible phase transition observed at 2.8 GPa, a transition pressure subsequently confirmed by powder neutron diffraction, IR and Raman spectroscopic study (Kagi et al., 2003). Kagi et al. (2005) compared the pressure response of the crystal structure, especially surrounding the H-bond, between KHCO$_3$ and NaHCO$_3$. Although some experimental results had been reported, the crystal structure of the high-pressure phase and the mechanism of the pressure-induced phase transition are still unclear. In this study, the crystal structure of the high-pressure phase of KHCO$_3$ was identified by analysis of single crystal X-ray diffraction data collected from sample mounted in a diamond anvil cell (DAC).

Experimental Method

Prismatic single crystals of phase II of KHCO$_3$ some 50-200µm on edge were grown from K$_2$CO$_3$ aqueous solution by slow evaporation at room temperature. A modified Merrill-Bassett type DAC (Kudoh and Takeda, 1986) was used for the high-pressure experiment. The SUS301 stainless steel plate with 250µm thickness and a 300 µm diameter hole in the center was used as a gasket. A 4:1 methanol-ethanol mixture was used for the pressure transmitting medium. No ruby chip for determining pressure was mounted to avoid the extra spots. Pressure was increased stepwise and a phase transition, accompanied by abrupt change in sample shape was visually observed. Above the phase transition pressure, X-ray oscillation photographs were taken using an imaging plate X-ray diffractometer (Rigaku, R-AXIS IV++) with rotating anode (MoK$_\alpha$, 50kV, 80mA). The observed reflections were indexed assuming a mixture of a monoclinic and a triclinic phase in the same crystal.

Pressure was determined approximately from the Raman band of the methanol-ethanol mixture in the DAC instead of the usual ruby fluorescence method. Raman spectra were measured by the JASCO NRS-2000 spectrometer with a nitrogen-cooled CCD detector. A microscope was used to focus the excitation laser beam (514.5 nm lines of a Princeton Instruments Inc., Ar$^+$ laser). The ν(CC) stretching mode of methanol-ethanol mixture was observed at 899 cm$^{-1}$. Wang et al. (2004) showed that the ν(CC) stretching mode was observed at 882 cm$^{-1}$ at ambient conditions, and that the frequency of this mode increased linearly by 3.7 cm$^{-1}$/GPa with increasing pressure. Hence, pressure was estimated to be about 4.6 GPa. All X-ray diffraction measurements in this study were carried out at this pressure.

X-ray diffraction measurements for determining the unit cell parameters and for collecting intensities of the monoclinic phase was performed using a four-circle X-ray diffractometer installed at the beam line BL-10A, Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. The wavelength of the synchrotron radiation was calibrated to be $\lambda = 0.6990(2)$ Å from the unit cell constants of a ruby standard crystal at ambient conditions. The cell parameters were determined by 27 centered reflections in the 2θ range between 35º and 45º. The X-ray diffraction intensities were collected up to sinθ/λ < 0.82 Å$^{-1}$ (maximum 2θ is 70º) by the ω-scan with the fixed φ method. Extinction and absorption corrections of the crystal were not applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F was based on 227 observed reflections [I > 3.00σ(I)] and 21 variable parameters. All calculations were performed using the Crystal Structure crystallographic software package.
Results and Discussion

Assignment of reciprocal lattices

Bragg reflections in the observed X-ray oscillation photographs above the phase transition pressure could be assigned to a monoclinic and a triclinic lattices (Fig. 1). Although both settings of these monoclinic and triclinic lattices are non-standard ones, these settings are chosen for comparison with the ambient pressure phase (phase II) as seen latter. These monoclinic and triclinic phases are different from three polymorphs described previously (phase I-III). Hereafter, the monoclinic phase is referred to as phase IV and the triclinic phase as phase V. The two lattices are superimposed on the a’ axis with a’ IV = 2 x a V, i.e., the bc plane is common to both lattices in real space. As seen in Fig. 1, the two reciprocal lattices coincide when h00:IV = 2 x hV. Overlapped reflections were not included in the Fourier synthesis for the crystal structure refinement, because the ratio of two phases could not be estimated. Diffuse streaks parallel to a’ were frequently observed. These diffuse streaks are indicative of lamellar stacking disorder of the common (100) planes of phases IV and V.
Table 1. Crystal data and structure refinements for high-pressure monoclinic phase (phase IV) of KHCO₃

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure, GPa</td>
<td>4.6</td>
</tr>
<tr>
<td>Space group</td>
<td>(P 2_1/b 11)</td>
</tr>
<tr>
<td>Lattice parameters, Å</td>
<td>(a = 10.024(3)) , (b = 6.912(5)) , (c = 4.1868(11)) , (\alpha = 115.92(4)^\circ)</td>
</tr>
<tr>
<td>Unit cell volume, Å³</td>
<td>(V = 260.9(2))</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated), g/cm³</td>
<td>2.55</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-15 \leq h \leq 4), (-11 \leq k \leq 9), (-6 \leq l \leq 6)</td>
</tr>
<tr>
<td>No. Observations ((I &gt; 3.00\sigma(I)))</td>
<td>227</td>
</tr>
<tr>
<td>No. Variables</td>
<td>21</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>10.81</td>
</tr>
<tr>
<td>(R_c) ((I &gt; 3.00\sigma(I)))</td>
<td>0.100</td>
</tr>
<tr>
<td>(R_w) ((I &gt; 3.00\sigma(I)))</td>
<td>0.110</td>
</tr>
</tbody>
</table>

\(a\)Pressure was approximated from the shift of the wavenumber of Raman spectra of the 4:1 methanol-ethanol mixture.  
\(b\)Standard setting for the monoclinic structure is \(P 12_1/c\) with \(a = 6.321(5)\), \(b = 10.024(3)\), \(c = 6.912(5)\), \(\beta = 143.45(3)\). The above setting \((P 2_1/b 11)\) is used so that a comparison can be made with the ambient pressure phase (phase II).  
\(c\)\(R = \Sigma [|F_o| - |F_c|] / \Sigma |F_o|\)  
\(d\)\(R_w = (\Sigma w[|F_o| - |F_c|]^2 / \Sigma wF_o^2]^{1/2}\), \(w = 1\) (unit weight).

Table 2. Atomic and isotropic displacement parameters \((U_{iso}, \AA^2)\)

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>(U_{iso})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0.1785(3)</td>
<td>0.5859(11)</td>
<td>0.237(2)</td>
<td>0.0181(8)</td>
</tr>
<tr>
<td>C</td>
<td>0.046(2)</td>
<td>0.206(4)</td>
<td>0.096(6)</td>
<td>0.017(3)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0812(12)</td>
<td>0.341(4)</td>
<td>0.482(5)</td>
<td>0.024(3)</td>
</tr>
<tr>
<td>O2</td>
<td>0.1397(10)</td>
<td>0.106(4)</td>
<td>-0.219(5)</td>
<td>0.019(2)</td>
</tr>
<tr>
<td>O3</td>
<td>-0.0759(11)</td>
<td>0.162(3)</td>
<td>-0.036(5)</td>
<td>0.017(3)</td>
</tr>
</tbody>
</table>

The unit cell parameters were determined from data collected on a four-circle X-ray diffractometer at the beam line of BL-10A. The results of phase IV are listed in Table 1. The unit cell parameters of phase V have not been refined precisely. The approximate values calculated from the observed Bragg reflection in oscillation photographs are \(a_V \approx 5.44\ \text{Å}\), \(b_V \approx 6.91\ \text{Å}\), \(c_V \approx 4.2\ \text{Å}\), \(\alpha_V \approx 115^\circ\), \(\beta_V \approx 94^\circ\) and \(\gamma_V \approx 69^\circ\). The space group of phase IV \([P 2_1/b 11\) (\#14)\] is determined uniquely from the reflection conditions \((0k\ell: k = 2n\) and \(00h: h = 2n\)\). This non-standard setting \((P 2_1/b 11; a', b', c')\) can be transformed to the standard monoclinic setting \((P 12_1/c1; a', b', c')\) through the following transformation matrix:

\[
\begin{pmatrix}
\mathbf{a}' \\
\mathbf{b}' \\
\mathbf{c}'
\end{pmatrix} =
\begin{pmatrix}
0 & -1 & -1 \\
-1 & 0 & 0 \\
0 & 1 & 0
\end{pmatrix}
\begin{pmatrix}
\mathbf{a} \\
\mathbf{b} \\
\mathbf{c}
\end{pmatrix}.
\]
The setting for phase V was chosen for taking the common $b$- and $c$-axes with phase IV. Accordingly, it was also non-standard triclinic setting.

Figure 2. Crystal structure of (a) the ambient pressure phase (phase II) and (b) the high-pressure monoclinic phase (phase IV), and schematic illustrating of (c) the ($\text{HCO}_3^-$)$_2$ dimers of phase III and (d) two $\text{CO}_3$ groups of the high pressure triclinic phase (phase V) as the ellipses. Only $\text{H}1$ site in phase II and no hydrogen sites in phase IV are described. The ($\text{HCO}_3^-$)$_2$ dimers and the two $\text{CO}_3$ groups are included in the ellipses in phase II and IV, respectively. Each unit cells are designated by parallelograms.
Figure 3. Schematic drawings of the relationship between the structures of (a) phase IV and (b) phase V in terms of the orientations of two \( \text{CO}_3 \) groups parallel to (100) planes. Each unit cell is shaded. There are two possible orientations for each pair of \( \text{CO}_3 \) groups. These orientations are labeled + and -. Only one of the two possible orientations was described as a phase V structure. (c) The observed relationship of phase IV and V. (d) The possible but unobserved relationship of phase IV and V.

Relationship between high-pressure phases and other polymorphs

Some parameters derived from the structure refinement of phase IV are listed in Table 1. The atomic positions and isotropic displacement parameters for non-hydrogen atoms are listed in Tables 2. A hydrogen position in phase IV could not be seen clearly determined from the Fourier difference map. The crystal structure of the new high-pressure monoclinic phase is illustrated in Fig. 2(b). Two \( \text{CO}_3 \) groups are almost on the plane parallel to (301) in the ambient pressure phases (phase I and II). Two \( \text{CO}_3 \) groups in phase IV are also on the
plane parallel to $(03\bar{1})$. These sets of two CO$_3$ groups are described as ellipses in Fig. 2(a) and 2(b), respectively. In phase II, two CO$_3$ groups take one of the two orientations, which are symmetric to the $a$ axis and the ordered structure in an anti-phase configuration. Also in phase IV, there are two orientations, which are symmetric to the $a$ axis, and the two CO$_3$ groups are ordered in an anti-phase configuration as seen in Fig. 2b. The Non-standard setting of phase IV adopted in this study makes clear the relationship between the crystal structures of the ambient pressure phase II and high-pressure phase IV. The observation that the two lattices of phase IV and V are superimposed along $a$ axis and that $a_{IV} = 2 \times a_{V}$ strongly suggests that phase V could be ordered with an in-phase configuration of two CO$_3$ groups as illustrated in Fig. 2d. It is likely that phase V contact with phase IV among $(100)$ plane, and the $d_{100}$ of phase IV is twice as that of phase V owing to the configuration of two CO$_3$ groups. Accordingly, the possible relationship of phase IV and V would be schematically drawn in Fig. 3c. However, this does not explain the observation that an expected $(100)$ twin for phase V was not observed in this experiment. If two CO$_3$ groups in phase V randomly adopt one of the two orientations, which are symmetric to the $a$ axis and the ordered structure in the in-phase configuration, both orientations should be statistically adopted in a crystal, resulting in the arrangement shown in Fig. 3d. The reason why only one of the two orientations was selected in this sample is still unclear. This 'broken symmetry' of two CO$_3$ groups deserves further investigation.

Conclusion

Phases IV and V, which are new high-pressure polymorphs of KHCO$_3$, were identified by single crystal X-ray diffraction analysis. Using synchrotron radiation, the crystal structure of phase IV without hydrogen positions was determined, and found to contain two CO$_3$ groups ordered in an anti-phase configuration. We predict that the crystal structure of phase V will contain two CO$_3$ groups in an ordered, in-phase configuration.

Acknowledgement

Figure 2 was drawn with VICS:Visualization of Crystal Structure developed by Dilanian and Izumi. We thank K. Momma to improvements of VICS for the adjustment to non-standard setting crystal. This work was supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for JSPS Fellows, 4681, 2005. This work was also supported by a Grant-in-aid for The 21st Century COE program for Advanced Science and Technology Center for the Dynamic Earth, and for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science, and Technology. JBP is grateful for support from NSF-EAR program.

References


