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X-RAY STUDY OF LOW AND HIGH SYMMETRY PHASES OF LiNaCO₃

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ABSTRACT

A new phase transition is found in a LiNaCO₃ crystal at 175°C. The structure of the high temperature hexagonal phase (b-phase) was determined using X-ray single crystal diffraction. The low symmetry phase (α-phase) is triclinic and can be described as distorted hexagonal phase. The structure of triclinic phase at room temperature was refined using X-ray powder diffraction data and the Rietveld method. The probable transformations of crystal structure at higher temperatures are discussed.

MATERIAL INDEX: carbonate, alkali metals

INTRODUCTION

Alkali metal carbonates are widely used in molten carbonate fuel cells (1). Other applications have been found in membrane reactors for methane conversion (2) and carbon dioxide sensors (3). A number of structural studies have been performed on the alkali metal carbonates, such as Li₂CO₃, Na₂CO₃ and K₂CO₃ (4-9), but little is known of the structure of the LiNaCO₃. The

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The early paper of Eitle & Skaliks should be mentioned (10). Christmann et al. (11) studied LiNaCO₂ using X-ray powder diffraction over a wide temperature range. The authors claimed the room temperature phase (α-phase) is monoclinic with unit cell parameters a = 14.285(5), b = 24.75(1), c = 3.302(2) Å, β = 91.7 (1) and space group C2 or C2/m. At 290° C and 415° C, the crystal undergoes phase transitions to the β and γ hexagonal phases, respectively.

For the γ-phase, the unit cell parameters, a = 8.297(5) and c = 3.380 Å and space group P6m2 or P62m were reported. Zehnder (12) with IR, FIR and Raman spectroscopy suggested that carbonate ions may be oriented parallel to the (001) plane. Here we present the results of our X-ray study of the LiNaCO₂ structure at room and high temperatures.

**EXPERIMENTAL**

The crystals with sizes about 3 mm were grown from a melt solution of 47% Na₂CO₃ and 53% Li₂CO₃. For single crystal measurements, a four-circle CAD4 (Enraf-Nonius) diffractometer, equipped with graphite monochromator (MoKα radiation) and a standard high-temperature device FR559 was used. Small pieces (about 0.1 mm) were obtained by breaking up the crystals. At room temperature, most of the reflections revealed multiple twinning with up to four or five components. However, the preliminary measurements led us to conclude that the primitive cell of the α-phase is triclinic. The least-square refinement of unit-cell parameters for all chosen samples indicated constant deviations from the direct angles of the previously reported monoclinic cell. With increasing temperature, the twinning angles decreased monotonically, and at 175° ± 5° C the phase transition to the uniform state occurred. The new high temperature phase (β-phase) was determined as hexagonal with unit-cell parameters a = b = 14.355(2), c = 3.341(1) Å. The space group, confirmed afterwards with a structure solution, is P6 space group. The data collection on CAD4 diffractometer was performed at 230°C over one sixth of the Ewald sphere in the range 0° ≤ 2θ ≤ 120° with checking the orientation matrix and monitoring of the intensity of three reflections as standards. No decomposition was observed. The SDP package (see (13)) was used to correct the data for Lorentz and polarization factors. Data collection led to 1460 reflections with I > 3(I) and 790 reflections were used for the structure solution and refinement after the averaging procedure (Rint = 2.8%). Due to multiple twinning for the structure analysis at room temperature, we used X-ray powder diffraction and the Rietveld method. The Rietveld refinement yields very precise unit-cell parameters and, in general, structural parameters, which are comparable with single-crystal studies (14). The specimen was prepared with a hand mortar, then mounted on a spin holder and flattened with a glass slide. The data were obtained on a Philips PW 1450 powder diffractometer in the range 10° ≤ 2θ ≤ 85° using CuKα radiation monochromatized with a β-Ni filter. The measuring time per 0.01° step was 20s.

**RESULTS**

The locations of the sodium atoms were determined from the Patterson synthesis, after which the positions of CO₃²⁻ groups on the difference map were indicated. The least-squares isotropic refinement resulted in a discrepancy factor Riso = 13%. Then the coordinates of the lithium atoms on the Fourier difference map were derived. All atoms except the Li atoms were refined anisotropically. The full-matrix least-squares refinement converged to the discrepancy factor Rfinal = 3.3%. The final difference Fourier synthesis showed no significant peaks. The positional parameters, relevant interatomic distances and angles are given in Tables 1a & 1b.
**Room temperature α-phase.** The P1 space group was chosen on the basis of the observation of a second harmonic signal. The atomic parameters of 54 atoms of α-phase were derived from the hexagonal structure with an appropriate matrix transformation. For the least-squares refinement, we used the MRJA-VAX package (15). Background was fitted by the Chebyshev polynomial function and the peak profile by the pseudo-Voigt function including the asymmetry correction. Following Cagliotti et al. (16) the width $H$ of the Bragg peak was modeled as function of the $\theta$ angle: $H = Utg^2 \theta + Vtg \theta + W$. The atomic parameters were fixed; the cell parameters, the scale factor, the background coefficients, and the peak width parameters were adjusted. A large discrepancy between the calculated and experimental peak intensities of 00l reflections was observed, which might be explained by preferred orientation. Thus, the March

<table>
<thead>
<tr>
<th>Table 1a. Atomic Coordinates.</th>
<th></th>
<th>Table 1b. Interatomic distances d(Å).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>Na (1) 0.1335 (2)</td>
<td>0.2247 (1)</td>
<td>0.5</td>
</tr>
<tr>
<td>Na (2) 0.4477 (2)</td>
<td>0.2554 (1)</td>
<td>0.5</td>
</tr>
<tr>
<td>Na (3) 0.1209 (2)</td>
<td>0.5788 (2)</td>
<td>0.5</td>
</tr>
<tr>
<td>C (1) 0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>O (1) -0.0920 (2)</td>
<td>-0.0052 (3)</td>
<td>0.0</td>
</tr>
<tr>
<td>C (2) 0.67</td>
<td>0.3333</td>
<td>0.0</td>
</tr>
<tr>
<td>O (2) 0.5808 (2)</td>
<td>0.3392 (3)</td>
<td>0.0</td>
</tr>
<tr>
<td>C (3) 0.33</td>
<td>0.6666</td>
<td>0.0</td>
</tr>
<tr>
<td>O (3) 0.2412 (3)</td>
<td>0.5831 (3)</td>
<td>0.0</td>
</tr>
<tr>
<td>C (4) -0.0120 (3)</td>
<td>0.3204 (3)</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Na(1)-O(1) | 2.364(2) | Na(2)-O(2) | 2.364(3) | Na(3)-O(3) | 2.380(4) |
| Na(1)-O(4)' | 2.496(5) | Na(2)-O(4) | 2.398(3) | Na(3)-O(4)* | 2.519(4) |
| Na(1)-O(5) | 2.446(2) | Na(2)-O(5)' | 2.400(3) | Na(3)-O(5)* | 2.377(4) |
| Li(1)-O(1) | 1.94(1) | Li(2)-O(3) | 1.88(1) | Li(3)-O(2) | 1.94(1) |
| Li(1)-O(4)' | 2.04(1) | Li(2)-O(4)* | 2.03(1) | Li(3)-O(4) | 2.06(1) |
| Li(1)-O(5)* | 1.93(1) | Li(2)-O(5) | 1.87(1) | Li(3)-O(5)* | 1.94(1) |

$d_{av}$ (C-O) 1.274 $\omega_{av}$ (O-C-O) 120°
### TABLE 2.
The Rietveld refinement results.

<table>
<thead>
<tr>
<th>Unit cell parameters</th>
<th>Peak width parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, Å 14.283 (1) α, (°) 89.00 (1)</td>
<td>u -0.015 (1)</td>
</tr>
<tr>
<td>b, Å 14.289 (1) β, (°) 91.70 (1)</td>
<td>v 0.016 (1)</td>
</tr>
<tr>
<td>c, Å 3.310 (1) γ, (°) 120.00 (1)</td>
<td>w 0.0064 (2)</td>
</tr>
</tbody>
</table>

March correction coefficient of preferred orientation (0 0 ℓ)  
G 0.60 (1)  
Mixing factor q 0.95 (1)  
(pseudo-Voigt function)  
Asymmetry -0.12 (2)

### FIG. 1.
Observed (points) and calculated X-ray powder patterns of α-phase LiNaCO₃. The vertical lines indicate the positions of Bragg reflections. The line near the bottom shows the difference between the observed and calculated patterns.
correction (see (17)) for preferred orientation was applied. The Rietveld refinement converged to the discrepancy factors $R_{wp} = 10\%$, $R_B = 24\%$ and $GOF = 12$. The results are given in Table 2. In Fig. 1 the plots of observed and calculated powder X-ray diffraction patterns are shown. The agreement seems to be quite reasonable. Therefore, the Rietveld method confirmed the triclinic symmetry of LiNaCO$_3$ crystal at room temperature.

**DISCUSSION**

In Fig. 2 the stereoview projection of the hexagonal LiNaCO$_3$ structure along c-axis is shown. The structure can be described as stacked hexagonal closed-packed layers of CO$_3^{2-}$ groups with Li or Na cations, normal to the c-axis. The lithium and sodium ions are placed inside different polyhedra: the lithium cations occupy the tetrahedral sites, and the sodium cations occupy the sites in the distorted square pyramid with respect to the oxygen atoms of CO$_3^{2-}$ groups.

The structure of the $\alpha$-phase is very similar to the $\beta$-phase and seems to be distorted with shifts of layers along the a0b plane with minor changes of layers. The triclinic parameters permit selection of the unit cell, close to the C-base monoclinic cell. However, the monoclinic symmetry requires the two-fold axis to be in the a0b plane or the mirror plane, normal to this direction, which are obviously inconsistent with determined crystal structure. A more detailed investigation of the $\alpha$-phase is desirable.

It is interesting to analyze the probable transformation of the crystal structure at higher temperatures. In Fig. 2 one can see that the unit cell of $\beta$-phase could be constructed from the hexagonal subcell with the unit cell parameters $a = a_0 / \sqrt{3}$ and $c = c_0$, and the existence of the
supercell is caused by the unique position of one CO$_2^-$ group. Therefore, the phase transition at 415° C to the hexagonal γ-phase with the unit cell parameters $a = 8.297(5)$, $c = 3.380(2)$ Å as reported by Christmann et al. (11) is very probably related to the rotation of this CO$_2^-$ group around the c-axis.

ACKNOWLEDGMENTS

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