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X-RAY STUDY OF LOW AND HIGH SYMMETRY PHASES OF LiNaCO_3

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ABSTRACT

A new phase transition is found in a LiNaCO_3 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 Li_2CO_3 , Na_2CO_3 and K_2CO_3 (4-9), but little is known of the structure of the LiNaCO_3 . The

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early paper of Eitle & Skaliks should be mentioned (10). Christmann *et al.* (11) studied LiNaCO_3 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, $\beta = 91.7(1)$ 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 LiNaCO_3 structure at room and high temperatures.

EXPERIMENTAL

The crystals with sizes about 3 mm were grown from a melt solution of 47% Na_2CO_3 and 53% Li_2CO_3 . For single crystal measurements, a four-circle CAD4 (Enraf-Nonius) diffractometer, equipped with graphite monochromator (MoK α 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 $175 \pm 5^\circ\text{C}$ 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 $0^\circ \leq 2\theta \leq 120^\circ$ 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 $I > 3\sigma(I)$, and 790 reflections were used for the structure solution and refinement after the averaging procedure ($R_{\text{int}} = 2.8\%$). 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 $10^\circ \leq 2\theta \leq 85^\circ$ using CuK_α radiation monochromatized with a β -Ni filter. The measuring time per 0.01° step was 20s.

RESULTS

High temperature β -phase. The locations of the sodium atoms were determined from the Patterson synthesis, after which the positions of CO_3^{2-} groups on the difference map were indicated. The least-squares isotropic refinement resulted in a discrepancy factor $R_w = 13\%$. 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 $R_w = 3.3\%$. 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 MRIA-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 θ angle: $H_2 = U\lg^2\theta + V\lg\theta + W$. 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 00 ℓ reflections was observed, which might be explained by preferred orientation. Thus, the March

TABLE 1a.
Atomic Coordinates.

Atom	x	y	z	Atom	x	y	z
Na (1)	0.1335 (2)	0.2247 (1)	0.5	O (4)	-0.0814 (2)	0.3515 (2)	0.5
Na (2)	0.4477 (2)	0.2554 (1)	0.5	O'(4)	-0.0430 (3)	0.2193 (2)	0.5
Na (3)	0.1209 (2)	0.5788 (2)	0.5	O''(4)	0.0885 (3)	0.3894 (3)	0.5
C (1)	0.0	0.0	0.0	C (5)	0.3357 (3)	0.3445 (3)	0.0
O (1)	-0.0920 (2)	-0.0052 (3)	0.0	O (5)	0.2528 (3)	0.3539 (3)	0.0
C (2)	0.67	0.3333	0.0	O'(5)	0.3257 (3)	0.2516 (2)	0.0
O (2)	0.5808 (2)	0.3392 (3)	0.0	O''(5)	0.4281 (3)	0.4279 (3)	0.0
C (3)	0.33	0.6666	0.0	Li (1)	0.2255 (6)	0.0991 (6)	0.0
O (3)	0.2412 (3)	0.5831 (3)	0.0	Li (2)	0.1811 (7)	0.4329 (6)	0.0
C (4)	-0.0120 (3)	0.3204 (3)	0.5	Li (3)	0.5262 (6)	0.1062 (6)	0.0

TABLE 1b.
Interatomic distances d(Å).

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			w_{av} (O-C-O)	120°

TABLE 2.
The Rietveld refinement results.

Unit cell parameters	Peak width parameters
a , Å 14.283 (1) α , (°) 89.00 (1)	U -0.015(1)
b , Å 14.289 (1) β , (°) 91.70 (1)	V 0.016(1)
c , Å 3.310 (1) γ , (°) 120.00 (1)	W 0.0064(2)
March correction coefficient of preferred orientation (0 0 ℓ)	Mixing factor η 0.95(1) (pseudo-Voigt function)
G 0.60(1)	Asymmetry -0.12(2)

FIG. 1.

Observed (points) and calculated X-ray powder patterns of α -phase LiNaCO_3 . The vertical lines indicate the positions of Bragg reflections. The line near the bottom shows the difference between the observed and calculated patterns.

FIG. 2.
The stereo projection of β -phase LiNaCO_3 along c -axis.

correction (see (17)) for preferred orientation was applied. The Rietveld refinement converged to the discrepancy factors $R_w = 10\%$, $R_B = 24\%$ 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 α -phase is very similar to the β -phase and seems to be distorted with shifts of layers along the a_0b 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 a_0b plane or the mirror plane, normal to this direction, which are obviously inconsistent with determined crystal structure. A more detailed investigation of the α -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 β -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_3^{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_3^{2-} group around the c -axis.

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