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BRIEF COMMUNICATION

Crystal Structure of $LiKCO_3$ by Neutron Powder Diffraction Analysis

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The crystal structure of $LiKCO_3$ was determined by neutron powder diffraction. A final weighted R-factor of 4.54% was obtained for the refinement of 2373 reflections by the Rietveld method from a sample synthesized using $^7Li_2CO_3$ and K_2CO_3 (99.9% pure). Slight distortion of the CO_3^{2-} units in the monoclinic cell was observed; the O(1)–C–O(2) angle and C–O(3) length are larger than the other C–O bond lengths and O–C–O angles. These local-structure characteristics can be explained by the difference in the ionic size of Li^+ and K^+, and the different electrostatic interactions between the cations and CO_3^{2-} units.

INTRODUCTION

The promising efficiency and attractive environmental features of molten carbonate fuel cells have attracted keen attention from electrochemists in recent years. In particular, concerns such as corrosion of electrodes and reduction processes of oxygen in mixed Li_2CO_3–K_2CO_3 molten salts have been the subject of intense studies. Both issues involve electroactive CO_3^{2-} species, their interaction with cations of the electrodes, and interdiffusion with O_2 and CO_2. These properties are closely related to the structural differences of the materials near and in between the eutectic compositions. Information regarding the configuration of CO_3^{2-} with respect to the alkali ions in molten and solid-state solutions of Li_2CO_3–K_2CO_3 is not complete. Recent molecular dynamics (MD) simulations of molten $LiKCO_3$ indicated that a Li^+ ion is located near one O atom of a CO_3^{2-} ion, and a K^+ ion is at an intermediate position between two O atoms of the CO_3^{2-} ion (1–3). Furthermore, simulations suggested that cation sites surrounding CO_3^{2-} ions change with the Li/K ratio (2). However, MD simulations (1–3) and *ab initio* calculations (4) do not determine the precise near-neighbor distances and angles, nor do they identify geometric changes in CO_3^{2-} units responding to preferential coordination of Li^+ and K^+ ions. Detailed crystal structure determinations can provide these insights. In particular, structural changes resulting from changes in Li/K ratio may be correlated with variations of thermodynamic properties and performance of the fuel cells. This letter reports the crystal structure of a $LiKCO_3$ powder by neutron-diffraction measurements.

Several authors have reported the solid–liquid phase diagram for mixtures of Li_2CO_3 and K_2CO_3 (5, 6). These data suggest that a solid solution with composition $Li_2CO_3 : K_2CO_3 = 0.5 : 0.5$ may form a single-phase material at room temperature. The crystal structure of $LiKCO_3$ has been studied by X-ray diffraction (7) and the lattice parameters and space group have been reported. However, a detailed crystal structure determination was not achieved. To the best of our knowledge, no neutron-diffraction studies of Li_2CO_3–K_2CO_3 have been reported so far. This may be in part due to difficulties encountered when analyzing neutron-diffraction data from samples containing natural Li (^6Li 7.42% + ^7Li 92.58%), since the neutron absorption coefficient of ^6Li is large. The samples used in this study were prepared by mixing $^7Li_2CO_3$ with K_2CO_3 to avoid this problem.

EXPERIMENTAL DETAILS

Li_2CO_3 powder of 99.9% purity and 99.9% ^7Li isotopic substitution, supplied by Tomiyama's High Purity Chemicals, and K_2CO_3 powder of 99.9% purity, supplied by Wako Pure Chemical Ind. Ltd., were used as starting materials. The carbonates were dried in air at 450°C for 12 h. Li_2CO_3 and K_2CO_3 were then mixed in a 1 : 1 molar ratio and placed in an alumina crucible for melting. The sample was first heated at a rate of 30°C/min to 650°C and kept for

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TABLE 1
The Lattice Parameters and Cell Volume for $LiKCO_3$ at Room Temperature

	Neutron	X-ray (7)
a (Å)	7.22284(7)	7.232(5)
b (Å)	7.07673(8)	7.080(4)
c (Å)	7.59397(9)	7.619(5)
β	127.421(1)	127.5(1)
V (Å)	308.272(3)	

Note. Numbers within parentheses are statistical standard deviations of the last significant digit.

1 h in air. The melt was then quenched to room temperature by pouring it on a copper plate in air. The quenched sample was placed in a dry box under flowing dry nitrogen gas and ground into a powder. The resulting sample was dried at 450°C for 1.5 h in air. This process was repeated once.

Time-of-flight (TOF) neutron powder diffraction was performed using the General Purpose Powder Diffractometer (GPPD) at Argonne's Intense Pulsed Neutron Source (IPNS) (8). A powder sample was enclosed in a thin-walled vanadium can (11 mm diameter, 50 mm long). Independent TOF data were recorded on eight detector banks positioned at scattering angles ranging from $\pm 15°$ to $\pm 150°$. The back-scattering geometry (at a mean scattering angle of $\pm 148°$) corresponds to the highest resolution ($\Delta d/d =$ 0.25% where d is the atomic spacing). For the measurement of $^7LiKCO_3$, 3.3 g of powder was used, and data were collected for 9 h at room temperature. The crystal structure was refined with the Rietveld technique (GSAS program (9)).

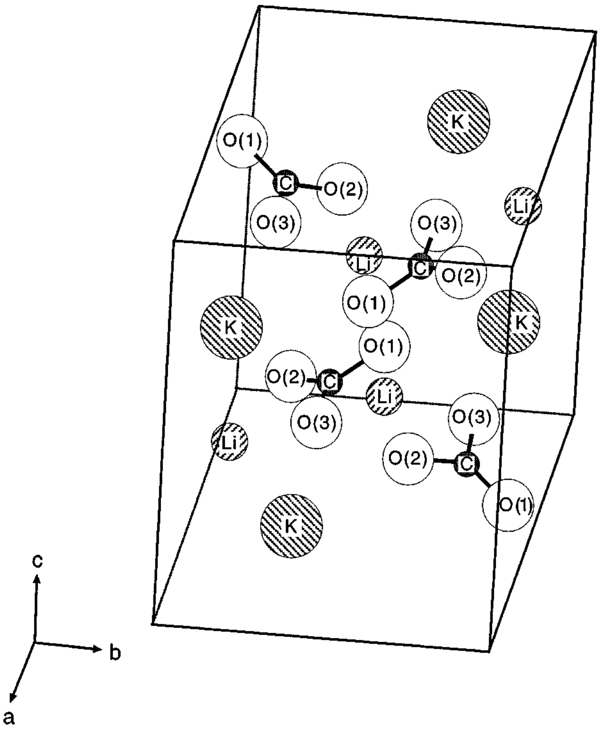

FIG. 1. The crystal structure (space group $P2_1/c$) of $LiKCO_3$. The unit cell is shown by the parallelepiped.

RESULTS AND DISCUSSION

The intensity profile of the $^7LiKCO_3$ sample was analyzed over a large d-spacing range from 0.5 to 2.9 Å, which consisted of 4910 data points and 2373 reflections. An initial refinement was carried out by assuming a monoclinic unit cell isostructural with K_2CO_3 (7). Subsequent analyses concluded a single-phase structure for $LiKCO_3$ of monoclinic symmetry (space group $P2_1/c$). The final refined parameters are listed in Tables 1 and 2, and the unit cell is shown in Fig. 1. Figure 2 illustrates the resulted profile fit, where good agreement between the observed and calculated patterns and a low R-factor ($R_{wp} = 4.54\%$) were obtained. The lattice parameters agree reasonably well with those previously obtained by Christmann and co-workers (7) from X-ray diffraction. As shown in Table 2, our results show that Li^+ and K^+ ions occupy different sites and that all cation sites are fully occupied, in good agreement with previous MD simulations (1).

TABLE 2
The Crystal Structural Parameters for $LiKCO_3$ at Room Temperature

Atom	Site	x	y	z	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{12} (Å^2)	U_{13} (Å^2)	U_{23} (Å^2)
Li	4e	0.4004(9)	0.0676(8)	0.1019(9)	0.0234(28)	0.0356(32)	0.0384(34)	0.0068(22)	0.0275(28)	0.0025(25)
K	4e	− 0.1716(5)	0.3553(4)	0.1685(5)	0.0225(17)	0.0220(18)	0.0447(23)	− 0.0010(11)	0.0234(17)	0.0023(13)
C	4e	0.2939(3)	0.3326(2)	0.2132(3)	0.0206(8)	0.0189(8)	0.0254(10)	− 0.0023(8)	0.0165(8)	− 0.0039(8)
O(1)	4e	0.7436(3)	− 0.0243(2)	0.2092(3)	0.0296(11)	0.0193(11)	0.0310(12)	0.0030(8)	0.0240(10)	0.0075(9)
O(2)	4e	0.1596(3)	0.1899(3)	0.1294(3)	0.0301(11)	0.0168(10)	0.0421(14)	− 0.0032(9)	0.0277(11)	− 0.0026(9)
O(3)	4e	0.4787(3)	0.3328(3)	0.2207(4)	0.0285(11)	0.0287(10)	0.0552(15)	− 0.0094(10)	0.0346(11)	− 0.0153(11)

Note. Rietveld refinements were based on a monoclinic structure (space group $P2_1/c$); see Table 1. The occupation factors of all atoms were fixed to unity. The R-factors were $R_{wp} = 4.54\%$, $R_p = 3.03\%$, and $R_{exp} = 2.82\%$.

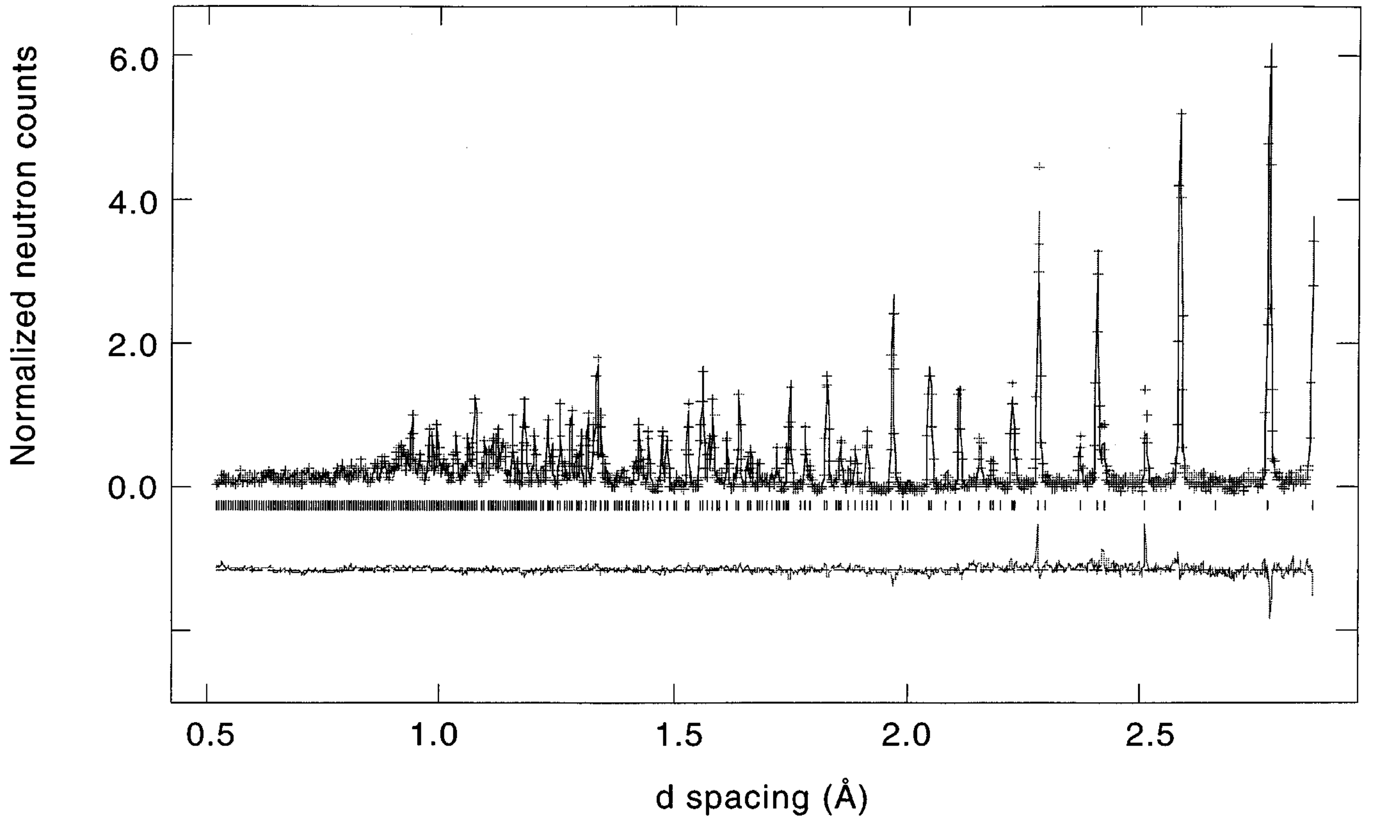

FIG. 2. Neutron powder diffraction data and Rietveld refinement profile fit for monoclinic $LiKCO_3$. The symbols (+) represent the background-subtracted data. The solid line is the calculated profile. Tick marks below the profile mark the positions of allowed Bragg reflections. The differences between the observed and calculated intensities are shown at the bottom.

TABLE 3
Selected Bond Lengths (in Å) and Bond Angles (in °) for $LiKCO_3$

C_1–$O(1)_5$	1.281(2)	$O(1)_5$–C_1–$O(2)_1$	123.2(2)
C_1–$O(2)_1$	1.271(2)	$O(2)_1$–C_1–$O(3)_1$	118.3(2)
C_1–$O(3)_1$	1.301(2)	$O(3)_1$–C_1–$O(1)_5$	118.5(2)
Li_1–$O(1)_4$	1.942(6)		
Li_1–$O(2)_1$	2.065(5)	Li_1–C_1–$O(1)_5$	174.5(2)
Li_1–$O(3)_6$	1.977(6)	Li_1–C_1–$O(2)_1$	60.5(2)
K_1–$O(1)_5$	2.767(3)	Li_1–C_1–$O(3)_1$	58.0(2)
K_1–$O(2)_2$	2.794(4)	Li_5–C_1–$O(2)_1$	170.8(2)
K_1–$O(3)_7$	2.789(3)		
C_1–Li_1	2.370(5)	K_1–C_1–$O(1)_5$	60.2(1)
C_1–Li_5	2.417(5)	K_1–C_1–$O(2)_1$	63.2(1)
C_1–K_1	3.172(3)	K_1–C_1–$O(3)_1$	175.9(2)
Li_1–K_3	3.396(6)		
Li_1–Li_4	2.843(1)	Li_1–C_1–K_1	123.7(2)
K_1–K_3	4.058(3)		

Note. Subscripts indicate the following equivalent positions.

(1)	x	y	z
(2)	$-x$	$y+(1/2)$	$-z+(1/2)$
(3)	$-x$	$y-(1/2)$	$-z+(1/2)$
(4)	$-x+1$	$-y$	$-z$
(5)	$-x+1$	$y+(1/2)$	$-z+(1/2)$
(6)	$-x+1$	$y-(1/2)$	$-z+(1/2)$
(7)	$x-1$	y	z

Selected bond lengths and angles from structural parameters are listed in Table 3. In contrast with the carbonate groups in isostructural K_2CO_3 (10), the CO_3 units in $LiKCO_3$ are slightly distorted. The O(1)–C–O(2) bond angle of 123.2 ± 0.2° is somewhat larger than that (118.4 ± 0.3°) of O(2)–C–O(3) and O(3)–C–O(1). In addition, a greater bond length of C–O(3) (1.301(2) Å) than of C–O(1) and C–O(2) (1.281(2) and 1.271(2) Å, respectively) was clearly identified. A selected portion of the crystal structure is shown in Fig. 3 to illustrate this situation. The seven atoms shown are located roughly in the plane of the figure. The observed differences in bond distances and angles within the CO_3 unit can be understood by comparison with K_2CO_3, where Li sites would be occupied by K atoms. While this group of atoms in K_2CO_3 closely follows a D_{3h} point symmetry around carbon, in $LiKCO_3$ the local symmetry is closer to C_{2v}. Furthermore, each Li^+ ion is fourfold coordinated, whereas K^+ exhibits seven-fold coordination. Because Li^+ is considerably smaller than K^+, these differences in local symmetry and coordination will strongly influence the bond lengths and angles. Local structural variations in $(Li_xK_{1-x})_2CO_3$ materials can therefore be explained by the difference in ionic size between Li^+ and K^+ and the consequent differences in electrostatic interactions.

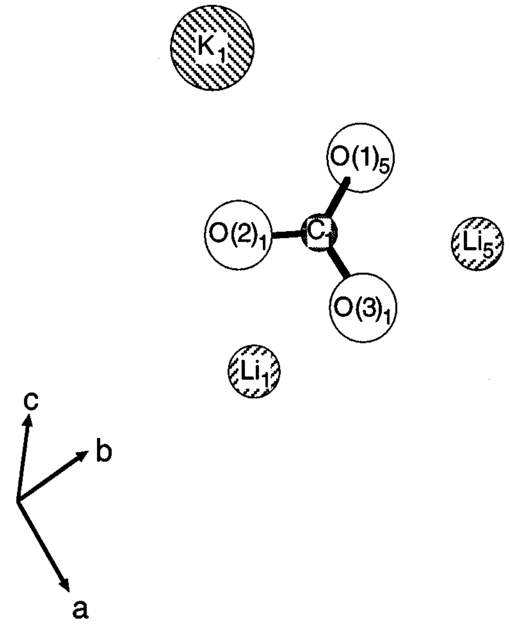

FIG. 3. A selected portion of crystal structure for $LiKCO_3$, illustrating the coordination of Li^+ and K^+ ions with the CO_3^{2-} units. Atoms are labeled according to the scheme given in Table 3.

A separate sample of $LiKCO_3$ was prepared, in the same manner as the first sample, using natural Li_2CO_3. As expected, a Rietveld refinement of the diffraction data from this sample resulted in a larger R_{wp} (5.28%) than that obtained with the ^7Li enriched sample (4.54%). The improvement from ^7Li enrichment is due to the lower absorption coefficient of ^7Li than ^6Li. Complete details of neutron-diffraction results for both the isotopic and natural Li_2CO_3, K_2CO_3, $(Li_{0.43}K_{0.57})_2CO_3$, and $(Li_{0.62}K_{0.38})_2CO_3$ samples will be reported in a separate paper.

CONCLUSION

The crystal structure of $LiKCO_3$ has been determined by TOF neutron powder diffraction. Asymmetry in the CO_3^{2-} units in terms of larger O(1)–C–O(2) bond angle and C–O(3) bond length than the other corresponding angles and lengths in the CO_3^{2-} unit was observed. Differences in bond angles and bond lengths are influenced by electrostatic interactions between the CO_3^{2-} units and the Li^+ ion and K^+ ions. The improved refinements — R_{wp} from 5.28% to 4.54% — by using isotopically enriched samples, prepared by using $^7Li_2CO_3$ instead of the natural compound, demonstrates that ^7Li isotopic substitution is effective for the determination of an accurate crystal structure by neutron diffraction.

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