INORGANIC COMPOUNDS

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Triclinic α-$LiNaCO_3$

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Abstract

The structure of room-temperature triclinic lithium sodium carbonate, $LiNaCO_3$, is built up of layers; one of them contains all the Na^+ cations and one-third of the carbonate anions, and the other contains all the Li^+ cations with the remaining anions. The triclinic unit cell is formed by the distortion of the high-temperature hexagonal unit cell.

Comment

Lithium sodium carbonate exhibits several phase transitions up to its melting point (Christmann, Sadeghi & Papin, 1978). A new phase transition at 448 K and the crystal structure of the hexagonal β phase ($P\bar{6}$, a = 14.355, c = 3.341 Å) above 448 K have been reported previously (Yatsenko *et al.*, 1995). The unit cell of the hexagonal γ phase (a = 8.297, c = 3.380 Å) was determined by Christmann *et al.* (1978) by X-ray powder diffraction. The results of the structural study of the α phase are presented below.

The unit cell of the α phase can be produced from the β unit cell by a uniform shift of the neighbouring layers by 0.06 Å in a direction close to $[\bar{1}10]$. The equivalence of these three directions in the $P\bar{6}$ space group leads to the formation of a domain-disordered structure of the α phase below the transition temperature. Separate atoms deviate from the planes of the layers by up to 0.27 Å. The α unit cell can be transformed to a pseudo monoclinic unit cell (a = 24.698, b = 14.274, c = 3.305 Å, α = 90.11, β = 91.90, γ = 89.98°), as proposed by Christmann *et al.* (1978) on the basis of powder diffraction data. However, the $|F|^2$-body as well as the crystal structure are not consistent with the monoclinic symmetry.

One can see from Fig. 1 that the unit cell contains a pseudo-hexagonal subcell with dimensions $a = b = a_0/(3^{1/2})$ (8.24 Å) and $c = c_0$, *i.e.* as for the unit cell of the γ phase. The supercell results from the rotation of one carbonate anion (related to C3) through 60°, so we can suppose that the origin of the $\beta \leftrightarrow \gamma$ phase transition is associated with the reorientation of this anion and the subcell becomes the true cell of the γ phase.

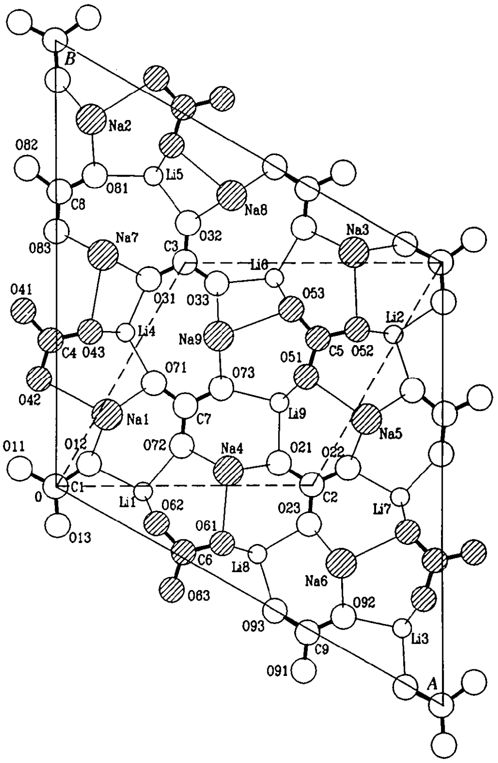

Fig. 1. Packing diagram viewed down the c axis. Shaded atoms have a z coordinate *ca* 0.5. The subcell is shown by the dashed line.

The Na^+ cations are surrounded by ten to eleven O atoms and the Na—O distances fall into two classes: principal (shorter than 2.55 Å) and additional (longer than 2.70 Å). Each Na^+ cation has five principal contacts and these O atoms form a tetragonal pyramid. Analysis of the Na—O bond valences (Brown & Altermatt, 1985) indicates that these five contacts account for 85–89% of the full valence of Na. All Li^+ cations are in a tetrahedral oxygen environment, as in Li_2CO_3 (Effenberger & Zemann, 1979). The C—O distances in the carbonate groups range from 1.265 (5) to 1.295 (6) Å.

Experimental

The monodomain specimen of $LiNaCO_3$ was cleaved from a large crystal grown from the melt solution of 50.5% Li_2CO_3 and 49.5% Na_2CO_3. The crystal density D_m was measured by flotation in a CCl_4/$CHBr_3$ mixture.

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Crystal data

$LiNaCO_3$
$M_r = 89.94$
Triclinic
$P1$
$a = 14.265\,(4)$ Å
$b = 14.261\,(3)$ Å
$c = 3.3050\,(10)$ Å
$\alpha = 88.41\,(2)°$
$\beta = 91.70\,(3)°$
$\gamma = 119.95\,(3)°$
$V = 582.2\,(3)$ Å^3
$Z = 9$
$D_x = 2.309$ Mg m^{-3}
$D_m = 2.29$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 15.0$–$17.5°$
$\mu = 0.351$ mm^{-1}
$T = 295\,(2)$ K
Plate
0.15 × 0.11 × 0.03 mm
Colourless

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
Profile data from ω scans
Absorption correction: none
3407 measured reflections
3407 independent reflections
2445 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 29.97°$
$h = 0 \rightarrow 20$
$k = -20 \rightarrow 17$
$l = -4 \rightarrow 4$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0455$
$wR(F^2) = 0.0701$
$S = 1.056$
3407 reflections
440 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0210P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.018$
$\Delta\rho_{\max} = 0.383$ e Å^{-3}
$\Delta\rho_{\min} = -0.338$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0179 (16)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{\rm iso}$ for Li atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Na1	0.1320	0.2250	0.5250	0.0179 (4)
Na2	0.0920 (2)	0.8665 (2)	0.5292 (10)	0.0187 (5)
Na3	0.7743 (2)	0.9085 (2)	0.4708 (10)	0.0171 (4)
Na4	0.4478 (2)	0.2562 (2)	0.4941 (9)	0.0206 (5)
Na5	0.8070 (2)	0.5514 (2)	0.4809 (11)	0.0210 (5)
Na6	0.7427 (2)	0.1913 (2)	0.5153 (9)	0.0204 (5)
Na7	0.1210 (2)	0.5770 (2)	0.4811 (9)	0.0244 (5)
Na8	0.4561 (2)	0.8775 (2)	0.5653 (11)	0.0222 (5)
Na9	0.4214 (2)	0.5448 (2)	0.4447 (10)	0.0224 (5)
C1	−0.0003 (4)	−0.0005 (4)	0.0092 (17)	0.0115 (9)
O11	−0.0933 (3)	−0.0066 (3)	−0.0169 (13)	0.0159 (7)
O12	0.0856 (3)	0.0927 (3)	0.0299 (13)	0.0153 (7)
O13	0.0059 (3)	−0.0871 (3)	0.0055 (13)	0.0161 (7)
C2	0.6661 (4)	0.3337 (4)	−0.0034 (17)	0.0124 (9)
O21	0.5802 (3)	0.3405 (3)	0.0034 (14)	0.0188 (8)
O22	0.7593 (3)	0.4190 (3)	−0.0120 (13)	0.0170 (8)
O23	0.6587 (3)	0.2396 (3)	−0.0015 (13)	0.0175 (8)
C3	0.3331 (4)	0.6673 (4)	0.0010 (15)	0.0087 (9)
O31	0.2403 (3)	0.5821 (3)	0.0046 (14)	0.0196 (8)
O32	0.3421 (3)	0.7587 (3)	0.0762 (13)	0.0167 (7)
O33	0.4162 (3)	0.6603 (3)	−0.0860 (14)	0.0192 (8)
C4	−0.0143 (4)	0.3188 (4)	0.5023 (16)	0.0116 (9)
O41	−0.0848 (3)	0.3488 (3)	0.4972 (13)	0.0179 (8)
O42	−0.0445 (3)	0.2168 (3)	0.5116 (13)	0.0191 (8)
O43	0.0874 (3)	0.3883 (3)	0.4977 (13)	0.0195 (8)
C5	0.6809 (4)	0.6687 (4)	0.4674 (16)	0.0110 (9)
O51	0.6500 (3)	0.5672 (3)	0.4683 (13)	0.0178 (8)
O52	0.7819 (3)	0.7393 (3)	0.4737 (13)	0.0180 (8)
O53	0.6105 (3)	0.6996 (3)	0.4642 (13)	0.0190 (8)
C6	0.3316 (4)	0.0129 (4)	0.5311 (16)	0.0112 (9)
O61	0.4329 (3)	0.0832 (3)	0.5175 (13)	0.0173 (7)
O62	0.2611 (3)	0.0435 (3)	0.5188 (14)	0.0176 (8)
O63	0.3001 (3)	−0.0885 (3)	0.5515 (13)	0.0175 (8)
C7	0.3353 (4)	0.3456 (4)	−0.0085 (16)	0.0104 (9)
O71	0.2529 (3)	0.3554 (3)	0.0555 (14)	0.0216 (8)
O72	0.3263 (3)	0.2531 (3)	−0.0394 (14)	0.0205 (8)
O73	0.4279 (3)	0.4310 (3)	−0.0476 (14)	0.0188 (8)
C8	0.0091 (4)	0.6635 (4)	0.0004 (16)	0.0103 (9)
O81	0.1016 (3)	0.7456 (3)	0.0728 (14)	0.0214 (8)
O82	−0.0745 (3)	0.6734 (3)	−0.0330 (14)	0.0215 (8)
O83	0.0010 (3)	0.5705 (3)	−0.0392 (13)	0.0196 (8)
C9	0.6543 (4)	−0.0088 (4)	0.0116 (15)	0.0093 (9)
O91	0.6433 (3)	−0.1008 (3)	−0.0817 (13)	0.0187 (8)
O92	0.7474 (3)	0.0736 (3)	0.0476 (14)	0.0200 (8)
O93	0.5692 (3)	−0.0020 (3)	0.0688 (13)	0.0164 (7)
Li1	0.2254 (7)	0.1002 (7)	0.010 (3)	0.018 (2)
Li2	0.8762 (8)	0.7753 (8)	−0.017 (3)	0.023 (2)
Li3	0.8989 (7)	0.1239 (7)	0.013 (3)	0.020 (2)
Li4	0.1792 (7)	0.4322 (7)	0.004 (3)	0.017 (2)
Li5	0.2525 (7)	0.8193 (7)	0.053 (3)	0.017 (2)
Li6	0.5662 (7)	0.7464 (7)	−0.051 (3)	0.020 (2)
Li7	0.8944 (7)	0.4196 (7)	−0.011 (3)	0.015 (2)
Li8	0.5251 (7)	0.1056 (7)	0.028 (3)	0.018 (2)
Li9	0.5802 (7)	0.4743 (7)	−0.029 (3)	0.018 (2)

Table 2. *Selected geometric parameters* (Å)

Na1—O12^{i}	2.330 (4)	Na9—O73^{i}	2.333 (4)
Na1—O12	2.353 (4)	Na9—O73	2.364 (4)
Na1—O71	2.374 (4)	Na9—O33	2.398 (4)
Na1—O42	2.460 (4)	Na9—O53	2.492 (4)
Na1—O71^{i}	2.511 (5)	Li1—O12	1.946 (9)
Na2—O13^{ii}	2.325 (4)	Li1—O62	2.006 (10)
Na2—O13^{iii}	2.358 (4)	Li1—O62^{viii}	2.021 (10)
Na2—O81	2.379 (4)	Li1—O72	1.926 (9)
Na2—O62^{iii}	2.473 (4)	Li2—O13^{iv}	1.912 (10)
Na2—O81^{i}	2.504 (5)	Li2—O52^{viii}	2.032 (11)
Na3—O11^{iv}	2.328 (4)	Li2—O52	2.026 (10)
Na3—O11^{v}	2.354 (4)	Li2—O82^{vii}	1.906 (10)
Na3—O91^{ii}	2.366 (4)	Li3—O11^{vii}	1.924 (9)
Na3—O52	2.469 (4)	Li3—O42^{ix}	2.011 (10)
Na3—O91^{iii}	2.530 (5)	Li3—O42^{vii}	2.024 (10)
Na4—O21	2.335 (4)	Li3—O92	1.913 (10)
Na4—O72^{i}	2.337 (4)	Li4—O31	1.862 (9)
Na4—O21^{i}	2.346 (4)	Li4—O43	2.005 (9)
Na4—O61	2.367 (4)	Li4—O43^{viii}	2.005 (10)
Na4—O72	2.421 (4)	Li4—O71	1.861 (9)
Na5—O22^{i}	2.333 (4)	Li5—O32	1.865 (9)
Na5—O22	2.345 (4)	Li5—O63^{x}	1.998 (9)
Na5—O82^{vi}	2.350 (4)	Li5—O63^{iii}	2.017 (10)
Na5—O51	2.359 (4)	Li5—O81	1.868 (9)
Na5—O82^{vii}	2.417 (5)	Li6—O33	1.863 (9)
Na6—O23^{i}	2.337 (4)	Li6—O53	2.011 (10)
Na6—O23	2.338 (4)	Li6—O53^{viii}	1.988 (10)
Na6—O92	2.340 (4)	Li6—O91^{iii}	1.889 (9)
Na6—O41^{vii}	2.364 (4)	Li7—O22	1.923 (9)
Na6—O92^{i}	2.421 (4)	Li7—O41^{vii}	2.027 (9)
Na7—O31	2.326 (4)	Li7—O41^{ix}	2.041 (9)
Na7—O83^{i}	2.334 (4)	Li7—O83^{vii}	1.919 (9)
Na7—O83	2.360 (5)	Li8—O23	1.912 (9)
Na7—O31^{i}	2.367 (5)	Li8—O61	2.032 (9)
Na7—O43	2.486 (4)	Li8—O61^{viii}	2.040 (10)
Na8—O32	2.317 (4)	Li8—O93	1.927 (9)
Na8—O93^{iii}	2.341 (4)	Li9—O21	1.908 (9)
Na8—O93^{ii}	2.358 (4)	Li9—O51	2.038 (10)
Na8—O32^{i}	2.370 (4)	Li9—O51^{viii}	2.042 (9)
Na8—O63^{iii}	2.502 (4)	Li9—O73	1.939 (9)
Na9—O33^{i}	2.323 (4)		

Symmetry codes: (i) $x, y, 1+z$; (ii) $x, 1+y, 1+z$; (iii) $x, 1+y, z$; (iv) $1+x, 1+y, z$; (v) $1+x, 1+y, 1+z$; (vi) $1+x, y, 1+z$; (vii) $1+x, y, z$; (viii) $x, y, z-1$; (ix) $1+x, y, z-1$; (x) $x, 1+y, z-1$.

The atomic coordinates of β-$LiNaCO_3$ were used as a starting set. The enantiomorphs are indistinguishable from the X-ray data (Flack, 1983).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTO* (Motherwell, 1974). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$KMoO_2AsO_4$

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Abstract

Potassium molybdyl arsenate consists of AsO_4 tetrahedra and MoO_6 octahedra sharing corners to form a three-dimensional framework containing intersecting tunnels where the K^+ ions are located. The covalent framework of $KMoO_2AsO_4$ (*Pnma*) is very similar to that of $Ba(MoO_2)_2(PO_4)_2$ ($P2_1/c$), $Pb(MoO_2)_2(PO_4)_2$ ($P2_1/c$), $NaMoO_2PO_4$ ($P2_1/n$) and $KMoO_2PO_4$ (*Fddd*).

Commentaire

Dans le cadre de l'élaboration de matériaux à structures ouvertes formées de charpentes covalentes mixtes, des études entreprises dans notre laboratoire, ont conduit à isoler les composés: $Na_3Sb_3As_2O_{14}$ (Haddad, Guedira & Jouini, 1988), KNb_4AsO_{13} (Haddad, Jouini, Jouini & Piffard, 1988), $K_2Nb_2As_2O_{11}$ et $K_3NbAs_2O_9$ (Zid, Jouini, Jouini & Omezzine, 1988, 1989), $K_3NbP_2O_9$ (Zid, Jouini & Piffard, 1992), $Tl_2NbO_2PO_4$ (Fakhfakh, Zid, Jouini & Tournoux, 1993), $RbAlAs_2O_7$ (Boughzala, Driss & Jouini, 1993), KYP_2O_7 (Hamady, Zid & Jouini, 1994), $NaAlAs_2O_7$ (Driss & Jouini, 1994), $Na_2V_3P_2O_{13}$ (Haddad & Jouini, 1994) dont les charpentes covalentes sont constituées d'octaèdres (MO_6, M = V, Nb, Sb, Al, Y) et de tétraèdres (XO_4, X = P, As) partageant des sommets. Dans ces matériaux les charpentes covalentes délimitent des tunnels ou bien des intercouches dans lesquels sont logés les cations. Le phosphate $KMoO_2PO_4$ de formulation analogue au composé étudié a été caractérisé (Peascoe & Clearfield, 1991). L'arséniate équivalent, à notre connaissance, est inconnu. La structure de $KMoO_2AsO_4$ est caractérisée par un enchaînement selon les trois directions *a*, *b* et *c* d'octaèdres MoO_6 et de tétraèdres AsO_4 partageant des sommets. Il en résulte une charpente tridimensionnelle possédant de larges canaux parallèles à la direction *b*. Les octaèdres MoO_6 sont irréguliers. Deux distances courtes $\langle d(\text{Mo—O})\rangle$ = 1,694 Å constituent le groupement molybdyl MoO_2. Les quatres autres distances $\langle d(\text{Mo—O})\rangle$ = 2,095 Å correspondent à des atomes d'oxygènes mis en commun avec les tétraèdres réguliers, AsO_4. Ces derniers ne sont pas directement reliés entre eux. L'organisation de la charpente dans $KMoO_2AsO_4$ est très similaire à celle observée dans $Ba(MoO_2)_2(PO_4)_2$ (Masse, Averbuch-Pouchot & Durif, 1985). Signalons que les composés $NaMoO_2PO_4$ (Kierkegaard, 1962) et $Pb(MoO_2)_2(PO_4)_2$ (Masse, Averbuch-Pouchot & Durif, 1985) possèdent la même organisation mais avec des chaînes plus incurvées. Plusieurs composés contenant des groupements molybdyl (Hazenkamp, Voogt & Blass, 1992),

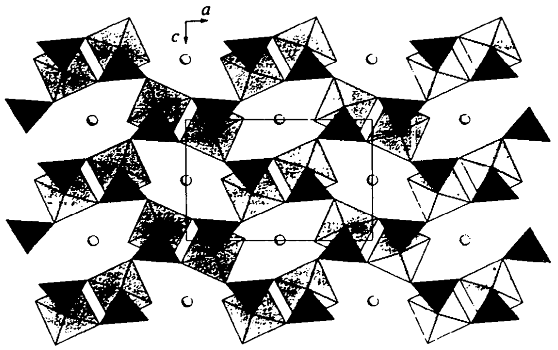

Fig. 1. Projection de la stucture de $KMoO_2AsO_4$ selon l'axe *b*.