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The Structure of β-LiIO$_3$

BY HEINZ SCHULZ

Institut für Kristallographie und Petrographie der ETH, Sonneggstrasse 5, 8006 *Zürich, Switzerland*

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β-LiIO$_3$ crystallizes in space group $P4_2/n$ with $a=9{\cdot}7329$ (7), $c=6{\cdot}1566$ (7) Å, $Z=8$. The intensities were collected with a diffractometer. The final R based on F is 0·059. The structure consists of discrete IO$_3$ groups in the form of distorted trigonal pyramids, and distorted LiO$_4$ tetrahedra. Each tetrahedron shares two corners with two other tetrahedra. The mean bond distances are I–O = 1·79, Li–O = 1·98 Å.

Introduction

Three modifications of LiIO$_3$ are known. α-LiIO$_3$ can be transformed reversibly into γ-LiIO$_3$ at about 250°C. The retransformation γ–α takes place at about 200°C. γ-LiIO$_3$ can be transformed irreversibly into β-LiIO$_3$ at about 300°C. β-LiIO$_3$ is stable up to the melting point (435°C) (Liebertz, 1969; Matsumura, 1971). The transformation behaviour is strongly influenced by contamination of LiIO$_3$ by small amounts of HIO$_3$ (Arend, Remoissenet & Staehlin, 1972). Furthermore, the α- and β-phases can be grown from neutral and acid aqueous solution at different temperatures (Desvignes & Remoissenet, 1971).

α-LiIO$_3$ crystallizes in space group $P6_3$ with $a=5{\cdot}18$, $c=5{\cdot}17$ Å. The iodine atoms are surrounded by six oxygens in a distorted octahedral arrangement. They form discrete trigonal IO$_3$ groups with I–O = 1·81 Å and O–I–O = 99°. Each oxygen is bonded to two iodine atoms forming a three-dimensional network of I–O bonds (Rosenzweig & Morosin, 1966; de Boer, van Bolhuis, Olthof-Hazekamp & Vos, 1966). The features of the I–O network agree with other iodate structures. The lithium atoms have an octahedral coordination with Li–O = 2·12 Å.

The orthohexagonal cell of γ-LiIO$_3$ was determined from high temperature powder diffractometer values by Matsumura (1971): $a=19{\cdot}1$, $b=11{\cdot}14$, $c=10{\cdot}44$ Å. This cell is closely related to the cell of α-LiIO$_3$. The structure of γ-LiIO$_3$ is not yet known.

Experimental

Polycrystalline samples were prepared from large single crystals (diameter about 1 cm) of β-LiIO$_3$ for a determination of the lattice constants with a Jagodzinski-Guinier camera and Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å). Silicon was used as an internal standard. The lat-

Table 1. *Structure parameters*

Numbers in parentheses are the standard deviations related to the last digit. Origin at $\bar{1}$.
All thermal parameters are in Å^2.

	x	y	z	U	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	0·0343 (1)	0·7576 (1)	0·1150 (1)	0·0207 (2)	0·0236 (5)	0·0236 (5)	0·0241 (5)	0·0009 (4)	0·0002 (4)	0·0001 (4)
Li	0·426 (4)	0·236 (5)	0·426 (9)	0·043 (9)	0·04 (2)	0·04 (2)	0·07 (3)	0·00 (2)	0·00 (2)	0·01 (2)
O(1)	0·836 (1)	0·121 (2)	−0·050 (3)	0·037 (3)	0·032 (7)	0·035 (7)	0·049 (9)	+0·008 (6)	0·001 (7)	−0·003 (7)
O(2)	0·094 (2)	0·209 (2)	0·094 (3)	0·046 (4)	0·042 (9)	0·054 (9)	0·047 (9)	+0·000 (7)	−0·011 (8)	−0·006 (8)
O(3)	0·847 (1)	0·552 (1)	0·172 (2)	0·031 (3)	0·032 (7)	0·038 (7)	0·026 (6)	−0·006 (6)	0·004 (6)	−0·002 (6)

tice constants (listed in the abstract) were obtained from a least-squares fit of 38 observed d values.

Precession photographs confirmed the space group determination of Liebertz (1969). β-LiIO$_3$ crystallizes in the centric space group $P4_2/n$.

A spherical crystal with a radius of 312 μm, and an on-line Siemens single-crystal diffractometer with filtered Mo radiation and θ–2θ scan were used for the collection of the intensities. 4300 reflexions within one half of reciprocal space were measured with $\theta < 30°$. These measurements were reduced to 836 and 157 independent reflexions with $F_o > 0$ and $F_o = 0$ respectively. ($F_o = 0$ if the net intensity is less than three times the standard deviation.) All independent reflexions were used for the structure investigation with weights calculated from the counting statistics. An absorption

Table 2. *Interatomic distances* (Å) *and angles* (°)

Numbers in parentheses are the standard deviations related to the last digit.
The atom designations refer to Fig. 1.

I coordination

I–O(1^{i})	1·77 (2)
I–O(3^{i})	1·79 (1)
I–O(2^{i})	1·82 (2)
I–O(3^{ii})	2·73 (1)
I–O(1^{ii})	2·95 (2)
I–O(1^{iii})	3·25 (1)

O(1^{i})–I–O(3^{i})	100·2 (7)
O(1^{i})–I–O(2^{i})	102·0 (8)
O(1^{i})–I–O(3^{ii})	172·8 (6)
O(1^{i})–I–O(1^{ii})	102·0 (7)
O(1^{i})–I–O(1^{iii})	66·6 (7)
O(3^{i})–I–O(2^{i})	96·1 (7)
O(3^{i})–I–O(3^{ii})	87·0 (7)
O(3^{i})–I–O(1^{ii})	67·6 (5)
O(3^{i})–I–O(1^{iii})	135·8 (5)
O(2^{i})–I–O(3^{ii})	76·4 (6)
O(2^{i})–I–O(1^{ii})	153·0 (6)
O(2^{i})–I–O(1^{iii})	127·4 (6)
O(3^{ii})–I–O(1^{ii})	81·3 (4)
O(3^{ii})–I–O(1^{iii})	108·7 (4)
O(1^{ii})–I–O(1^{iii})	74·2 (3)

O–O distances < 3·7 Å

O(1^{i})–O(3^{i})	2·73 (2)
O(1^{i})–O(2^{i})	2·80 (2)
O(1^{i})–O(1^{iii})	3·02 (2)
O(3^{i})–O(2^{i})	2·69 (2)
O(3^{i})–O(3^{ii})	3·18 (2)
O(3^{i})–O(1^{ii})	2·81 (2)
O(2^{i})–O(3^{ii})	2·90 (2)

LiO$_4$–tetrahedra

Li–O(3^{iii})	1·87 (5)
Li–O(2^{ii})	1·90 (5)
Li–O(1^{iv})	2·03 (4)
Li–O(2^{iii})	2·13 (6)
O(3^{iii})–O(2^{ii})	3·32 (2)
O(3^{iii})–O(1^{iv})	2·81 (2)
O(3^{iii})–O(2^{iii})	3·62 (2)
O(2^{ii})–O(1^{iv})	3·29 (2)
O(2^{ii})–O(2^{iii})	2·94 (3)
O(1^{iv})–O(2^{iii})	3·28 (2)

O(3^{iii})–Li–O(2^{ii})	123 (3)
O(3^{iii})–Li–O(1^{iv})	92 (2)
O(3^{iii})–Li–O(2^{iii})	130 (2)
O(2^{ii})–Li–O(1^{iv})	114 (2)
O(2^{ii})–Li–O(2^{iii})	93 (2)
O(1^{iv})–Li–O(2^{iii})	104 (2)

Table 3. *Main axes and their directions of the thermal vibrational ellipsoids*

Numbers in parentheses are the standard deviations related to the last digit.

	Length of main axes (Å)	Angle with axis (°)		
		a	b	c
I	0·151 (2)	134 (13)	45 (13)	88 (17)
	0·155 (2)	73 (25)	71 (25)	154 (32)
	0·157 (2)	49 (16)	52 (17)	64 (32)
Li	0·19 (6)	23 (180)	71 (180)	102 (60)
	0·20 (6)	68 (180)	153 (147)	76 (49)
	0·28 (6)	84 (29)	72 (32)	19 (31)
O(1)	0·16 (2)	40 (19)	51 (19)	88 (17)
	0·20 (2)	52 (21)	136 (24)	109 (37)
	0·22 (2)	80 (26)	106 (30)	19 (37)
O(2)	0·18 (3)	41 (20)	79 (21)	51 (17)
	0·23 (2)	56 (29)	135 (44)	117 (35)
	0·24 (2)	69 (30)	47 (43)	129 (29)
O(3)	0·15 (2)	54 (40)	79 (35)	142 (50)
	0·17 (2)	127 (42)	123 (25)	125 (52)
	0·21 (2)	122 (19)	35 (22)	102 (20)

Table 4. *Observed and calculated structure factors*

Observed structure factors marked with * have a net intensity less than three times the standard deviation.

[illegible]

correction was applied. [$\mu=240$ cm^{-1} and $\mu r=7\cdot5$; the density was taken from Liebertz (1969).]

Structure determination and refinement

The positions of the iodine atoms were derived from a Patterson synthesis. The best R given by these positions was 0·13. This model was used for calculation of a difference synthesis which showed resolved positions for all oxygen and lithium atoms. After inclusion of these atoms in the structure refinement, R for isotropic and anisotropic temperature factors dropped to 0·063 and 0·059. The scattering curves for Li^+, I^{5+} and O^{2-} were taken from *International Tables for X-ray Crystallography* (1962), Thomas & Umeda (1957), and Suzuki (1960) respectively. The difference synthesis of the final model showed a minimum and maximum residual electron density of about $-3e$ Å^{-3} at the I positions and of about $+2e$ Å^{-3} at the O positions respectively. The results are listed in Tables 1–4.

Description of the structure

The main features of the structure are distorted trigonal IO_3 groups and distorted LiO_4 tetrahedra (Fig. 2). Each

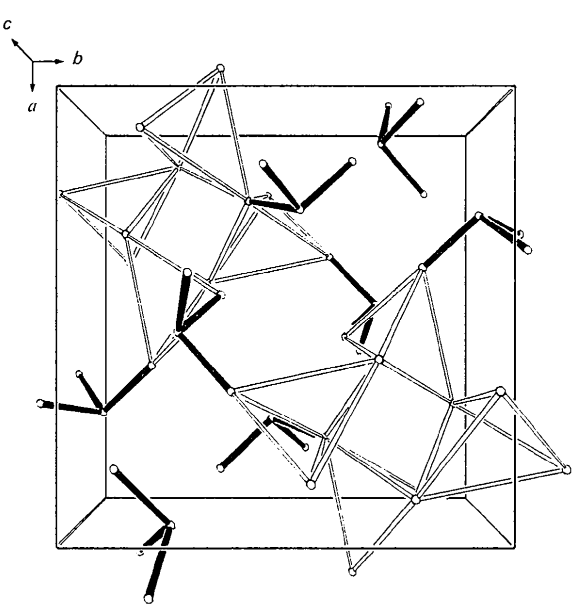


Fig. 2. Central projection of IO_3 groups and LiO_4 tetrahedra. The IO_3 groups are shown by black lines, the O–O connexions of the LiO_4 tetrahedra are shown by open white lines. Origin at $\bar{1}$.

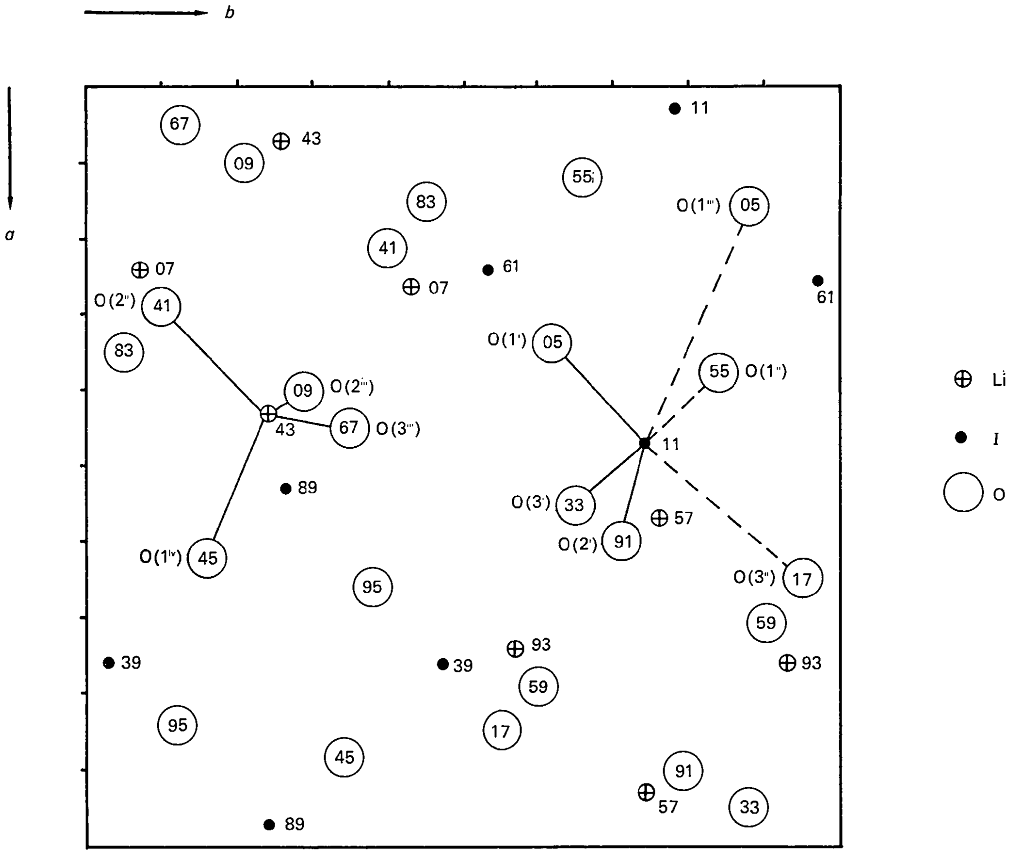


Fig. 1. Parallel projection of β-$LiOI_3$ on (001). The numbers in the drawing are the z coordinates multiplied by 100. The atom designations refer to Table 2. Origin at $\bar{1}$.

LiO_4 tetrahedron shares two corners with two other tetrahedra. The LiO_4 tetrahedra form isolated rings, each of which contains four tetrahedra. Each elementary cell contains two rings. The rings of LiO_4 tetrahedra are connected to each other by IO_3 groups.

1. *Iodine atoms*

Each iodine atom forms six iodine–oxygen bonds, three short (I–O) bonds and three long (I--O) bonds. The three short I–O distances range from 1·77 to 1·92 Å, and the corresponding O–I–O bond angles from 96 to 102°. These values show that the IO_3 groups deviate significantly from a trigonal pyramid. The long I--O distances have values between 2·73 and 3·25 Å. Short and long iodine–oxygen bonds form a three-dimensional network, which is shown in Fig. 3. Only two of the three short I–O bonds of each iodine atom participate in the network of I–O bonds.

O–I--O–I--O··· bonds form helices running parallel to **c**. Two of these helices run through each elementary cell. In Fig. 3(*a*) these helices occupy the upper right and the lower left corners. Long I--O bonds run through the inner part of the helices, which are connected to each other by O–I--O bonds. Referred to an elementary cell, each helix is formed by four O–I--O bonds and four I--O bonds. The helices are connected to each other by two O–I--O bonds.

The thermal motion of the iodine atoms is isotropic (Table 3).

2. *Lithium atoms*

The distorted LiO_4 tetrahedra have Li–O distances from 1·87 to 2·13 Å and angles from 92 to 123°. The Li–O bonds are shown in Fig. 4.

The rings of LiO_4 tetrahedra (Fig. 1) are parallel to (001). They are connected to each other parallel to **c** by four IO_3 groups and perpendicular to **c** by two IO_3 groups. Although the main thermal axes of the lithium atoms do not differ greatly (Table 3), their orientations suggest a preferred thermal motion of the lithium atoms perpendicular to the LiO_4 tetrahedra rings.

3. *Oxygen atoms*

Each oxygen atom is bonded three times to iodine or lithium atoms. O(1) atoms form one short I–O and two long I--O bonds, O(2) atoms form one O–I and two Li–O bonds, O(3) atoms form one I–O, one I--O and one Li–O bond. The largest thermal motion is shown by the O(2) atoms which are bonded only once to the iodine atoms. The main thermal axes of the oxygens are equal within the standard deviations. The smallest main thermal axes of all oxygens point approximately in the directions of the strong I–O bonds.

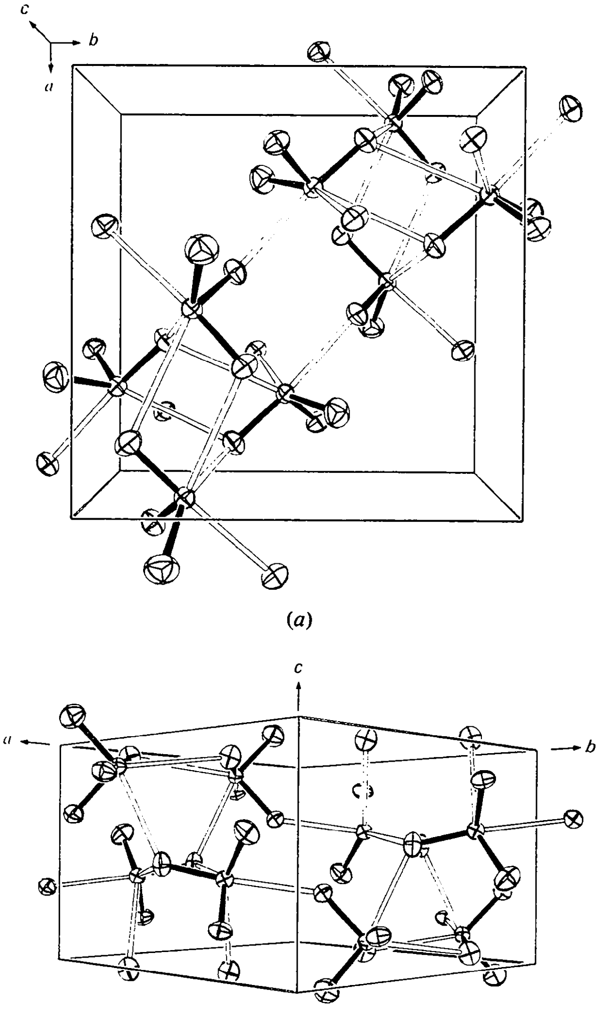
4. *Thermal expansion*

The thermal expansion coefficients reported by Matsumura (1971) are: $5{\cdot}4\times10^{-6}$ parallel to and $3{\cdot}1\times10^{-5}\,^{\circ}K^{-1}$ perpendicular to *c*. The structure explains this behaviour. More iodine–oxygen bonds are used for the formation of helices of these bonds than for the interconnexion of the helices.

The helices run parallel to **c**, and their connexion bonds are approximately perpendicular to **c** (§ 4.1). Furthermore, the connexion of LiO_4 tetrahedra rings by IO_3 groups is twice as strong parallel to **c** as perpendicular to it (§ 2).

Comparison between α- and β-LiIO$_3$

The transformation from α-LiIO$_3$ to β-LiIO$_3$ is a reconstructive one (Buerger, 1961). The oxygen arrangement in α-LiIO$_3$ can be described as distorted hexagonal closest packing. Its packing density is 52%, if 1·40 Å



(*a*)

(*b*)

Fig. 3. Central projection of the network formed by the iodine–oxygen bonds. The short I–O bonds (1·77–1·82 Å) are indicated by black lines, and the long I--O bonds (2·73–3·25 Å) by open white lines. The thermal vibrational ellipsoids are scaled to include 50% probability. Origin at $\bar{1}$. (*a*) Central projection on (001). (*b*) Central projection on (110).

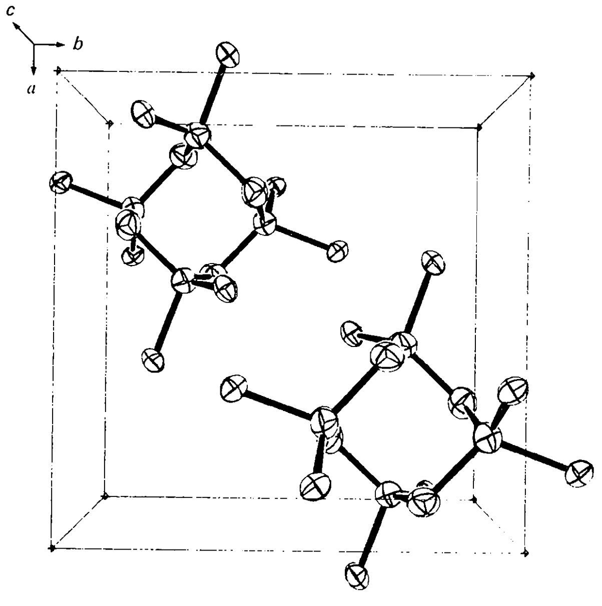


Fig. 4. Central projection of Li–O bonds on (001). The thermal vibrational ellipsoids are scaled to include 50% probability. Origin at $\bar{1}$.

is taken as the radius of the oxygen atoms. In β-$LiIO_3$ this value is reduced to 47%. The oxygen arrangement of β-$LiIO_3$ does not show similarities to closest packing. In α-$LiIO_3$ all oxygens participate in the formation of the three-dimensional network of O–I--O bonds. In β-$LiIO_3$ only $\frac{2}{3}$ of the oxygen atoms [O(1) and O(3) atoms] contribute to the network. The IO_3 groups form a trigonal pyramid in α-$LiIO_3$, but only a distorted trigonal pyramid in β-$LiIO_3$.

In spite of these differences the mean values of bond distances and angles are in good agreement in both structures: I–O = 1·81 and 1·79 Å, O–I–O = 99·5 and 99·4°, I--O = 2·89 and 2·98 Å in α- and β-$LiIO_3$ respectively.

The main differences between the modifications are found in the lithium atoms. In α-$LiIO_3$ they are surrounded by six oxygens in the form of an octahedron. The octahedra form chains parallel to **c** by sharing two corners with two other octahedra. The Li–O distance is 2·12 Å. In β-$LiIO_3$ isolated rings containing four LiO_4 tetrahedra are present. The mean Li–O distance is 1·98 Å, which agrees well with the mean Li–O distance in fourfold oxygen coordination.

The single crystals of β-$LiIO_3$ used were supplied by Dr Remoissenet, Laboratoire de Diélectriques, Université de Dijon, France. The author is indebted to Dr Arend (Labor. für Festkörperphysik der ETH, Zürich) and to Dr Remoissenet for discussions on the optical, electrical and thermal properties of the α, β and γ modifications of $LiIO_3$. The single-crystal diffractometer used for the measurements was made available by the Owens Illinois Co., Toledo, Ohio, U.S.A., who also supported the work financially.

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