Acta Cryst. (1965). **18**, 481

The Crystal Structure of $LiGaO_2$

BY M. MAREZIO

Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.

(*Received* 6 *May* 1964)

$LiGaO_2$ is orthorhombic, space group $Pna2_1$ with four molecules in a cell of dimensions $a=5{\cdot}402$, $b=6{\cdot}372$, $c=5{\cdot}007$ Å. The positions of all atoms have been determined with high precision. The final R index is less than 2% and bond lengths have been determined to an accuracy of 0·004 Å for Ga–O bonds and 0·020 Å for Li–O bonds. Each atom is tetrahedrally coordinated and the structure consists of an infinite three-dimensional array of tetrahedra having only vertices in common. An experimental check of the new formula for secondary extinction correction developed by Zachariasen is included.

Introduction

The structure of $LiGaO_2$ has been determined as part of a program for finding new refractory piezoelectric substances. The first single crystals were grown by J. P. Remeika from a flux, and he found them to be very strongly piezoelectric with a high coupling coefficient. This material appears to be harder than quartz with an acoustic loss comparable to or better than that of quartz (Remeika & Ballman, 1964).

The crystals are orthorhombic with cell dimensions

$a=5{\cdot}402\pm0{\cdot}001$, $b=6{\cdot}372\pm0{\cdot}001$, $c=5{\cdot}007\pm0{\cdot}001$ Å.

These values are in good agreement with those of Hoppe (1959) whose cell dimensions from powder were: $a=5{\cdot}404$, $b=6{\cdot}374$ and $c=5{\cdot}010$ Å. The cell contains four molecules, the calculated density being 4·187 g.cm^{-3}. The only systematic absences among the reflections are: $0kl$ when $k+l$ is odd and $h0l$ when h is odd. From these absences and the fact that the crystals are piezoelectric one is led to the space group symmetry $Pna2_1$ with all atoms in general position

(x, y, z) $(\bar{x}, \bar{y}, \frac{1}{2}+z)$ $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z)$ $(\frac{1}{2}+x, \frac{1}{2}-y, z)$,

and 11 positional degrees of freedom (one z coordinate can be chosen at will).

Determination of the structure

All intensity measurements were taken with a General Electric XRD 3 spectrometer rebuilt for single-crystal work, a proportional counter and filtered Cu $K\alpha$ radiation being used. All data were taken on one crystal which had been ground into a sphere of radius $R=0{\cdot}0121\pm0{\cdot}0005$ cm, corresponding to $\mu R=2{\cdot}16$. The intensities of all reflections $hk0$, $hk1$ $h0l$, $h1l$, $0kl$, $1kl$ were measured. The lattice constants were determined by measuring the 2θ values for 19 reflections in the back-reflection region. The least-squares method described by Mueller & Heaton (1960,1961) was used. Their program was modified by J. L. Bernstein for use on an IBM 7090 computer.

According to the space group symmetry $Pna2_1$ the projection of the structure on the XY plane has a center of symmetry. The first step towards the solution of the structure was therefore based on the $hk0$ data. It was immediately evident from the $hk0$ experimental structure factors that the gallium atom was very nearly at $(x=\frac{1}{12}, y=\frac{1}{8})$. A Fourier synthesis carried out with strong $|F_{hk0}|$ having the signs of the relative gallium contribution gave the approximate positions of the other three atoms, and quite precise x and y coordinates were obtained by least-squares refinements based on all experimental $|F_{hk0}|$ data.

An accurate XY-projection of the structure having been deduced and the z coordinate for the gallium atom chosen at zero, it was a simple task to find the approximate z coordinates of the other atoms so that refinements using the full set of three-dimensional data could be made. The Martin–Busing–Levy IBM-7090 least-squares refinement program was used with the f curves (for neutral atoms) given in *International Tables for* X-*Ray Crystallography*. The one for gallium was corrected for anomalous dispersion.

During these refinements it was found that there was still considerable secondary extinction in the specimen, in spite of surface grinding and thermal

Table 1. *Final parameters*

Atom	x	y	z	B
Ga	0·0821±0·0001	0·1263±0·0001	0	0·431±0·017 Å^2
O_I	0·4066±0·0007	0·1388±0·0005	0·8927±0·0010	0·460±0·060
O_{II}	0·0697±0·0007	0·1121±0·0005	0·3708±0·0010	0·400±0·061
Li	0·4207±0·0014	0·1267±0·0011	0·4936±0·0097	0·612±0·146

Table 2. *Observed and calculated structure factors*

Reflections 0 k ℓ and 1 k ℓ

h k ℓ	F_o	0.8239 | F_c |	A	B
*011	54.41	59.57	-0.03	72.31
020	2.11	1.68	-2.04	0
*002	83.71	92.10	102.62	-44.33
022	1.84	1.92	-2.33	0.16
031	41.48	41.21	-5.95	49.66
013	42.85	43.18	3.68	52.28
*040	86.78	89.66	-108.82	0
*042	62.60	63.41	-73.30	23.47
033	39.51	38.84	-1.69	47.11
004	37.15	37.91	45.82	-4.16
051	39.33	39.13	-3.36	-47.38
024	1.72	1.20	-1.07	0.98
060	2.04	2.47	3.00	0
053	28.55	27.89	-4.85	-33.50
015	24.67	24.65	2.52	29.82
044	31.46	31.05	-37.57	2.87
062	2.52	2.99	3.63	-0.11
035	23.78	24.01	4.04	28.86
071	19.85	19.38	4.64	-23.06
006	33.72	33.45	38.97	11.38
064	1.86	2.27	2.12	-1.75
026	nil	0.24	0.23	0.19
073	23.75	22.88	3.33	-27.57
*080	40.01	40.53	49.20	0
055	16.61	17.02	-0.29	-20.66
*110	50.21	51.97	63.08	0
111	26.97	27.33	-0.42	33.16
*120	55.91	59.96	-72.77	0
*121	48.68	51.82	-24.87	57.77
112	36.91	37.96	45.97	-3.14
130	36.08	36.35	-44.12	0
122	38.63	39.34	-44.68	16.82
131	25.87	25.39	-2.37	-30.73
132	33.97	33.19	-40.12	-3.64
113	20.64	20.62	1.40	24.99
140	1.41	1.66	2.02	0
141	1.62	1.54	-0.46	-1.82
*123	64.63	66.33	-16.90	78.72
142	1.34	1.47	1.70	-0.59
133	17.39	17.21	-3.16	-20.65
150	32.88	33.31	-40.43	0
151	14.64	14.52	1.92	-17.51
114	26.21	26.41	31.84	3.64
124	17.80	17.55	-21.19	2.14
143	nil	0.80	0.66	-0.72
152	24.96	24.93	-29.75	5.53
134	27.79	27.13	-32.72	-3.63
160	29.18	29.04	35.25	0
161	32.63	32.09	8.86	-37.92
153	14.66	14.35	0.88	-17.39
115	12.13	11.95	1.30	14.44
144	nil	0.79	0.54	-0.80
162	22.12	21.99	25.78	-6.87
125	44.46	44.66	7.61	53.69
170	18.35	17.94	21.78	0
135	10.06	9.95	-0.34	-12.07
163	39.00	38.91	8.19	-46.51
171	14.14	14.30	1.92	17.25
154	16.40	15.83	-19.14	-1.77
172	19.17	19.16	22.88	4.15
145	2.01	1.78	1.14	-1.84
116	19.66	20.45	24.72	2.16
164	11.00	11.85	14.33	-1.17
126	13.78	15.21	-17.73	-5.14
173	8.94	9.72	2.58	11.51
180	1.55	1.47	-1.79	0

Reflections h 0 ℓ and h 1 ℓ

h k ℓ	F_o	0.8281 | F_c |	A	B
*200	60.67	63.03	76.12	0
*002	84.54	92.57	102.62	-44.33
*201	48.24	50.84	-24.08	56.47
202	40.25	40.64	45.67	-17.96
*203	65.32	65.12	-16.97	76.79
400	36.56	36.87	-44.53	0
401	40.55	40.38	-13.71	46.80
004	38.33	38.10	45.82	-4.16
402	27.34	27.34	-31.70	9.25
204	18.91	18.00	21.70	-1.24
403	49.89	50.29	-11.27	59.67
205	44.42	44.33	6.94	53.08
404	14.27	13.78	-16.48	2.28
600	50.12	49.88	-60.24	0
601	1.97	1.80	-1.00	1.94
602	38.11	37.79	-43.93	12.33
006	34.13	33.62	38.97	11.38
405	36.61	36.38	6.56	43.44
206	16.47	16.78	19.43	5.76
603	2.66	2.86	0.03	3.46
*110	49.42	52.23	63.08	0
*011	53.12	59.88	-0.03	72.31
111	27.33	27.47	-0.42	33.16
210	37.75	39.39	-47.56	0
211	24.23	23.80	-2.49	28.63
112	37.69	38.16	45.97	-3.14
212	35.21	34.84	-41.93	-3.40
310	5.16	5.09	6.15	0
311	41.24	40.74	-2.40	49.13
013	44.36	43.40	3.68	52.28
113	20.95	20.73	1.40	24.99
312	3.61	3.52	1.04	-4.12
213	21.37	21.03	-0.25	25.39
410	32.62	32.47	-39.21	0
411	20.18	20.06	-2.84	-24.06
313	34.49	35.27	0.59	42.58
114	26.79	26.54	31.84	3.64
412	26.91	27.02	-32.62	1.00
214	27.62	27.90	-33.47	-3.86
510	23.34	23.29	-28.13	0
511	13.05	12.76	-3.42	15.03
413	13.28	12.92	-3.47	-15.21
314	1.77	1.67	-2.00	-0.23
015	25.01	24.78	2.52	29.82
512	21.32	21.34	-25.72	-1.44
115	11.96	12.01	1.30	14.44
215	13.11	12.74	1.89	15.26
414	20.73	20.60	-24.74	-2.55
513	15.02	15.22	-2.28	18.24
610	4.26	4.58	-5.53	0
611	24.43	24.23	-0.09	-29.25
315	21.63	21.83	2.92	26.20
612	3.66	3.50	-1.29	4.02
116	20.14	20.55	24.72	2.16
514	17.91	18.15	-21.81	-2.23
415	7.21	7.42	0.28	-8.95
216	19.00	20.02	-24.18	0
613	20.23	20.69	-1.45	-24.94

Reflections h k 0 and h k 1

h k ℓ	F_o	0.8278 | F_c |	A	B
*110	49.66	52.22	63.08	0
020	1.44	1.69	-2.04	0
*120	58.23	60.24	-72.77	0
*200	61.05	63.01	76.12	0
210	39.45	39.37	-47.56	0
220	nil	0.05	-0.06	0
130	36.50	36.52	-44.12	0
310	5.46	5.09	6.15	0
230	39.30	37.69	-45.53	0
*040	90.36	90.08	-108.82	0
*320	89.19	89.43	-108.04	0
140	1.34	1.67	2.02	0
330	3.95	3.79	-4.58	0
240	41.74	41.14	-49.70	0
400	36.98	36.86	-44.53	0
410	32.52	32.46	-39.21	0
420	2.79	1.28	1.54	0
150	33.75	33.47	-40.43	0
340	1.69	1.94	2.34	0
250	24.04	23.31	28.16	0
430	30.80	31.05	-37.51	0
510	23.23	23.29	-28.13	0
060	1.98	2.48	3.00	0
160	29.46	29.18	35.25	0
350	2.37	2.76	-3.34	0
440	27.41	27.50	33.22	0

Reflections h k 0 and h k 1

h k ℓ	F_o	0.8278 | F_c |	A	B
520	31.18	31.77	-38.38	0
260	1.19	0.31	0.38	0
530	18.97	19.03	22.99	0
450	20.91	20.75	25.07	0
360	51.26	50.32	60.79	0
600	49.78	49.87	-60.24	0
170	18.11	18.03	21.78	0
540	nil	0.52	-0.64	0
610	4.28	4.58	-5.53	0
620	nil	0.69	0.83	0
270	21.50	21.91	26.47	0
460	2.90	2.24	-2.71	0
630	3.76	4.16	-5.03	0
550	18.13	18.49	22.33	0
370	1.96	1.69	2.04	0
*080	40.65	40.73	49.20	0
180	1.69	1.48	-1.79	0
*640	40.08	40.49	48.92	0
*011	54.55	59.86	-0.03	72.31
111	27.20	27.46	-0.42	33.16
*121	47.88	52.06	-24.87	57.77
*201	47.06	50.83	-24.09	56.47
211	23.85	23.79	-2.49	28.63
031	40.40	41.40	-5.95	49.66
221	1.14	0.44	0.18	-0.50
131	25.74	25.52	-2.37	-30.73
311	40.59	40.72	-2.40	49.13
231	17.79	17.67	-4.29	20.92
321	2.13	1.55	-0.96	1.60
141	1.67	1.55	-0.46	-1.82
331	40.04	39.66	-1.87	-47.87
241	39.55	39.66	12.84	-46.16
401	39.13	40.37	-13.71	46.80
411	19.90	20.05	-2.84	-24.06
051	39.48	39.32	-3.36	-47.38
421	1.78	0.96	-0.43	-1.07
151	14.73	14.59	1.92	-17.51
341	2.04	1.29	-1.04	-1.17
251	17.58	17.31	-0.46	-20.90
431	16.24	15.62	-0.98	-18.84
511	13.16	12.76	-3.42	15.03
161	32.12	32.24	8.86	-37.92
351	24.64	24.25	4.04	-29.02
441	31.49	32.13	9.28	-37.69
521	29.96	30.23	8.47	-35.52
261	1.20	1.04	-0.17	1.25
531	12.84	12.77	1.63	-15.34
451	15.08	15.12	2.67	18.07
361	1.18	0.90	0.49	-0.97
071	19.49	19.47	4.64	-23.06
601	1.80	1.80	-1.00	1.94
171	14.22	14.37	1.92	17.25
541	1.53	0.48	-0.51	0.28
611	24.20	24.22	-0.09	-29.25
621	1.72	0.86	-0.69	-0.77
271	8.69	8.81	2.95	-10.22
461	1.53	1.83	0.81	2.06
631	19.20	19.58	1.82	-23.58
551	7.84	8.43	3.42	-9.60
371	23.23	24.69	2.76	29.70

shock treatment in liquid nitrogen. Therefore, the early refinements were made with only weak reflections for which secondary extinction is negligible. The structure factors corresponding to strong reflections could thus be calculated and corrected for secondary extinction.

Since in the first formula of the next paragraph only the linear term is taken into consideration, the

reflections for which the extinction correction was larger than 40% were left out of the final refinement which gave a conventional R index of 0·019 (including the 'zeros'), and the atomic parameters shown in Table 1. The degree of agreement between observed and calculated structure factors is shown in Table 2. The values marked with an asterisk are those which were left out of the final refinement.

Extinction correction

The new formula for secondary extinction correction developed by Zachariasen (1963) was used:

$$F_{\text{corr}} \approx F_o(1+\beta(2\theta)CJ_o)\,,$$

where F_o is the observed structure factor, F_{corr} the value corrected for secondary extinction, J_o the observed integrated intensity on an arbitrary scale, C is a constant to be found, while $\beta(2\theta)$ takes account of the angular variation of the extinction correction. For an unpolarized incident beam the expression for $\beta(2\theta)$ is

$$\beta(2\theta) = \frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\,\frac{A^{*\prime}(2\theta)}{A^{*\prime}(0)}$$

where $A^{*\prime}(2\theta)$ is the value of $dA^{*\prime}/d\mu$ at 2θ and $A^{*\prime}(0)$ the value at $2\theta=0$.

Although the purpose of this structure determination was not intended as an experimental test of this new formula, after the high precision attained in the last refinement it was thought worthwhile to show the agreement between the theoretical $\beta(2\theta)C$ and the experimental one. This is shown in Fig. 1 for $hk0$, $h0l$ and $0kl$ reflections only.

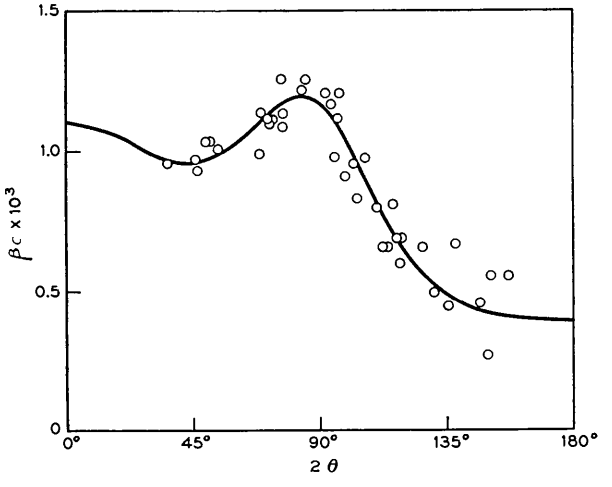

Fig. 1. The experimental values βC obtained with a sphere of $LiGaO_2$ for which $\mu R = 2{\cdot}16$. The curve is the theoretical one, calculated with $C = 1{\cdot}1.10^{-3}$.

Discussion of the structure

The coordinates listed in Table 1 give the interatomic distances and angles reported in Tables 3 and 4, respectively.

Table 3. *Bond lengths*

Tetrahedron about Ga

Ga–O_I	1·835 ± 0·004 Å	O_I–O_{II}	3·012 ± 0·006 Å
–O_{II}	1·860 ± 0·005	–O_I'	3·050 ± 0·003
–O_I'	1·852 ± 0·004	–O_{II}'	3·032 ± 0·005
–O_{II}'	1·844 ± 0·004	O_{II}–O_I'	3·004 ± 0·006
Average	1·848 ± 0·004 Å	–O_{II}'	2·980 ± 0·004
		O_I'–O_{II}'	3·021 ± 0·005
		Average	3·016 ± 0·005

Tetrahedron about Li

Li–O_I	2·001 ± 0·026 Å	O_I–O_{II}	3·189 ± 0·006 Å
–O_{II}	1·995 ± 0·018	–O_I'	3·227 ± 0·004
–O_I'	1·997 ± 0·018	–O_{II}'	3·182 ± 0·005
–O_{II}'	1·949 ± 0·019	O_{II}–O_I'	3·251 ± 0·006
Average	1·985 ± 0·020	–O_{II}'	3·222 ± 0·004
		O_I'–O_{II}'	3·360 ± 0·005
		Average	3·239 ± 0·005

Tetrahedron about O_I		Tetrahedron about O_{II}	
Ga–Ga	3·128 Å	Ga–Ga	3·106 Å
Li–Li	3·100	Li–Li	3·125
Li–Ga	3·189	Li–Ga	3·184
	3·132		3·057
	3·057		3·159
	3·075		3·075

Table 4. *Bond angles*

O_I–Ga–O_{II}	109·2°	O_I–Li–O_{II}	105·9°
O_I–Ga–O_I'	111·7	O_I–Li–O_I'	107·7
O_I–Ga–O_{II}'	111·0	O_I–Li–O_{II}'	107·3
O_{II}–Ga–O_I'	108·1	O_{II}–Li–O_I'	109·1
O_{II}–Ga–O_{II}'	107·1	O_{II}–Li–O_{II}'	109·6
O_I'–Ga–O_{II}'	109·7	O_I'–Li–O_{II}'	116·8
Ga–O_I–Ga	116·1°	Ga–O_{II}–Ga	114·0°
Li–O_I–Li	101·7	Li–O_{II}–Li	104·8
Li–O_I–Ga	111·8	Li–O_{II}–Ga	114·1
Li–O_I–Ga	109·7	Li–O_{II}–Ga	106·8
Li–O_I–Ga	107·5	Li–O_{II}–Ga	110·7
Li–O_I–Ga	109·1	Li–O_{II}–Ga	105·7

The structure consists of an infinite three dimensional array of tetrahedra having only vertices in common, as shown in Fig. 2. At the vertices there are oxygen atoms and at the centers gallium and lithium atoms. Each oxygen is shared among four tetrahedra, two Ga-centered and two Li-centered; it shares then $(\frac{3}{4}+\frac{3}{4})$ valence with the gallium atom and $(\frac{1}{4}+\frac{1}{4})$ with the lithium atom. Actually the same scheme would be obtained if the tetrahedra were drawn by putting the gallium and the lithium atoms at the vertices and the O_I and O_{II} atoms at the centers. This means that in this structure each is tetrahedrally coordinated.

The mean bond lengths are: Ga–4O = 1·848 Å and Li–4O = 1·985 Å. In β–Ga_2O_3 Geller (1960) found that the distance Ga–O for tetrahedrally coordinated gallium is 1·83 Å.

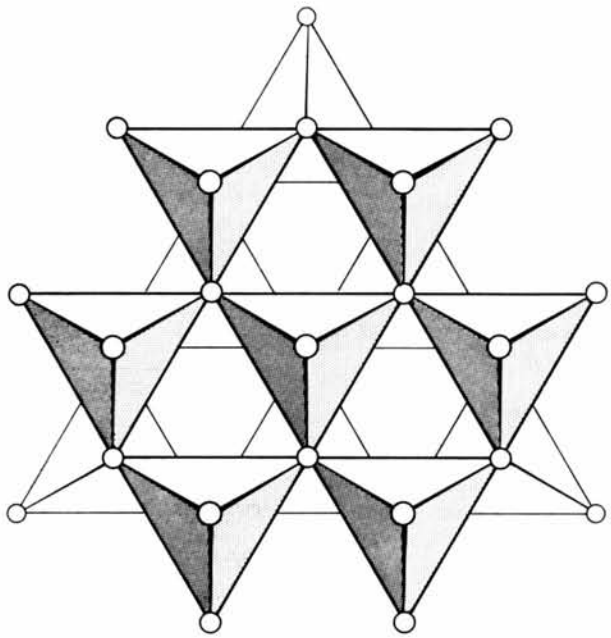

Fig. 2. A plane view of the arrangement of the tetrahedra in the structure. The oxygen atoms are located at the vertices of the vertices–linked tetrahedra. (The Ga and Li atoms are omitted from this diagram.)

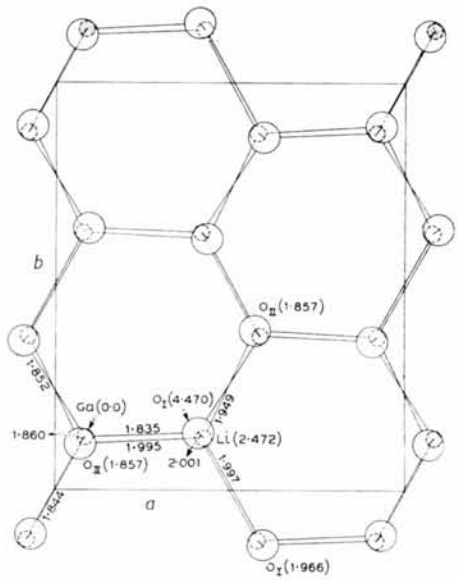

Fig. 3. A projection of the structure on the XY plane. The heights of the atoms in Å are given in parenthesis. The bond lengths are also shown.

During the last refinement anisotropic thermal coefficients were tried, but this did not give any improvement in precision. The correlation matrix obtained from the refinement program shows that the interdependence among the scale factors and the atomic parameters is fairly weak. One is led then to say that in this structure there is negligible thermal anisotropy.

Note added in proof.—An arrangement similar to the one of $LiGaO_2$ has been found by Bertaut & Blum (1954) for $NaFeO_2$. The two compounds seem to be isostructural.

As can be seen from Fig. 2, $LiGaO_2$ has the arrangement of a wurtzite-like structure. The departure from the hexagonal symmetry is due to the need for accommodating metallic atoms of different sizes.

The experimental data for this work were taken at the University of Chicago and I am indebted to Professor W. H. Zachariasen for permission to use his X-ray equipment. I wish also to thank J. P. Remeika who supplied the crystal of lithium metagallate and S. Geller for helpful discussions.

References

Bertaut, F. & Blum, P. (1954). *C. R. Acad. Sci., Paris,* **239**, 429.

Geller, S. (1960). *J. Chem. Phys.* **33**, 676.

Hoppe, R. (1959). *Angew. Chem.* **71**, 457.

Mueller, M. H. & Heaton, Le R. (1961). *Determination of Lattice Parameters with the Aid of a Computer.* Argonne National Laboratory Report, ANL–6176, January, 1961.

Mueller, M. H., Heaton, Le R. & Miller, K. T. (1960). *Acta Cryst.* **13**, 828.

Remeika, J. P. & Ballman, A. A. (1964). *Appl. Phys. Letters.* **5** (9), 180.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139.