Short Communications

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The crystal and molecular structure of 4,4′-dibromo- and 4,4′-dichloro-dibenzoyl peroxide*.

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4,4′-Dichlorodibenzoyl peroxide crystallizes in the monoclinic system, space group $P2_1/a$, with $a=25{\cdot}47\pm0{\cdot}05$, $b=7{\cdot}80\pm0{\cdot}02$, $c=6{\cdot}85\pm0{\cdot}02$ Å and $\beta=98{\cdot}60\pm0{\cdot}17°$, and 4 molecules in the unit cell: 4,4′-dibromodibenzoyl peroxide, isomorphous with the chloro compound, has $a=25{\cdot}94\pm0{\cdot}05$, $b=7{\cdot}91\pm0{\cdot}02$, $c=6{\cdot}83\pm0{\cdot}02$ Å and $\beta=96{\cdot}83\pm0{\cdot}17°$. The length of the peroxide O–O bond was determined as $1{\cdot}48\pm0{\cdot}02$ Å, and the dihedral angle about this bond as $81{\cdot}1\pm3{\cdot}4°$.

The dimensions of the peroxide group in an organic molecule were undetermined when the present study was begun. The simplest stable organic molecule containing the peroxide group appeared to be dibenzoyl peroxide, $C_6H_5CO.OO.COC_6H_5$. A trial model for this crystal structure was arrived at some years ago, but had not been refined. Recently, an independent study of dibenzoyl peroxide was published by Sax & McMullan (1967). The crystal structures of the halogeno-substituted dibenzoyl peroxides were initially solved in 1956, and in the present paper we report this together with the results of a three-dimensional study of 4,4′-dichlorodibenzoyl peroxide. An account of the non-isostructural difluoro- and diiodo-dibenzoyl peroxides will be presented separately.

4,4′-Dibromo- and 4,4′-dichloro-dibenzoyl peroxide, hereafter DBBP and DCBP respectively, crystallize in the monoclinic system, with crystal data as given in Table 1. Reflections are present, for both crystals, in all orders except for $h0l$ with $h=2n+1$ and for $0k0$ with $k=2n+1$. The space group is $P2_1/a$ (C_{2h}^5). The intensity distribution together with the data in Table 1 indicate the two crystals to be isostructural. For DCBP, $\mu=4{\cdot}46$ mm^{-1} for Cu $K\alpha$ radiation.

DBBP and DCBP were prepared by the reaction between bromobenzoyl chloride (or chlorobenzoyl chloride) and hydrogen peroxide, following a synthesis method of Tucker (1955). Well-developed prismatic crystals, bounded by {100}, {210} and {101}, were grown from benzene solution.

Lattice constants were measured, using the precession camera, with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). Preliminary estimates of the intensities of $hk0$ and $h0l$ reflections were made photographically. Final measurements, on DCBP, were made by counter methods, with use of a Weissenberg-geometry manually operated single-crystal diffractometer (Caticha-Ellis, 1963). Lorentz, polarization and absorption corrections were made on the 763 independent measured reflections, listed under F_{meas} in Table 2.

The x, y, and z coordinates of the bromine atoms of DBBP were determined from two-dimensional Patterson functions. The method of Hargreaves (1946, 1957) gave the signs of the $F(hk0)$ terms: the z coordinates of the remaining atoms were evaluated geometrically. Least-squares refinement of these two-dimensional data, with Busing & Levy's (1959) *ORXLS* program, reduced the agreement index $R=\Sigma\,||F_{meas}|-|F_{calc}||/\Sigma\,|F_{meas}|$ from 0·295 to 0·173. The resulting model was somewhat distorted, and further refinement was not pursued. The coordinates were used, instead, as starting values in refining the DCBP model.

Initially, two-dimensional DCBP data only were available. Refinement was accomplished by a combination of Fourier-series and least-squares methods, and resulted in a final $R=0{\cdot}251$. The 763 three-dimensional structure factors, measured later, were used to refine these coordinates, using Busing, Martin & Levy's (1962) ORFLS program. With isotropic temperature factors, having average values of 7·0 Å^2 for Cl, 6·2 Å^2 for O and 5·3 Å^2 for C, the best value of R was 0·153; with anisotropic thermal coefficients having a maximum anisotropy for each kind of atom, expressed as B_{max} Å^2/B_{min} Å^2, of 1·4 for Cl, 2·6 for O and 3·5 for C, R decreased to 0·104. The position coordinates from these two refinement sets differed by less than a maximum of 2·5 pooled standard deviations. Structure factor magnitudes calculated on the basis of the anisotropic thermal coefficients are given in Table 2 under F_{calc}. The individual thermal coefficients have not been listed because of lack of confidence in their physical significance.

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Table 1. *Crystal data for* 4,4′-*dibromo- and* 4,4′-*dichloro-dibenzoyl peroxide**

	a	b	c	β	Z	D_m	D_x	m.p.†	M.W.
DBBP	25·94 ± 5 Å	7·91 ± 2 Å	6·83 ± 2 Å	96·83 ± 17°	4	1·90 ± 2	1·909	143·5 °C	402·052
DCBP	25·47 ± 5	7·80 ± 2	6·85 ± 2	98·60 ± 17	4	1·53 ± 2	1·535	138–142	313·140

* Error values here and in Table 3 without decimal point correspond to the least significant digit in the value of the function.
† Melting, in both crystals, is accompanied by decomposition.

Table 2. *Measured and calculated structure factors for* 4,4′-dichlorodibenzoyl peroxide *at* 25°C

h	k	l	Fmeas	Fcalc
2	0	0	29	25
6	0	0	27	28
8	0	0	10	10
10	0	0	25	25
12	0	0	20	16
14	0	0	30	31
16	0	0	35	35
18	0	0	21	20
20	0	0	6	6
22	0	0	6	6
24	0	0	44	42
26	0	0	2	2
28	0	0	3	1
1	1	0	20	15
2	1	0	34	30
3	1	0	26	22
4	1	0	13	8
5	1	0	47	51
6	1	0	14	15
7	1	0	4	5
8	1	0	4	4
9	1	0	10	11
10	1	0	4	3
11	1	0	16	12
12	1	0	51	49
13	1	0	13	15
14	1	0	11	9
15	1	0	9	7
16	1	0	9	6
17	1	0	7	17
19	1	0	11	6
20	1	0	11	9
21	1	0	28	25
22	1	0	5	4
23	1	0	3	3
27	1	0	4	6
0	2	0	54	58
1	2	0	59	60
2	2	0	155	145
3	2	0	116	105
4	2	0	40	36
5	2	0	50	43
6	2	0	78	68
7	2	0	58	54
8	2	0	18	19
9	2	0	8	7
10	2	0	37	38
11	2	0	10	13
12	2	0	18	15
13	2	0	6	5
14	2	0	5	6
15	2	0	13	12
16	2	0	7	8
17	2	0	15	18
18	2	0	14	16
19	2	0	17	17
20	2	0	9	8
22	2	0	30	25
24	2	0	4	4
26	2	0	11	7
1	3	0	58	60
2	3	0	49	48
3	3	0	10	10
4	3	0	5	5
6	3	0	31	31
7	3	0	31	29
8	3	0	11	11
10	3	0	34	31
13	3	0	4	4
14	3	0	6	7
15	3	0	14	13
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23	3	0	10	10
24	3	0	16	15
0	4	0	13	11
1	4	0	17	19
3	4	0	47	40
4	4	0	40	35
5	4	0	8	8
6	4	0	7	8
7	4	0	10	9
8	4	0	10	7
9	4	0	10	9
10	4	0	16	12
11	4	0	14	12
13	4	0	22	22
14	4	0	6	7
15	4	0	4	5
16	4	0	5	5
19	4	0	9	7
20	4	0	10	10
1	5	0	27	25
2	5	0	5	4
4	5	0	18	18
5	5	0	14	11
6	5	0	25	21
7	5	0	5	6
8	5	0	7	8
9	5	0	5	6
10	5	0	7	6
12	5	0	6	7
13	5	0	6	4
14	5	0	12	12
15	5	0	8	7
17	5	0	12	13
18	5	0	16	18
19	5	0	2	3
0	6	0	25	25
1	6	0	6	7
2	6	0	4	4
3	6	0	3	2
4	6	0	10	9
5	6	0	9	6
6	6	0	7	6
7	6	0	5	5
8	6	0	7	6
9	6	0	11	11
10	6	0	6	6
11	6	0	4	5
12	6	0	7	7
15	6	0	6	7
3	7	0	12	12
4	7	0	8	10
9	8	0	4	5
0	0	1	13	5
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2	0	1	38	41
4	0	1	7	8
-4	0	1	87	83
-6	0	1	15	17
6	0	1	68	74
-8	0	1	79	83
8	0	1	50	62
-10	0	1	47	44
10	0	1	37	38
-12	0	1	27	30
12	0	1	6	6
14	0	1	7	5
16	0	1	7	7
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13	6	2	10	8
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11	7	2	15	16
-13	7	2	9	10
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2	0	3	4	3
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4	0	3	38	47
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6	0	3	58	58
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8	0	3	20	21
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20	0	3	7	6
-22	0	3	4	5
22	0	3	3	3
24	0	3	11	8
2	1	3	66	66
3	1	3	5	6
4	1	3	13	17
5	1	3	27	24
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6	1	3	23	18
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7	1	3	7	5
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8	1	3	22	23
-9	1	3	11	10
9	1	3	34	41
-9	1	3	7	7
10	1	3	21	22
-10	1	3	4	8
-11	1	3	4	5
11	1	3	17	23
12	1	3	20	19
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-13	1	3	31	32
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14	1	3	8	9
15	1	3	9	11
16	1	3	2	2
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17	1	3	9	8
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19	1	3	14	13
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0	2	3	11	9
1	2	3	5	3
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3	2	3	17	15
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4	2	3	79	77
-4	2	3	7	7
5	2	3	52	43
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6	2	3	6	5
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7	2	3	29	32
8	2	3	14	16
-8	2	3	42	38
9	2	3	4	5
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11	2	3	5	6
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15	2	3	11	11
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11	3	3	15	15
12	3	3	10	12
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-13	3	3	14	12
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-18	3	3	8	8
-20	3	3	15	17
0	4	3	26	8
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2	4	3	27	29
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3	4	3	33	28
-3	4	3	18	15
4	4	3	9	11
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5	4	3	8	9
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-8	4	3	12	13
-9	4	3	10	13
9	4	3	20	18
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10	4	3	15	15
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11	4	3	30	30
12	4	3	13	13
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13	4	3	20	22
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15	4	3	12	11
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18	4	3	5	6
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1	5	3	8	6
-1	5	3	15	17
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4	5	3	8	8
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8	5	3	5	5
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-9	5	3	14	16
10	5	3	17	15
-10	5	3	19	17
12	5	3	11	12
-13	5	3	7	5
14	5	3	5	6
-14	5	3	17	16
15	5	3	12	10
-15	5	3	5	3
-2	6	3	10	10
-4	6	3	8	8
-6	6	3	9	8
-7	5	3	5	4
-9	6	3	24	19
-10	6	3	14	13
-12	6	3	6	6
-5	7	3	7	5
-7	7	3	13	13
-2	0	4	29	29
2	0	4	2	2
-4	0	4	17	20
4	0	4	21	21
-6	0	4	12	12
6	0	4	56	68
-8	0	4	42	42
8	0	4	23	26
10	0	4	6	6
-10

The final atomic position coordinates obtained with use of anisotropic thermal coefficients are listed in Table 3 and the corresponding interatomic distances are indicated in Fig. 1. The standard deviations in these distances may be estimated in several ways, since we suspect the primary intensity data to be subject to appreciable systematic error: (1) directly from the least-squares correlation matrix, (2) from the maximum difference between corresponding distances obtained with isotropic and anisotropic temperature motion models, and (3) as the mean standard deviation obtained from corresponding differences in distance between these models. Values of these various 'standard' deviations are given in Table 4. The least-squares derived values are probably too small since the assumption of random error only is not applicable. The second and third estimates are likely to be closer to true standard deviations.

Table 3. *Final atomic position coordinates for 4,4′-dichlorodibenzoyl peroxide**

	x	*y*	*z*
Cl(1)	4036 ± 1	5704 ± 6	7736 ± 7
Cl(2)	−0233 ± 2	7084 ± 7	−8509 ± 9
O(1)	2315 ± 4	5436 ± 16	−0477 ± 14
O(2)	1851 ± 4	5238 ± 14	−2045 ± 19
O(3)	1839 ± 3	3827 ± 12	1342 ± 14
O(4)	1501 ± 4	7278 ± 15	−0296 ± 18
C(1)	2698 ± 5	4901 ± 17	2733 ± 27
C(2)	3147 ± 5	5865 ± 17	2468 ± 27
C(3)	3539 ± 5	6106 ± 18	4018 ± 32
C(4)	3532 ± 5	5361 ± 19	5894 ± 28
C(5)	3095 ± 5	4399 ± 20	6248 ± 24
C(6)	2684 ± 5	4081 ± 20	4682 ± 30
C(7)	2200 ± 6	4589 ± 21	1017 ± 35
C(8)	1062 ± 4	6459 ± 18	−3484 ± 29
C(9)	1113 ± 5	5655 ± 22	−5295 ± 20
C(10)	0708 ± 5	5884 ± 20	−6869 ± 24
C(11)	0287 ± 5	6786 ± 22	−6551 ± 24
C(12)	0221 ± 5	7548 ± 22	−4656 ± 31
C(13)	0615 ± 5	7465 ± 22	−3145 ± 22
C(14)	1483 ± 5	6363 ± 21	−1685 ± 25

* $\times 10^4$; see footnote to Table 1.

Table 4. *Value of estimated standard deviations in the interatomic distances**

Bond	Least squares	Max (iso-aniso)	Mean (iso-aniso)
Cl–C	0·01 Å	0·04 Å	0·03 Å
O–C	0·02	0·04	0·03
O–O	0·01	0·02	0·02
C–C_{arom}	0·02	0·06	0·03
C–C_{aliph}	0·02	0·07	0·05

* See text for discussion.

The average bond lengths found are: Cl–C, 1·72; O=C, 1·16; O–C, 1·32; O–O, 1·48; C–C (aromatic), 1·40; and C–C (aliphatic), 1·56 Å. The individual distances in Fig. 1 do not differ significantly from these average lengths, although they correspond to an apparently highly distorted molecule.

The principal purpose of this investigation was the determination of the dimensions of the peroxide group in an organic molecule, *i.e.* of the O–O bond length and the C–O–O–C dihedral angle. The distortions from regularity in the present molecular model are large, as also were those found in the comparable study on dibenzoyl peroxide (Sax & McMullan, 1967). The C–C distances in the benzene rings, for example, range from 1·34 to 1·42 Å in dibenzoyl peroxide and from 1·33 to 1·46 Å in DCBP: *in neither case, however, is this variation from the mean significant.* The O–O bond length in both studies appears to be among the more accurate of the quantities determined. A comparison of bond lengths and dihedral angles in various peroxides is made in Table 5. The remaining bond lengths found in the present study may be compared with the selected standard values given by Sutton (1965): Cl–C, 1·70 ± 0·01; O=C, 1·17 to 1·24; O–C, 1·31 to 1·36; C–C (aromatic), 1·394 ± 0·005 and C–C (aliphatic), 1·505 ± 0·005 Å. With the exception of the C–C (aliphatic) bond, the average distances determined in the present study are in excellent agreement with Sutton's values. The large error (Table 4) associated with the C–C (aliphatic) bond length indicates this discrepancy to be of low significance.

The six independent determinations of the peroxide bond length, in Table 5, have a mean value of 1·47 Å. There is no significant difference between this mean value and any of the experimental values. The peroxide dihedral angle, by contrast, appears strongly dependent upon its environment.

The smallest intermolecular distance in this crystal is 3·26 Å, between O(4) and C(5) in neighboring molecules.

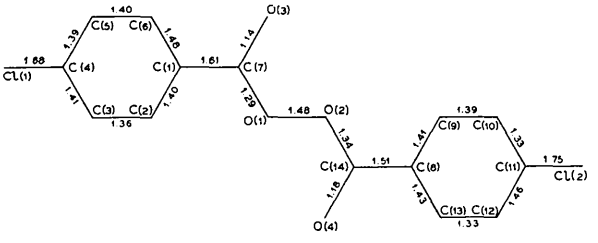

Fig. 1. Bond lengths (Å) in 4,4′-dichlorodibenzoyl peroxide. The variations in the benzene ring C–C distances are not significantly different from the mean value of 1·40 Å (see text).

Table 5. *Dimensions of the peroxide group*

Compound	O–O bond length	Dihedral angle	Reference
H_2O_2	1·49 ± 0·02 Å	94°*	Abrahams, Collin & Lipscomb (1951)
	1·453 ± 0·007	90·2 ± 0·6°	Busing & Levy (1965)
$H_2O_2.2H_2O$	1·481 ± 0·009	138·8°*	Olovsson & Templeton (1960)
BaO_2	1·49 ± 0·04	—	Abrahams & Kalnajs (1954)
Dibenzoyl peroxide	1·46 ± 0·02	91 ± 2°	Sax & McMullan (1967)
DCBP	1·48 ± 0·02	81·1 ± 3·4°	Present paper

* The H–O–O–H dihedral angle in this X-ray work was based on the assumption of identity with the corresponding O...O–O...O angle.

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Siliziumhaltiges β-AlB_{12} und $AlBeB_{24}$ vom Typ des BeB_{12}.

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At 1550°C in the presence of small amounts of silicon orthorhombic β-AlB_{12} is formed from aluminum and boron. The ratio Al:B of selected crystals varies between 1:12–1:14, the amount of Si being smaller than 0·2%. If Al is partly substituted by Be one obtains under the same conditions tetragonal crystals of $Al_{\sim 0,6}Be_{\sim 0,4}B_{12}$. The unit cell of this composition is the same as that of tetragonal B or BeB_{12}.

Über die als β-AlB_{12} bezeichnete Phase des Systems Aluminium–Bor sind in der Literatur keine einheitlichen Angaben vorhanden. Von Biltz (1908, 1910) wurde die Verbindung als ternäres Borid mit der Zusammensetzung $Al_3C_2B_{48}$ bezeichnet. Dann fanden Naray-Szabo (1936) und Kohn, Katz & Giardini (1958) praktisch kohlenstoffreie Kristalle mit der Zusammensetzung AlB_{12}. Neuerdings geben Matkovich, Economy & Giese (1964) wieder einen stöchiometrischen Kohlenstoffgehalt entsprechend der alten Formulierung an. 'β-AlB_{12}' bzw. $Al_{0,75}C_{0,5}B_{12}$ kristallisiert bei Normaltemperatur in rhombischen Formen mit Elementarzellen, die nach Matkovich, Economy & Giese (1965) zueinander in einfachen geometrischen Beziehungen stehen. Diese Zellen stellen beide schwach rhombisch verzerrte grössere Einheiten der Elementarzelle des tetragonalen Bors bzw. des mit diesem vergleichbaren BeB_{12} dar. Dieser Zusammenhang wird besonders deutlich durch die Existenz einer oberhalb 850°C auftretenden Hochtemperaturform des β-AlB_{12}, deren Elementarzelle nach Matkovich *et al.* (1965) der des tetragonalen Bors entspricht. Man kann daher im β-AlB_{12} mit einer ähnlichen Anordnung ikosaedrischer B_{12}-Einheiten wie im tetragonalen Bor rechnen, zwischen welchen bei letzterem je Zelle zwei Bor-, beim BeB_{12} vier Beryllium- und beim β-AlB_{12} vermutlich Aluminium- und gegebenenfalls Kohlenstoff-Atome angeordnet sind (Becher, 1964*a*, *b*). Bei unseren (Becher, 1960) Untersuchungen im System Aluminium–Bor sowie über die Bildung von Boriden aus Aluminiumschmelzen stellten wir in Übereinstimmung mit Matkovich *et al.* (1964, 1965) fest, dass reines Bor in Aluminiumschmelzen, die auf 1400–1500°C erhitzt wurden, neben AlB_2 nur α-AlB_{12} ergibt. Setzt man aber den Schmelzen Silizium in Form von gesintertem SiB_4 und SiB_6 zu, unterbleibt die Bildung von α-AlB_{12} vollständig. Silizium wird grösstenteils in feiner Form als Element ausgeschieden. Als kristalline Phase, in Kristallgrössen bis 3 mm, hinterbleibt nach Weglösen des überschüssigen Aluminiums β-AlB_{12}. Die Kristalle enthalten nur etwa 0,2 Gewichtsprozent Silizium. Es handelt sich um Zwillingskristalle beiden beschriebenen rhombischen Formen des β-AlB_{12} (Matkovich *et al.*, 1965). Wir beobachteten aber aus verschiedenen Ansätzen ein mengenmässig unterschiedliches Auftreten der beiden Formen, begleitet von kleinen Änderungen in den Achsenabmessungen, in den Dichten und im Aluminiumgehalt. Letzterer wurde durch Analyse und in einigen Fällen durch Untersuchung an Einkristallen mit der Mikrosonde bestimmt. Einige Werte lagen bei 17%, entsprechend der Formel AlB_{12}, andere bei 14–15%, entsprechend der Formel AlB_{14}. Guinieraufnahmen bei 900°C bestätigten die von Matkovich beobachtete Umwandlung in eine einfachere tetragonale Elementarzelle.

Offensichtlich vermag ein geringer Siliziumeinbau zur Bildung der β-AlB_{12}-Phase zu führen, in welcher wahrscheinlich in kleinem Ausmass eine Besetzung von Aluminium-Plätzen durch Bor möglich ist. Die Widersprüche in den Literaturangaben zur Zusammensetzung des β-AlB_{12} wären dann verständlich. Weitere Beobachtungen in unserem Arbeitskreis zeigten ferner die Bildung von β-AlB_{12}-Kristallen oder mit diesen verwandten Gittertypen, wenn den Schmelzen kleine Mengen Mangan oder Nickel zugesetzt wurden.

Wenn man dem Reaktionssystem ausser Silizium etwas Beryllium zuführt, das zuvor mit Bor in einem Verhältnis Be:B wie 1:8 bis 1:14 zusammengesintert wird, kristallisiert neben den schon beschriebenen Mischkristallen aus α-AlB_{12} und Be_2B_{12} vom α-AlB_{12}-Typ ein weiteres berylliumhaltiges Aluminiumborid. Für dieses fanden wir wiederum die tetragonale Elementarzelle mit den Achsen $a=8{,}82$, und $c=5{,}08$ Å, die mit nur geringfügigen Abweichungen beim tetragonalen Bor, beim BeB_{12} und bei der Hochtemperaturform des β-AlB_{12} auftritt. Durch den Berylliumeinbau bleibt demnach die Hochtemperaturform