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Trigonal B_2O_3 with Higher Space-Group Symmetry: Results of a Reevaluation

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Summary. A new crystal structure refinement based on published X-ray diffraction data [1] of the normal pressure modification of B_2O_3 (B_2O_3 form I) shows that the correct space group is (152) $P3_121$ instead of (144) $P3_1$ within limits of error.

Keywords. B_2O_3 form I; Trigonal diboron trioxide; Space group correction.

Introduction

At normal pressure, B_2O_3 has a trigonal structure (form I) characterized by a three-dimensional network of corner-linked BO_3 triangles [1]; at high pressure, an orthorhombic modification (form II) prevails consisting of a framework of linked BO_4 tetrahedra [2]. In the opinion of the authors of Ref. [1] the three earlier publications on the crystal structure of B_2O_3–I [3–5], all based on space group $P3_1$, have to be considered as obsolete.

The structural data published for B_2O_3–I by *Gurr*, *Montgomery*, *Knutson*, and *Gorres* [1] are presented in Table 1. Transforming the unit cell according to $(010/100/00\bar{1})$ followed by an origin shift of (0,0,0.204) leads to positional atom coordinates which fit approximately for a structure description in the higher symmetrical space group (152) $P3_121$. To verify this hypothesis, the 130 observed structure amplitude values F_{obs} which had been obtained from single-crystal diffractometer measurements [1] were converted to a computer file which was then used for new structure refinements.

Results and Discussion

Structure refinements were performed both in space group $P3_1$ and $P3_121$. The atomic coordinates given in Table 1 were used in the starting set for space group $P3_1$. The same parameters, but after cell transformation and origin shift, served as the starting set for space group $P3_121$. The complex scattering functions for neutral atoms [6], unit weights, and the program SHELXL-97 [7] were employed.

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Table 1. Structure data for trigonal B_2O_3 form I as published by *Gurr et al.* in 1970 [1]

Cell data	hP15 (144) $P3_1$-a^5 $a = 4.3358(5)$ Å, $c = 8.3397(18)$ Å, $\gamma = 120°$				
Atom	*Wyckoff* position	x	y	z	B/Å^2
B1	3a	0.2229(48)	0.3926(47)	−0.0198(26)	1.28(0.39)
B2	3a	0.8281(43)	0.6031(45)	0.0921(24)	0.81(0.36)
O1	3a	0.5468(30)	0.3972(32)	0.0000(00)	0.82(0.16)
O2	3a	0.1485(21)	0.6004(33)	0.0775(09)	0.75(0.16)
O3	3a	0.0045(24)	0.1608(36)	−0.1291(23)	0.58(0.12)

Isotropic displacement parameters were allowed to vary; the small amount of data does not allow to refine significant anisotropic displacement parameters for the atoms.

The results of structure refinements in the space groups $P3_1$ and $P3_121$ differ only insignificantly (Table 2). In any case, the enlargement of the number of refined parameters is not justified. The increase of the space group symmetry increases also the *Laue* symmetry from $\bar{3}$ to $\bar{3}$m. For the latter, the volume of the asymmetric unit is only half as big, and in particular the *hkil* reflections must have now the same intensity as the *khil* reflections. In the data set of *Gurr et al.* [1] there are 18 such reflection pairs. The internal R value based on these reflections is 0.029 which supports our choice of the higher *Laue* symmetry. In addition, there are larger elements in the correlation matrix after refinement in $P3_1$. More details on the refinement can be obtained from the data in CIF format which have been deposited at the Inorganic Crystal Structure Database at the Fachinformationszentrum Karlsruhe under the deposition number CSD 411992.

The new positional atom coordinates of trigonal B_2O_3 form I described in space group (152) $P3_121$ can be found in Table 3. These data have been standardized with

Table 2. Comparison of structural refinements in space group $P3_1$ and $P3_121$

	$P3_1$	$P3_121$
$R_1 = \Sigma(F_o - F_c)/\Sigma F_o$	0.052	0.052
$wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2)^{0.5}; w = 1$	0.121	0.122
$GooF = (\Sigma(w(F_o^2 - F_c^2)^2)/(n-p))^{0.5}$	0.675	0.703
Number of free variables (p)	21	11
Number of reflections (n)	130	112
Final difference *Fourier* map (eÅ^{-3})	−0.28 to +0.38	−0.31 to +0.37

Table 3. New structure data for trigonal B_2O_3 form I

Cell data	hP15 (152) $P3_121$-c^2a $a = 4.3358$ Å, $c = 8.3397$ Å, $\gamma = 120°$				
Atom	*Wyckoff* position	x	y	z	U_{iso}
B	6c	0.3954(19)	0.2299(23)	0.2244(9)	0.0102(14)
O1	6c	0.6009(12)	0.1477(10)	0.1282(5)	0.0101(11)
O2	3a	0.1607(14)	0	1/3	0.0092(14)

Table 4. Interatomic bond lengths (Å) and bond angles (°)

Bond lengths		Bond angles	
B–O1[a]	1.375(9)	O1[a]–B–O2	116.3(6)
B–O2	1.356(8)	O1[a]–B–O1	120.4(6)
B–O1	1.373(8)	O2–B–O1	123.1(7)
		B–O1–B[b]	130.9(5)
		B–O2–B[c]	135.0(8)

Symmetry codes other than x,y,z: [a] $-x+1,-x+y+1,-z+1/3$; [b] $-x+1,-x+y,-z+1/3$; [c] $x-y,-y,-z+2/3$

the computer program STRUCTURE TIDY [8]. Selected bond lengths and angles are presented in Table 4.

The B atom is triangularly coordinated to O atoms. The BO_3 triangle is very close to planar, the sum of the three O–B–O angles being 359.8(6)°. The two crystallographically independent O atoms have site symmetry 1 and 2, respectively. They are coordinated to two B atoms each. The coordination figures are more regular than in the $P3_1$ structure. The new structure description is in accordance with results from NMR measurements which show that the B atoms are in a trigonal planar environment [9]. The absence of more than one distinguishable splitting suggests that all BO_3 groups in the normal pressure modification of B_2O_3 are bonded in one configuration only. Contrary to the old structure proposal, the trigonal B_2O_3–I modification does not have a polar axis which allows to make some statements about selected physical properties as *e.g.* on pyroelectricity which cannot occur in this compound.

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