Boron-Carbon Order and Symmetry Control: Single-Crystal X-Ray Study of SmB_2C_2

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

The title compound was prepared from the elements by arc-melting followed by annealing in silica tubes at 1270 K for one week. The crystal structure was investigated by means of X-ray single crystal diffraction: space group $P4/mbm$, $a = 5.366(1)$, $c = 3.690(1)$ Å, $Z = 2$, $R1 = 0.010$, $wR2 = 0.022$ for 245 unique reflections with $I_o > 2\sigma(I_o)$ and 12 refined parameters. Group-subgroup relationships of $M B_6$ and $M B_2C_2$ structure models are discussed.

Key words: Samarium Boride Carbide, Crystal Structure, Group-Subgroup Relationships

Introduction

Metal boride carbides are one target in the extensive research of Jeitschko adressing the interesting question of bonding within the anionic substructure. For Mo_2BC he has shown [1] that B and C are well separated into B-B bonded domains and single C atoms. The less electron-rich BC substructures in $M B_2C_2$ phases serve somewhat related problems.

LnB_2C_2 compounds (Ln = lanthanides, Y) exhibit tetragonal symmetry, and a unit cell with $a \approx 3.8$ and $c \approx 4.0$ Å has been chosen for the description of their structures [2]. B and C atoms form planar 4.8^2 nets of four- and eight-membered rings stacked directly above one another with the cations occupying positions between eight-membered rings [3 – 5]. Early on, a doubling of the c axis length has been suggested on the basis of single crystal data for LaB_2C_2 [4], and the model in $P\bar{4}2c$ contained alternating boron and carbon atoms within the four-membered rings and connections between those rings *via* B-B and C-C bonds, respectively. The doubling of c is due to a rotation of successive BC nets by 90°, see Figs. 1a and 2. Later a description of this model in $P4_2/mmc$ has been chosen [6]. In any case the model deviates from an earlier one [7, 8] with no doubling of the c axis and the choice of the diagonal of the ab plane as a axis, where regular squares and octagons have been assumed with only heteroatomic B-C bonds, see Fig. 1b.

Two essential structural features of the LaB_2C_2 models hence remain uncertain. They adress the questions, firstly, whether B and C atoms within the eight-membered rings are alternating or arranged in pairs and, secondly, whether B and C atoms are stacked identically or alternatingly along c. The underlying coloring problem in extended networks and the correlation between symmetry and electronic stability has been thoroughly treated by Burdett *et al.* [9, 10], and on the basis of Extended Hückel calculations they reached the conclusion that a coloring scheme with only heteroatomic B-C bonds in contrast to [4] should represent the stable pattern in the LaB_2C_2 structure family. The stabilization of a structure with only heteroatomic bonds reminds of the case of SiC.

A recent reinvestigation of the structures of LnB_2C_2 (Ln = La-Nd, Tb-Tm, Lu) has been performed using neutron powder data [11 – 14]. Refinements in $P4/mbm$ are in agreement with the predicted structure characterized by only heteroatomic B-C bonds, however, in distorted squares and octagons as shown in Fig. 1c, in contrast to the structural model proposed in [7, 8].

X-ray powder diffraction experiments on CaB_2C_2 also resulted in a structure with no homoatomic bonding in the BC sheets [15]. Besides those experimental verifications of the predicted structure new DFT calculations for $M B_2C_2$ (M = Mg, Ca, Sc, Y, La, Ce, Lu) corroborate the coloring pattern with only heteroatomic B-C bonds [16].
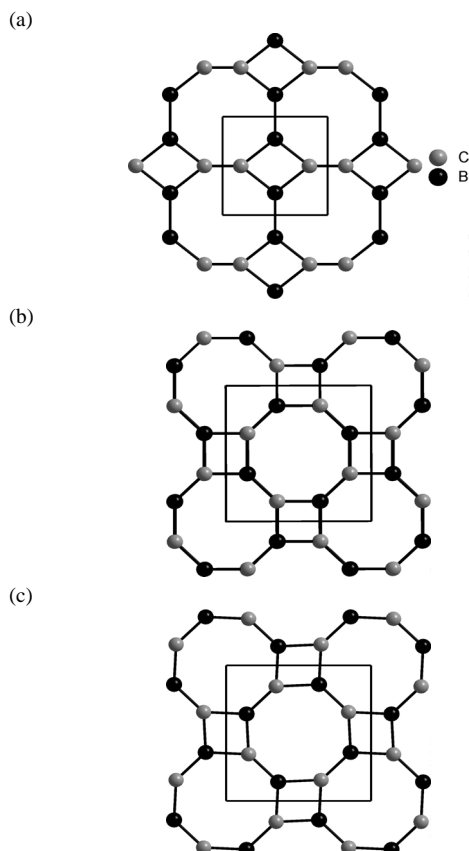
(a)

(b)

(c)

Fig. 1. Projections of BC nets in different structure models: (a) Bauer model [3], (b) Smith model [7, 8], (c) Onimaru, van Duijn and Albert model [11 – 13, 15].

Here we report on single crystal X-ray investigations of SmB$_2$C$_2$, a phase with interesting magnetic properties [17, 18]. The different structural models and the underlying coloring problem are rationalized in terms of group-subgroup relationships [19].

Experimental Section

Synthesis and electron probe microanalysis

SmB$_2$C$_2$ samples were prepared from commercially available pure elements: samarium metal with a claimed purity of 99.99 at-%, Rhône Poulenc, Arizona, USA; crystalline boron powder, purity 99.99 at-%, H. C. Starck, Germany; graphite powder, purity 99.98 at-%, Carbone-Lorraine, France. The powders were mixed and compacted in stainless steel dies. The pellets were arc-melted on a water-cooled copper hearth using tungsten electrodes in a Ti gettered high purity argon atmosphere. The buttons of approx. 1 g were turned over and remelted three times to ensure their homogeneity. Subsequently the samples were wrapped

Table 1. Crystallographic data for SmB$_2$C$_2$.

Empirical formula	SmB$_2$C$_2$
Crystal system	tetragonal
Space group	*P*4/*mbm* (No. 127)
Pearson symbol	tP10
Lattice parameters	
a [Å]	5.366(1)
c [Å]	3.690(1)
Unit cell volume [Å^3]	106.26(3)
Calculated density [g/cm^3]	6.126
Absorption coefficient [cm^{-1}]	27.171
Crystal size [mm^3]	0.1 × 0.08 × 0.03
Radiation and wavelength [Å]	Ag-K$_\alpha$, 0.56086
Diffractometer	NONIUS CAD4
Data reduction program	HELENA [22]
Absorption correction	semiempirical, ψ-scan [23]
Structure refinement	SHELX97 [24]
Refined parameters	12
Collected reflections	5026
hkl Range	$-12 < h < 12,$
	$-12 < k < 12,$
	$-8 < l < 8$ ($2\vartheta_{\max} = 80°$)
Independent reflections	397 ($R_{\mathrm{int}} = 0.065$)
Reflections with $I_\mathrm{o} > 2\sigma(I_\mathrm{o})$	245 ($R_\sigma = 0.022$)
Final *R*1 (*R*1 all data)[a]	0.010 (0.022)
Weighted *wR*2 (*wR*2 all data)[b]	0.022 (0.025)
Goodness-of-fit on F^2	1.1
Max./min. residual electron density [e/Å^3]	$-1.78/2.36$

[a] *R*1 is defined as $\frac{\Sigma||F_\mathrm{o}|-|F_\mathrm{c}||}{\Sigma|F_\mathrm{o}|}$; [b] *wR*2 is defined as $\sqrt{\frac{\Sigma[w(F_\mathrm{o}^2-F_\mathrm{c}^2)^2]}{\Sigma[w(F_\mathrm{o}^2)^2]}}$, $w = [\sigma^2(F_\mathrm{o}^2) + (aP)^2 + bP]^{-1}$, $P = \frac{1}{3} \cdot [2F_\mathrm{c}^2 + \mathrm{Max}(F_\mathrm{o}^2, 0)]$ with $a = 0.0081$ and $b = 0.0000$.

in molybdenum foil and annealed in silica tubes under argon atmosphere for one week at 1270 K. Shiny black plate-like single crystals were isolated from the crushed sample. All handling was carried out under argon atmosphere in a glove box or using Schlenk technique.

For metallographic inspection and electron probe microanalysis (EPMA), samples of the alloy were embedded in Woods metal (Fluka Chemie, Switzerland). The embedded samples were polished on a nylon cloth using chromium oxide (Bühler Isomet) with grain sizes of $1 – 5$ μm. Quantitative and qualitative composition analyses were performed by energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy (WDX) on a scanning electron microscope TESCAN 5130 MM with an Oxford Si-detector and with an Oxford INCA WAVE 700 detector. SmB$_4$ [20] and SmBC [21] standards were used to deduce the composition La$_{20(1)}$B$_{40(1)}$C$_{40(2)}$. For chemical microprobe analysis, the polishing procedure had to be performed or repeated just before the measurements.

X-ray powder and single crystal diffraction

X-ray powder diffraction patterns were obtained on a STOE STADI P with Mo-K$_\alpha$ radiation, using capillar-
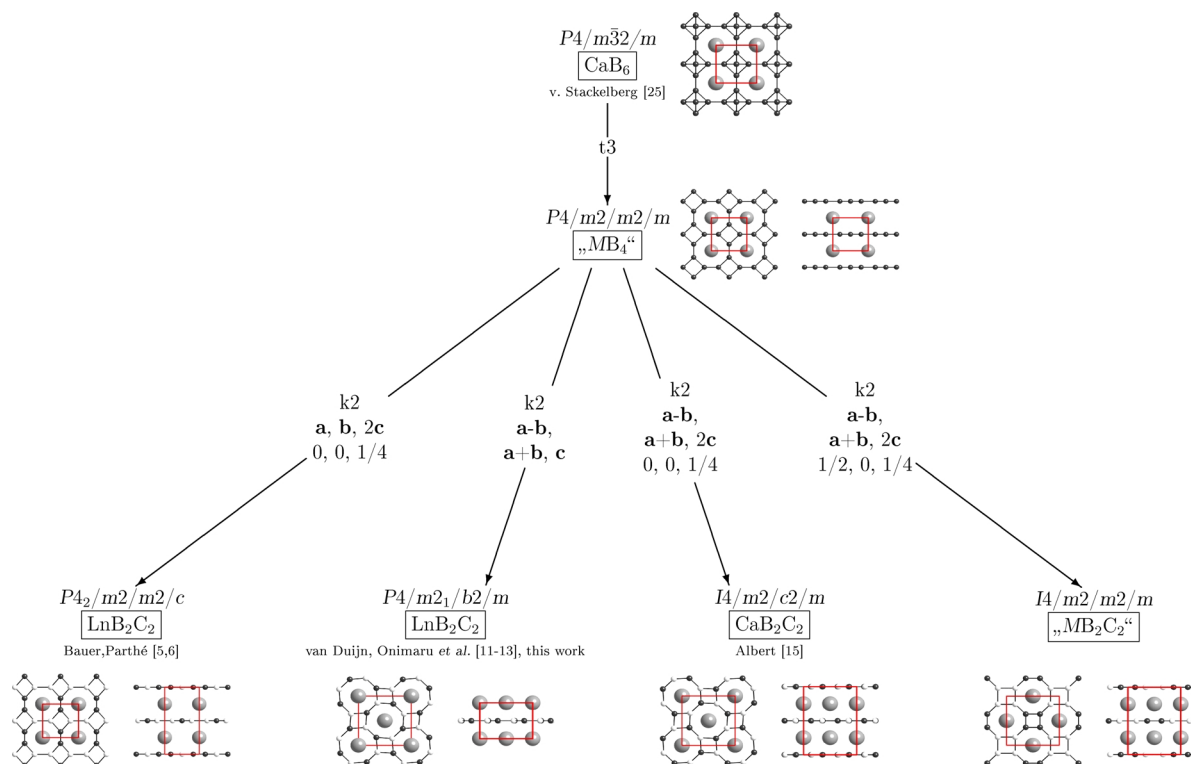
Fig. 2. *Bärnighausen* tree for the group-subgroup relationships of CaB$_6$ and MB$_2$C$_2$.

ies sealed under dried argon to avoid hydrolysis. The unit cell parameters refined from powder data are $a = 5.3719(2)$, $c = 3.6960(2)$ Å. Small and irregularly shaped single crystals sealed under argon were first examined by Laue and Buerger precession exposures in order to examine their suitability for intensity collection. Data of half of the Ewald sphere were collected on an Enraf Nonius CAD4 four-circle diffractometer with scintillation counter using graphite monochromatized Ag-K$_\alpha$ radiation. The reflections were measured at diffractometer settings optimized for minimum absorption. Collected data were corrected for Lorentz and polarization effects [22], and a semi-empirical absorption correction was applied [23] on the basis of ψ-scan data. Relevant crystallographic data are given in Table 1. Single crystal lattice parameters used for further calculations were determined from 25 centered high-indexed reflections. The starting atomic parameters were anisotropically refined with the program SHELX-97 [24] (full-matrix least-squares on F^2). The refinement converged well, and the final difference Fourier synthesis was flat.

Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) by quoting the depository number ICSD-416178.

Table 2. Atomic coordinates and displacement parameters [Å$^2 \cdot 10^{-5}$] for SmB$_2$C$_2$. Sm at 2a; B, C at 4h; U_{ij} is defined as $\exp\{-2\pi^2[U_{11}(ha^*)^2 + \ldots + 2U_{12}hka^*b^*]\}$.

Atom	x	U_{eq}	U_{11}	U_{33}	U_{12}
Sm	0	426(3)	451(3)	376(4)	0
B	0.3600(6)	620(70)	600(80)	660(12)	260(80)
C	0.1594(6)	590(50)	610(60)	530(90)	140(60)

Results and Discussion

Three different structural models proposed by Bauer [4], Smith [8], Onimaru and van Duijn [12, 13] were checked. No doubling of the c axis was observed for SmB$_2$C$_2$. The single crystal data showed superstructure reflections that all could be indexed in a tetragonal $\sqrt{2}a \times \sqrt{2}b \times c$ unit cell referring to the earlier chosen subcell with $a \approx 3.8$ and $c \approx 4.0$ Å. This is the first single crystal data which shows that an enlargement of the cell is needed, however, only in a. The metrics of the unit cell alone leads to the structural model proposed by Onimaru and van Duijn [12, 13], space group $P4/mbm$ with alternating B and C atoms. On the basis of our X-ray single crystal data, the final $R1$ value for this model was 1.0% ($wR2 = 2.2\%$).
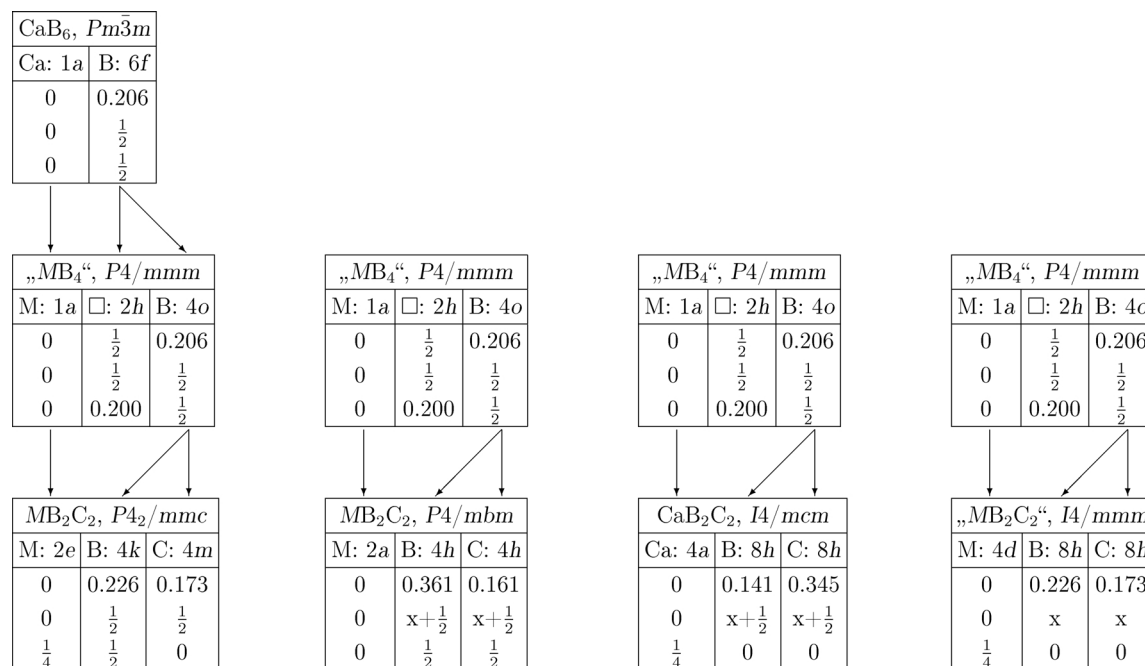
CaB_6, $Pm\bar{3}m$	
Ca: 1a	B: 6f
0	0.206
0	$\frac{1}{2}$
0	$\frac{1}{2}$

„MB_4", $P4/mmm$		
M: 1a	□: 2h	B: 4o
0	$\frac{1}{2}$	0.206
0	$\frac{1}{2}$	$\frac{1}{2}$
0	0.200	$\frac{1}{2}$

„MB_4", $P4/mmm$		
M: 1a	□: 2h	B: 4o
0	$\frac{1}{2}$	0.206
0	$\frac{1}{2}$	$\frac{1}{2}$
0	0.200	$\frac{1}{2}$

„MB_4", $P4/mmm$		
M: 1a	□: 2h	B: 4o
0	$\frac{1}{2}$	0.206
0	$\frac{1}{2}$	$\frac{1}{2}$
0	0.200	$\frac{1}{2}$

„MB_4", $P4/mmm$		
M: 1a	□: 2h	B: 4o
0	$\frac{1}{2}$	0.206
0	$\frac{1}{2}$	$\frac{1}{2}$
0	0.200	$\frac{1}{2}$

MB_2C_2, $P4_2/mmc$		
M: 2e	B: 4k	C: 4m
0	0.226	0.173
0	$\frac{1}{2}$	$\frac{1}{2}$
$\frac{1}{4}$	$\frac{1}{2}$	0

MB_2C_2, $P4/mbm$		
M: 2a	B: 4h	C: 4h
0	0.361	0.161
0	x+$\frac{1}{2}$	x+$\frac{1}{2}$
0	$\frac{1}{2}$	$\frac{1}{2}$

CaB_2C_2, $I4/mcm$		
Ca: 4a	B: 8h	C: 8h
0	0.141	0.345
0	x+$\frac{1}{2}$	x+$\frac{1}{2}$
$\frac{1}{4}$	0	0

„MB_2C_2", $I4/mmm$		
M: 4d	B: 8h	C: 8h
0	0.226	0.173
0	x	x
$\frac{1}{4}$	0	0

Fig. 3. Evolution of the atomic coordinates for CaB_6 and the MB_2C_2 structures present in the *Bärnighausen* tree in Fig. 2.

The atomic coordinates and displacement parameters are given in Table 2, respectively. Interatomic distances and bond angles are reported in Table 3. Two types of B-C bonds are present: long bonds, 1.610(4) Å, with B-C-B angle 138.7(3)°, in the four- and eight-membered rings and short bonds, 1.522(6) Å, with B-C-B angle 82.6(2)°, unique to the eight-membered rings. The Sm atoms located above the centers of the eight-membered rings have slightly shorter contacts to C (2.734(1) Å) than to B (2.775(1) Å). The Sm atoms are packed in a slightly distorted simple cubic array. The Sm-Sm distances are 3.689(1) Å parallel to [001] and 3.7946(7) Å in (001). They are comparable with other Ln-Ln distances observed in the neutron diffraction studies taking into account the lanthanoid contraction.

Group-subgroup relationships for CaB_6 and MB_2C_2

The structure models of the boride carbides MB_2C_2 can be derived from the aristotype CaB_6 [25] using group-subgroup relationships represented in a *Bärnighausen* tree [19], see Figs 2 and 3. This formalism is used to analyze the problem of coloring the 4.8^2 nets of B and C atoms which occur in the structures. Furthermore, all possible BC net types can be deduced systematically.

Table 3. Bond lengths [Å] and angles [°] with multiplicities for SmB_2C_2.

Atoms	Bond length	Atoms	Angle
Sm-Sm (2×)	3.689(1)	C-B-C (2×)	131.3(2)
Sm-Sm (4×)	3.7946(7)	C-B-C (1×)	97.4(3)
Sm-B (8×)	2.775(1)	B-C-B (2×)	138.7(3)
Sm-C (8×)	2.734(1)	B-C-B (1×)	82.6(2)
B-C (2×)	1.610(4)		
B-C (1×)	1.522(6)		

The first step of symmetry reduction in order to obtain the structures of MB_2C_2 boride carbides from the CaB_6 structure leads to a hypothetical „MB_4" structure in the *translationengleiche* subgroup $P4/mmm$ of index 3. Lowering the symmetry to the tetragonal system leads to a splitting of the 6f boron site into a fourfold 4o site ($x, \frac{1}{2}, \frac{1}{2}$) corresponding to the equatorial plane of the B_6 octahedron and a twofold 2h site ($\frac{1}{2}, \frac{1}{2}, x$) corresponding to the apical positions of the octahedron which is left empty in „MB_4", having the consequence that the three-dimensional network of octahedra is transformed into 4.8^2 nets. The proposed structures crystallize in direct *klassengleiche* subgroups of index 2 of the hypothetical „MB_4" structure.

The first structure model for MB_2C_2 described by Bauer in space group $P\bar{4}2c$ [5] and later transformed into $P4_2/mmc$ by Parthé [6] can be deduced from the

„*M*B$_4$" structure by transforming the former boron position into two independent 4k and 4m sites, which allows a slight shift of the atomic positions from 0.207, $\frac{1}{2}$, $\frac{1}{2}$ (B in CaB$_6$) to 0.226, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, 0.173, $\frac{1}{2}$ (B and C in LaB$_2$C$_2$, respectively) and yields homoatomic contacts B-B and C-C of different bond lengths.

The alternative structure model introduced by Smith and Onimaru *et al.* [7, 8, 11, 12], in space group *P*4/*mbm* agrees with the single crystal data for SmB$_2$C$_2$ reported here. The model with only heteroatomic contacts between boron and carbon atoms can be deduced from the „ *M*B$_4$" structure by transforming the boron site into two 4h sites (0.361, $x + \frac{1}{2}$, $\frac{1}{2}$ and 0.161, $x + \frac{1}{2}$, $\frac{1}{2}$ for B and C atoms in LaB$_2$C$_2$, respectively), actually by doubling the a and b vector of the initial „*M*B$_4$" cell, thus transforming into *C*4/*mmm* and subsequently replacing the mirror plane in (100) by a glide plane. The standard setting of the resulting space group *C*4/*mmd* is *P*4/*mbm*, shown in Figs 2 and 3.

The boride carbide CaB$_2$C$_2$ published by Albert and Schmitt [15] crystallizes in *I*4/*mcm* and shows a similar topology with only heteroatomic contacts between boron and carbon in the nets. The difference is the alternating stacking sequence of these nets ...A-B-A-B... where A is rotated by 90° against B. Similar to the preceding case doubling of all base vectors, shifting the origin into the BC plane and replacing the mirror plane in (100) by a glide plane leads to *F*4/*mmc* which is a non-standard setting of *I*4/*mcm*. The boron site in „*M*B$_4$" transforms into two 8h sites $x, x + \frac{1}{2}, 0$ with $x = 0.141$ and 0.345 for B and C, respectively.

One can easily construct further colorings for the 4.8^2 nets by applying group-subgroup relationships on the aristotype CaB$_6$ *via* „*M*B$_4$". As one example a fourth possibility of *klassengleiche* symmetry reduction of index 2 from *P*4/*mmm* is shown. For this structure model in space group *I*4/*mmm* there is no

representative found in the chemistry of metal boride carbides and such a model will be improbable from chemical reasoning. The structure exhibits squares of B atoms which are connected to squares of C atoms and *vice versa*. In Figs 2 and 3 the two independent 8h positions for B and C at $x, x, 0$ were fixed to $x = 0.226$ and 0.173 in order to give visibly different sizes for the two squares.

Another variant would be an alternating ...A-B-A-B... stacking of homoatomic 4.8^2 nets of only carbon (A) or boron atoms (B), respectively. The corresponding transition from *P*4/*mmm* to the isomorphous subgroup *P*4/*mmm* results in a doubled c axis. All other polytypic stacking variants of such homoatomic nets can also be described in isomorphous subgroups *P*4/*mmm* of index n with n-fold c vectors ($n =$ prime number > 2).

A branch of the symmetry tree which has not been mentioned yet leads to orthorhombic structures *via* the direct *translationengleiche* subgroup *Pmmm* of index 2. In orthorhombic variants the nets can exhibit alternatingly connected homoatomic chains or ribbons of B and C atoms.

In summary, each subgroup of *P*4/*mmm* in which the 4o site in „*M*B$_4$" transforms into (at least) two independent sites is adequate to generate coloring variants of the 4.8^2 nets in „*M*B$_4$". The direct subgroups and the resulting net variants have been shown in detail for *klassengleiche* subgroups and indicated for isomorphous and *translationengleiche* subgroups.

So far, the systematization of the proposed structural models for *M*B$_2$C$_2$ phases seems an academic exercise as the heteroatomic bonding is the preferred configuration at least in the isolated BC layer. However, due to varying cation-anion interactions this situation could change in structures with different cations in an ordered array leading to other coloring patterns.

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