Synthesis and Crystal Structure of the New High-Pressure Phase CdB$_2$O$_4$

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Abstract: The use of high-pressure/high-temperature conditions (7.5 GPa and 1100°C; Walker-type multianvil apparatus) led to the synthesis of a new cadmium borate CdB$_2$O$_4$, starting from stoichiometric mixtures of the oxides. The crystal structure was determined on the basis of single crystal X-ray diffraction data, to reveal the hexagonal space group $P6_3$ with $a =$ 885.2(2), $c = 716.72(8)$ pm, $Z = 8$, $R_1 =$ 0.0178, and $wR_2 = 0.0388$ (all data). CdB$_2$O$_4$ is built up from interconnected layers of BO$_4$-tetrahedra and exhibits for the first time the basic structure of

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a family of compounds, represented by BaGa$_2$O$_4$, KAlSiO$_4$, KGeAlO$_4$, KCoPO$_4$, CaP$_2$N$_4$ and the recently discovered SrP$_2$N$_4$. The lack of superstructure ordering in CdB$_2$O$_4$ was confirmed by electron diffraction. Additionally, a B−O−B angle of 180° was found in this borate for the first time.

Introduction

In the last few years, detailed investigations into the high-pressure chemistry of oxoborates has led to a large diversity of new polymorphs and compositions. In the field of rare-earth oxoborates, we synthesised new high-pressure polymorphs like γ-REBO$_3$ ($RE =$ Dy, Er[1]), γ-REBO$_3$ ($RE =$ La–Nd[2,3]) and δ-REBO$_3$ ($RE =$ La, Ce[4,5]). With 3d-transition metals and main group metals, polymorphs like β-MB$_4$O$_7$ ($M =$ Mn,[6] Ni ,[6] Cu,[6] Zn ,[7] Ca,[8] Hg[9]) and the new non-centrosymmetric δ-BiB$_3$O$_6$[10] could be prepared. The compounds β-SnB$_4$O$_7$[11] and β-MB$_2$O$_5$ ($M =$ Hf,[12] Zr[13]) are the first representatives of ternary phases in the according borate systems.

Under high-pressure/high-temperature conditions, also new structural features are observed. RE_4B$_6$O$_{15}$ ($RE =$ Dy, Ho),[14–16] α-RE_2B$_4$O$_9$ ($RE =$ Sm-Ho),[17–19] and the recently found HP-NiB$_2$O$_4$[20] show, besides new compositions, the new strucural motif of edge-sharing BO$_4$-tetrahedra. HP-NiB$_2$O$_4$ is the first borate, in which every BO$_4$-group shares one common edge with an adjacent BO$_4$-tetrahedron.

In connection with recent high-pressure studies on phase formation and crystal chemistry of the group IIb tetraborates β-ZnB$_4$O$_7$ (orthorhombic, $Cmcm$)[7] and β-HgB$_4$O$_7$ (orthorhombic, $Pmn2_1$),[9] we have turned our attention to the high-pressure and high-temperature synthesis of phases in the system CdO−B$_2$O$_3$. Until now only three cadmium borates have been structurally characterised at ambient pressure; the tetraborate CdB$_4$O$_7$,[21] a member of the isotypic MB$_4$O$_7$ family (orthorhombic, $Pbca$) with $M =$ Mg,[22] Mn,[23] Co,[24] Zn[25] and Hg,[26] the orthoborate Cd$_3$(BO$_3$)$_2$,[27,28] which adopts the kotoite (Mg$_3$(BO$_3$)$_2$)[29] structure type (orthorhombic, $Pnnm$) and the diborate CdB$_2$O$_5$,[30] which is isotypic with its Mg[31] and Co[24] analogues (triclinic, $P\bar{1}$).

Under high-pressure and high-temperature conditions, we have now obtained a new cadmium borate with the formula CdB$_2$O$_4$. We report the synthesis and the crystal structure of this compound, including a comparative discussion concerning the related structures of BaGa$_2$O$_4$,[32] KAlSiO$_4$,[33] KGeAlO$_4$,[34,35] KCoPO$_4$,[36] CaP$_2$N$_4$[37] and SrP$_2$N$_4$.[38] In contrast to CdB$_2$O$_4$, all these phases form a superstructure, whereas CdB$_2$O$_4$ exhibits the basic structure of this family for the first time.

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Results and Discussion

Crystal structure: CdB_2O_4 is built up exclusively from corner-sharing BO_4-tetrahedra, forming layers, which are interconnected to a three-dimensional network. The layers spread out perpendicularly to [001] and consist of "sechser" rings (a ring with six tetrahedral centers)[39,40] (Figure 1).
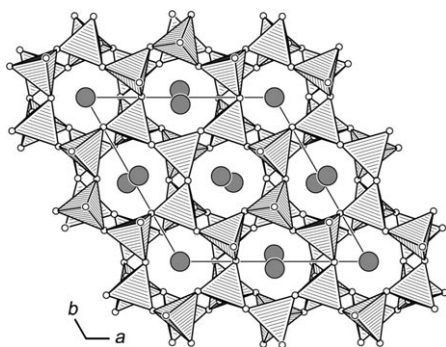

Figure 1. Crystal structure of CdB_2O_4 with a view along [00$\bar{1}$]. Grey spheres represent Cd-atoms, white spheres O-atoms; light-shaded polyhedra show BO_4-groups.

These rings show two types of topologies with respect to the orientation of the containing tetrahedra (U=up, D= down): one fourth of the rings reveals an UDUDUD topology, and the remaining rings adopt an UUUDDD topology. Figure 2 gives a view of the two arrangements inside of a layer.
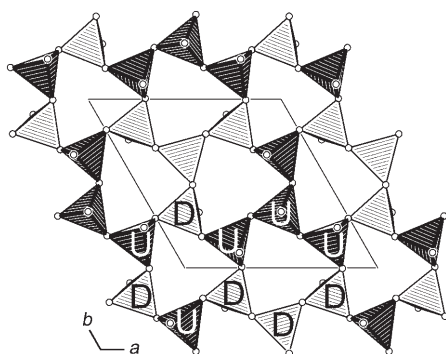

Figure 2. One layer of CdB_2O_4 consists of two different types of "sechser" rings[39,40] (topology: UUUDDD, UDUDUD). White spheres represent O-atoms. Light-shaded BO_4-polyhedra face downwards (D), dark-shaded polyhedra face upwards (U) (view along [00$\bar{1}$]).

The layers are interconnected through the atoms O1 and O2, building further B_6O_6-"sechser", as well as B_4O_4-"vierer"-rings. Figure 3 shows the connection of the layers, whereas adjacent layers are marked in white and grey for better demonstration. The layers are equivalent and can be transformed into one another by a rotation of 60° along [001] and a translation of [00$^1/_2$].
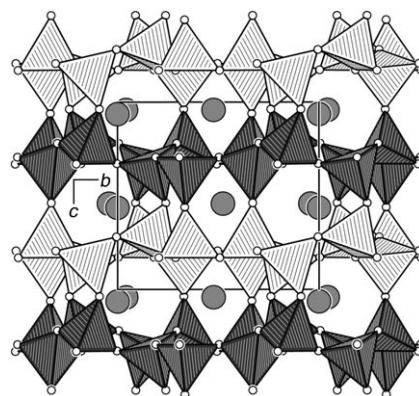

Figure 3. Crystal structure of CdB_2O_4 with a view along [100]. Adjacent layers are shown in different colours. Grey spheres represent Cd-atoms and the white spheres O-atoms.

Figure 4 displays the coordination sphere of the Cd^{2+}-ions. Cd1 is surrounded by six oxygen atoms in the range of 218–277 pm with an average value of 223.4 pm. This value is smaller than the average Cd–O distance of 231.9 pm in $Cd_2B_2O_5$[30] or 232.9 pm in $Cd_3(BO_3)_2$,[27] which both exhibit cadmium in a six-fold coordination as well. However, Cd2 possesses 12 (9+3) next-near neighbours with Cd–O distances from 234.1(2) to 285.0(2) pm with a mean distance of 257.4 pm. As far as we know, no cadmium borate with a comparably high coordination-sphere at a Cd^{2+}-ion has been described up to now.

Cd2-O3a = 234.1(2) pm
Cd2-O3b = 249.1(2) pm
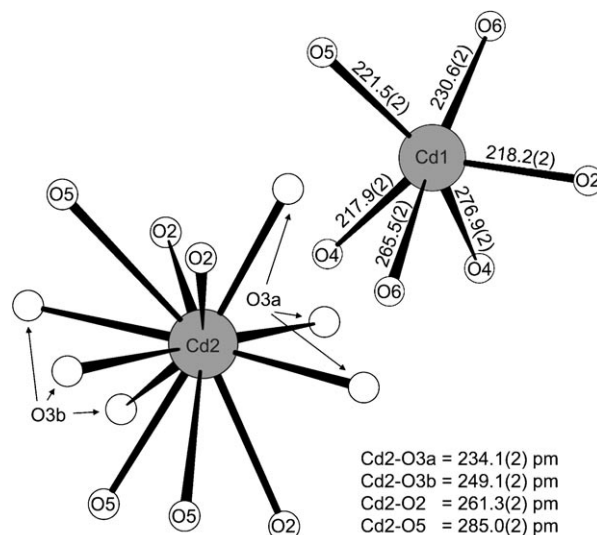Cd2-O2 = 261.3(2) pm
Cd2-O5 = 285.0(2) pm

Figure 4. Coordination spheres of Cd1 and Cd2. Distances are given in pm.

Within the BO_4-network, the B–O bond-lengths reach from 139 to 150 pm with a mean value of 147.3 pm, which corresponds to the known average value of 147.6 pm for B–O distances in BO_4 tetrahedra.[41,42] The O–B–O bond angles range from 107.4(2) to 112.8(2)° with a mean value

of 109.5°. Additionally, we calculated bond-valence sums for CdB_2O_4 with the bond-length/bond-strength and CHARDI concepts[43–45] (Table 1). The formal ionic charges of the atoms, as calculated from the results of the X-ray structure analysis, were in agreement within the limits of both concepts.

Table 1. Charge distribution in CdB_2O_4 calculated with the bond-length/bond-strength concept (ΣV) and the CHARDI concept (ΣQ).

	Cd1	Cd2	B1	B2	B3	B4
ΣV	1.94	2.21	3.16	3.06	3.00	2.96
ΣQ	2.00	1.96	3.04	3.15	2.95	2.99
	O1	O2	O3	O4	O5	O6
ΣV	−1.87	−2.07	−2.03	−2.06	−2.00	−1.93
ΣQ	−1.96	−2.10	−2.02	−1.98	−2.04	−1.88

Related compounds: The structure of CdB_2O_4 is closely related to the structure-type of the compounds $BaGa_2O_4$,[32] $KAlSiO_4$,[33] $KGeAlO_4$,[34,35] $KCoPO_4$,[36] CaP_2N_4,[37] and SrP_2N_4.[38] Both structure types consist of layers of tetrahedra, forming "sechser" rings[39,40] with an identical orientation of the tetrahedra. Excepting CdB_2O_4, all other compounds form a superstructure, which means that CdB_2O_4 is the first representative, showing a threefold smaller basic cell. Table 2 lists the lattice parameters of CdB_2O_4 in com-

Table 2. Lattice parameters of CdB_2O_4 and related structures, all in space group $P6_3$.

	Ref.	a [pm]	c [pm]	V [nm^{-3}]
CdB_2O_4		885.2(2)	716.72(8)	0.486(1)
$BaGa_2O_4$	[32]	1864.03(7)	868.01(2)	2.6119(2)
$KAlSiO_4$	[33]	1811.11(8)	846.19(4)	2.4037(2)
$KGeAlO_4$	[34,35]	1841.3(1)	859.0(1)	2.5222(2)
$KCoPO_4$	[36]	1820.6(1)	851.35(8)	2.4438(2)
CaP_2N_4	[37]	1684.66(4)	785.5(2)	1.9307(1)
SrP_2N_4	[38]	1710.29(8)	810.318(5)	2.05270(2)

parison to related compounds. The superstructure can be obtained from the basic structure by the following lattice transformation: $a_{super} = 2a_{basic} + b_{basic}$; $b_{super} = -a_{basic} + b_{basic}$; $c_{super} = c_{basic}$. This corresponds to an isomorphic transition of index 3. Figure 5 shows the crystal structure of SrP_2N_4 ($P6_3$) with the position of the according subcell of CdB_2O_4.

In SrP_2N_4, this superstructure is caused by avoiding one P−N−P angle of 180° at nitrogen N15. The isotypic compounds $BaGa_2O_4$,[32] $KAlSiO_4$,[33] $KGeAlO_4$,[34,35] $KCoPO_4$,[36] and CaP_2N_4[37] do not show the linear arrangement at the corresponding position. By contrast, the associated B−O−B angle in CdB_2O_4 adopts a value of 180° at oxygen O1 on thermal average (Figure 6). From our knowledge, this is the first example of a linear B−O−B arrangement in the structural chemistry of borates. There exists a molecular compound divinylborinic anhydride $[(CH_2=CH)_2B]_2O$, in which the vibrational data indicate that the molecule possesses C_1
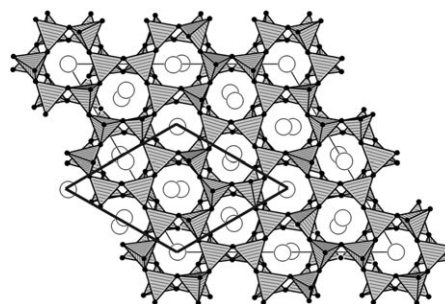

Figure 5. Structure of SrP_2N_4[38] with a view along [001]. Polyhedra represent PN_4 tetrahedra, white spheres show Sr^{2+}-ions. The according basic unit cell of CdB_2O_4 is drawn in thick black lines.
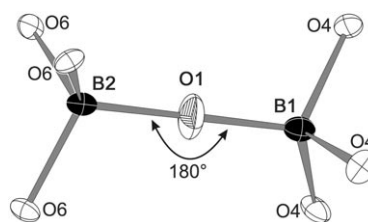

Figure 6. Linear environment of O1 in CdB_2O_4, drawn with 90% thermal probability ellipsoids.

symmetry and a linear B−O−B angle.[46] In a theoretical work, Geisinger et al. investigated the potential energy curves for molecules, containing a B−O−B group.[47] These results showed that a linear arrangement is energetically unfavourable. In other solids, comparable linear arrangements with different atoms could be found in silicates as zunyite $Al_{13}Si_5O_{16}(OH,F)_{15}O_4Cl$,[48] thortveitite $Sc_2Si_2O_7$,[49] or $(Ag-SiO_4)\cdot Ag_{10}Si_4O_{13}$[50] and in the nitridosilicate $Ba_2Nd_7Si_{11}N_{23}$.[51] Liebau examined the influence of thermal vibrations on the Si−O−Si bond-angles[39] with the following observation: the stronger the displacement at the bridging atom, the smaller the deviation from linearity.[39,52] Further analysis of the thermal displacement parameters at the bridging atom showed that the oscillation amplitude, perpendicular to the T−T-vector (T = tetrahedral centre), is considerably larger. Figure 6 gives a view of the linear B−O−B arrangement in CdB_2O_4, drawn with 90% thermal probability ellipsoids. It also shows that the thermal displacement parameter at oxygen O1 has the largest value perpendicular to the B−B-vector, which corresponds to Liebau's observations.

The existence of the basic cell in CdB_2O_4 is confirmed by electron diffraction. The electron diffraction pattern (along zone axis [001]) of CdB_2O_4 (left) in comparison to that of SrP_2N_4 (right) can be seen in Figure 7. The reciprocal unit cells of both phases are shown in solid lines. The dashed line in the right pattern (SrP_2N_4) designates the basic cell. In contrast to the pattern of CdB_2O_4, where no additional reflections can be found, the pattern of SrP_2N_4 clearly exhibits the supercell reflections.
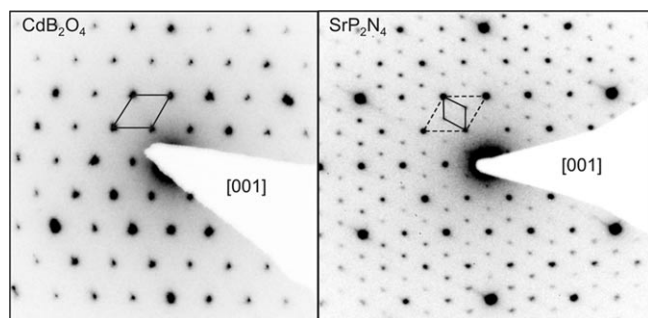
Figure 7. Electron diffraction patterns (zone axis [001]) of CdB_2O_4 (left) and SrP_2N_4 (right).[38] The reciprocal unit cells are drawn in black solid lines. In dashed lines (right picture) the basic unit cell is drawn.

Thermal behaviour: Temperature-programmed X-ray powder diffraction investigations were performed to study the thermal stability and the metastable character of CdB_2O_4. Evidence to show that the compound remains stable up to a temperature of 600°C can bee seen in Figure 8. Between $T = 600$ and 650°C, decomposition occurs into the normal-pressure borates $Cd_2B_2O_5$ and CdB_4O_7, and above 850°C only an amorphous phase can be detected, which remains during and after cooling to room-temperature.

Structure analysis: First, the structure refinement of CdB_2O_4 converged with residuals of $R1 = 6.9\%$, $wR2 = 19\%$. Additionally, a high electron density close to one oxygen atom remained. The consideration of twinning by merohedry and the introduction of a twofold rotation axis according to the twin matrix $(010\ 100\ 00\bar{1})$ led to a twin ratio of 0.55:0.45 with satisfactory residuals ($R1 = 1.8\%$, $wR2 = 3.9\%$) without any significant electron density. The checking of a possible higher symmetry, by using the program PLATON,[53] did not reveal an additional symmetry. Further details of the data collection and refinement are summarised in Table 3, atomic parameters are given in Table 4.

The powder diffraction pattern of CdB_2O_4 was obtained in transmission geometry from a flat sample, using a STOE
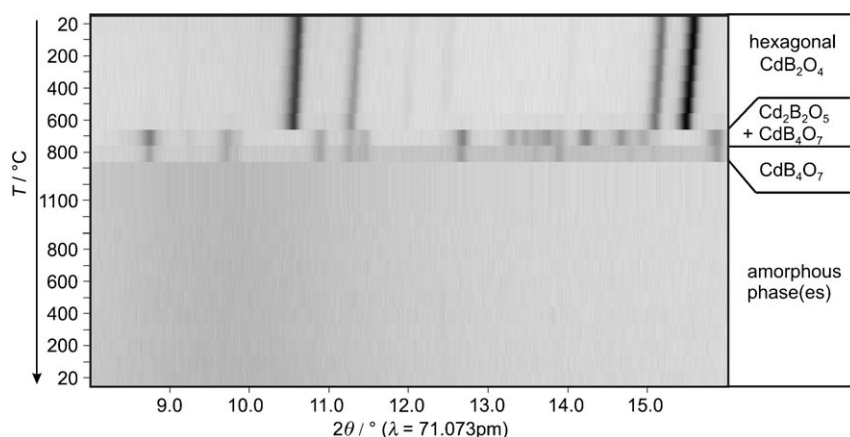
Table 3. Crystal data and structural refinement for CdB_2O_4 (standard deviations in parantheses).

empirical formula	CdB_2O_4
molar mass [gmol^{-1}]	198.02
crystal system	hexagonal
space group	$P6_3$
formula units per cell	8
single crystal diffractometer	CAD4 (Nonius)
radiation	MoK_α
crystal size [mm^3]	$0.23 \times 0.18 \times 0.14$
T [K]	293
Single crystal data	
a [pm]	885.2(2)
c [pm]	716.72(8)
V [nm^3]	0.486(1)
Powder data	
a [pm]	886.64(3)
c [pm]	717.38(3)
V [nm^3]	0.488(1)
F (000)	720
absorption coefficient [mm^{-1}]	8.756
θ range [°]	$2.66 \leq \theta \leq 44.88$
range in hkl	$\pm 17, \pm 17, \pm 14$
scan type	$\omega/2\theta$
total no. reflections	16090
independent reflections	2691 ($R_{int} = 0.0365$)
reflections with $I > 2\sigma(I)$	2598 ($R_\sigma = 0.0167$)
absorption correction	numerical
transm. ratio (max./min.)	0.4572/0.2449
extinction coefficient χ	0.0600(9)
data/parameters	2691/87
largest difference peak/deepest hole [$e\,\text{Å}^{-3}$]	0.985/−2.349
goodness-of-fit (F^2)	1.154
final R indices ($I > 2\sigma(I)$)	$R1 = 0.0163$
	$wR2 = 0.0383$
R indices (all data)	$R1 = 0.0178$
	$wR2 = 0.0388$

STADI P powder diffractometer with monochromatised CuK_α radiation ($\lambda = 154.051$ pm). The diffraction pattern was indexed with the program Ito[54] on the basis of a hexagonal unit cell. Table 3 lists the lattice parameters, which were obtained from the least-square fits of the powder data. The correct indexing of the pattern was confirmed by intensity calculations ,[55] taking the atomic positions from the structure refinement (Table 4). The lattice parameters, determined from the powder and the single crystal data agree well.

Conclusion

The high-pressure synthesis of the cadmium borate CdB_2O_4 is an illustrating example for the introduction of new synthetic possibilities in long known borate systems by applying extreme synthetic conditions. Investigations into the physical properties of CdB_2O_4, based on

Figure 8. Temperature-programmed X-ray powder patterns, showing the decomposition of CdB_2O_4.

Table 4. Atomic coordinates and equivalent isotropic displacement parameters $U_{eq}/\text{Å}^2$ for CdB_2O_4 (space group $P6_3$). U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor (standard deviations in parentheses).

Atom	Wyckoff position	x	y	z	U_{eq}
Cd1	6c	0.48061(3)	0.95729(2)	0.54204(2)	0.00703(2)
Cd2	2a	0	0	0.56427(2)	0.00740(3)
B1	2b	2/3	1/3	0.7548(5)	0.0047(4)
B2	2b	2/3	1/3	0.3653(4)	0.0042(4)
B3	6c	0.3273(2)	0.1522(4)	0.7318(3)	0.0045(4)
B4	6c	0.1514(4)	0.8227(4)	0.8454(3)	0.0042(4)
O1	2b	2/3	1/3	0.5612(3)	0.0098(3)
O2	6c	0.3289(2)	0.0899(2)	0.5378(2)	0.0053(2)
O3	6c	0.18459(18)	0.0034(2)	0.8284(2)	0.0056(2)
O4	6c	0.4927(2)	0.2048(2)	0.8307(2)	0.0051(2)
O5	6c	0.2934(2)	0.2986(2)	0.7198(2)	0.0055(2)
O6	6c	0.3069(2)	0.8106(2)	0.7942(2)	0.0041(2)

the non-centrosymmetric structure, are planned for the future. Especially the increase of the coordination number of boron from three to four in high-pressure borates allows the synthesis of denser borates with structural analogies to for example, aluminates, gallates, silicates and nitridophosphates. In this context, several new borates can be expected for the future.

Experimental Section

Synthesis of CdB_2O_4: The compound CdB_2O_4 was synthesised under high-pressure/high-temperature conditions of 7.5 GPa and 1100 °C. As starting reagents, CdO and B_2O_3 (Strem Chemicals, Newburyport, USA, 99 + %) were ground together in the stoichiometric ratio $CdO:B_2O_3 = 1:1$. The mixture was filled into a boron nitride crucible (Henze BNP GmbH, HeBoSint® S10, Kempten, Germany) of an 18/11-assembly. The compound was compressed and heated by means of a multianvil assembly, based on a Walker-type module and a 1000 t press (Voggenreiter, Mainleus, Germany). Therefore, the boron nitride crucible was positioned inside the centre of an 18/11 assembly, which was compressed by eight tungsten carbide cubes (TSM-10, Ceratizit, Reutte, Austria) with truncated corners. A detailed description of the assembly can be found in refs. [56–60]. For the synthesis of CdB_2O_4, the sample was compressed within 3 h to 7.5 GPa. After reaching constant pressure, the sample was heated to 1100 °C in the following 10 min (cylindrical graphite furnace). After holding this temperature for 5 min, the sample was cooled down to 650 °C in another 15 min. Afterwards, the sample was quenched to room temperature by switching off the heating, followed by decompression over a period of 9 h. The recovered pressure medium (MgO octahedron) was broken apart and the sample carefully separated from the surrounding boron nitride crucible, gaining the air- and water-resistant, colourless, crystalline compound CdB_2O_4. A powder diffraction pattern showed no crystalline impurities, and EDX measurements confirmed the chemical composition of CdB_2O_4.

Single crystal X-ray diffraction: Prior to single crystal measurements, the quality of selected crystals was checked under a polarizing microscope. For the data collection, a colourless fragment ($0.23 \times 0.18 \times 0.14$ mm) was used. Intensity data were measured on a CAD4 diffractometer (Nonius) in the $\omega/2\theta$ technique, scanning the whole reciprocal sphere up to 90°/2θ. A numerical absorption correction, based on an optimisation of the crystal shape, was applied using the program HABITUS.[61] The crystal structure of CdB_2O_4 was solved by direct methods in space group $P6_3$ and refined with the SHELXTL program package.[62,63] Additional information

of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crystdata@fiz-karlsruhe.de), on quoting the depository number CSD-419180.

Temperature programmed X-ray powder diffraction: Temperature programmed X-ray powder diffraction experiments were performed on a STOE STADI P powder diffractometer [MoK$_\alpha$] radiation ($\lambda = 71.073$ pm)] with a computer controlled STOE furnace. The sample was enclosed in a silica capillary and heated from room temperature to 500 °C in 100 °C steps, and from 500 °C to 1100 °C in 50 °C steps. Afterwards, the sample was cooled down to 500 °C in 50 °C steps, and from 500 °C to room temperature in 100 °C steps. After each heating step, a diffraction pattern was recorded over the angular range $8° \leq 2\theta \leq 16°$.

Electron diffraction experiments: Electron diffraction was carried out on a FEI Titan 80–300, equipped with a field emission gun, operating at 300 kV. The sample was ground in an agate mortar and dispersed in ethyl alcohol suspension. A small amount of the suspension was subsequently dispersed on a copper grid, coated with holey carbon film. The grids were mounted on a double tilt holder with a maximum tilt angle of 30° and subsequently transferred into the microscope. The diffraction patterns were recorded on a Gatan UltraScan 1000 P CCD camera.

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