

CdZn₂KB₂O₆F, a new fluoride borate
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During an attempt to grow crystals of the nonlinear optical material Cd₃Zn₃B₄O₁₂ using a KBF₄ flux, crystals of a new cadmium dizinc potassium borate fluoride compound, CdZn₂KB₂O₆F, were unexpectedly isolated. The structure consists of layers constructed of distorted corner-sharing ZnO₃F tetrahedra and BO₃ triangles. Both Zn and B reside on threefold rotation axes, while the F⁻ anion is located at a site of 3.2 symmetry. The Cd^{II} (site symmetry $\bar{3}$) and K⁺ (site symmetry 3.2) ions occupy six- and nine-coordinate interlayer sites, respectively. The BO₃ triangles and ZnO₃F tetrahedra share bridging O atoms with each other to form an extended [ZnBO₃] layer parallel to (001). Although these layers are similar to the [MBO₃] layers seen in other compounds, they are uniquely bridged here by the Cd centres and F⁻ anions to form a three-dimensional framework. In so doing, a series of channels is formed along the [010] direction and the K⁺ cations are found in these channels.

Comment

Recently, numerous studies have been carried out on inorganic nonlinear optical (NLO) borate crystals, which are widely used in optical communications, laser medicine and signal processing (Becker, 1998). Some fluoride borates display good NLO properties, including KBe₂BO₃F₂ (Wu *et al.*, 1996), Ln₃(BO₃)₂F₃ (Ln = Sm, Eu and Gd; Corbel *et al.*, 1998), BaMBO₃F₂ (M = Ga and Al; Park & Barbier, 2000) and ABe₂BO₃F₂ (McMillen & Kolis, 2008). In the present work, KBF₄ was added as a flux in the ternary CdO–ZnO–B₂O₃ system in an attempt to grow the NLO crystal Cd₃Zn₃B₄O₁₂ (Zhang, 2008), of interest in part due to its reported fluorescence behaviour (Harrison & Hummel, 1959). The title new fluoride borate crystal, CdZn₂KB₂O₆F, was unexpectedly obtained and has been structurally characterized.

CdZn₂KB₂O₆F belongs to the trigonal $P\bar{3}1c$ space group and the structure consists of (001) layers formed by corner-

sharing ZnO₃F tetrahedra and BO₃ triangles, linked by Cd^{II} ions occupying six-coordinate interlayer sites with K⁺ ions in interlayer channels (Fig. 1). The Zn^{II} ion is coordinated by three O atoms and an F⁻ ion to form a slightly flattened ZnO₃F tetrahedron (O–Zn–O angles ~117° and O–Zn–F angles ~100°). The BO₃ triangles are planar, with ideal angles, as required by the threefold symmetry, and with B–O bonds comparable with those in other borates (Sun *et al.*, 2003; Haberer & Huppertz, 2009).

The [BO₃] triangles and [ZnO₃] pyramids from the [ZnO₃F] tetrahedra share bridging O atoms to form an extended [ZnBO₃] layer (Fig. 2), which is related to the layers observed in the crystal structures of Sr₂Be₂B₂O₇ (SBBO), KBe₂BO₃F₂ (KBBF) and BaAlBO₃F₂ (BABF) (Becker, 1998). In the title crystal structure, the [ZnBO₃] layers are stacked along the (001) direction, connected by Cd and F atoms. In SBBO, the [BO₃] groups are linked through [BeO₄] tetrahedra to form [Be₂B₂O₇] layers, which are stacked in a coplanar orientation along [001] (Chen *et al.*, 1995). In KBBF and BABF, [BO₃] and [BeO₃F]/[AlO₃F₂] sheets are very similarly stacked along [001]. The layers in these structures are essentially the same as those in CdZn₂KB₂O₆F, with the Zn sites occupied by Be/Al atoms instead. Unlike the structures of SBBO, KBBF and BABF, in the title compound a series of CdO₆ octahedra and bridging F atoms links adjacent ZnBO₃ layers alternately to form a unique three-dimensional framework (Fig. 3).

Six O atoms from adjacent layers coordinate the Cd atoms to form slightly distorted CdO₆ octahedra. The F atoms are two-coordinate and bridge two Zn^{II} ions from different layers. The Zn–F bonds make the Zn^{II} ions deviate slightly from the BO₃ layers by 0.327 (1) Å. The bridging Cd^{II} and F⁻ ions together connect the [ZnBO₃] layers to form a three-dimensional open framework. In this way, channels are formed along the [010] direction and the K⁺ cations occupy these channels. Each K⁺ ion is surrounded by six O atoms and three F⁻ ions (Table 1). The six O atoms form a trigonal antiprismatic

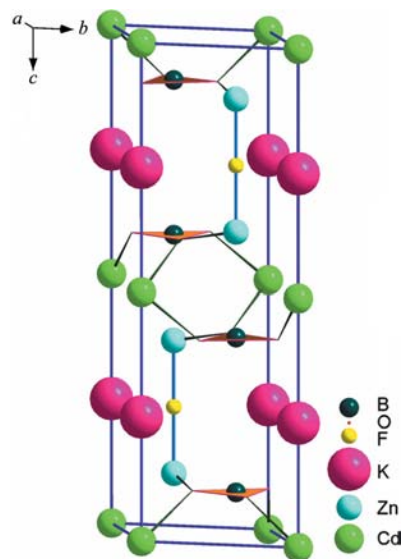


Figure 1
The unit cell of CdZn₂KB₂O₆F.

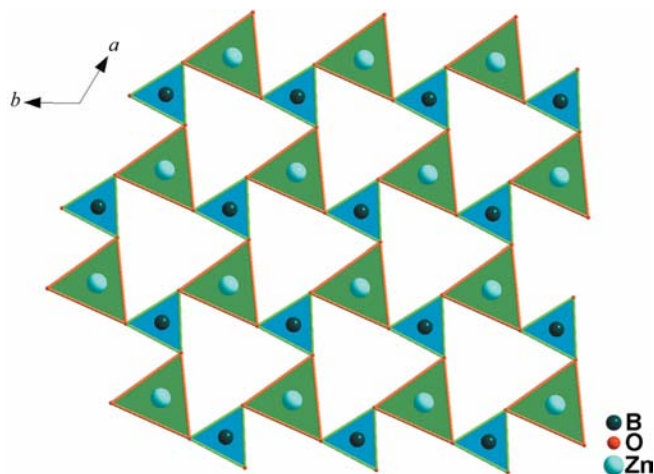


Figure 2
A single $[\text{ZnBO}_3]_n$ layer, viewed along the c axis, showing the BO_3 (smaller) and ZnO_3 (larger) triangles connected to each other *via* shared corners.

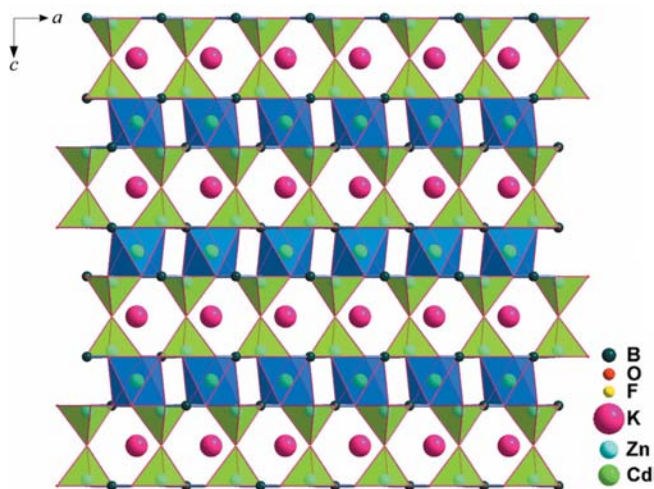


Figure 3
The extended structure of $\text{CdZn}_2\text{KB}_2\text{O}_6\text{F}$, viewed along the b axis, with the CdO_6 octahedra (dark; rectangular in this projection) and K^+ ions (large spheres) filling the channels. The remaining polyhedra (triangular in this projection) are the $[\text{ZnO}_3\text{F}]$ tetrahedra.

arrangement, with the three F atoms capping edges linking the opposite trigonal faces. In this way, the six O atoms and three F atoms form a tetrakaidecahedron around the K^+ ion.

The crystalline powder of $\text{CdZn}_2\text{KB}_2\text{O}_6\text{F}$ exhibits distinct blue photoluminescence, with emission peaks at 471 and 483 nm on excitation at 389 and 400 nm, respectively. The luminescence may be caused by the planar sandwich layers coordinated to the Cd^{II} ions, which affect the charge transfer between the Cd^{II} ions and the layers in a process similar to ligand-to-metal charge transfer (LMCT).

Experimental

The precursor $\text{Cd}_3\text{Zn}_3\text{B}_4\text{O}_{12}$ was synthesized from CdO (99.8%), ZnO (99.95%) and H_3BO_3 (99.99%) according to the published

procedure of Zhang *et al.* (2008). $\text{Cd}_3\text{Zn}_3\text{B}_4\text{O}_{12}$ and KBF_4 (99.0%) (mole ratio 1:4) were mixed and ground to a fine powder in a mortar and compressed into a Pt crucible. The sample was gradually heated to 1073 K and kept at this temperature for 1 d for complete melting. It was then cooled to 973 K at a rate of 1 K h^{-1} , followed by cooling to room temperature at a rate of 20 K h^{-1} . Colourless crystals of the title compound of millimetre dimensions were isolated mechanically from the solidified melt for further study.

Crystal data

$\text{CdZn}_2\text{KB}_2\text{O}_6\text{F}$	$Z = 2$
$M_r = 418.86$	Mo $K\alpha$ radiation
Trigonal, $P\bar{3}1c$	$\mu = 10.93 \text{ mm}^{-1}$
$a = 5.0381(6) \text{ \AA}$	$T = 295 \text{ K}$
$c = 15.1550(19) \text{ \AA}$	$0.14 \times 0.1 \times 0.1 \text{ mm}$
$V = 333.13(7) \text{ \AA}^3$	

Data collection

Bruker $P4$ diffractometer	599 independent reflections
Absorption correction: empirical (using intensity measurements) (North <i>et al.</i> , 1968)	547 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.243$, $T_{\text{max}} = 0.335$	$R_{\text{int}} = 0.053$
2534 measured reflections	3 standard reflections every 97 reflections
	intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	23 parameters
$wR(F^2) = 0.083$	$\Delta\rho_{\text{max}} = 1.55 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\text{min}} = -2.29 \text{ e \AA}^{-3}$
599 reflections	

Table 1

Selected bond lengths (\AA).

$\text{Cd1}-\text{O1}$	2.297 (3)	$\text{K1}-\text{F1}$	2.9087 (3)
$\text{Zn1}-\text{O1}$	1.933 (3)	$\text{K1}-\text{O1}^{\text{i}}$	2.954 (3)
$\text{Zn1}-\text{F1}$	2.0228 (7)	$\text{B1}-\text{O1}$	1.382 (3)

Symmetry code: (i) $-x + y, y + 1, -z + \frac{1}{2}$.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3218). Services for accessing these data are described at the back of the journal.

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