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Syntheses and crystal structures of two new hydrated borates, $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)]\cdot 1.5H_2O$

Xuean Chen[a,*], Yinghua Zhao[a], Xinan Chang[a], Jianlong Zuo[a], Hegui Zang[a], Weiqiang Xiao[b]

[a] College of Materials Science and Engineering, Beijing University of Technology, Ping Le Yuan 100, Beijing 100022, PR China
[b] Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100022, PR China

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Abstract

Two new hydrated borates, $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)]\cdot 1.5H_2O$, have been prepared by hydrothermal reactions at 170 °C. Single-crystal X-ray structural analyses showed that $Zn_8[(BO_3)_3O_2(OH)_3]$ crystallizes in a non-centrosymmetric space group $R32$ with $a = 8.006(2)$ Å, $c = 17.751(2)$ Å, $Z = 3$ and $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ in a triclinic space group $P\bar{1}$ with $a = 6.656(2)$ Å, $b = 6.714(2)$ Å, $c = 10.701(2)$ Å, $\alpha = 99.07(2)°$, $\beta = 93.67(2)°$, $\gamma = 118.87(1)°$, $Z = 2$. $Zn_8[(BO_3)_3O_2(OH)_3]$ represents a new structure type in which Zn-centered tetrahedra are connected via common vertices leading to helical ribbons $^1_\infty[Zn_8O_{15}(OH)_3]^{17-}$ that pack side by side and are further condensed through sharing oxygen atoms to form a three-dimensional $^3_\infty[Zn_8O_{11}(OH)_3]^{9-}$ framework. The boron atoms are incorporated into the channels in the framework to complete the final structure. $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ is a layered compound containing double ring $[B_5O_8(OH)]^{2-}$ building units that share exocyclic oxygen atoms to form a two-dimensional layer. *Symmetry-center*-related layers are stacked along the *c*-axis and held together by interlayer Pb^{2+} ions and water molecules via electrostatic and hydrogen bonding interactions. The IR spectra further confirmed the existence of both triangular BO_3 and OH groups in $Zn_8[(BO_3)_3O_2(OH)_3]$, and BO_3, BO_4, OH groups as well as guest water molecules in $Pb[B_5O_8(OH)]\cdot 1.5H_2O$.

Keywords: Zinc borate; Lead borate; Hydrothermal synthesis; Crystal structure

1. Introduction

Borate materials are of considerable interest because they show a great variety of physical properties ranging from nonlinear optical (NLO), ferroelectric to semiconducting behaviors and in addition, a boron atom may adopt triangular or tetrahedral oxygen coordination, the BO_3 and BO_4 groups may be further linked via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, leading to the rich structural chemistry [1,2]. Zinc-containing hydrated borates have been previously studied because $Zn[B_3O_4(OH)_3]$ is a industrially important material primarily used as a polymer additive and as a preservative in wood composites [3]. In the system of $ZnO–B_2O_3–H_2O$, four compounds have been structurally characterized including $Zn_2(OH)BO_3$ [4], $Zn(H_2O)B_2O_4\cdot xH_2O$ ($x \approx 0.12$) [5], $Zn[B_3O_4(OH)_3]$ [3], and $Zn[B_3O_3(OH)_5]\cdot H_2O$ [6]. They span a range of B_2O_3/ZnO mole ratios from 0.25 to 1.5, with $Zn_2(OH)BO_3$ crystallizing in chiral group $P2_1$, the others in centrosymmetric space groups. Several other hydrated borates like $6ZnO5\cdot B_2O_3\cdot 3H_2O$ and $ZnO\cdot 5B_2O_3\cdot 4.5H_2O$ have only been proposed on the basis of powder XRD results, but their crystal structures remain as yet undetermined [7]. In contrast, lead-containing hydrated borates are relatively more explored, and at least five phases, i.e., $Pb_5B_3O_8(OH)_3\cdot H_2O$ [8], $Pb_6B_{11}O_{18}(OH)_9$ [9], $Pb_3B_9O_{16}(OH)\cdot B(OH)_3$ [10], $Pb_2B_5O_9(OH)\cdot H_2O$ [11] as well as $PbB_8O_{11}(OH)_4$ [12] have been characterized in detail. Among them, the first three compounds [8–10] exhibit NLO properties because the presence of the $6s^2$ lone pair on Pb^{2+} may induce the asymmetry in the structure.

In an attempt to synthesize non-centrosymmetric compounds that are potentially applicable as NLO materials,

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*Corresponding author.
E-mail address: xueanchen@bjut.edu.cn (X. Chen).

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we have successfully isolated $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$. Our X-ray structural analyses established that the former compound is a ZnO-rich hydrated borate ($B_2O_3/ZnO \approx 0.2$) crystallizing in a new structure-type with the non-centrosymmetric space group $R32$ and the latter is a new lead borate containing two-dimensional sheets of 3, 9-membered boron rings. Herein, we report their syntheses and crystal structures.

2. Experimental

2.1. Sample preparation and general characterization

The title compounds were synthesized by a two-step process. First, the polycrystalline samples of $Zn_3B_2O_6$ and $PbBiBO_4$ were prepared in the following way: a powder mixture of 13.500 mmol ZnO and 4.500 mmol B_2O_3 was transferred to a Pt crucible. The sample was gradually heated to 600 °C and annealed there for 2 weeks with an intermediate grinding, followed by cooling to room temperature at a rate of 30 °C/h. The resulting product was found to be a single-phase $Zn_3B_2O_6$ based on powder X-ray diffraction analysis. The $PbBiBO_4$ precursor was prepared in the same way, except that the starting materials contained 9.000 mmol PbO, 4.500 mmol Bi_2O_3 and 4.500 mmol B_2O_3 powder, and the annealed temperature was lower (500 °C 2 weeks). Then, 0.200 g (0.637 mmol) of $Zn_3B_2O_6$, 0.2 ml CH_3COOH, 0.2 ml $NH_2CH_2CH_2NH_2$, and 1 ml H_2O were weighed and sealed in a 15-ml Teflon-lined stainless steel vessel. This was heated in an oven at 170 °C for 1 week under autogenous pressure, then cooled slowly to room temperature. The product consisted of colorless, plate-like crystals of $Zn_8[(BO_3)_3O_2(OH)_3]$ with the largest dimension of $0.8 \times 0.6 \times 0.3\,mm^3$ in colorless mother liquor. The final pH of the reaction system was about 6.0. The crystals in about 20% yield (based on Zn) were isolated by washing the reaction product with deionized water and anhydrous ethanol followed by drying with anhydrous acetone.

$Pb[B_5O_8(OH)] \cdot 1.5H_2O$ was synthesized from a hydrothermal reaction of 0.200 g (0.525 mmol) $Na_2B_4O_7 \cdot 10H_2O$, 0.100 g (0.204 mmol) $PbBiBO_4$ in 0.2 ml HNO_3, 0.2 ml $NH_2CH_2CH_2NH_2$, and 1 ml H_2O. The same heating and isolation procedures as previously described for $Zn_8[(BO_3)_3O_2(OH)_3]$ were used and colorless, block-like crystals were obtained in about 30% yield (based on Pb). Both $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$ appear to be relatively stable in air and water.

Powder X-ray diffraction measurements were performed using the monochromatized Cu$K\alpha$ radiation of a Bruker D8 ADVANCE diffractometer. Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer 1730 FT-IR spectrometer from KBr pellets.

2.2. Structure determination

X-ray data collections of both compounds were carried out at room temperature (298 K) on an automated Rigaku AFC7R four-circle diffractometer using monochromatized Mo$K\alpha$ radiation. Cell dimensions were obtained from a least-square refinement with 25 automatically centered reflections in the range $40.72° \leqslant 2\theta \leqslant 44.89°$ for $Zn_8[(BO_3)_3O_2(OH)_3]$ and $40.52° \leqslant 2\theta \leqslant 44.88°$ for $Pb[B_5O_8(OH)] \cdot 1.5H_2O$. Three standard reflections were re-measured after every 150 reflections. No decay was observed except the statistic fluctuation in a range of $\pm 1.46\%$ for $Zn_8[(BO_3)_3O_2(OH)_3]$ and $\pm 1.24\%$ for $Pb[B_5O_8(OH)] \cdot 1.5H_2O$. The raw intensity data were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data.

The crystal structures were solved by direct methods and refined in SHELX-97 system [13] by full-matrix least-squares methods on $F_o^2 \cdot$ For $Zn_8[(BO_3)_3O_2(OH)_3]$, all non-hydrogen atoms were refined anisotropically. The H atoms were placed geometrically and allowed to ride on the atoms to which they are attached with fixed isotropic displacement parameters. The refinement of 41 parameters with 944 observed reflections $[I \geqslant 2\sigma(I)]$ resulted in the residuals of $R_1/wR_2 = 0.0378/0.1112$. For $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, the H atoms were not located because of the presence of the heavy Pb atom. After introduction of anisotropic displacement parameters for all non-hydrogen atoms, the reliability factors converged to $R_1/wR_2 = 0.0310/0.0813$ for 3384 observed reflections and 155 variables. The final difference electron density maps were featureless, with the highest electron density of 1.29 e $Å^{-3}$ for $Zn_8[(BO_3)_3O_2(OH)_3]$ and 3.28 e $Å^{-3}$ for $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, both very close to the heavy atomic sites. Details of crystal parameters, data collection and structure refinements are given in Table 1 and the atomic coordinates and the equivalent isotropic displacement parameters are summarized in Table 2. Listings of the anisotropic displacement parameters and the structure factors are available from the authors.

Table 1
Crystallographic data for $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$

Formula	$Zn_8[(BO_3)_3O_2(OH)_3]$	$Pb[B_5O_8(OH)] \cdot 1.5H_2O$
Formula weight	782.41	431.26
Space group	$R32$ (No. 155)	$P\bar{1}$ (No. 2)
a (Å)	8.006(2)	6.656(2)
b (Å)	8.006(2)	6.714(2)
c (Å)	17.751(2)	10.701(2)
α (deg)	90	99.07(2)
β (deg)	90	93.67(2)
γ (deg)	120	118.87(1)
V ($Å^3$), Z	985.3(4), 3	408.08(19), 2
d_{calc} (g/cm^3)	3.956	3.510
λMo$K\alpha$ (Å)	0.71073	0.71073
μ (mm^{-1})	14.418	20.719
$2\theta_{max}$ (deg)	69.94	69.92
Unique reflection	976	3582
Observed $[I \leqslant 2\sigma(I)]$	944	3384
No. of variables	41	155
GOF on F_o^2	1.119	1.069
R_1/wR_2 $[I \geqslant 2\sigma(I)]$	0.0378/0.1112	0.0310/0.0813
R_1/wR_2 (all data)	0.0389/0.1116	0.0340/0.0826

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$

Atoms	*X*	*Y*	*Z*	U_{eq}	BVS
$Zn_8[(BO_3)_3O_2(OH)_3]$					
Zn1	1/3	2/3	0.25968(5)	0.00809(17)	2.004
Zn2	0.42859(8)	0.12159(7)	0.07865(3)	0.00958(14)	1.999
B	1/3	0.3662(8)	1/6	0.0077(9)	2.963
O1	1/3	0.1945(6)	1/6	0.0130(8)	2.012
O2	0.2390(5)	0.4036(5)	0.22319(19)	0.0115(5)	1.961
O3	0.2330(7)	0	0	0.0161(9)	1.012
O4	1/3	2/3	0.3702(3)	0.0090(8)	2.015
H3	0.117(3)	0	0	0.024	
$Pb[B_5O_8(OH)] \cdot 1.5H_2O$					
Pb	0.36602(2)	0.69233(2)	0.117845(13)	0.01021(5)	1.909
B1	0.1805(9)	0.3381(8)	0.6014(5)	0.0115(7)	3.026
B2	0.9461(7)	0.2099(7)	0.1670(4)	0.0081(6)	3.013
B3	0.2545(7)	0.1160(7)	0.1487(4)	0.0064(6)	3.035
B4	0.8824(7)	0.8242(7)	0.2014(4)	0.0070(6)	3.025
B5	0.3112(7)	0.6013(7)	0.8087(4)	0.0075(6)	3.038
O1	0.9304(6)	0.8470(6)	0.3412(3)	0.0131(5)	1.754
O2	0.4749(5)	0.1750(5)	0.1309(3)	0.0091(5)	1.961
O3	0.3026(5)	0.4081(5)	0.8606(3)	0.0074(4)	1.937
O4	0.7996(5)	0.9884(5)	0.1789(3)	0.0096(5)	2.046
O5	0.1089(5)	0.6248(5)	0.8439(3)	0.0107(5)	1.961
O6	0.1800(5)	0.2772(5)	0.1611(3)	0.0102(5)	2.157
O7	0.3041(7)	0.5601(6)	0.6714(3)	0.0153(6)	1.857
O8	0.1019(5)	0.8906(5)	0.1502(3)	0.0112(5)	1.998
O9	0.1723(8)	0.3024(7)	0.4708(4)	0.0238(8)	.992
O10	0.3695(8)	0.7469(8)	0.3542(4)	0.0156(9)	.356
O11	0.5127(9)	0.9870(9)	0.4300(5)	0.0129(11)	.030

Note: U_{eq} is defined as one-third of the trace of the orthogonalized **U** tensor. For $Zn_8[(BO_3)_3O_2(OH)_3]$, O3 is an OH group. The H atom was located from the difference electron density map. The positional parameters of the H atom were refined by fixing the H–O distance at 0.93 Å. The U_{eq} (H) was fixed to a value that is 1.5 times U_{eq} (O3). For $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, O9 is an OH group, O10 and O11 are disordered water molecules with occupancies of 0.836(13) and 0.664(13), respectively.

3. Results and discussion

Hydrothermal synthesis is a relatively complex process. Many factors such as initial reactants, concentration, pH, and temperature may affect the product compositions. In the syntheses of the title compounds, when H_3BO_3 or B_2O_3 was used as boron source, colorless plate-like H_3BO_3 crystals prefer to crystallize from solution first. The use of precursors $Zn_3B_2O_6$ and $PbBiBO_4$ as starting reagents can avoid the formation of H_3BO_3 crystals. Ethylenediamine (en) is used to adjust the pH value of the reaction system. In the absence of en molecules, no crystals of the title compounds appear in the reaction products. Although Bi did not incorporate into the final structure of $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, $PbBiBO_4$ was found to play an important role in the formation of this phase. In a similar hydrothermal synthesis using $Pb(NO_3)_2$ instead of $PbBiBO_4$, colorless hexagonal prismatic crystals of the known phase, $Pb_5B_3O_8(OH)_3 \cdot H_2O$ [8] was obtained, which has a hexagonal cell with $a = 9.092(3)$ Å, $c = 24.717(6)$ Å, and $V = 1769.8(9)$ Å^3.

$Zn_8[(BO_3)_3O_2(OH)_3]$ contains a four ring $[Zn_8O_{18}(OH)_3]^{23-}$ as the basic building unit, which has crystallographically imposed C_2 symmetry and is composed of two Zn1-centered and six Zn2-centered tetrahedra, as depicted in Fig. 1. Three of such units are stacked rhombohedrally along the *c*-axis to build the unit cell and linked together via common O1 atoms leading to a ribbon ${}^1_\infty[Zn_8O_{15}(OH)_3]^{17-}$, which is arranged around a 3_1 screw axis, as illustrated in Fig. 2. These ${}^1_\infty[Zn_8O_{15}(OH)_3]^{17-}$ ribbons pack side by side in a hexagonal motif and are further condensed through sharing O2 and O4 atoms to form a three-dimensional (3D) ${}^3_\infty[Zn_8O_{11}(OH)_3]^{9-}$ framework (Fig. 3). The 3D framework affords 1D open channels running along the [001] direction. The boron atoms are located inside the channels around the 3_1 screw axes and interact with the framework via B–O bonds to complete the final structure resulting in the formula $Zn_8[(BO_3)_3O_2(OH)_3]$. Each BO_3 triangle shares its three vertices with six neighboring ZnO_4 tetrahedra, while BO_3 triangles are separated from each other. To the best of our knowledge, a similar 3D framework has not been encountered in the structures of zinc-containing borates.

In this structure, zinc atoms occupy two different crystallographic sites. They are all coordinated with four oxygen atoms forming tetrahedral geometries (Fig. 1). There is a crystallographic three-fold rotational axis passing through Zn1 atoms, thus resulting in two sets of bond lengths (Zn1–O2 = 3 × 1.959(3), and Zn1–O4 = 1 × 1.962(5) Å, Table 3). Two pairs of O–Zn1–O angles deviate slightly from those (109.5°) in a perfect tetrahedron with 109.63(10)° and 109.31(10)°, respectively. In contrast, Zn2 atoms occupy general sites and the Zn2-centered tetrahedra are more distorted, with Zn2–O distances varying from 1.951(2) to 1.980(3) Å and O–Zn2–O angles

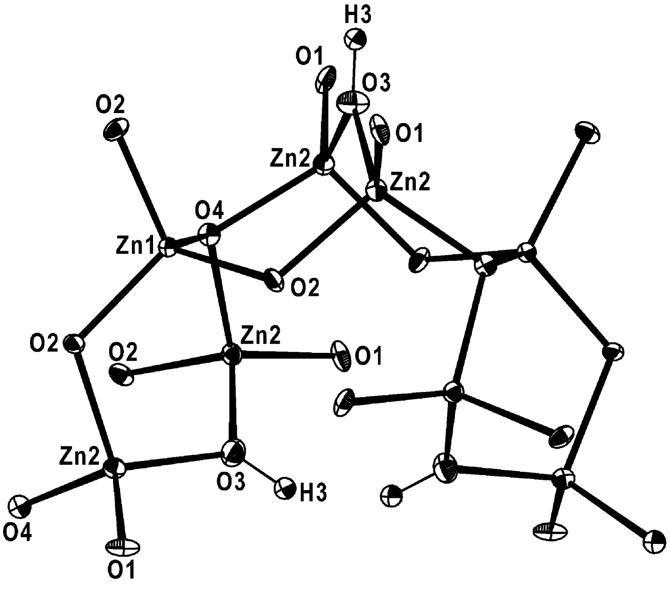

Fig. 1. An ORTEP representation of the $[Zn_8O_{18}(OH)_3]^{23-}$ structural building block to show the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

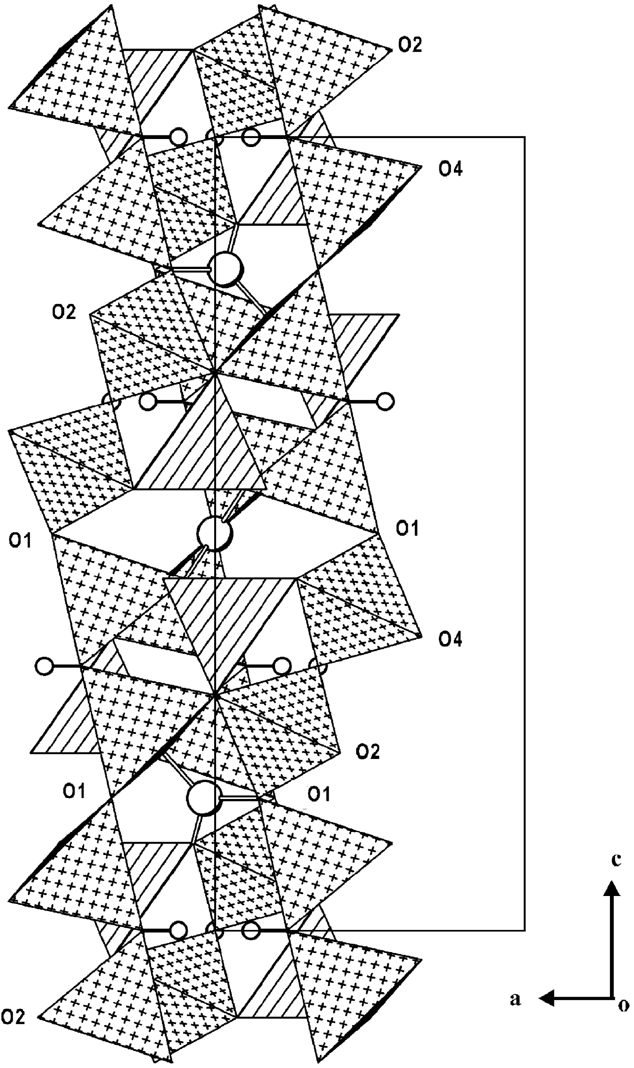

Fig. 2. The $^{1}_{\infty}[Zn_8O_{15}(OH)_3]^{17-}$ helical ribbon viewed along the *b*-axis. H: small spheres; B: large spheres; $Zn(1)O_4$: tetrahedra with parallel lines; $Zn(2)O_4$: tetrahedra with crosses.

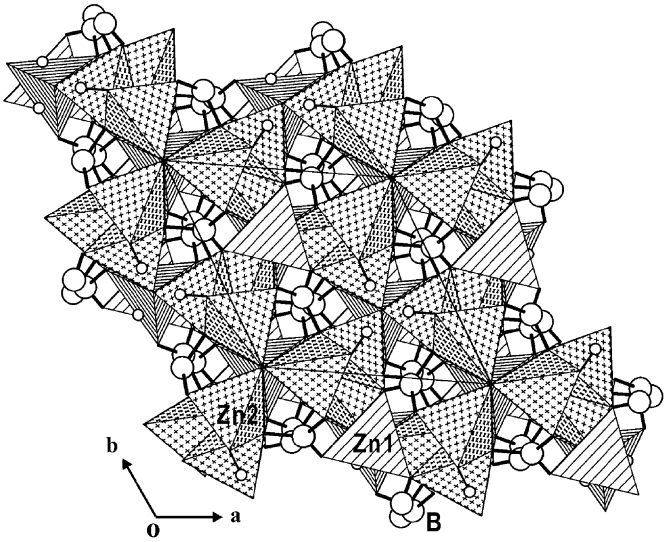

Fig. 3. The crystal structure of $Zn_8[(BO_3)_3O_2(OH)_3]$ projected along the [001] direction. H: small empty circles; B: large filled circles; $Zn(1)O_4$: tetrahedra with parallel lines; $Zn(2)O_4$: tetrahedra with crosses.

covering a wide range between 103.93(11) and 113.68(14)°. Depending on the considered sites, the mean values of Zn–O distances are 1.960 Å for Zn1 and 1.961 Å for Zn2, which are closely comparable to those found in $BaZn_2(BO_3)_2$ (1.945–1.952 Å), $Ba_2Zn(BO_3)_2$ (1.975–1.980 Å), and $Zn(H_2O)B_2O_4 \cdot xH_2O$ ($x \approx 0.12$) (1.978 Å), all featuring tetrahedrally coordinated Zn^{2+} [5,14,15]. Bond valence analyses [16] produced reasonable values of 2.004 for Zn1 and 1.999 for Zn2, respectively.

There is one crystallographically independent B atom in the asymmetric unit, which lies on a two-fold axis, giving two sets of B–O bond distances (B–O1 = 1.375(8) and B–O2 = 2 × 1.376(4) Å) and O–B–O angles (O1–B–O2 = 2 × 119.5(3)° and O2–B–O2 = 1 × 121.1(5)°). The sum of O–B–O angles is equal to 360.1°, indicating that the triangular coordination around the B atom deviates slightly from the ideal planar geometry. The average B–O distance is 1.376 Å, very close to those reported in other compounds having BO_3 groups, e.g. $Li_3In(BO_3)_2$ (1.371–1.372 Å) [17], $SrBe_2(BO_3)_2$ (1.372–1.374 Å) [18], and $PbZn_2(BO_3)_2$ (1.376 Å) [19]. A bond valence sum of 2.963 can be computed for B, in good agreement with its expected formal valence.

Of the four unique oxygen atoms, two (O1 and O2) are three-coordinate, binding to two Zn and one B centers in an approximately triangular manner, as indicated by interatomic angles (115.35(17)–122.0(3)°) near 120°; one (O4) is surrounded by four Zn centers to constitute a $(OZn_4)^{6+}$ tetrahedron [six tetrahedral angles are: Zn2–O4–Zn2 = 3 × 106.51(14)°, Zn2–O4–Zn1 = 3 × 112.29(13)°]; the remaining one (O3) is connected to two Zn centers with the Zn2–O3–Zn2 angle of 113.0(3)°. As far as the charge balance is concerned, there are three hydrogen atoms per formula $Zn_8[(BO_3)_3O_2(OH)_3]$. Bond valence sum (BVS) calculations produced a BVS value of 1.012 for O3, which is significantly lower than those for the rest of O atoms (from 1.961 for O2 to 2.015 for O4 (see Table 2)). This suggests that the hydrogen atoms are most likely attached to O3 atoms. Our difference Fourier analysis indeed revealed the residual electron density at ~1 Å from the O3 position and the presence of OH groups is further confirmed by the IR spectrum in Fig. 7, where the stretch ing vibration of hydroxyl groups at about 3570 cm^{-1} is clearly observed.

As mentioned above, in the system of $ZnO–B_2O_3–H_2O$, four hydrated borates, $Zn_2(OH)BO_3$, $Zn(H_2O)B_2O_4 \cdot xH_2O$ ($x \approx 0.12$), $Zn[B_3O_4(OH)_3]$, and $Zn[B_3O_3(OH)_5] \cdot H_2O$ have been structurally characterized [3–6]. However, their crystal structures are quite different from that of $Zn_8[(BO_3)_3O_2(OH)_3]$ presented here. In $Zn_2(OH)BO_3$, ZnO_4 tetrahedra share corners to form helical chains running along the crystallographic 2_1 screw axes. There are

Table 3
Selected bond lengths (Å) and angles (°) for $Zn_8[(BO_3)_3O_2(OH)_3]$ and $Pb[B_5O_8(OH)]\cdot 1.5H_2O$

$Zn_8[(BO_3)_3O_2(OH)_3]$			
Zn1–O2 × 3	1.959(3)	Zn2–O4	1.956(2)
Zn1–O4/	1.962(5)	Zn2–O2	1.980(3)
Zn2–O1	1.951(2)	B–O1	1.375(8)
Zn2–O3	1.956(3)	B–O2 × 2	1.376(4)
O2–Zn1–O2 × 3	109.63(10)	O1–Zn2–O2	108.54(15)
O2–Zn1–O4 × 3	109.31(10)	O3–Zn2–O2	106.86(13)
O1–Zn2–O3	112.64(13)	O4–Zn2–O2	103.93(11)
O1–Zn2–O4	113.68(14)	O1–B–O2 × 2	119.5(3)
O3–Zn2–O4	110.58(14)	O2–B–O2	121.1(5)
$Pb[B_5O_8(OH)]\cdot 1.5H_2O$			
Pb–O10	2.494(4)	B2–O5	1.344(5)
Pb–O4	2.552(3)	B2–O4	1.362(5)
Pb–O6	2.581(3)	B2–O6	1.405(5)
Pb–O3	2.606(3)	B3–O2	1.357(5)
Pb–O8	2.679(3)	B3–O8	1.359(5)
Pb–O2	2.937(3)	B3–O6	1.385(5)
Pb–O5	2.938(3)	B4–O3	1.450(5)
Pb–O3	2.969(3)	B4–O1	1.477(6)
Pb–O2	3.033(3)	B4–O8	1.478(5)
Pb–O5	3.149(3)	B4–O4	1.494(5)
Pb–O11	3.415(5)	B5–O7	1.444(6)
B1–O7	1.358(6)	B5–O3	1.468(5)
B1–O1	1.370(6)	B5–O2	1.487(5)
B1–O9	1.374(6)	B5–O5	1.494(5)
O7–B1–O1	121.4(4)	O1–B4–O8	108.2(3)
O7–B1–O9	118.2(4)	O3–B4–O4	106.8(3)
O1–B1–O9	120.4(4)	O1–B4–O4	108.3(3)
O5–B2–O4	127.1(4)	O8–B4–O4	109.2(3)
O5–B2–O6	114.6(4)	O7–B5–O3	111.4(3)
O4–B2–O6	118.3(3)	O7–B5–O2	108.9(3)
O2–B3–O8	118.8(3)	O3–B5–O2	111.1(3)
O2–B3–O6	121.8(3)	O7–B5–O5	111.2(3)
O8–B3–O6	119.4(3)	O3–B5–O5	107.1(3)
O3–B4–O1	111.3(3)	O2–B5–O5	107.1(3)
O3–B4–O8	112.9(3)		

two independent types of –Zn–O–Zn– chains: one in the center and another in the corners of the unit cell when viewed the structure along the *b*-axis. These chains are crossed-linked by the common O atoms to form a 3D Zn–O framework, with the boron atoms incorporated into the triangular hollows of oxygen atoms within this framework to strengthen the structure [4]. In $Zn(H_2O)B_2O_4\cdot xH_2O$ ($x\approx 0.12$), six BO_4 tetrahedra and six BO_3 triangles are linked together through sharing corners to create a six-membered cyclic borate polyanion of the formula $[B_{12}O_{24}]^{12-}$. The addition of Zn^{2+} ions to the polyborate anion, $[B_{12}O_{24}]^{12-}$, gives rise to the zincoborate cluster $Zn_6B_{12}O_{24}$. The zincoborate clusters, thus formed, are interconnected through Zn–O–B bonds resulting in a 3D network, with eight-membered 1D channels in the network hosting water molecules [5]. In $Zn[B_3O_4(OH)_3]$, one triangular BO_3 and two tetrahedral $[BO_3(OH)$ and $BO_2(OH)_2]$ groups share oxygen vertexes to form a three-membered cyclic polyanion $[B_3O_5(OH)_3]^{4-}$. These triborate moieties link into infinite chains ${}^{1}_{\infty}[B_3O_4(OH)_3]^{2-}$ by sharing an exocyclic oxygen between BO_3 and $BO_3(OH)$ polyhedra. The polytriborate chains are cross-linked by coordination with zinc and further integrated by hydrogen bonding [3]. $Zn[B_3O_3(OH)_5]\cdot H_2O$ contains similar three-membered cyclic polyanions of the composition $[B_3O_3(OH)_5]^{2-}$ which are bridged by Zn^{2+} ions to generate 1D zigzag chains [6]. A common feature of the three B-rich zincoborates, $Zn(H_2O)B_2O_4\cdot xH_2O$ ($x\approx 0.12$), $Zn[B_3O_4(OH)_3]$, and $Zn[B_3O_3(OH)_5]\cdot H_2O$, is the presence of boron in both triangular and tetrahedral coordinations, different from the situation observed in the two ZnO-rich phases ($Zn_2(OH)BO_3$ and the newly prepared $Zn_8[(BO_3)_3O_2(OH)_3]$), where the boron atoms are all triangularly coordinated by oxygen. To the best of our knowledge, $Zn_8[(BO_3)_3O_2(OH)_3]$ represents a new structure type and the ZnO-richest hydrated borate isolated so far in the $ZnO–B_2O_3–H_2O$ system.

The basic building unit in $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ is a double ring $[B_5O_8(OH)]^{2-}$ composed of two BO_4 tetrahedra (□) and three borate triangles (Δ) (Fig. 4), which can be written as $3\Delta 2\square{:}<2\Delta\square>-<2\square>$ according to the definition given by Burns et al. [2,20]. This unit is very common as found in $Na_2[B_5O_8(OH)]\cdot 2H_2O$, $Ce[B_5O_8(OH)]\cdot NO_3\cdot 3H_2O$, $Ba[B_5O_8](OH)]\cdot H_2O$, and $[H_3N(C_6H_{10})NH_3]B_5O_8(OH)]$ [21–24]. Each $[B_5O_8(OH)]^{2-}$ unit is connected to four others through exocyclic oxygen atoms to form a 2D infinite layer ${}^{2}_{\infty}[B_5O_8(OH)]^{2-}$ extending in the (001) plane. The borate layer is characterized by 3, 9-membered boron rings, as shown in Fig. 5. Applying the *inversion* operations at the cell origin and center to the layer at $z=1/4$ produces adjacent equivalent layers along the [001] direction. Pb^{2+} ions and water molecules are located between these layers and arranged alternately along the *c*-axis to balance charge and also to hold the layers together through electrostatic and hydrogen bonding interactions (Fig. 6).

Each Pb^{2+} is coordinated to 11 O atoms, six of which are from one ${}^{2}_{\infty}[B_5O_8(OH)]^{2-}$ layer, three from the

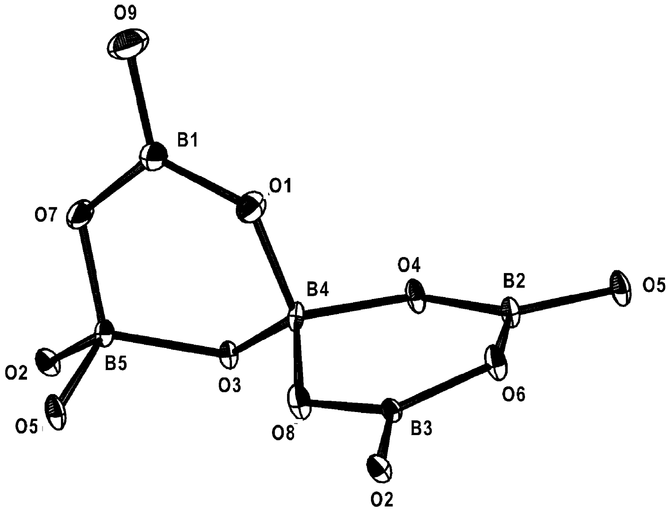

Fig. 4. The $[B_5O_8(OH)]^{2-}$ building unit found in $Pb[B_5O_8(OH)]\cdot 1.5H_2O$, where the OH group is located in the O9 site.

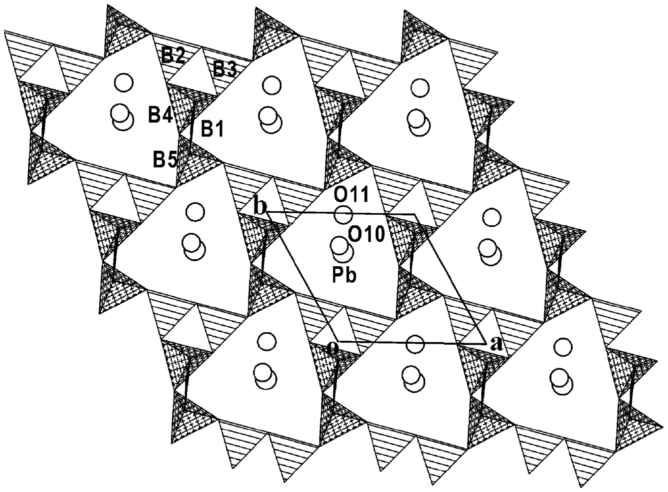

Fig. 5. The $^{2}_{\infty}[B_5O_8(OH)]^{2-}$ layer parallel to the (001) plane. The filled and empty circles represent Pb atoms and O atoms of water molecules (O_w), respectively.

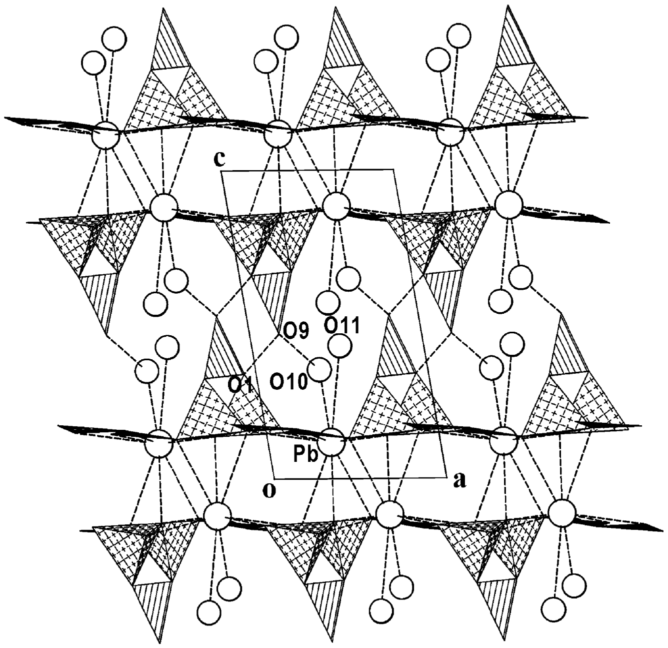

Fig. 6. View of the $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ structure along the *b*-axis, where the O···O contacts <3.20 Å and Pb–O distances of 2.494(4)–3.415(5) Å are drawn with dashed lines. O_w: empty circles; Pb: filled circles; BO_3: triangles filled by parallel lines; BO_4: tetrahedra filled by crosses.

neighboring layer, and the other two from water molecules. The Pb–O distances are divided into two sets: a set of five shorter distances range from 2.494(4) to 2.679(3) Å, and others are between 2.937(3) and 3.415(5) Å (Table 3). Taking all these 11 bonds into account, the concept of bond valence [16] allows us to calculate a valence sum equal to 1.909 for Pb which proves that the long bonds indeed participate in the metal coordination scheme. The PbO_{11} polyhedron is irregular with all the short Pb–O distances falling within the same hemisphere around lead, an environment typical of a lone-pair cation. A similar highly distorted lead coordination geometry has also been observed in $Pb_2(B_5O_9)(OH)\cdot H_2O$ with 11 Pb–O distances of 2.425(8)–3.507(11) Å [11].

There are five symmetrically independent B atoms, of which B1, B2, and B3 are in triangular coordination and B4, B5 in tetrahedral coordination. The B–O bonds in the triangles range from 1.344(5) to 1.405(5) Å, and the O–B–O angles from 114.6(4) to 127.1(4)°; in the tetrahedra the respective ranges are 1.444(6)–1.494(5) Å and 106.8(3)–112.9(3)° (Table 3). These geometric parameters are comparable to those observed in the five known lead-containing borates [8–12]. As far as the charge balance is concerned, there exists one H atom of the hydroxyl group per formula $Pb[B_5O_8(OH)]\cdot 1.5H_2O$. Bond valence sum calculations (Table 2) clearly showed that this hydrogen atom is likely to be located near the O9 site. Similarly, O10 and O11 were identified to be the O atoms of guest water molecules, judged from their very low BVS values. The presence of short O···O contacts such as O9–H1···O1 = 2.736(5) Å and O10–H2···O9 = 3.129(6) Å indicates the hydrogen bonding interactions, although the hydrogen positions cannot be precisely determined due to the presence of heavy element of Pb. The hydrogen bonds involve not only the H-atoms of hydroxyl groups and ring O-atoms of neighboring sheets, but also the H-atoms of water molecules and O-atoms of hydroxyl groups, as depicted in Fig. 6.

The crystal structure of $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ is closely related to those of biringuccite $Na_2[B_5O_8(OH)]\cdot H_2O$ and $Ba[B_5O_8(OH)]\cdot H_2O$ [21,23]. All of these three compounds contain topologically identical $^{2}_{\infty}[B_5O_8(OH)]^{2-}$ layers. However, $Na_2[B_5O_8(OH)]\cdot H_2O$ crystallizes in a monoclinic structure with the space group $P2_1/c$, where each $^{2}_{\infty}[B_5O_8(OH)]^{2-}$ sheet has two adjacent equivalent sheets related by 2_1 axes and by symmetry centers, respectively, whereas the neighboring sheets in $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ are all related by symmetry centers only. $Ba[B_5O_8(OH)]\cdot H_2O$ is almost isostructural with the newly prepared $Pb[B_5O_8(OH)]\cdot 1.5H_2O$, except for water molecules which occupy orderly one crystallographic site, different from the case of $Pb[B_5O_8(OH)]\cdot 1.5H_2O$ where 1.5 water molecules are found to be disordered over two distinct sites. This may result from the larger interlayer space when Ba^{2+} is replaced by Pb^{2+}. Several recently characterized borates such as $Ce[B_5O_8(OH)]\cdot NO_3\cdot 3H_2O$ and $[H_3N(C_6H_{10})NH_3]B_5O_8(OH)]$ also contain the double ring $[B_5O_8(OH)]^{2-}$ building units [22,24]. However, the neighboring units are linked and arranged in such a way that the $BO_2(OH)$ triangles bridging two BO_4 tetrahedra appear on both sides of each $^{2}_{\infty}[B_5O_8(OH)]^{2-}$ sheet, instead of on one side of each sheet in $Pb[B_5O_8(OH)]\cdot 1.5H_2O$.

In a variety of borate crystals [25,26], four fundamental vibrations attributed to BO_3 groups are observed in the following ranges: ν_s~850–960, γ~650–800, ν_{as}~1100–1450, and δ~500–600 cm^{-1}. Infrared spectrum of

$Zn_8[(BO_3)_3O_2(OH)_3]$ was shown in Fig. 7, where the bands with the frequency of 861 cm^{-1} were assigned as the BO_3 symmetric stretching vibrations (ν_s); the bands at 653 and 730 cm^{-1} are caused by the out-of-plane bending vibrations (γ); the band near 1249 cm^{-1} arises from the antisymmetric stretch (ν_{as}); and those at about 513 cm^{-1} due to the in-plane modes (δ). The BO_3 group in $Zn_8[(BO_3)_3O_2(OH)_3]$ is distorted from the ideal D_{3h} symmetry. This removes the degeneracy of the infrared active vibrations resulting in the band split and also allows the non-active vibration ν_s to absorb energy in the infrared region. Moreover, the O–H stretching vibration was observed at 3570 cm^{-1}. The IR spectrum confirmed the existence of both triangular BO_3 and OH groups, consistent with the results obtained from the single-crystal X-ray structural analysis. Fig. 7 also shows IR spectrum of $Pb[B_5O_8(OH)] \cdot 1.5H_2O$. Again, the strong bands at about 1363 cm^{-1} are consistent with the existence of trigonally coordinated boron, the bands near 918 cm^{-1} are characteristic of tetrahedral boron. The presence of the lattice water and OH groups in this structure are confirmed by the O–H stretching near 3270, 3329 cm^{-1} and the H–O–H bending at about 1585 cm^{-1}.

Of the two compounds presented in this work, $Zn_8[(BO_3)_3O_2(OH)_3]$ crystallizes in a chiral space group *R*32 with the crystal class of 32, and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$ contains polar sheets ${}^2_\infty[B_5O_8(OH)]^{2-}$. However, these sheets are arranged in an antiparallel manner resulting in a structure without polarity. To confirm these, SHG measurements were performed on crushed crystals of both compounds using a modified Kurtz–NLO system with a 1064 nm light source [27]. The second-harmonic signal at 532 nm was clearly observed for $Zn_8[(BO_3)_3O_2(OH)_3]$, supporting the assignment of this structure in a noncentrosymmetric setting. No green light of 532 nm was observed for $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, confirming the centrosymmetric structure.

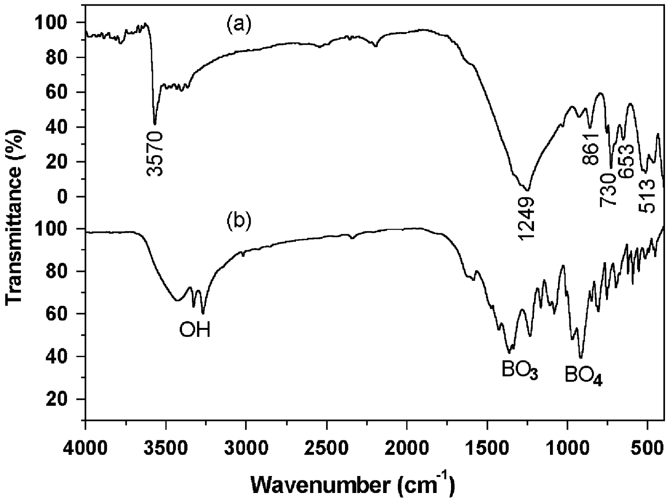

Fig. 7. Infrared spectra of $Zn_8[(BO_3)_3O_2(OH)_3]$ (a) and $Pb[B_5O_8(OH)] \cdot 1.5H_2O$ (b).

4. Conclusions

Two hydrated borates have been synthesized from hydrothermal reactions in the presence of amines and their crystal structures have been investigated. $Zn_8[(BO_3)_3O_2(OH)_3]$ is the ZnO-richest hydrated borate isolated so far. It consists of an original 3D polar network formed by Zn-centered tetrahedra and BO_3 triangles. $Pb[B_5O_8(OH)] \cdot 1.5H_2O$ is a new phase found in the $PbO–B_2O_3–H_2O$ system and it contains very popular ${}^2_\infty[B_5O_8(OH)]^{2-}$ layers. The successful syntheses of the title compounds indicate that the hydrothermal synthetic route is still promising for the preparation of more metal borates with unusual structures and properties.

Auxiliary material: Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein- Leopoldshafen, Germany (Fax: (+49)7247 808 666; Email: crysdata@fiz-karlsruhe.de) on quoting depository numbers CSD416894 for $Zn_8[(BO_3)_3O_2(OH)_3]$ and CSD416895 for $Pb[B_5O_8(OH)] \cdot 1.5H_2O$, respectively.

Acknowledgments

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References

[1] P. Becker, Adv. Mater. 10 (1998) 979.
[2] J.D. Grice, P.C. Burns, F.C. Hawthorne, Can. Mineral. 37 (1999) 731.
[3] D.M. Schubert, F. Alam, M.Z. Visi, C.B. Knobler, Chem. Mater. 15 (2003) 866.
[4] Z.-T. Yu, J.-J. Xu, Y.-S. Jiang, Z. Shi, Y. Guo, D.-J. Wang, J.-S. Chen, J. Mater. Chem. 13 (2003) 2227.
[5] A. Choudhury, S. Neeraj, S. Natarajan, C.N.R. Rao, J. Chem. Soc. Dalton Trans. 7 (2002) 1535.
[6] J. Ozols, I.V. Tetere, A. Ievins, Izv. Akad. Latv. Nauk. SSR. Ser. Kim. 1 (1973) 3.
[7] H.-A. Lehmann, K. Sperschneider, G. Kessler, Z. Anorg. Allg. Chem. 354 (1967) 37.
[8] R.K. Rastsvetaeva, A.V. Araksheeva, D.Y. Pushcharovsky, S.A. Vinogradova, O.V. Dimitrova, S.Y. Stefanovich, Z. Kristallogr. 213 (1998) 240.
[9] Z.T. Yu, Z. Shi, Y.S. Jiang, H.M. Yuan, J.S. Chen, Chem. Mater. 14 (2002) 1314.
[10] E.L. Belokoneva, S.Yu. Stefanovich, T.A. Borisova, O.V. Dimitrova, Russ. J. Inorg. Chem. 46 (2001) 1621.
[11] E.L. Belokoneva, O.V. Dimitrova, T.A. Korchemkina, S.Yu. Stefanovich, Kristallografiya 43 (1998) 864.
[12] G.-M. Wang, Y.-Q. Sun, G.-Y. Yang, J. Solid State Chem. 179 (2006) 398.
[13] G.M. Sheldrick, SHELX-97: program for structure refinement, University of Goettingen, Germany, 1997.
[14] R.W. Smith, D.A. Keszler, J. Solid State Chem. 100 (1992) 325.
[15] R.W. Smith, L.J. Koliha, Mater. Res. Bull. 29 (1994) 1203.
[16] I.D. Brown, D. Altermatt, Acta Crystallogr. B 41 (1985) 244.
[17] N. Penin, M. Touboul, G. Nowogrocki, Solid State Sci. 3 (2001) 461.
[18] K.I. Schaffers, D.A. Keszler, J. Solid State Chem. 85 (1990) 270.
[19] X.-A. Chen, Y.-H. Zhao, X.-A. Chang, L. Zhang, H.-P. Xue, Acta Crystallogr. C 62 (2006) i11.

[20] P.C. Burns, J.D. Grice, F.C. Hawthorne, Can. Mineral. 33 (1995) 1131.

[21] E. Corazza, S. Menchetti, C. Sabelli, Am. Mineral. 59 (1974) 1005.

[22] L.Y. Li, X.L. Jin, G.B. Li, Y.X. Wang, F.H. Liao, G.Q. Yao, J.H. Lin, Chem. Mater. 15 (2003) 2253.

[23] D.Yu. Pushcharovsky, S. Merlino, O. Ferro, S.A. Vinogradova, O.V. Dimitrova, J. Alloys Compd. 306 (2000) 163.

[24] G.-M. Wang, Y.-Q. Sun, G.-Y. Yang, J. Solid State Chem. 177 (2004) 4648.

[25] S. Filatov, Y. Shepelev, R. Bubnova, N. Sennova, A.V. Egorysheva, Y.F. Kargin, J. Solid State Chem. 177 (2004) 515.

[26] J. Li, S. Xia, S. Gao, Spectrochim. Acta 51A (1995) 519.

[27] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.