



# Sr<sub>10</sub>[(PO<sub>4</sub>)<sub>5.5</sub>(BO<sub>4</sub>)<sub>0.5</sub>](BO<sub>2</sub>): Growth and crystal structure of a strontium phosphate orthoborate metaborate closely related to the apatite-type crystal structure

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## ABSTRACT

Single crystals of the strontium phosphate orthoborate metaborate, Sr<sub>10</sub>[(PO<sub>4</sub>)<sub>5.5</sub>(BO<sub>4</sub>)<sub>0.5</sub>](BO<sub>2</sub>), were grown from the melt and investigated by X-ray diffraction (space group *P*<sub>3</sub>, No. 147; *a*=9.7973(8) Å, *c*=7.3056(8) Å, *V*=607.29(10) Å<sup>3</sup>, *Z*=1). The crystal structure is closely related to apatite and contains linear metaborate groups, [BO<sub>2</sub>]<sup>−</sup> (point group *D*<sub>∞h</sub>, B–O=1.284(11) Å) taking positions within the channels running along the three-fold inversion axis. Strontium sites are found to be fully occupied while [PO<sub>4</sub>]<sup>3−</sup> tetrahedra are partially replaced by [BO<sub>4</sub>]<sup>5−</sup> groups.

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## 1. Introduction

Apart from vacancies and their specific distributions, natural and synthetic apatites are represented by the general formula M<sub>10</sub>(ZO<sub>4</sub>)<sub>6</sub>X<sub>2</sub> with M=Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup>, Pb<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, La<sup>3+</sup>, etc.; Z=P<sup>5+</sup>, As<sup>5+</sup>, V<sup>5+</sup>, Si<sup>4+</sup>, etc.; and X=F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, OH<sup>−</sup>, O<sup>2−</sup>, etc., which shows the wide range of tolerance of this structure type to chemical substitutions [1–3]. In addition, there are also reports on linear [BO<sub>2</sub>]<sup>−</sup> groups taking the position of X [4,5]. Generally, boron as a main constituent of solid inorganic compounds prefers to form either planar [BO<sub>3</sub>] complexes or tetrahedral [BO<sub>4</sub>] groups as manifested in the huge number of crystalline borates or in the newly established class of borophosphates [6]. Therefore, the presence of a [BO<sub>2</sub>]<sup>−</sup> metaborate unit is still questionable bearing in mind the sometimes challenging crystallography connected to the crystal structure solutions of apatites [7].

During our extensive studies on borophosphates [6] and biomimetic apatite composites [8] the metaborate ion has not been observed so far. The only examples of single crystal structure

determinations reporting the presence of [BO<sub>2</sub>]<sup>−</sup> are the apatite-type structures Sr<sub>9.402</sub>Na<sub>0.209</sub>(PO<sub>4</sub>)<sub>6</sub>(B<sub>0.996</sub>O<sub>2</sub>) [5] and Ca<sub>9.64</sub>(P<sub>5.73</sub>-B<sub>0.27</sub>O<sub>24</sub>)(BO<sub>2</sub>)<sub>0.73</sub> [9]. As a first step we reduced the chemical system to the ternary system SrO–B<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> by avoiding the alkali metal component similar to the experimental strategies applied for the system CaO–B<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> [9–13].

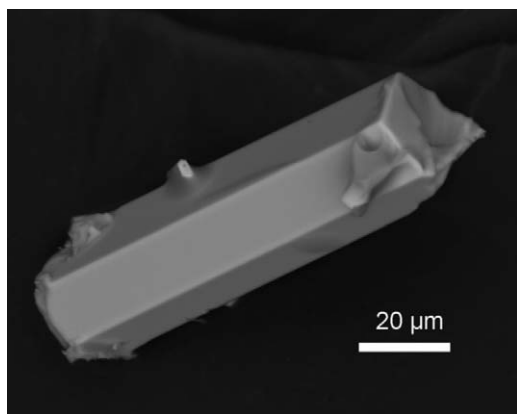
Here, we report on the strontium phosphate orthoborate metaborate, Sr<sub>10</sub>[(PO<sub>4</sub>)<sub>5.5</sub>(BO<sub>4</sub>)<sub>0.5</sub>](BO<sub>2</sub>), which was grown from the melt and structurally characterized by single-crystal X-ray diffraction.

## 2. Experimental

### 2.1. Synthesis

Sr<sub>10</sub>[(PO<sub>4</sub>)<sub>5.5</sub>(BO<sub>4</sub>)<sub>0.5</sub>](BO<sub>2</sub>) was first prepared by solid-state reactions from SrCO<sub>3</sub> (0.443 g, 3 mmol, Sigma-Aldrich, ≥ 98%), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (0.115 g, 1 mmol, Sigma-Aldrich, 98+%) and H<sub>3</sub>BO<sub>3</sub> (0.124 g, 2 mmol, Sigma-Aldrich, 99.5%). The mixed raw materials were heated to 773 K in a closed alumina crucible in air for 3 h to liberate CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O. Then the preheated mixture was ground again and subsequently heated to 1423 K for 8 h in an alumina crucible. The final reaction product is a white powder,

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**Fig. 1.** SEM image of a representative single crystal of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  with hexagonal prismatic shape.

which, according to powder X-ray diffraction, exclusively consists of the crystalline phase  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ . Excess boron results in the formation of a glassy phase according to visual inspection under an optical microscope. Least-squares fittings by use of the program WinCSD [14] revealed the lattice parameters  $a=9.7411(5)\text{\AA}$  and  $c=7.3318(4)\text{\AA}$ . White transparent single crystals of hexagonal prismatic shape (Fig. 1) were obtained in the course of thermogravimetric investigations after cooling from 1823 K (STA409 NETZSCH, corundum crucible, heating and cooling rates 10 K/min, argon). A broad endothermic effect during heating between 1623 and 1723 K indicates melting of the sample. A total weight loss of not more than 0.2 wt% is observed during the whole thermogravimetric investigation. Powder XRD proved the presence of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  after cooling but with slightly different lattice parameters ( $a=9.7934(22)\text{\AA}$ ,  $c=7.3089(10)\text{\AA}$ ).

## 2.2. Single crystal structure determination

Data collection was carried out with a Rigaku AFC7 (Mercury CCD) diffractometer equipped with graphite monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda=0.71073\text{\AA}$ ) at room temperature. A prismatic specimen ( $0.025 \times 0.025 \times 0.070\text{ mm}^3$ ) was selected under a light microscope. Diffraction data were collected with index ranges  $-9 \leq h \leq 12$ ,  $-11 \leq k \leq 11$ ,  $-9 \leq l \leq 9$ . No systematic absences were observed and the space group  $P\bar{3}$  (No. 147) was chosen. The crystal structure was solved with the program SHELXS-97 [15] and refined with the program SHELXL-97 [15] included in the program package WinGX [16]. Direct methods and subsequent Fourier difference analyses were used to locate the Sr, P and O positions. The boron position was determined from the Fourier difference map. The assignment of atom labels follows the suggested pattern which allows for easy comparison between different apatite crystal structures [2]. No carbon or nitrogen was found by chemical analyses (CHNS 932 LECO), L.O.D:  $\text{C} \leq 0.05\text{ wt\%}$ ,  $\text{N} \leq 0.18\text{ wt\%}$ . The initial chemical formula obtained during the structure refinement was “ $\text{Sr}_{10}(\text{PO}_4)_6(\text{BO}_2)^+$ ”. In order to fulfill electroneutrality, we first tried to refine the occupancy of the Sr positions [4,5,9,10] showing that the Sr sites are fully occupied (more than 99%). In a next step we used a model with boron partially substituting the phosphorous site as previously proposed for the calcium compound  $\text{Ca}_{9.64}[(\text{PO}_4)_{5.73}(\text{BO}_4)_{0.27}](\text{BO}_2)_{0.73}$  [9]. This model was refined to an occupation of 95(1)% phosphorous and 5% boron. In the final refinement cycle the site occupation was fixed to 11/12 P (91.7%) and 1/12 B to achieve charge balance ( $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ ). Supporting EDX measurements on two different single crystals gave Sr:P ratios of 1.72 and 1.82 also

indicating a deficiency on the phosphorous site (“ $\text{Sr}_{10}(\text{PO}_4)_6(-\text{BO}_2)^+$ ”, calc. Sr:P=1.67). Aluminum as a possible impurity originating from the corundum crucible used was not detected. A summary of the crystallographic data and refinement parameters are given in Table 1. The crystallographic data were deposited at FIZ Karlsruhe under the CSD number 421389.

## 2.3. FT-IR spectroscopy

The FT-IR spectrum was recorded at room temperature with a Fourier transform infrared spectrometer (Bruker, IFS 66v/S; Globar (MIR), KBr, DTGS-detector, program Opus/IR 3.0.3). 3 mg of the sample were mixed with 150 mg KBr in an agate mortar. The mixture was isostatically pressed and a transparent pellet was obtained. A pure KBr pellet prepared under the same conditions was used as a reference. All manipulations were conducted in an argon filled glove box ( $\text{MBraun}$ ,  $p(\text{O}_2) < 1\text{ ppm}$ ,  $p(\text{H}_2\text{O}) < 1\text{ ppm}$ ).

## 3. Results and discussion

$\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  crystallizes in the trigonal system, space group  $P\bar{3}$  (No. 147), with one formula unit per unit cell ( $a=9.7973(8)\text{\AA}$ ,  $c=7.3056(8)\text{\AA}$ ,  $V=607.29(10)\text{\AA}^3$ ). Atomic positions are given in Table 2.  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  is a derivative of the apatite crystal structure. Sr ions occupy the Wyckoff positions 2d (Sr1, Sr2) and 6g (Sr3).  $[\text{PO}_4]^{3-}$  tetrahedra (6g) are partially replaced by  $[\text{BO}_4]^{5-}$  groups. Therefore,  $\text{ZO}_4$  with  $Z=11/12\text{ P}+1/12\text{ B}$  will be used in the following text when referring to this structural entity. The linear  $[\text{BO}_2]^-$  units are located within the channels formed by Sr3 ions and running along the three-fold inversion axis (Fig. 2). The space group symmetry of the title compound is reduced to  $P\bar{3}$  by displacement of the  $\text{ZO}_4$  tetrahedra destroying the mirror plane characteristic for the parent apatite crystal structure ( $P6_3/m$ ) [5], which is found for strontium fluorapatite  $\text{Sr}_{10}[\text{PO}_4]_6\text{F}_2$  [17]. A comparison of the nearest neighbors around  $[\text{BO}_2]^-$  and  $\text{F}^-$  located within the channels is shown in Fig. 3.  $\text{F}^-$  ions ( $0, 0, \frac{1}{4}$ ) are situated on the mirror plane in the center of a Sr triangle. As a result constant  $\text{F}\cdots\text{F}$  distances of  $3.64\text{\AA}$  ( $a/2$ ) are observed along  $[001]$  (Fig. 3b). In  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ , the incorporation of boron atoms between two O atoms draw these atoms closer ( $d(\text{O}-\text{B}-\text{O})=2.57\text{\AA}$ ) and at the same time increase the gaps between two neighboring  $[\text{BO}_2]^-$  units ( $d(\text{O}\cdots\text{O})=4.73\text{\AA}$ ), which results in alternating  $\text{O}\cdots\text{O}$  distances along the  $c$  axis (Fig. 3a). Accordingly,

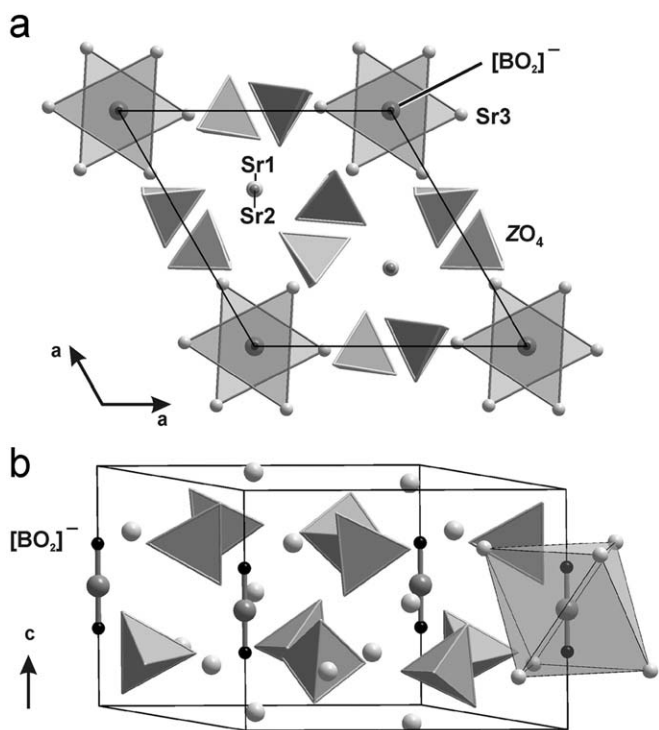
**Table 1**  
Crystallographic data and refinement parameters for  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ .

Formula	$\text{Sr}_{10}\text{P}_{5.50}\text{B}_{1.50}\text{O}_{26}$
Space group	$P\bar{3}$
$a/\text{\AA}$	9.7973(8)
$b/\text{\AA}$	$=a$
$c/\text{\AA}$	7.3056(8)
$V/\text{\AA}^3$	607.29(10)
$Z$	1
Density (calculated)	4.043 $\text{mg}/\text{m}^3$
Diffractometer	Rigaku AFC7
Radiation	$\text{Mo-K}\alpha$ , $\lambda=0.71073\text{\AA}$
$T/\text{K}$	293
$2\theta$ range/ $^\circ$	$4.8^\circ \leq 2\theta \leq 55.9^\circ$
Reflections collected	3321
Goodness-of-fit on $F^2$	1.188
$R1$ [ $I > 2\sigma(I)$ ]	0.0447
$R1$ (all data)	0.0522
$wR2$ [ $I > 2\sigma(I)$ ]	0.0765
$wR2$ (all data)	0.0787

**Table 2**  
 $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ : atomic coordinates and equivalent displacement parameters.

Atom	Site	x	y	z	$U^{eq}$
Sr1	2d	1/3	2/3	0.0069(1)	0.019(1)
Sr2	2d	1/3	2/3	0.5064(1)	0.016(1)
Sr3	6g	0.2491(1)	-0.0158(1)	0.2459(1)	0.023(1)
Z <sup>a</sup>	6g	0.3993(2)	0.3678(2)	0.2508(2)	0.014(1)
O1	6g	0.3345(6)	0.4823(5)	0.2539(6)	0.018(1)
O2	6g	0.5779(6)	0.4590(6)	0.2323(7)	0.025(1)
O3	6g	0.3293(7)	0.2538(6)	0.0899(7)	0.032(1)
O4	6g	0.3585(7)	0.2704(7)	0.4281(7)	0.033(1)
B	1b	0	0	1/2	0.047(7)
O5	2c	0	0	0.3243(16)	0.047(3)

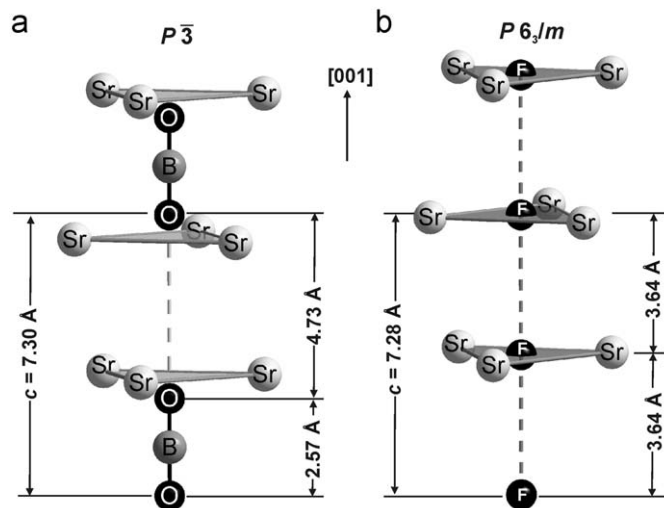
<sup>a</sup> Z=11/12 P+1/12 B.



**Fig. 2.** Crystal structure of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ : (a) projection along [001] showing the channels formed by Sr3 (gray triangles) and the positions of the  $\text{ZO}_4$  tetrahedra (gray; Z=11/12 P+1/12 B). (b) Side view with emphasized  $[\text{BO}_2]^-$  groups and the coordinating trigonal antiprism formed by Sr3.

because of the movement of O atoms, they do not take positions within the triangle formed by Sr3 species but stay in between two Sr triangles. Along with these changes an expansion of the unit cell parameters  $a$  by 1.2% and  $c$  by 0.4% is observed in comparison to  $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$  ( $a=9.678 \text{ \AA}$ ,  $c=7.275 \text{ \AA}$ ,  $V=590.1 \text{ \AA}^3$ ) [17].

Selected interatomic distances are listed in Table 3. Sr1 and Sr2 are nine-fold coordinated ( $d(\text{Sr1}-\text{O})=2.529(5) \text{ \AA}$ – $3.075(6) \text{ \AA}$ ,  $d(\text{Sr2}-\text{O})=2.586(4) \text{ \AA}$ – $2.804(6) \text{ \AA}$ ). Sr3 is surrounded by seven oxygen atoms forming a distorted pentagonal bipyramid ( $d(\text{Sr}-\text{O})=2.481(5) \text{ \AA}$ – $2.789(5) \text{ \AA}$ ). One of the vertices stems from an oxygen atom belonging to the linear metaborate unit ( $d(\text{Sr}-\text{O5})=2.586(3) \text{ \AA}$ ). The  $\text{ZO}_4$  group is slightly distorted and Z–O distances vary from  $1.522(5) \text{ \AA}$  to  $1.540(5) \text{ \AA}$  with an average Z–O distance of  $1.532 \text{ \AA}$ . Compared with the average P–O distance of  $1.537 \text{ \AA}$  in pure phosphates [18] and average B–O distance of  $1.475 \text{ \AA}$  in borates [19], the Z–O distance of  $1.532 \text{ \AA}$  is in good agreement with the calculated mean value ( $1.537 \text{ \AA} \times 11/12 + 1.475 \text{ \AA} \times 1/12 = 1.5318 \text{ \AA}$ ).



**Fig. 3.** Comparison of the arrangement of  $[\text{BO}_2]^-$  and  $\text{F}^-$  ions within the Sr-channels of (a)  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  and (b)  $\text{Sr}_{10}(\text{PO}_4)_6\text{F}_2$  [17].

**Table 3**

Selected interatomic distances in the crystal structure of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ .

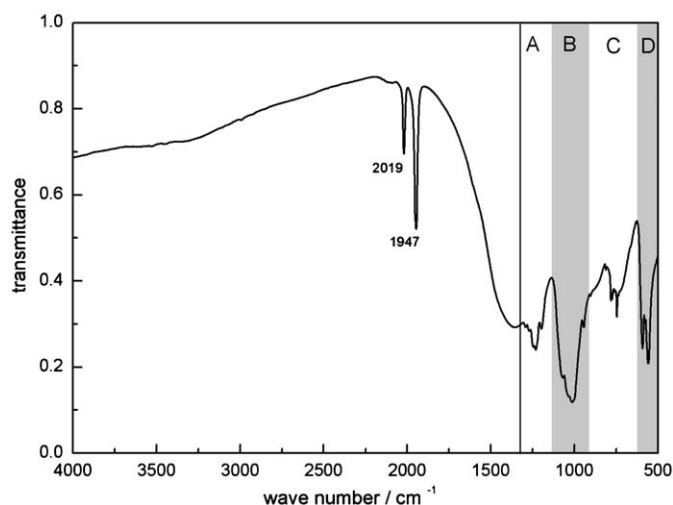
Atom contacts	/Å	Atom contacts	/Å
Sr3–O2	2.481(5)	Sr1–O2	2.529(5)...3 ×
Sr3–O4	2.523(5)	Sr1–O1	2.557(5)...3 ×
Sr3–O3	2.528(5)	Sr1–O3	3.075(6)...3 ×
Sr3–O5	2.586(3)		
Sr3–O3	2.611(5)	Z <sup>a</sup> –O2	1.522(5)
Sr3–O1	2.764(5)	Z <sup>a</sup> –O3	1.527(5)
Sr3–O4	2.789(5)	Z <sup>a</sup> –O4	1.539(5)
Sr2–O1	2.586(4)...3 ×	Z <sup>a</sup> –O1	1.540(5)
Sr2–O2	2.643(5)...3 ×		
Sr2–O4	2.804(6)...3 ×	B–O5	1.284(11)...2 ×

<sup>a</sup> Z=11/12 P+1/12 B.

The B–O distance of  $1.284(11) \text{ \AA}$  in the symmetric linear  $[\text{BO}_2]^-$  unit is in the same range compared with the values reported for  $\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6(\text{B}_{0.996}\text{O}_2)$  ( $1.253(10) \text{ \AA}$ ) [5] and  $\text{Ca}_{9.64}[(\text{PO}_4)_{5.73}(\text{BO}_4)_{0.27}](\text{BO}_2)_{0.73}$  ( $1.277(8) \text{ \AA}$ ) [9]. This distance is shorter than the average ones in  $\text{B}\Phi_3$  and  $\text{B}\Phi_4$  ( $\Phi=\text{O}, \text{OH}$ ) units where values of  $1.37 \text{ \AA}$  and  $1.48 \text{ \AA}$  are reported (ICSD database) [19]. Recent DFT calculations for the linear  $[\text{BO}_2]^-$  group yielded  $1.264 \text{ \AA}$  [20] which was interpreted as a B=O double bond similar to the isoelectronic  $\text{CO}_2$  molecule.

The FT-IR spectrum of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  is shown in Fig. 4. The prominent features of the spectrum are the two strong absorption bands at  $2019$  and  $1947 \text{ cm}^{-1}$ . In accordance with the results of single-crystal X-ray diffraction they are attributed to the asymmetric stretches of the linear  $[\text{BO}_2]^-$  and  $[\text{BO}_2]^-$  units (natural abundance of boron: 19.9%  $^{10}\text{B}$  and 80.1%  $^{11}\text{B}$ ). This pattern was first observed for metaborate containing (contaminated) alkali metal halides (NaCl:  $2067$  and  $1997 \text{ cm}^{-1}$ ) [21,22]. Later it was also reported for metaborate containing calcium apatite ( $2007$  and  $1939 \text{ cm}^{-1}$ ) [10], the noble gas matrix isolated  $[\text{BO}_2]^-$  (argon:  $2000$  and  $1931 \text{ cm}^{-1}$ ) [23], and metaborate containing sodalite ( $2002$  and  $1930 \text{ cm}^{-1}$ ) [24].

In contrast to the straightforward assignment of the metaborate bands the interpretation of the remaining part of the FT-IR spectrum is not that clear. A comparison with a published IR spectrum of  $\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2$  suggests that the bands in the regions B and D (Fig. 4) are mainly caused by  $\text{PO}_4$  vibration modes [25]. In agreement with the interpretation of the IR spectrum of



**Fig. 4.** FT-IR spectrum of  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$  (KBr pellet): The wave numbers of the asymmetric stretch of the linear  $[\text{}^{10}\text{B}\text{O}_2]^-$  and  $[\text{}^{11}\text{B}\text{O}_2]^-$  are given. The gray ranges B and D are attributed to  $\text{PO}_4$  vibrational modes. Ranges A and C were not assigned. For further details see text.

metaborate containing calcium apatite the bands in region A and C (Fig. 4) should stem from borate ions [10]. The authors assumed that  $\text{BO}_3$  and/or  $\text{BO}_2$  units are responsible for the observed bands and summarized their results with the chemical formula  $\text{Ca}_{9.5+0.5x}\{(\text{PO}_4)_{6-x}(\text{BO}_3)_x\}\{(\text{BO}_2)_{1-x}\text{O}_x\}$  where  $\text{BO}_3$  units replace  $\text{PO}_4$  units and oxygen atoms partly replace  $\text{BO}_2$  units in the channels [10]. However, the bands of region C could be also explained by  $\text{BO}_4$  vibrational modes [26]. Keeping in mind that also amorphous boron containing compounds could be present which were not detected the powder XRD the final assignment of the band of regions A and C remains an open question.

With respect to the question whether  $\text{BO}_3$  or  $\text{BO}_4$  units replace  $\text{PO}_4$  groups a comparison with carbonate containing calcium apatites may be useful. The carbonate anion  $\text{CO}_3^{2-}$  and the borate anion  $\text{BO}_3^{3-}$  are both planar. Therefore the space requirement and the arrangement in the structure should be similar. For the carbonated apatites it is known that the replacement of the phosphate tetrahedra (type B [27]) leads to an under-occupation of the phosphorus and one oxygen position, along with a shortage of one of the P–O distances as well as a shrinkage of the tetrahedral volume by 3.6% [28]. These structural changes are due to the quite different geometries of the two complex anions. In the title compound neither a pronounced shortage of the P–O distance (Table 3) nor a shrinkage in the tetrahedral volume ( $V=1.844\text{Å}^3$ ) are found, an observation which underlines the conclusion that a tetrahedral anion replaces the  $\text{PO}_4$  group.

#### 4. Conclusion

Single crystals of strontium phosphate orthoborate metaborate,  $\text{Sr}_{10}[(\text{PO}_4)_{5.5}(\text{BO}_4)_{0.5}](\text{BO}_2)$ , were grown from the melt and investigated by X-ray diffraction. The crystal structure is closely related to apatite and contains linear  $[\text{BO}_2]^-$  metaborate groups ( $\text{B–O}=1.284(11)\text{Å}$ ), isoelectronic to  $\text{CO}_2$ . It is interesting to note, that even linear  $[\text{CuO}]^-$  chains with  $d(\text{Cu–O})=1.854\text{Å}$  can be inserted into the channels as observed in a strontium vanadate apatite  $\text{Sr}_5(\text{VO}_4)_3(\text{CuO})$  [29]. Also discrete linear  $[\text{CuO}_2]^{3-}$  groups

with  $d(\text{Cu–O})=1.825\text{Å}$  have been inserted in strontium phosphate apatite  $\text{Sr}_5(\text{PO}_4)_3(\text{CuO}_2)_{1/3}$  [30]. All these findings emphasize the exceptional tolerance of the apatite crystal structure even for a wide variety of complex anions.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.12.026.

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