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The new silver borate $Ag_3B_5O_9$

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ABSTRACT

Single crystals of $Ag_3B_5O_9$ were obtained *via* high-pressure synthesis at 3 GPa and 600 °C, using a Walker-type multianvil high-pressure device. $Ag_3B_5O_9$ crystallizes with $a=674.7(2)$, $b=943.5(2)$, $c=1103.5(2)$ pm, $V=0.7025(2)$ nm^3, and $Z=4$ in the noncentrosymmetric space group $P2_12_12_1$ (no. 19). The orthorhombic structure was refined from 3740 independent reflections with $R1=0.0496$ and $wR2=0.587$ (all data). It is built up from infinite corner-sharing chains of BO_4 tetrahedra along the *a* axis, which are interconnected by BO_3 groups to form a network. In the structure, three crystallographically independent sites are occupied with Ag^+ cations exhibiting argentophillic interactions. The synthetic conditions as well as the results of the single crystal structure analysis are presented.

1. Introduction

During our research in the field of high-pressure alkali metal borates, we noticed that HP-RbB_3O_5 is isotypic to HP-KB_3O_5, [1] according to the similar ionic radii of the alkali metal cations differing by 7 pm (K: 173 pm, Rb: 180 pm) [2]. Consequently, pseudo alkali metal borates with comparable ionic radii can form isotypic structures or substitution variants, as can be seen in the compounds HP-$(NH_4)B_3O_5$ or HP-TlB_3O_5 [3]. Even the significantly larger cesium ion (195 pm) [2] fits into this structure type, if it is occupying not more than one half of the M^+ positions, as was demonstrated in the compound HP-$Cs_{1-x}(H_3O)_xB_3O_5$ ($x=0.5$–0.7) [4]. Another structure type present in lighter high-pressure alkali metal borates is found in the sodium tetraborate HP-$Na_2B_4O_7$ [5]. With the knowledge that the radius of the pseudo alkali metal ion silver (142 pm) differs by just 10 pm from the value of the sodium ion (132 pm), [2] we started investigations in the system Ag–B–O.

Under ambient-pressure conditions, seven ternary borate phases are known in this system: the metaborate $AgBO_2$, [6] the orthoborates Ag_3BO_3-I [7] and Ag_3BO_3-II, [8] two forms of $Ag_2B_8O_{13}$, [9] as well as $Ag_2B_4O_7$ and AgB_9O_{14} [10].

Within these ambient-pressure phases, there are examples for silver borates being isotypic to sodium borates like β-$Ag_2B_8O_{13}$ to β-$Na_2B_8O_{13}$ [9b]. However, there are also examples for phases possessing a different structure. For example, $AgBO_2$ crystallizes in a different structure than $NaBO_2$ or KBO_2. In literature, this difference is used to underline a structure influencing factor of Ag^+ ions that, for example, is also observed in the system Ag–Si–O [6]. This fascinating structure influencing factor is caused by the fully occupied 4*d* orbitals of the Ag^+ ions (electronic configuration: [Kr]$4d^{10}$). Homoatomic d^{10}–d^{10} interactions lead to shortened distances between the Ag^+ cations in the range between 253.35(5) pm (Ag–Ag single bond) and 344 pm (double van der Waals radius). These argentophillic interactions lead to substructures of the silver cations of different complexity, ranging from simple dimers up to complex networks [11].

The question arises, how the system Ag–B–O behaves under high-pressure conditions. Is there a silver borate isotypic to HP-$Na_2B_4O_7$ or does the structural chemistry differ due to argentophillic interactions? Interestingly, no high-pressure silver borates were known until we started our investigations in this system. With the compound AgB_3O_5, we recently synthesized the first high-pressure silver borate with an interesting, noncentrosymmetric structure [12]. Noncentrosymmetric borates are highly interesting materials due to their industrial application as non-linear optical materials, e.g. β-BaB_2O_4 (BBO) [13]. In this work, the second high-pressure silver borate possessing the composition $Ag_3B_5O_9$ will be presented. Synthetic conditions as well as the crystal structure of the new compound will be described.

2. Results and discussion

2.1. Crystal structure

The silver borate $Ag_3B_5O_9$ crystallizes with four formula units ($Z=4$) in the orthorhombic space group $P2_12_12_1$ (no. 19). The

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dimensions of the unit cell are $a=674.7(2)$, $b=943.5(2)$, $c=1103.5(2)$ pm, and $V=0.7025(2)$ nm^3 (see Table 1). Fig. 1 displays the unit cell down the *a* axis. The fundamental building block is presented in Fig. 2 together with the atom labeling (for atomic coordinates and displacement parameters see Tables 2 and 3). BO_4 tetrahedra and BO_3 groups are linked by common oxygen atoms to form a noncentrosymmetric B–O network structure.

Three crystallographically independent BO_4 tetrahedra are present in the structure. They exhibit B–O bond lengths between 145.0(6) and 149.9(6) pm (av. 147.2 pm), 144.7(6) and 149.7(6) pm (av. 147.5 pm), and 145.5(6) and 149.1(6) pm (av. 147.5 pm) for the tetrahedra around B1, B3, and B4, respectively (see Table 4). The O–B–O bond angles in these tetrahedra are distributed from 106.0(3)° to 112.2(4)°, 105.1(3)° to 112.1(4)°, and 105.9(4)° to 112.4(4)° (see Table 5). The mean O–B–O bond angle in the tetrahedra around B1 and B3 is 109.5°, while the tetrahedron around B4 exhibits a value of 109.4°. The B–O bond lengths within the two independent BO_3 groups range from 137.0(7) to 140.3(6) pm (av. 138.3 pm) and from 136.1(6)° to 138.0(6) pm (av. 137.2 pm) with O–B–O bond angles from 115.1(4)° to 121.6(4)° (av. 119.2°) and 117.8(4)° to 121.4(4)° (av. 120.0°) for $B2O_3$ and $B5O_3$, respectively. These values are within the range of the values found in literature for BO_4 tetrahedra (137.3–169.9 pm, av. 147.6(3.5) pm and 95.7–119.4°, av. 109.4(2.8)°) [14] and for BO_3 groups (135.1–140.3 pm, av. 137.0 pm and 109–129°, av. 120.0°) [15].

The BO_4 tetrahedra are linked by common oxygen atoms to form chains along the *a* axis (see Fig. 1, bottom). In each chain, corners of two neighboring BO_4 tetrahedra ($B3O_4$ to $B4O_4$ and $B4O_4$ to $B1O_4$) are additionally connected by BO_3 groups ($B5O_3$ and $B2O_3$, respectively), yielding two crystallographically different "dreier" rings [16]. The remaining corner of the BO_3 groups connect to the remaining corner of BO_4 tetrahedra in the neighbored chains (see Fig. 3), resulting in a network of BO_3 and BO_4 groups. Within this network, channels are formed along [1 0 1] and [1 0 0] which incorporate the Ag1 and Ag2 sites, respectively. The Ag3 site is stacked with the $B5O_3$ groups along the *a* axis. As shown in Fig. 4, the silver ions are surrounded by five (Ag1, Ag3) and four (Ag2) oxygen atoms with distances from 217.2(4) to 270.3(4) pm (av. 248.5 pm), 226.5(3) to 254.1(3) pm (av. 242.5 pm), and from 234.6(3) to 304.5(4) pm (av. 255.5 pm)), for Ag1, Ag2, and Ag3, respectively. According to the ECoN values (effective coordination numbers), [17] the coordination numbers of the silver ions in $Ag_3B_5O_9$ (CN=4, 5) are within the range of coordination numbers found in other phases of the system Ag–B–O (CN=2 [7]–8 [12]). The value for the shortest ($Ag–O_{min}$) as well as for the longest ($Ag–O_{max}$) Ag–O bond length within the coordination spheres of the silver ions is comparable to other silver borates. ($Ag–O_{min}=211.1(2)$ [8] to 237.2(4) pm [12], $Ag–O_{max}=212.5(7)$ [7] to 304.6(6) pm [12]). The average Ag–O distances for Ag1, Ag2, and Ag3 are 248.5, 242.5, and 255.5 pm, respectively. Other phases show average values in the same region (212.5 [7] to 278.1 pm [6]). Compared to the recently discovered high-pressure phase AgB_3O_5, the surrounding of the silver ions in $Ag_3B_5O_9$ resembles the ambient-pressure phases rather than AgB_3O_5. Solely the $Ag–O_{min}$ and $Ag–O_{max}$ value of the ion Ag3 (234.6(3) and 304.5(4) pm) are comparable to the values in AgB_3O_5 (237.2(4) and 304.6(6) pm) [12]. The shortest distances between the silver ions are 286.56(7) (Ag1···Ag3), 294.89(8) (Ag1···Ag2), 301.47(9) (Ag2···Ag3), and 324.73(8) pm (Ag1···Ag2) compared to 295.4(2) and 306.2(1) pm in $AgBO_2$ [6] and Ag_3BO_3-II [8], respectively. The first distance is even shorter than the distance found in metallic silver (289 pm). These short distances clearly indicate the presence of argentophillic interactions, which also explain the color of the crystals [11]. A representation of the resulting silver substructure is displayed in Fig. 5. With the bond-length/bond-strength – (ΣV) [18] and the Chardi-(charge distribution in solids, ΣQ) [19] concepts, the bond-valence sums for $Ag_3B_5O_9$ were calculated. The formal ionic charge of each atom fits to the expected values within the limits of the concepts (see Table 6).

Table 1
Crystal data and structure refinement of $Ag_3B_5O_9$ (standard deviations in parentheses).

Empirical formula	$Ag_3B_5O_9$
Molar mass (g/mol)	521.66
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
Single crystal diffractometer	Enraf-Nonius Kappa CCD
Radiation	MoKα ($\lambda=71.073$ pm) (graded multilayer X-ray optics)
Single crystal data	
a (pm)	674.7(2)
b (pm)	943.5(2)
c (pm)	1103.5(2)
V (nm^3)	0.7025(2)
Formula units per cell	$Z=4$
Calculated density (g/cm^3)	4.932
Crystal size (mm^3)	0.037 × 0.035 × 0.020
Temperature (K)	293(2)
Absorption coefficient (mm^{-1})	8.316
F(0 0 0)	952
θ range (°)	2.84–37.72
Range in *hkl*	$-11 \geq h \geq 11$, $-13 \geq k \geq 16$, $-18 \geq l \geq 18$
Total no. of reflections	10,856 ($R_{int}=0.0560$)
Independent reflections	3,740 ($R_\sigma=0.0579$)
Reflections with $I \geq 2\sigma(I)$	3,150
Data / parameters	3,740/154
Absorption correction	Multi-scan (Scalepack [23])
Goodness-of-fit on F_i^2	1.052
Flack-parameter	−0.05(3)
Final *R* indices [$I \geq 2\sigma(I)$]	$R1=0.0367$ $wR2=0.0557$
Final *R* indices (all data)	$R1=0.0496$ $wR2=0.0587$
Largest diff. peak and hole (e/Å^3)	1.341/−1.633