

## Supporting Information (SI)

### Exploration of Silver Borates with Diverse Low Dimensional Anion Frameworks by Introducing Monovalent Heteroanions

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### Supporting Information Index

#### Tables and Figures

- 1) **Table S1.** Crystal Data and Structure Refinement Parameters.
- 2) **Table S2.** Important bond lengths (Å) for **(1)**, **(2)**, **(3)** and **(4)**.
- 3) **Table S3.** Selected bond angles (deg) for **(1)**, **(2)**, **(3)** and **(4)**.
- 4) **Table S4.** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{Å}^2 \times 10^3$ ) for **(1)**, **(2)**, **(3)** and **(4)**.  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.
- 5) **Table S5.** Assignment of the absorption peaks observed in the IR spectra of **(1)**, **(2)**, **(3)** and **(4)**.
- 6) **Table S6.** Reported inorganic stoichiometric Ag-borates with B–O framework.
- 7) **Figure S1.** Rietveld refinement for the powder X-ray diffraction pattern of **(1)**.
- 8) **Figure S2.** Rietveld refinement for the powder X-ray diffraction pattern of **(2)**.
- 9) **Figure S3.** Rietveld refinement for the powder X-ray diffraction pattern of **(3)**.
- 10) **Figure S4.** Rietveld refinement for the powder X-ray diffraction pattern of **(4)**.
- 11) **Figure S5.** Asymmetric units of these compounds, and the coordination environments of atoms.
- 12) **Figure S7.** (a) 2D structure of **(2)** along the *ab* plane, (b) 12-MR channel, (c) 20-MR channel, and (d) 16-MR channel.
- 13) **Figure S7.** (a) 2D structure of **(3)** along the *ab* plane, (b) 12-MR channel, (c) 20-MR channel, and (d) 16-MR channel.
- 14) **Figure S8.** The calculated refractive indices of **(1)**, **(2)**, **(3)** and **(4)**.

**Table S1** Crystal Data and Structure Refinement Parameters.

Compounds	(1)	(2)	(3)	(4)
Empirical formula	Ag <sub>7</sub> B <sub>9</sub> O <sub>16</sub> (OH) <sub>2</sub>	Ag <sub>8</sub> B <sub>8</sub> O <sub>15</sub> Cl <sub>2</sub>	Ag <sub>8</sub> B <sub>8</sub> O <sub>15</sub> (OH)Br	Ag <sub>11</sub> B <sub>8</sub> O <sub>16</sub> I <sub>3</sub>
<i>Mr</i> (g·mol <sup>-1</sup> )	1142.40	1260.34	1286.36	1909.75
Cryst syst.	Monoclinic	Monoclinic	Triclinic	Monoclinic
<i>T</i> (K)			296	
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> (Å)	8.826(4)	13.7794(8)	8.7338(3)	13.4121(5)
<i>b</i> (Å)	8.825(3)	10.7272(6)	8.8080(3)	12.5734(4)
<i>c</i> (Å)	20.483(9)	21.5856(12)	10.8986(3)	25.1948(9)
$\alpha$ (°)	90	90	79.573(10)	90
$\beta$ (°)	100.220(2)	95.604(2)	89.317(10)	93.062(10)
$\gamma$ (°)	90	90	75.242(10)	90
<i>V</i> (Å <sup>3</sup> )	1570.10(11)	3175.40(3)	796.84(4)	4242.70(3)
<i>Z</i>	4	8	2	8
<i>D<sub>c</sub></i> (g·cm <sup>-3</sup> )	4.833	5.273	5.361	5.980
$\mu$ (mm <sup>-1</sup> )	8.653	10.071	12.212	14.354
<i>F</i> (000)	2080.0	4560.0	1160.0	6752.0
<i>R</i> <sub>int</sub>	0.0322	0.0718	0.0313	0.0275
Radiation	MoK $\alpha$ ( $\lambda$ = 0.71073)			
$2\theta$ range for data collection/ <sup>o</sup>	5.038 to 55.002	3.792 to 55.062	4.826 to 54.966	3.238 to 55.068
Index ranges	-11 ≤ <i>h</i> ≤ 9, -11 ≤ <i>k</i> ≤ 10, -26 ≤ <i>l</i> ≤ 26	-15 ≤ <i>h</i> ≤ 17, -13 ≤ <i>k</i> ≤ 13, -28 ≤ <i>l</i> ≤ 27	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -14 ≤ <i>l</i> ≤ 14	-17 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 16, -32 ≤ <i>l</i> ≤ 32
Reflns collected	7797	15737	14123	32864
GOF on <i>F</i> <sup>2</sup>	1.030	1.041	1.022	1.075
Final <i>R</i> indexes [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0280, w <i>R</i> <sub>2</sub> = 0.0556	<i>R</i> <sub>1</sub> = 0.0438, w <i>R</i> <sub>2</sub> = 0.0514	<i>R</i> <sub>1</sub> = 0.0233, w <i>R</i> <sub>2</sub> = 0.0455	<i>R</i> <sub>1</sub> = 0.0219, w <i>R</i> <sub>2</sub> = 0.0398
Final <i>R</i> indexes [all data] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0384, w <i>R</i> <sub>2</sub> = 0.0592	<i>R</i> <sub>1</sub> = 0.0886, w <i>R</i> <sub>2</sub> = 0.0580	<i>R</i> <sub>1</sub> = 0.0307, w <i>R</i> <sub>2</sub> = 0.0480	<i>R</i> <sub>1</sub> = 0.0272, w <i>R</i> <sub>2</sub> = 0.0412

<sup>a</sup>*R*<sub>1</sub> =  $\sum ||F_o| - |F_c|| / \sum |F_o|$  and w*R*<sub>2</sub> =  $[w(F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$  for *F*<sub>o</sub><sup>2</sup> > 2σ(*F*<sub>o</sub><sup>2</sup>)

**Table S2(a).** Important bond lengths for (1).

<b>Bond Length(Å) for (1)</b>			
B(1)—O(1)	1.353(6)	B(1)—O(2)	1.403(6)
B(1)—O(3)	1.380(6)	B(2)—O(2)	1.501(6)
B(2)—O(4)	1.454(6)	B(2)—O(5) <sup>13</sup>	1.454(6)
B(2)—O(7) <sup>13</sup>	1.495(6)	B(2) <sup>11</sup> —O(5)	1.454(6)
B(2) <sup>11</sup> —O(7)	1.495(6)	B(3)—O(3)	1.491(6)
B(3)—O(4)	1.461(6)	B(3)—O(5)	1.482(6)
B(3)—O(6)	1.468(6)	B(4)—O(6)	1.382(6)
B(4)—O(7)	1.388(6)	B(4)—O(8)	1.363(6)
B(5)—O(8) <sup>3</sup>	1.495(5)	B(5)—O(8)	1.495(5)
B(5)—O(9) <sup>3</sup>	1.459(5)	B(5)—O(9)	1.459(6)
Ag(1)—O(2)	2.139(3)	Ag(1)—O(2) <sup>10</sup>	2.139(3)
Ag(2) <sup>9</sup> —O(1)	2.174(4)	Ag(2)—O(1) <sup>6</sup>	2.174(4)
Ag(2)—O(5)	2.300(3)	Ag(2)—O(7)	2.652
Ag(2)—O(9)	2.665	Ag(3)—O(4)	2.232(3)
Ag(3)—O(5) <sup>2</sup>	2.507(3)	Ag(3)—O(7) <sup>3</sup>	2.536(3)
Ag(3)—O(9) <sup>4</sup>	2.348(4)	Ag(3) <sup>2</sup> —O(5)	2.507(3)
Ag(3) <sup>3</sup> —O(7)	2.536(3)	Ag(3) <sup>12</sup> —O(9)	2.348(4)
Ag(4)—O(1) <sup>8</sup>	2.349(4)	Ag(4)—O(1) <sup>9</sup>	2.507(4)
Ag(4) <sup>8</sup> —O(1)	2.349(4)	Ag(4) <sup>6</sup> —O(1)	2.507(4)
Ag(4)—O(6)	2.499(3)		

<sup>1</sup> -x, +y, 1/2-z; <sup>2</sup> 1/2-x, 1/2-y, 1/2-z; <sup>3</sup> 1-x, +y, 1/2-z; <sup>4</sup> -1/2+x, 3/2-y, +z; <sup>5</sup> +x, -1+y, +z;

<sup>6</sup> 1/2-x, -1/2+y, -z; <sup>7</sup> +x, 1+y, +z; <sup>8</sup> -x, 1-y, -z; <sup>9</sup> 1/2-x, 1/2+y, -z; <sup>10</sup> -x, -y, -z;

<sup>11</sup> 1/2+x, 1/2-y, +z; <sup>12</sup> 1/2+x, 3/2-y, +z; <sup>13</sup> -1/2+x, 1/2-y, +z

**Table S2(b).** Important bond lengths for **(2)**.

<b>Bond Length(Å) for (2)</b>			
B(1)—O(13)	1.365(9)	B(1)—O(14)	1.365(9)
B(1)—O(15)	1.358(10)	B(2)—O(12)	1.461(8)
B(2)—O(12) <sup>5</sup>	1.461(8)	B(2)—O(13)	1.494(9)
B(2)—O(13) <sup>5</sup>	1.494(9)	B(3)—O(6)	1.477(9)
B(3)—O(7)	1.462(9)	B(3)—O(12)	1.459(9)
B(3)—O(14)	1.509(9)	B(4)—O(5)	1.472(9)
B(4)—O(7)	1.472(9)	B(4)—O(8)	1.491(9)
B(4)—O(11)	1.434(9)	B(5)—O(3)	1.478(9)
B(5)—O(4)	1.497(9)	B(5)—O(5)	1.458(9)
B(5)—O(6)	1.458(9)	B(6)—O(2)	1.475(8)
B(6)—O(2) <sup>5</sup>	1.474(8)	B(6)—O(3)	1.455(8)
B(6)—O(3) <sup>5</sup>	1.455(8)	B(7)—O(1)	1.379(9)
B(7)—O(2)	1.351(9)	B(7)—O(4)	1.375(9)
B(8) <sup>13</sup> —O(1)	1.472(9)	B(8)—O(1) <sup>2</sup>	1.472(9)
B(8)—O(10)	1.504(9)	B(8)—O(11)	1.407(9)
B(8)—O(15) <sup>3</sup>	1.494(9)	B(8) <sup>7</sup> —O(15)	1.494(9)
B(9)—O(8)	1.362(10)	B(9)—O(9)	1.333(9)
B(9)—O(10)	1.392(9)	Ag(1)—O(5) <sup>8</sup>	2.196(5)
Ag(1)—O(9)	2.104(5)	Ag(1)—Cl(2) <sup>9</sup>	2.923(2)
Ag(1) <sup>10</sup> —Cl(2)	2.923(2)	Ag(1) <sup>8</sup> —O(5)	2.196(5)
Ag(2) <sup>6</sup> —Cl(1)	2.742(2)	Ag(2) <sup>8</sup> —O(1)	2.439(5)
Ag(2) <sup>10</sup> —Cl(2)	2.772(2)	Ag(2)—Cl(1) <sup>6</sup>	2.742(2)
Ag(2)—Cl(2) <sup>9</sup>	2.772(2)	Ag(2)—O(1) <sup>8</sup>	2.439(5)
Ag(2)—O(10)	2.311(5)	Ag(3)—Cl(1)	2.556(2)
Ag(3)—O(6) <sup>4</sup>	2.489(5)	Ag(3)—O(9)	2.316(5)
Ag(3)—O(14) <sup>4</sup>	2.361(5)	Ag(3) <sup>4</sup> —O(14)	2.361(5)
Ag(3) <sup>4</sup> —O(6)	2.489(5)	Ag(4) <sup>6</sup> —Cl(1)	2.670(2)
Ag(4) <sup>12</sup> —Cl(2)	2.819(2)	Ag(4)—Cl(1) <sup>6</sup>	2.670(2)
Ag(4)—Cl(1)	2.632(2)	Ag(4)—O(7)	2.320(5)
Ag(4)—Cl(2) <sup>11</sup>	2.819(2)	Ag(5) <sup>4</sup> —O(8)	2.521(5)

Ag(5) <sup>4</sup> —O(4)	2.420(5)	Ag(5)—Cl(1)	2.774(2)
Ag(5)—O(4) <sup>4</sup>	2.420(5)	Ag(5)—O(15)	2.448(5)
Ag(5)—O(8) <sup>4</sup>	2.521(5)	Ag(6)—O(3) <sup>11</sup>	2.317(4)
Ag(6)—O(7)	2.306(5)	Ag(6)—O(12)	2.580(5)
Ag(6) <sup>12</sup> —O(3)	2.317(4)	Ag(7)—O(6)	2.320(4)
Ag(7)—O(3) <sup>5</sup>	2.451(4)	Ag(7)—O(12) <sup>5</sup>	2.388(5)
Ag(7)—Cl(2) <sup>5</sup>	2.545(19)	Ag(7) <sup>5</sup> —O(12)	2.388(5)
Ag(7) <sup>5</sup> —O(3)	2.451(4)	Ag(8) <sup>13</sup> —O(2)	2.458(5)
Ag(8) <sup>7</sup> —O(13)	2.388(5)	Ag(8)—O(2) <sup>2</sup>	2.458(5)
Ag(8)—O(11)	2.311(5)	Ag(8)—O(13) <sup>3</sup>	2.388(5)
Ag(8)—Cl(2)	2.519(2)		

<sup>1</sup> -x, +y, 1/2-z; <sup>2</sup> -1/2+x, -1/2+y, +z; <sup>3</sup> -1/2+x, 1/2+y, +z; <sup>4</sup> 1-x, 1-y, 1-z; <sup>5</sup> 1-x, +y, 1/2-z;  
<sup>6</sup> 1/2-x, 1/2-y, 1-z; <sup>7</sup> 1/2+x, -1/2+y, +z; <sup>8</sup> 1/2-x, 3/2-y, 1-z; <sup>9</sup> +x, 1-y, 1/2+z; <sup>10</sup> +x, 1-y, -1/2+z;  
<sup>11</sup> 1/2-x, -1/2+y, 1/2-z; <sup>12</sup> 1/2-x, 1/2+y, 1/2-z; <sup>13</sup> 1/2+x, 1/2+y, +z

**Table S2(c).** Important bond lengths for **(3)**.

<b>Bond Length(Å) for (3)</b>			
B(1)—O(1)	1.497(6)	B(1)—O(2)	1.478(5)
B(1)—O(3)	1.441(6)	B(1) <sup>13</sup> —O(13)	1.479(6)
B(1)—O(13) <sup>1</sup>	1.479(6)	B(2)—O(3)	1.448(6)
B(2)—O(4)	1.476(6)	B(2)—O(6)	1.443(6)
B(2)—O(7)	1.504(6)	B(3)—O(4)	1.371(6)
B(3)—O(5)	1.392(6)	B(3)—O(15) <sup>16</sup>	1.344(6)
B(3) <sup>16</sup> —O(15)	1.344(6)	B(4)—O(5)	1.486(6)
B(4)—O(6)	1.423(5)	B(4)—O(9)	1.493(6)
B(4)—O(11)	1.487(6)	B(5)—O(8)	1.369(6)
B(5)—O(9)	1.369(6)	B(5)—O(10)	1.369(6)
B(6)—O(1) <sup>4</sup>	1.469(6)	B(6)—O(7) <sup>4</sup>	1.466(6)
B(6)—O(14) <sup>7</sup>	1.475(6)	B(6)—O(10)	1.502(5)
B(6) <sup>2</sup> —O(1)	1.469(6)	B(6) <sup>2</sup> —O(7)	1.466(6)
B(6) <sup>7</sup> —O(14)	1.475(6)	B(7)—O(11)	1.365(6)
B(7)—O(12)	1.379(6)	B(7)—O(13)	1.360(6)
B(8) <sup>1</sup> —O(2)	1.466(6)	B(8)—O(2) <sup>13</sup>	1.466(6)
B(8) <sup>7</sup> —O(8)	1.479(6)	B(8)—O(8) <sup>7</sup>	1.479(6)
B(8)—O(12)	1.473(6)	B(8)—O(14)	1.463(6)
Ag(1)—O(1)	2.292(3)	Ag(1)—O(2) <sup>3</sup>	2.477(3)
Ag(1) <sup>13</sup> —O(14)	2.398(3)	Ag(1)—O(14) <sup>1</sup>	2.398(3)
Ag(1)—Br(1) <sup>3</sup>	2.6158(6)	Ag(1) <sup>3</sup> —Br(1)	2.6158(6)
Ag(2)—O(2) <sup>14</sup>	2.336(3)	Ag(2) <sup>14</sup> —O(2)	2.337(3)
Ag(2)—O(3)	2.184(3)	Ag(2)—Br(1) <sup>14</sup>	2.8618(7)
Ag(2) <sup>14</sup> —Br(1)	2.8618(7)	Ag(3)—O(10)	2.411(3)
Ag(3)—O(11) <sup>6</sup>	2.452(3)	Ag(3)—O(16) <sup>5</sup>	2.516(4)
Ag(3) <sup>6</sup> —O(11)	2.452(3)	Ag(3) <sup>11</sup> —O(16)	2.516(4)
Ag(4)—O(6)	2.317(3)	Ag(4)—O(8)	2.513(3)
Ag(4)—O(12)	2.364(3)	Ag(5)—O(7) <sup>8</sup>	2.567(3)
Ag(5)—O(7)	2.567(3)	Ag(5)—O(14) <sup>8</sup>	2.325(3)
Ag(5)—O(14)	2.325(3)	Ag(6)—O(7)	2.151(3)
Ag(6)—O(15)	2.096(3)	Ag(7)—O(1) <sup>13</sup>	2.389(3)

Ag(7) <sup>1</sup> —O(1)	2.389(3)	Ag(7)—O(15)	2.287(4)
Ag(7)—O(16)	2.358(4)	Ag(8)—O(16) <sup>12</sup>	2.101(4)
Ag(8)—O(16)	2.101(4)	Ag(9)—O(5) <sup>11</sup>	2.387(3)
Ag(9) <sup>5</sup> —O(5)	2.387(3)	Ag(9)—O(9) <sup>10</sup>	2.569(3)
Ag(9) <sup>10</sup> —O(9)	2.569(3)	Ag(9)—O(16)	2.406(4)

<sup>1</sup> -1+x, +y, +z; <sup>2</sup> +x, -1+y, +z; <sup>3</sup> -x, 1-y, 1-z; <sup>4</sup> +x, 1+y, +z; <sup>5</sup> -1+x, 1+y, +z;  
<sup>6</sup> 1-x, 2-y, 2-z; <sup>7</sup> 1-x, 2-y, 1-z; <sup>8</sup> 1-x, 1-y, 1-z; <sup>9</sup> 1+x, -1+y, 1+z; <sup>10</sup> 2-x, 1-y, 2-z;  
<sup>11</sup> 1+x, -1+y, +z; <sup>12</sup> 2-x, -y, 2-z; <sup>13</sup> 1+x, +y, +z; <sup>14</sup> -x, 2-y, 1-z; <sup>15</sup> -1+x, 1+y, -1+z; <sup>16</sup> 1-x, 1-y, 2-z

**Table S2(d).** Important bond lengths for **(4)**.

<b>Bond lengths (Å) for (4)</b>			
B(1)—O(1)	1.343(6)	B(1)—O(2)	1.390(6)
B(1)—O(3)	1.377(6)	B(2)—O(2)	1.473(6)
B(2)—O(4)	1.465(5)	B(2)—O(5) <sup>13</sup>	1.482(5)
B(2)—O(14) <sup>12</sup>	1.479(5)	B(2) <sup>9</sup> —O(14)	1.479(5)
B(2) <sup>13</sup> —O(5)	1.482(5)	B(3)—O(3)	1.517(6)
B(3)—O(4)	1.449(5)	B(3)—O(8)	1.453(6)
B(3)—O(9)	1.489(6)	B(4)—O(5)	1.380(6)
B(4)—O(6)	1.371(6)	B(4)—O(7)	1.353(6)
B(5)—O(9)	1.386(6)	B(5)—O(10)	1.349(6)
B(5)—O(11)	1.371(6)	B(6)—O(8)	1.455(6)
B(6)—O(11)	1.480(6)	B(6)—O(12)	1.485(6)
B(6)—O(13)	1.483(6)	B(7) <sup>17</sup> —O(6)	1.480(6)
B(7)—O(12)	1.454(6)	B(7)—O(14)	1.473(6)
B(7)—O(15)	1.473(6)	B(7)—O(6) <sup>18</sup>	1.480(6)
B(8)—O(13)	1.371(6)	B(8)—O(15)	1.378(6)
B(8)—O(16)	1.355(6)	Ag(1)—O(1)	2.211(3)
Ag(1)—O(3)	2.139(3)	Ag(1)—I(1)	2.6965(5)
Ag(1)—O(12) <sup>6</sup>	2.575(3)	Ag(1) <sup>6</sup> —O(12)	2.575(3)
Ag(2)—O(1)	2.243(3)	Ag(2)—O(14) <sup>6</sup>	2.292(3)
Ag(2) <sup>6</sup> —O(14)	2.292(3)	Ag(2)—I(2) <sup>2</sup>	2.8962(6)
Ag(2) <sup>2</sup> —I(2)	2.8962(6)	Ag(3) <sup>1</sup> —I(3)	2.8532(5)
Ag(3)—I(3) <sup>14</sup>	2.8532(5)	Ag(3)—O(2)	2.387(3)
Ag(3)—O(10) <sup>14</sup>	2.346(3)	Ag(3) <sup>1</sup> —O(10)	2.346(3)
Ag(4)—O(5)	2.308(3)	Ag(4)—O(7) <sup>13</sup>	2.447(3)
Ag(4) <sup>13</sup> —O(7)	2.447(3)	Ag(4) <sup>1</sup> —I(3)	2.8113(5)
Ag(4)—I(3) <sup>14</sup>	2.8112(5)	Ag(5)—O(4)	2.440(3)
Ag(5)—O(7)	2.249(3)	Ag(5)—O(15) <sup>12</sup>	2.424(3)
Ag(5) <sup>9</sup> —O(15)	2.424(3)	Ag(6)—O(9)	2.255(3)
Ag(6)—O(14) <sup>12</sup>	2.404(3)	Ag(6) <sup>9</sup> —O(14)	2.404(3)
Ag(6)—I(2) <sup>3</sup>	2.7774(5)	Ag(6) <sup>3</sup> —I(2)	2.7774(5)
Ag(7)—O(10)	2.255(3)	Ag(7)—O(12) <sup>4</sup>	2.449(3)



Ag(7) <sup>4</sup> —O(12)	2.449(3)	Ag(7)—I(2)	2.7408(6)
Ag(8)—O(10)	2.239(3)	Ag(8)—O(1) <sup>1</sup>	2.559(3)
Ag(8)—O(3) <sup>4</sup>	2.306(3)	Ag(8) <sup>14</sup> —O(1)	2.559(3)
Ag(8) <sup>4</sup> —O(3)	2.306(3)	Ag(9)—O(13)	2.359(3)
Ag(9)—O(16) <sup>11</sup>	2.240(3)	Ag(9) <sup>11</sup> —O(16)	2.239(3)
Ag(9)—I(3)	2.6886(5)	Ag(10)—O(16)	2.303(3)
Ag(10)—O(6) <sup>9</sup>	2.486(3)	Ag(10) <sup>12</sup> —O(6)	2.486(3)
Ag(10)—O(8) <sup>11</sup>	2.381(3)	Ag(10) <sup>11</sup> —O(8)	2.381(3)
Ag(10)—I(1) <sup>8</sup>	2.9118(5)	Ag(10) <sup>5</sup> —I(1)	2.9118(5)
Ag(11)—O(7) <sup>11</sup>	2.184(6)	Ag(11) <sup>11</sup> —O(7)	2.184(6)
Ag(11)—I(1) <sup>4</sup>	2.703(9)	Ag(11) <sup>4</sup> —I(1)	2.703(9)
Ag(11)—O(16)	2.214(5)	Ag(12)—O(16)	2.372(5)
Ag(12)—O(7) <sup>11</sup>	2.321(4)	Ag(12) <sup>11</sup> —O(7)	2.321(4)
Ag(12)—I(1) <sup>4</sup>	2.997(5)	Ag(12) <sup>4</sup> —I(1)	2.997(5)
Ag(12)—I(2) <sup>4</sup>	2.916(7)	Ag(12) <sup>4</sup> —I(1)	2.916(7)

<sup>1</sup>-1/2+x, -1/2+y, +z, <sup>2</sup>2-x, 1-y, 1-z, <sup>3</sup>3/2-x, 1/2-y, 1-z, <sup>4</sup>1-x, 1-y, 1-z, <sup>5</sup>1/2+x, 3/2-y, -1/2+z,  
<sup>6</sup>3/2-x, 3/2-y, 1-z, <sup>7</sup>-1/2+x, 3/2-y, -1/2+z, <sup>8</sup>-1/2+x, 3/2-y, 1/2+z, <sup>9</sup>-1/2+x, 1/2+y, +z, <sup>10</sup>-1+x, +y, +z,  
<sup>11</sup>1-x, +y, 3/2-z, <sup>12</sup>1/2+x, -1/2+y, +z, <sup>13</sup>2-x, +y, 3/2-z, <sup>14</sup>1/2+x, 1/2+y, +z, <sup>15</sup>1/2+x, 3/2-y, 1/2+z,  
<sup>16</sup>1+x, +y, +z, <sup>17</sup>3/2-x, -1/2+y, 3/2-z, <sup>18</sup>3/2-x, 1/2+y, 3/2-z

**Table S3(a).** Selected bond angles (deg) for **(1)**.

<b>Bond Angles (deg) for (1)</b>			
O(1)—B(1)—O(2)	117.6(4)	O(1)—B(1)—O(3)	124.2(5)
O(3)—B(1)—O(2)	118.2(4)	O(4)—B(2)—O(2)	109.1(4)
O(4)—B(2)—O(7) <sup>13</sup>	111.7(4)	O(5) <sup>13</sup> —B(2)—O(4)	108.7(4)
O(5) <sup>13</sup> —B(2)—O(2)	111.2(4)	O(5) <sup>13</sup> —B(2)—O(7) <sup>13</sup>	109.8(4)
O(7) <sup>13</sup> —B(2)—O(2)	106.4(4)	O(4)—B(3)—O(5)	108.4(4)
O(4)—B(3)—O(3)	110.0(4)	O(4)—B(3)—O(6)	109.1(4)
O(5)—B(3)—O(3)	110.9(4)	O(6)—B(3)—O(5)	110.6(4)
O(6)—B(3)—O(3)	107.9(4)	O(8)—B(4)—O(6)	123.0(4)
O(8)—B(4)—O(7)	116.8(4)	O(6)—B(4)—O(7)	120.2(4)
O(8)—B(5)—O(8) <sup>3</sup>	109.7(5)	O(9)—B(5)—O(8) <sup>3</sup>	110.9(2)
O(9)—B(5)—O(8)	108.71(19)	O(9) <sup>3</sup> —B(5)—O(8)	110.9(2)
O(9) <sup>3</sup> —B(5)—O(8) <sup>3</sup>	108.71(19)	O(9)—B(5)—O(9) <sup>3</sup>	107.8(6)

<sup>1</sup> -x, +y, 1/2-z; <sup>2</sup> 1/2-x, 1/2-y, 1/2-z; <sup>3</sup> 1-x, +y, 1/2-z; <sup>4</sup> -1/2+x, 3/2-y, +z; <sup>5</sup> +x, -1+y, +z;

<sup>6</sup> 1/2-x, -1/2+y, -z; <sup>7</sup> +x, 1+y, +z; <sup>8</sup> -x, 1-y, -z; <sup>9</sup> 1/2-x, 1/2+y, -z; <sup>10</sup> -x, -y, -z;

<sup>11</sup> 1/2+x, 1/2-y, +z; <sup>12</sup> 1/2+x, 3/2-y, +z; <sup>13</sup> -1/2+x, 1/2-y, +z

**Table S3(b).** Selected bond angles (deg) for **(2)**.

<b>Bond Angles (deg) for (2)</b>			
O(1)—B(1)—O(11)	116.4(3)	O(7) <sup>1</sup> —B(1)—O(1)	124.4(3)
O(13)—B(1)—O(14)	120.3(7)	O(15)—B(1)—O(14)	117.0(7)
O(15)—B(2)—O(13)	122.7(7)	O(13)—B(2)—O(13) <sup>5</sup>	104.2(8)
O(12)—B(2)—O(13) <sup>5</sup>	108.9(3)	O(12)—B(2)—O(13)	110.1(3)
O(12) <sup>5</sup> —B(2)—O(13)	108.9(3)	O(12) <sup>5</sup> —B(2)—O(13) <sup>5</sup>	110.1(3)
O(12)—B(2)—O(12) <sup>5</sup>	114.2(9)	O(6)—B(3)—O(14)	105.7(5)
O(7)—B(3)—O(6)	111.2(6)	O(7)—B(3)—O(14)	107.7(6)
O(12)—B(3)—O(6)	114.0(6)	O(12)—B(3)—O(14)	110.8(6)
O(12)—B(3)—O(7)	107.3(6)	O(11)—B(4)—O(5)	109.9(6)
O(11)—B(4)—O(7)	108.9(6)	O(11)—B(4)—O(8)	110.9(6)
O(5)—B(4)—O(7)	108.9(6)	O(5)—B(4)—O(8)	109.2(6)
O(7)—B(4)—O(8)	109.0(6)	O(6)—B(5)—O(3)	112.8(6)
O(6)—B(5)—O(4)	108.7(6)	O(5)—B(5)—O(6)	111.0(6)
O(5)—B(5)—O(3)	106.3(6)	O(5)—B(5)—O(4)	109.1(6)
O(3)—B(5)—O(4)	108.8(6)	O(3) <sup>5</sup> —B(6)—O(3)	114.6(9)
O(3) <sup>5</sup> —B(6)—O(2)	108.1(3)	O(3) <sup>5</sup> —B(6)—O(2) <sup>5</sup>	110.3(3)
O(3)—B(6)—O(2) <sup>5</sup>	108.1(3)	O(3)—B(6)—O(2)	110.3(3)
O(2) <sup>5</sup> —B(6)—O(2)	105.0(8)	O(2)—B(7)—O(4)	120.3(7)
O(2)—B(7)—O(1)	122.1(7)	O(4)—B(7)—O(1)	117.5(7)
O(11)—B(8)—O(1) <sup>2</sup>	114.1(6)	O(11)—B(8)—O(15) <sup>3</sup>	114.7(6)
O(11)—B(8)—O(10)	111.3(6)	O(1) <sup>2</sup> —B(8)—O(15) <sup>3</sup>	105.7(6)
O(1) <sup>2</sup> —B(8)—O(10)	106.7(6)	O(15) <sup>3</sup> —B(8)—O(10)	103.5(5)
O(8)—B(9)—O(10)	119.8(7)	O(9)—B(9)—O(10)	122.4(7)
O(9)—B(9)—O(8)	117.7(7)		

<sup>1</sup> -x, +y, 1/2-z; <sup>2</sup> -1/2+x, -1/2+y, +z; <sup>3</sup> -1/2+x, 1/2+y, +z; <sup>4</sup> 1-x, 1-y, 1-z; <sup>5</sup> 1-x, +y, 1/2-z;  
<sup>6</sup> 1/2-x, 1/2-y, 1-z; <sup>7</sup> 1/2+x, -1/2+y, +z; <sup>8</sup> 1/2-x, 3/2-y, 1-z; <sup>9</sup> +x, 1-y, 1/2+z; <sup>10</sup> +x, 1-y, -1/2+z;  
<sup>11</sup> 1/2-x, -1/2+y, 1/2-z; <sup>12</sup> 1/2-x, 1/2+y, 1/2-z; <sup>13</sup> 1/2+x, 1/2+y, +z

**Table S3(c).** Selected bond angles (deg) for **(3)**.

<b>Bond Angles (deg) for (3)</b>			
O(1)—B(1)—O(3)	109.7(4)	O(2)—B(1)—O(3)	109.4(4)
O(3)—B(1)—O(13) <sup>2</sup>	110.6(4)	O(2)—B(1)—O(1)	110.8(4)
O(2)—B(1)—O(13) <sup>2</sup>	110.1(3)	O(1)—B(1)—O(13) <sup>2</sup>	106.2(3)
O(6)—B(2)—O(7)	109.3(4)	O(6)—B(2)—O(3)	108.9(4)
O(6)—B(2)—O(4)	111.8(4)	O(3)—B(2)—O(7)	107.9(4)
O(3)—B(2)—O(4)	111.5(4)	O(4)—B(2)—O(7)	107.3(3)
O(4)—B(3)—O(5)	120.6(4)	O(15) <sup>16</sup> —B(3)—O(5)	121.5(4)
O(15) <sup>16</sup> —B(3)—O(4)	117.8(4)	O(6)—B(4)—O(9)	113.0(4)
O(6)—B(4)—O(11)	114.8(4)	O(6)—B(4)—O(5)	112.0(4)
O(11)—B(4)—O(9)	106.0(4)	O(5)—B(4)—O(9)	105.4(3)
O(5)—B(4)—O(11)	104.9(3)	O(9)—B(5)—O(8)	121.4(4)
O(9)—B(5)—O(10)	118.4(4)	O(10)—B(5)—O(8)	120.3(4)
O(14) <sup>7</sup> —B(6)—O(10)	110.2(3)	O(14) <sup>7</sup> —B(6)—O(7) <sup>5</sup>	106.7(3)
O(1) <sup>1</sup> —B(6)—O(7) <sup>5</sup>	111.2(3)	O(10)—B(6)—O(7) <sup>5</sup>	108.3(4)
O(14) <sup>7</sup> —B(6)—O(1) <sup>5</sup>	112.7(4)	O(10)—B(6)—O(1) <sup>5</sup>	107.7(3)
O(12)—B(7)—O(11)	121.7(4)	O(13)—B(7)—O(11)	118.0(4)
O(12)—B(7)—O(12)	120.3(4)	O(14)—B(8)—O(8) <sup>7</sup>	109.8(4)
O(14)—B(8)—O(2) <sup>13</sup>	113.8(4)	O(14)—B(8)—O(12)	108.8(4)
O(2) <sup>13</sup> —B(8)—O(8) <sup>7</sup>	107.6(4)	O(2) <sup>13</sup> —B(8)—O(12)	110.5(4)
O(12)—B(8)—O(8) <sup>7</sup>	106.1(4)		

<sup>1</sup> -1+x, +y, +z; <sup>2</sup> +x, -1+y, +z; <sup>3</sup> -x, 1-y, 1-z; <sup>4</sup> +x, 1+y, +z; <sup>5</sup> -1+x, 1+y, +z;

<sup>6</sup> 1-x, 2-y, 2-z; <sup>7</sup> 1-x, 2-y, 1-z; <sup>8</sup> 1-x, 1-y, 1-z; <sup>9</sup> 1+x, -1+y, 1+z; <sup>10</sup> 2-x, 1-y, 2-z;

<sup>11</sup> 1+x, -1+y, +z; <sup>12</sup> 2-x, -y, 2-z; <sup>13</sup> 1+x, +y, +z; <sup>14</sup> -x, 2-y, 1-z; <sup>15</sup> -1+x, 1+y, -1+z; <sup>16</sup> 1-x, 1-y, 2-z

**Table S3(d).** Selected bond angles (deg) for **(4)**.

<b>Bond Angles (deg) for (4)</b>			
O(2)—B(1)—O(3)	119.4(4)	O(1)—B(1)—O(3)	123.3(4)
O(1)—B(1)—O(2)	117.2(4)	O(4)—B(2)—O(14) <sup>12</sup>	113.4(4)
O(4)—B(2)—O(5) <sup>13</sup>	106.9(3)	O(4)—B(2)—O(2)	110.2(3)
O(14) <sup>12</sup> —B(2)—O(5) <sup>13</sup>	110.7(3)	O(2)—B(2)—O(14) <sup>12</sup>	107.9(3)
O(2)—B(2)—O(5) <sup>13</sup>	107.5(3)	O(8)—B(3)—O(9)	109.1(3)
O(8)—B(3)—O(3)	110.0(4)	O(4)—B(3)—O(8)	111.2(4)
O(4)—B(3)—O(9)	110.2(4)	O(4)—B(3)—O(3)	110.2(3)
O(9)—B(3)—O(3)	105.9(3)	O(7)—B(4)—O(5)	119.9(4)
O(7)—B(4)—O(6)	121.5(4)	O(5)—B(4)—O(6)	118.6(4)
O(10)—B(5)—O(9)	120.0(4)	O(10)—B(5)—O(11)	121.3(4)
O(11)—B(5)—O(9)	118.6(4)	O(13)—B(6)—O(12)	109.5(3)
O(8)—B(6)—O(13)	108.7(4)	O(8)—B(6)—O(12)	112.9(4)
O(11)—B(6)—O(8)	110.8(3)	O(11)—B(6)—O(13)	108.3(4)
O(11)—B(6)—O(12)	106.6(4)	O(14)—B(7)—O(6) <sup>18</sup>	111.0(4)
O(14)—B(7)—O(12)	109.4(4)	O(12)—B(7)—O(15)	111.6(4)
O(12)—B(7)—O(6) <sup>18</sup>	109.4(4)	O(15)—B(7)—O(14)	107.0(3)
O(15)—B(7)—O(6) <sup>18</sup>	108.4(4)	O(13)—B(8)—O(15)	118.7(4)
O(16)—B(8)—O(13)	121.8(4)	O(16)—B(8)—O(15)	119.5(4)

<sup>1</sup>-1/2+x, -1/2+y, +z; <sup>2</sup>2-x, 1-y, 1-z; <sup>3</sup>3/2-x, 1/2-y, 1-z; <sup>4</sup>1-x, 1-y, 1-z; <sup>5</sup>1/2+x, 3/2-y, -1/2+z;  
<sup>6</sup>3/2-x, 3/2-y, 1-z; <sup>7</sup>-1/2+x, 3/2-y, -1/2+z; <sup>8</sup>-1/2+x, 3/2-y, 1/2+z; <sup>9</sup>-1/2+x, 1/2+y, +z; <sup>10</sup>-1+x, +y, +z;  
<sup>11</sup>1-x, +y, 3/2-z; <sup>12</sup>1/2+x, -1/2+y, +z; <sup>13</sup>2-x, +y, 3/2-z; <sup>14</sup>1/2+x, 1/2+y, +z;  
<sup>15</sup>1/2+x, 3/2-y, 1/2+z; <sup>16</sup>1+x, +y, +z; <sup>17</sup>3/2-x, -1/2+y, 3/2-z; <sup>18</sup>3/2-x, 1/2+y, 3/2-z

**Table S4(a).** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **(1)**.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a/\text{\AA}^2$
Ag(1)	0	0	0	44.6(2)
Ag(2)	3410.1(6)	101.6(5)	999.5(2)	29.39(14)
Ag(3)	1643.0(5)	3795.6(5)	2636.4(2)	23.95(14)
Ag(4)	1691.4(5)	7063.4(5)	889.3(3)	30.10(15)
B(1)	1238(6)	3155(6)	172(3)	11.4(11)
B(2)	409(6)	2161(6)	1241(3)	8.8(10)
B(3)	2719(6)	3827(6)	1255(3)	9.4(10)
B(4)	4976(6)	5431(6)	1710(3)	10.7(11)
B(5)	5000	7664(8)	2500	9.0(14)
O(1)	972(4)	3082(4)	-498.9(17)	16.1(7)
O(2)	478(4)	2104(4)	513.9(16)	14.2(7)
O(3)	2220(4)	4181(4)	537.5(16)	12.9(7)
O(4)	1392(4)	3382(4)	1547.3(15)	9.8(7)
O(5)	3847(3)	2567(4)	1347.6(16)	9.3(7)
O(6)	3402(4)	5204(4)	1586.4(17)	12.2(7)
O(7)	5953(4)	4349(4)	1519.2(17)	12.6(7)
O(8)	5650(4)	6689(4)	2020.6(17)	12.7(7)
O(9)	6221(4)	8637(4)	2845.3(18)	14.8(8)
H(9)	7030(70)	8380(70)	2880(30)	19(17)

**Table S4(b).** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **(2)**.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckhoff site	$x$	$y$	$z$	$U_{\text{eq}}^a/\text{\AA}^2$
Ag(1)	<i>8f</i>	2482.4(5)	6616.7(6)	6183.8(3)	28.58(18)
Ag(2)	<i>8f</i>	977.8(5)	4323.8(6)	5441.9(3)	26.73(18)
Ag(3)	<i>8f</i>	4524.3(5)	4812.7(6)	5604.4(3)	28.22(19)
Ag(4)	<i>8f</i>	2693.9(6)	3051.8(6)	4111.0(3)	37.3(2)
Ag(5)	<i>8f</i>	5686.6(4)	2626.1(6)	5174.5(3)	19.80(17)
Ag(6)	<i>8f</i>	2373.9(5)	3261.4(6)	2621.5(3)	34.3(2)
Ag(7)	<i>8f</i>	6157.3(4)	5642.2(6)	3060.2(3)	17.93(16)
Ag(8)	<i>8f</i>	1189.5(4)	5718.7(6)	2577.8(3)	17.91(16)
Cl(1)	<i>8f</i>	3683.9(15)	2800.4(19)	5210.0(10)	24.6(5)
Cl(2)	<i>8f</i>	2033.1(14)	5894.2(18)	1597.3(9)	17.4(5)
B(1)	<i>8f</i>	5151(6)	2606(8)	3625(4)	9(2)
B(2)	<i>4e</i>	5000	3225(11)	2500	14(3)
B(3)	<i>8f</i>	4126(6)	4483(8)	3279(4)	6.0(18)
B(4)	<i>8f</i>	2732(6)	5670(8)	3672(4)	10(2)
B(5)	<i>8f</i>	4082(6)	6902(8)	3268(4)	8.6(19)
B(6)	<i>4e</i>	5000	8157(11)	2500	11(3)
B(7)	<i>8f</i>	5067(6)	8820(8)	3609(4)	7.6(19)
B(8)	<i>8f</i>	1051(6)	5672(7)	4101(4)	4.5(18)
B(9)	<i>8f</i>	2613(6)	5772(8)	4831(4)	12(2)
O(1)	<i>8f</i>	5342(3)	9643(4)	4084(2)	9.7(12)
O(2)	<i>8f</i>	5312(3)	8993(4)	3024(2)	11.7(12)
O(3)	<i>8f</i>	4161(3)	7424(4)	2641(2)	7.9(11)
O(4)	<i>8f</i>	4502(3)	7818(4)	3745(2)	7.8(11)
O(5)	<i>8f</i>	3043(3)	6759(4)	3327(2)	8.0(11)
O(6)	<i>8f</i>	4592(3)	5718(4)	3368(2)	9.0(11)
O(7)	<i>8f</i>	3100(3)	4531(4)	3396(2)	8.3(11)
O(8)	<i>8f</i>	3151(3)	5760(5)	4334(2)	17.0(13)
O(9)	<i>8f</i>	3086(4)	5917(4)	5395(2)	16.7(13)
O(10)	<i>8f</i>	1604(3)	5651(4)	4737(2)	9.2(11)
O(11)	<i>8f</i>	1688(3)	5616(4)	3630(2)	9.1(11)
O(12)	<i>8f</i>	4169(3)	3965(4)	2657(2)	9.0(11)
O(13)	<i>8f</i>	5328(4)	2369(4)	3025(2)	14.7(12)
O(14)	<i>8f</i>	4648(3)	3647(4)	3766(2)	10.5(12)
O(15)	<i>8f</i>	5462(3)	1841(4)	4105(2)	9.8(12)

**Table S4(c).** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **(3)**.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/\text{\AA}^2$
Ag(1)	<i>2i</i>	-1066.3(4)	3774.7(4)	6147.5(4)	15.93(9)
Ag(2)	<i>2i</i>	535.1(5)	10381.3(5)	6106.5(5)	35.53(13)
Ag(3)	<i>2i</i>	3119.4(5)	13366.0(5)	9719.0(3)	18.79(10)
Ag(4)	<i>2i</i>	3762.4(5)	8829.5(5)	5165.8(3)	18.04(10)
Ag(5)	<i>1h</i>	5000	5000	5000	33.54(17)
Ag(6)	<i>2i</i>	5435.3(5)	4567.2(5)	7820.1(4)	19.71(10)
Ag(7)	<i>2i</i>	9817.3(5)	4194.2(6)	8792.0(4)	33.22(13)
Ag(8)	<i>1a</i>	10000	0	10000	27.43(15)
Ag(9)	<i>2i</i>	13448.6(5)	-228.0(5)	10743.5(4)	21.12(10)
Br(1)	<i>2i</i>	2613.9(6)	8393.1(6)	3125.3(5)	17.87(12)
B(1)	<i>2i</i>	-229(6)	6883(6)	6530(4)	7.4(10)
B(2)	<i>2i</i>	2360(6)	7059(6)	7383(5)	7.7(10)
B(3)	<i>2i</i>	2893(6)	6707(6)	9683(5)	8.5(10)
B(4)	<i>2i</i>	4216(6)	8519(6)	8227(4)	6.0(9)
B(5)	<i>2i</i>	3326(6)	11524(6)	7312(5)	7.9(10)
B(6)	<i>2i</i>	2319(6)	14506(6)	6615(4)	6.4(9)
B(7)	<i>2i</i>	6950(6)	7585(6)	7196(4)	6.4(9)
B(8)	<i>2i</i>	7416(6)	7374(6)	4953(5)	7.8(10)
O(1)	<i>2i</i>	613(3)	5144(4)	6753(3)	7.4(6)
O(2)	<i>2i</i>	-962(4)	7405(4)	5257(3)	8.0(6)
O(3)	<i>2i</i>	877(4)	7807(4)	6684(3)	9.9(6)
O(4)	<i>2i</i>	2095(4)	6445(4)	8698(3)	13.8(7)
O(5)	<i>2i</i>	3865(4)	7752(4)	9491(3)	8.8(6)
O(6)	<i>2i</i>	3314(4)	8192(4)	7274(3)	7.4(6)
O(7)	<i>2i</i>	3205(3)	5652(4)	6817(3)	7.8(6)
O(8)	<i>2i</i>	3201(4)	11308(4)	6108(3)	12.4(7)
O(9)	<i>2i</i>	3888(4)	10258(4)	8264(3)	10.2(6)
O(10)	<i>2i</i>	2868(4)	13024(4)	7592(3)	9.7(6)
O(11)	<i>2i</i>	5962(4)	7945(4)	8141(3)	11.2(7)
O(12)	<i>2i</i>	6378(4)	7718(4)	5997(3)	10.6(7)
O(13)	<i>2i</i>	8535(4)	7073(4)	7470(3)	10.7(7)
O(14)	<i>2i</i>	7298(4)	5861(4)	4638(3)	7.5(6)
O(15)	<i>2i</i>	7256(4)	4117(5)	9176(3)	18.6(8)
O(16)	<i>2i</i>	11040(4)	1846(4)	10209(3)	20.2(8)
H(15)	<i>2i</i>	7900(200)	4400(300)	8700(200)	420(160)



**Table S4(d).** Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **(4)**.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/\text{\AA}^2$
Ag(1)	<i>8f</i>	8162.1(3)	7006.8(3)	4191.4(2)	23.47(9)
Ag(2)	<i>8f</i>	10317.2(3)	6249.2(4)	4842.3(2)	35.44(12)
Ag(3)	<i>8f</i>	10276.0(3)	7147.8(3)	5975.2(2)	31.13(11)
Ag(4)	<i>8f</i>	11037.8(4)	6413.8(3)	7843.7(2)	34.19(11)
Ag(5)	<i>8f</i>	8031.3(3)	3921.7(3)	7137.5(2)	18.20(8)
Ag(6)	<i>8f</i>	7593.0(3)	2987.0(3)	5831.0(3)	43.53(14)
Ag(7)	<i>8f</i>	6073.4(3)	3488.8(4)	4686.9(2)	30.20(11)
Ag(8)	<i>8f</i>	3593.6(3)	3716.3(3)	5168.4(2)	28.85(10)
Ag(9)	<i>8f</i>	5974.0(3)	4806.9(3)	7205.7(2)	24.66(9)
Ag(10)	<i>8f</i>	3099.9(3)	7331.1(3)	7971.9(2)	19.99(9)
Ag(11)	<i>8f</i>	2577(6)	5143(11)	6853(6)	47(2)
Ag(12)	<i>8f</i>	2420(3)	5446(4)	6690(2)	37.8(8)
I(1)	<i>8f</i>	6547.5(2)	6605.0(3)	3538.3(2)	23.06(8)
I(2)	<i>8f</i>	7957.2(2)	4082.5(3)	4435.9(2)	22.45(8)
I(3)	<i>8f</i>	6255.3(2)	2750.2(2)	6962.8(2)	16.64(7)
B(1)	<i>8f</i>	8475(4)	6134(4)	5430(2)	10.9(9)
B(2)	<i>8f</i>	9038(3)	4946(4)	6194.1(19)	8.6(9)
B(3)	<i>8f</i>	7177(3)	5436(4)	6049.7(19)	9.4(9)
B(4)	<i>8f</i>	9492(4)	4548(4)	8151(2)	12.0(10)
B(5)	<i>8f</i>	5635(4)	4487(4)	5696(2)	10.9(9)
B(6)	<i>8f</i>	5422(4)	6172(4)	6215(2)	10.6(9)
B(7)	<i>8f</i>	4728(4)	8040(4)	6339(2)	10.5(9)
B(8)	<i>8f</i>	4180(4)	6591(4)	6915.5(19)	11.4(10)
O(1)	<i>8f</i>	8752(2)	6713(3)	5014.5(13)	17.7(7)
O(2)	<i>8f</i>	9229(2)	5663(2)	5748.2(12)	12.3(6)
O(3)	<i>8f</i>	7496(2)	6015(3)	5558.4(12)	13.3(6)
O(4)	<i>8f</i>	8043(2)	5146(2)	6386.5(12)	10.7(6)
O(5)	<i>8f</i>	10231(2)	5210(2)	8363.4(12)	12.6(6)
O(6)	<i>8f</i>	9433(2)	3532(2)	8344.7(14)	17.4(7)
O(7)	<i>8f</i>	8835(2)	4914(3)	7768.2(13)	17.1(7)
O(8)	<i>8f</i>	6493(2)	6095(2)	6334.3(12)	13.6(6)
O(9)	<i>8f</i>	6641(2)	4463(2)	5852.6(13)	13.0(6)
O(10)	<i>8f</i>	5215(2)	3658(2)	5427.8(13)	14.9(7)
O(11)	<i>8f</i>	5088(2)	5369(2)	5814.5(13)	14.9(7)
O(12)	<i>8f</i>	5113(2)	7224(2)	5995.3(12)	11.2(6)
O(13)	<i>8f</i>	4900(2)	5964(2)	6709.1(12)	14.4(7)
O(14)	<i>8f</i>	4179(2)	8841(2)	6011.7(12)	10.1(6)
O(15)	<i>8f</i>	4021(2)	7594(2)	6707.3(13)	16.8(7)
O(16)	<i>8f</i>	3602(2)	6238(3)	7303.3(13)	15.9(7)

**Table S5.** Assignment of the absorption peaks observed in the IR spectra of (1), (2), (3) and (4).

<b>Mode description of (1)</b>	<b>Absorption peaks (cm<sup>-1</sup>)</b>
V <sub>as</sub> (BO <sub>3</sub> )	1348.00, 1220.72
V <sub>s</sub> (BO <sub>3</sub> )	1031.73, 966.16, 916.02
V <sub>s</sub> (BO <sub>4</sub> )	846.60, 813.81
δ <sub>out</sub> (BO <sub>3</sub> )	684.61, 611.33
δ(BO <sub>3</sub> , BO <sub>4</sub> )	566.97, 534.19
V <sub>c</sub> (OH)	3278.40

<b>Mode description of (2)</b>	<b>Absorption peaks (cm<sup>-1</sup>)</b>
V <sub>as</sub> (BO <sub>3</sub> )	1361.50, 1295.93, 1249.65
V <sub>as</sub> (BO <sub>4</sub> )	1143.58, 1116.58
V <sub>s</sub> (BO <sub>3</sub> )	993.16, 931.45, 896.74
V <sub>s</sub> (BO <sub>4</sub> )	829.31, 792.60, 725.11
δ <sub>out</sub> (BO <sub>3</sub> )	663.39, 603.61
δ(BO <sub>3</sub> , BO <sub>4</sub> )	541.90, 457.05

<b>Mode description of (3)</b>	<b>Absorption peaks (cm<sup>-1</sup>)</b>
V <sub>as</sub> (BO <sub>3</sub> )	1292.22, 1247.72
V <sub>s</sub> (BO <sub>3</sub> )	1052.95, 995.09, 892.88
V <sub>s</sub> (BO <sub>4</sub> )	829.24, 790.67, 723.18
δ <sub>out</sub> (BO <sub>3</sub> )	667.25
δ(BO <sub>3</sub> , BO <sub>4</sub> )	579.83, 534.19, 433.91
V <sub>c</sub> (OH)	3411.47

<b>Mode description of (4)</b>	<b>Absorption peaks (cm<sup>-1</sup>)</b>
V <sub>as</sub> (BO <sub>3</sub> )	1340.28, 1261.22, 1216.87
V <sub>as</sub> (BO <sub>4</sub> )	1062.59, 1018.23
V <sub>s</sub> (BO <sub>3</sub> )	875.23
V <sub>s</sub> (BO <sub>4</sub> )	821.53
δ <sub>out</sub> (BO <sub>3</sub> )	669.25, 632.53
δ(BO <sub>3</sub> , BO <sub>4</sub> )	555.40

**Table S6.** Reported inorganic stoichiometric Ag-borates with B–O framework.

No.	Compounds	Space group	B–O Units	Dimension	Ref.
1	$\text{Ag}_7\text{B}_9\text{O}_{16}(\text{OH})_2$	$C2/c$	$\text{B}_{15}\text{O}_{30}(\text{OH})_4$	1	This work (1)
2	$\text{Ag}_8\text{B}_8\text{O}_{15}\text{Cl}_2$	$C2/c$	$\text{B}_{18}\text{O}_{40}, \text{B}_{16}\text{O}_{36},$ $\text{B}_{12}\text{O}_{26}$	2	This work (2)
3	$\text{Ag}_8\text{B}_8\text{O}_{15}(\text{OH})\text{Br}$	$P \bar{1}$	$\text{B}_{18}\text{O}_{38}(\text{OH})_2, \text{B}_{16}\text{O}_{36},$ $\text{B}_{12}\text{O}_{26}$	2	This work (3)
4	$\text{Ag}_{11}\text{B}_8\text{O}_{16}\text{I}_3$	$C2/c$	$\text{B}_9\text{O}_{20}$	1	This work (4)
5	$\text{AgBO}_2(\text{I})$	$Pbca$	$\text{B}_3\text{O}_8$	1	1
6	$\text{AgBO}_2(\text{II})$	$Cc$	$\text{B}_3\text{O}_8$	1	2
7	$\text{Ag}_2\text{O}(\text{B}_2\text{O}_3)_4$	$P2_1/c$	$\text{B}_5\text{O}_{10}$	3	3
8	$\text{Ag}_3\text{BO}_3(\text{I})$	$R32$	$\text{BO}_3$	0	4
9	$\text{Ag}_3\text{BO}_3(\text{II})$	$R \bar{3}c$	$\text{BO}_3$	0	5
10	$\text{Ag}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6] \cdot 3\text{H}_2\text{O}$	$P2_1/c$	$\text{B}_{12}\text{O}_{18}(\text{OH})_6$	0	6
11	$\beta\text{-Ag}_2\text{B}_8\text{O}_{13}$	$P2_1/c$	$\text{BO}_3$	0	7
12	$\text{AgB}_3\text{O}_5$	$Pna2_1$	$\text{BO}_3, \text{BO}_4$	3	8
13	$\text{Ag}_3\text{B}_5\text{O}_9$	$P2_12_12_1$	$\text{BO}_3, \text{BO}_4$	3	9
14	$\text{Ag}_2\text{B}_4\text{O}_7$	$P2_1/c$	$\text{BO}_3, \text{BO}_4$	3	10
15	$\alpha\text{-Ag}_2\text{B}_8\text{O}_{13}$	$P2_1/c$	$\text{BO}_3$	0	11
16	$\beta\text{-Ag}_2\text{B}_8\text{O}_{13}$	$P2_1/c$	$\text{B}_8\text{O}_{13}$	0	12
17	$\text{Ag}_{16}\text{B}_4\text{O}_{10}$	$I4_1/a$	$\text{B}_4\text{O}_{10}$	1	13
18	$\text{Ag}_3\text{B}_6\text{O}_{10}\text{I}$	$Pnma$	$\text{B}_6\text{O}_{10}$	3	14
19	$\text{Ag}_4\text{B}_7\text{O}_{12}\text{Cl}$	$P \bar{1}$	$\text{B}_4\text{O}_9, \text{B}_3\text{O}_7$	2	15
20	$\text{Ag}_4\text{B}_7\text{O}_{12}\text{Br}$	$P \bar{1}$	$\text{B}_4\text{O}_9, \text{B}_3\text{O}_7$	2	15
21	$\text{Ag}_4\text{B}_7\text{O}_{12}\text{I}$	$P \bar{1}$	$\text{B}_4\text{O}_9, \text{B}_3\text{O}_7$	2	15
22	$\text{Ag}_4\text{B}_4\text{O}_7\text{Br}_2$	$P6_122$	$\text{B}_3\text{O}_8$	3	16
23	$\text{Ag}_4\text{B}_4\text{O}_7\text{I}_2$	$P6_122$	$\text{B}_3\text{O}_8$	3	16
24	$\text{Ag}_3\text{B}_6\text{O}_{10}\text{Br}$	$Pnm2_1$	$\text{B}_6\text{O}_{10}$	3	17
25	$\text{Ag}_2\text{Cs}[\text{B}_{15}\text{O}_{24}]$	$P2_12_12$	$\text{B}_{15}\text{O}_{24}$	3	18
26	$\text{AgSr}(\text{B}_7\text{O}_{12})$	$C2/c$	$\text{B}_7\text{O}_{12}$	2	19
27	$\text{Ag}_2\text{B}_{10}\text{O}_{14}(\text{OH})_4 \cdot \text{H}_2\text{O}$	$P \bar{1}$	$\text{B}_5\text{O}_8(\text{OH})_2$	2	20
28	$\text{Ag}_2\text{B}_5\text{O}_8(\text{OH}) \cdot \text{H}_2\text{O}$	$P2_1/c$	$\text{B}_5\text{O}_{10}(\text{OH})$	1	20

Figure S1. Rietveld refinement for the powder X-ray diffraction pattern of (1).

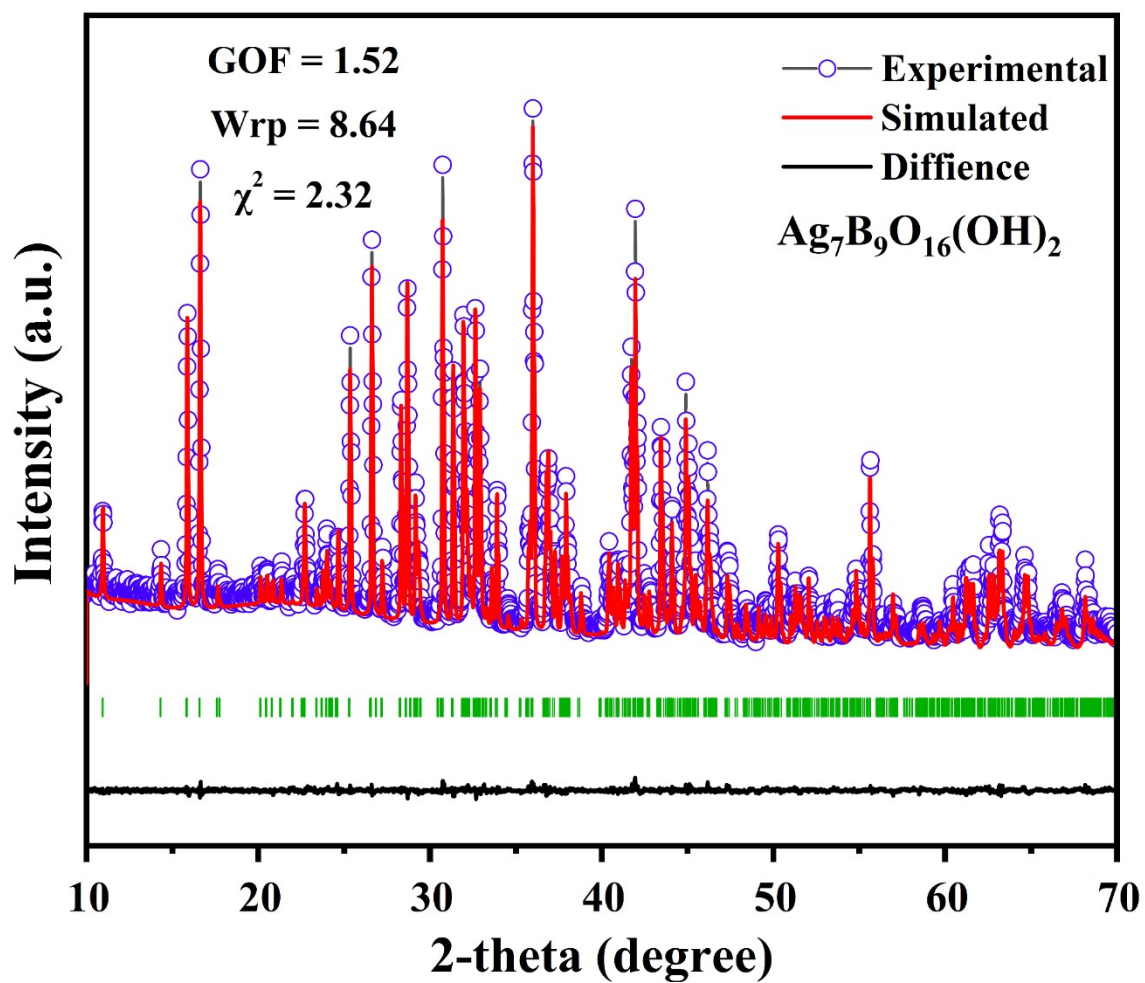


Figure S2. Rietveld refinement for the powder X-ray diffraction pattern of (2).

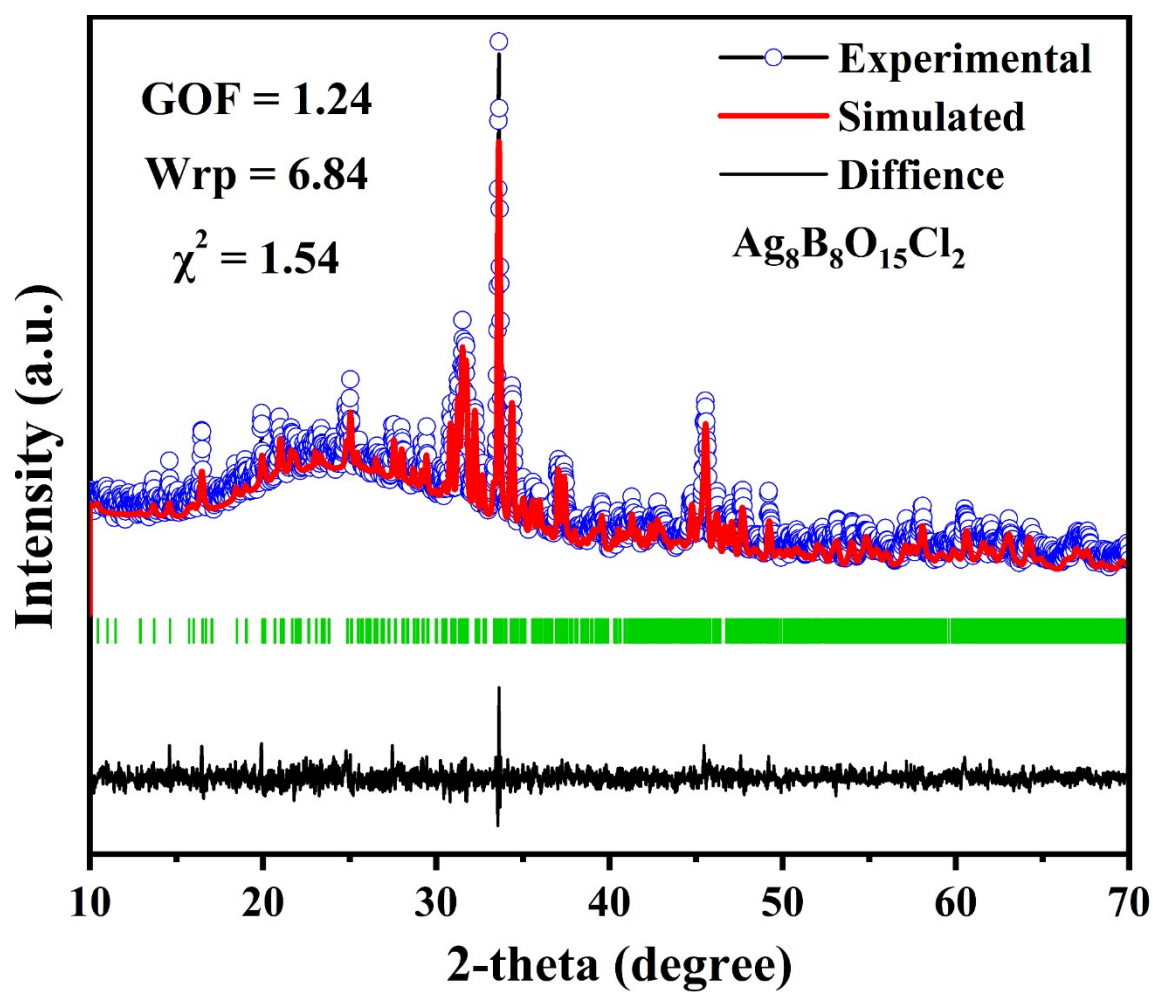


Figure S3. Rietveld refinement for the powder X-ray diffraction pattern of (3).

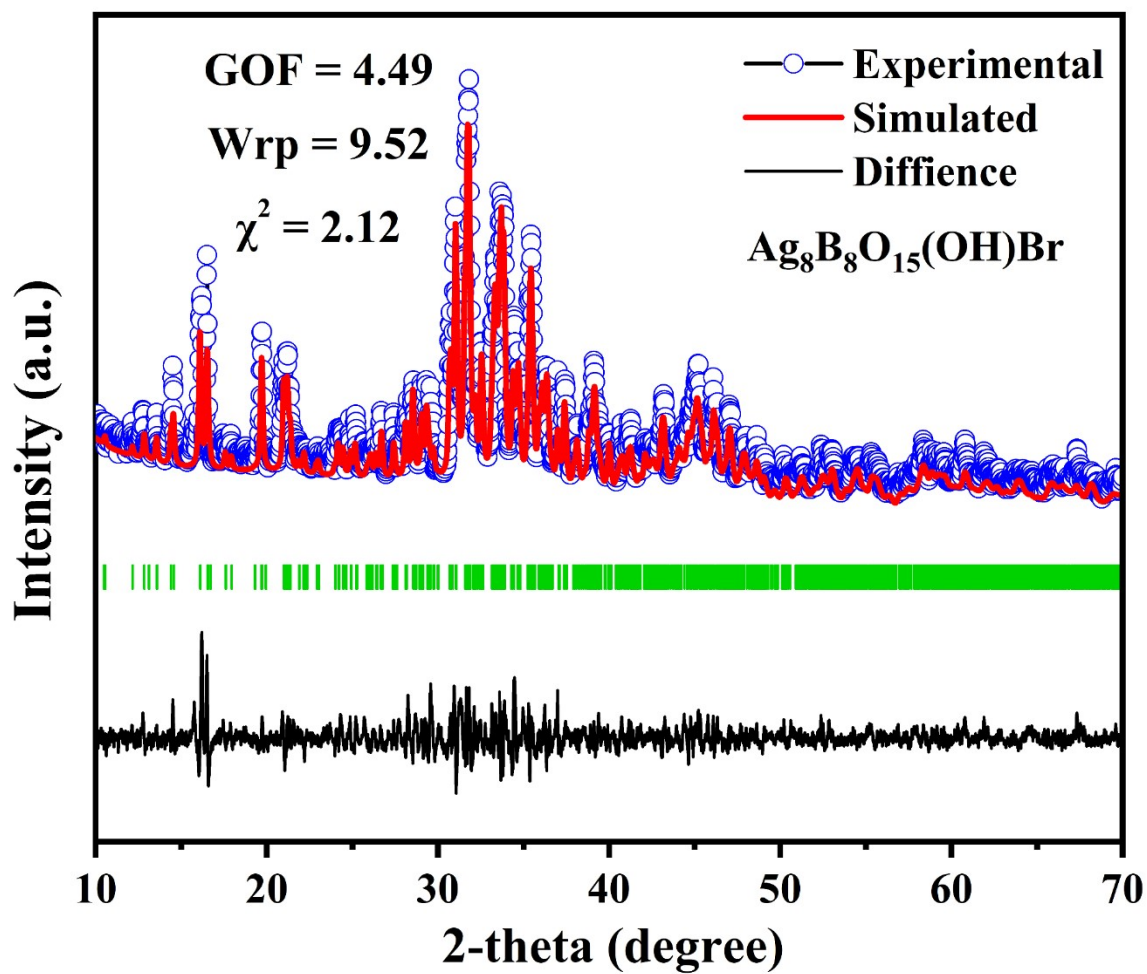


Figure S4. Rietveld refinement for the powder X-ray diffraction pattern of (4).

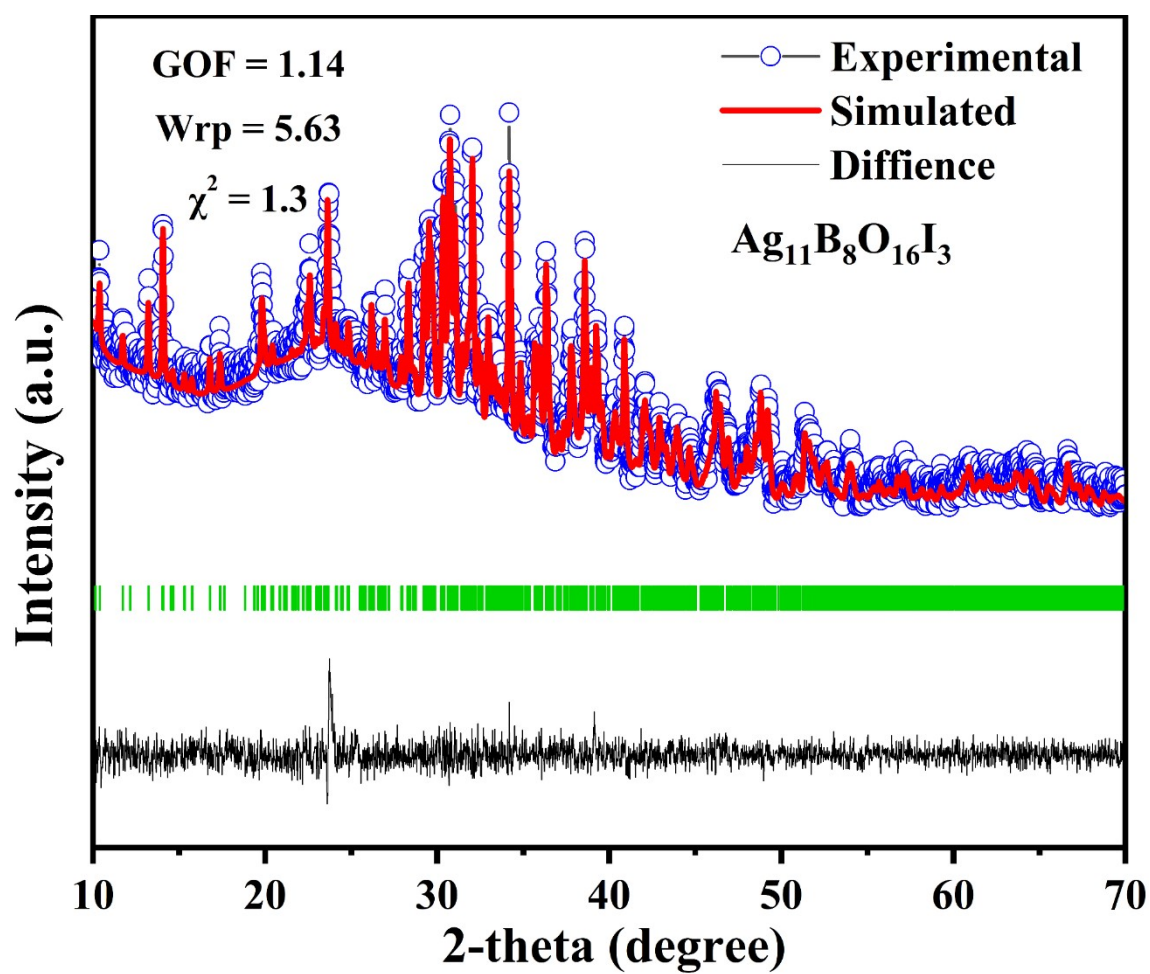
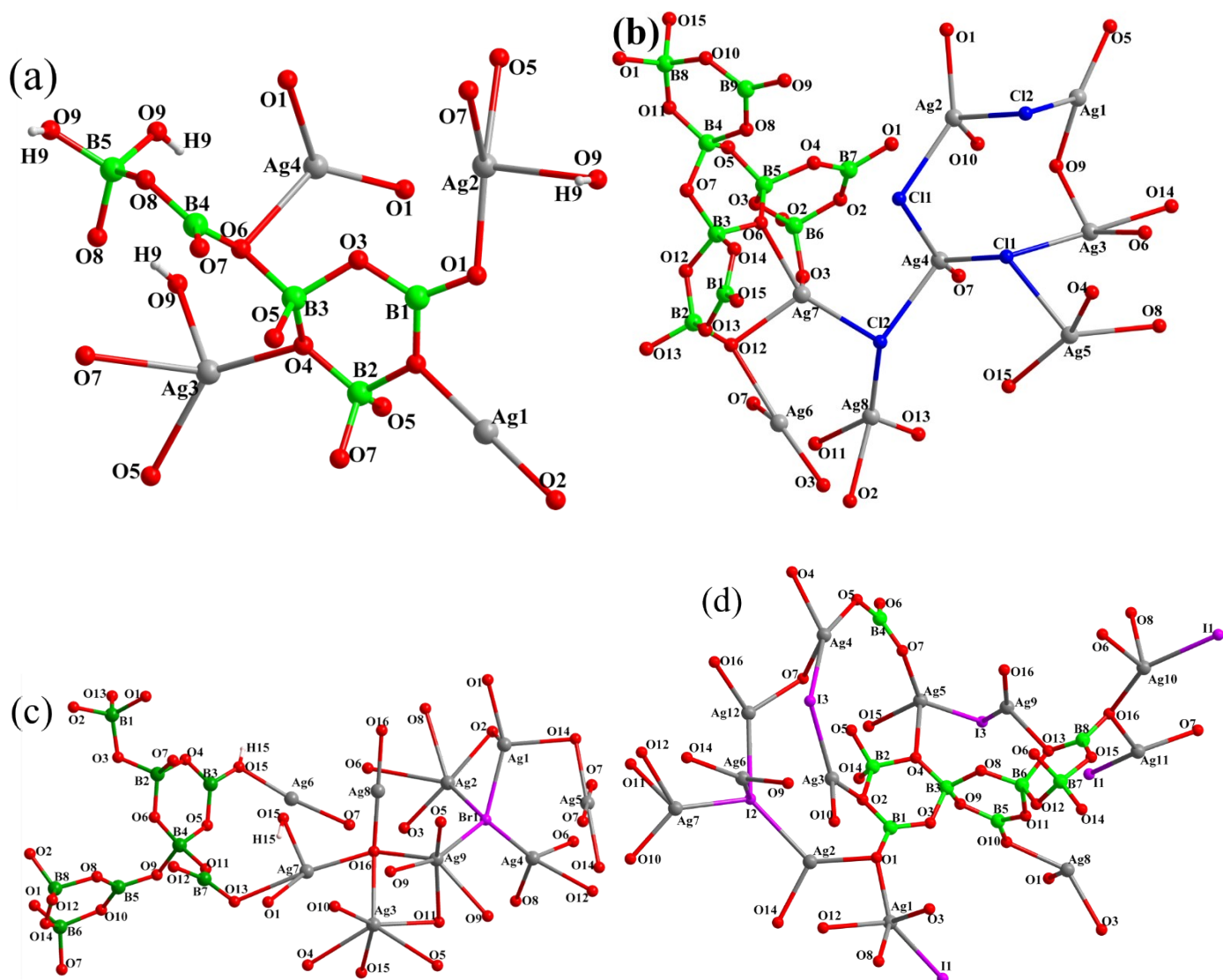
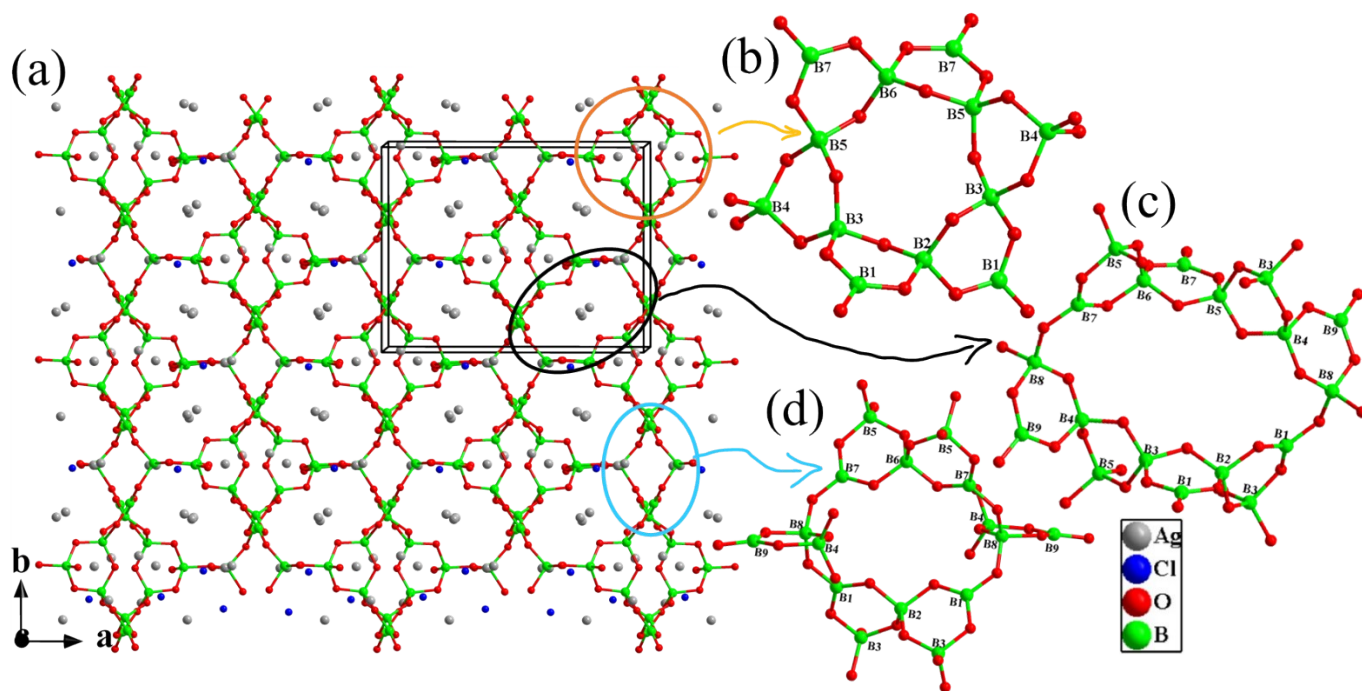


Figure S5. Asymmetric units of (1) to (4), and the coordination environments of atoms.

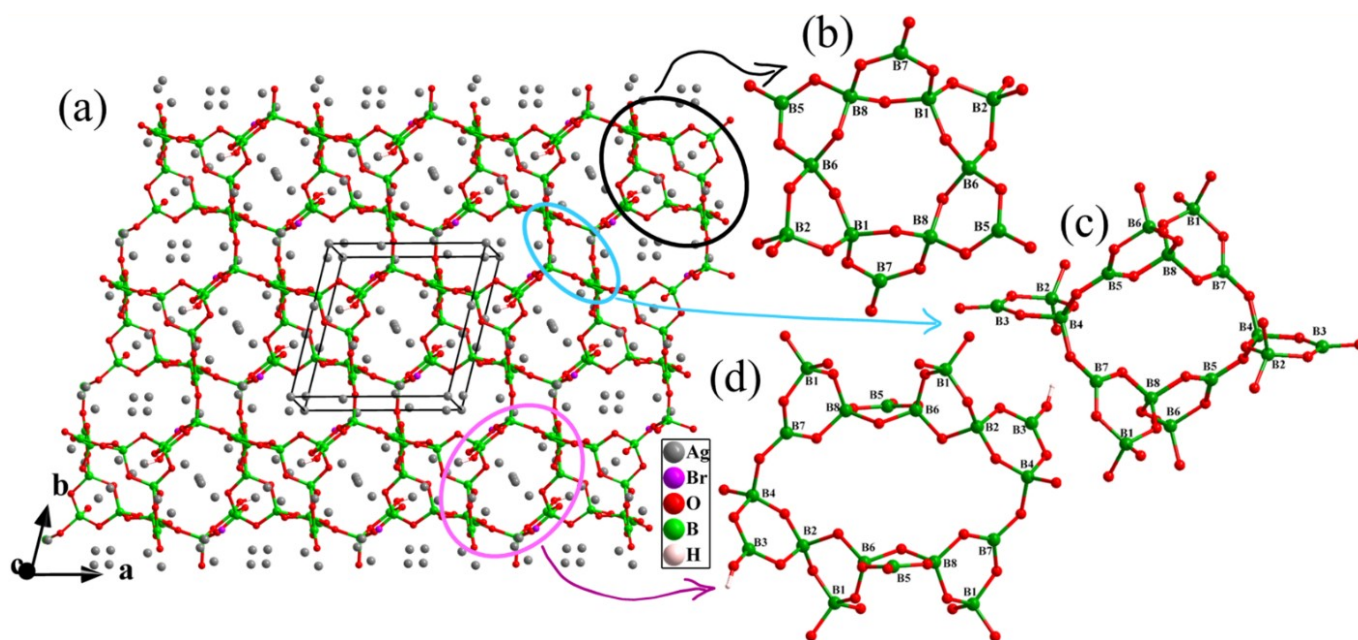




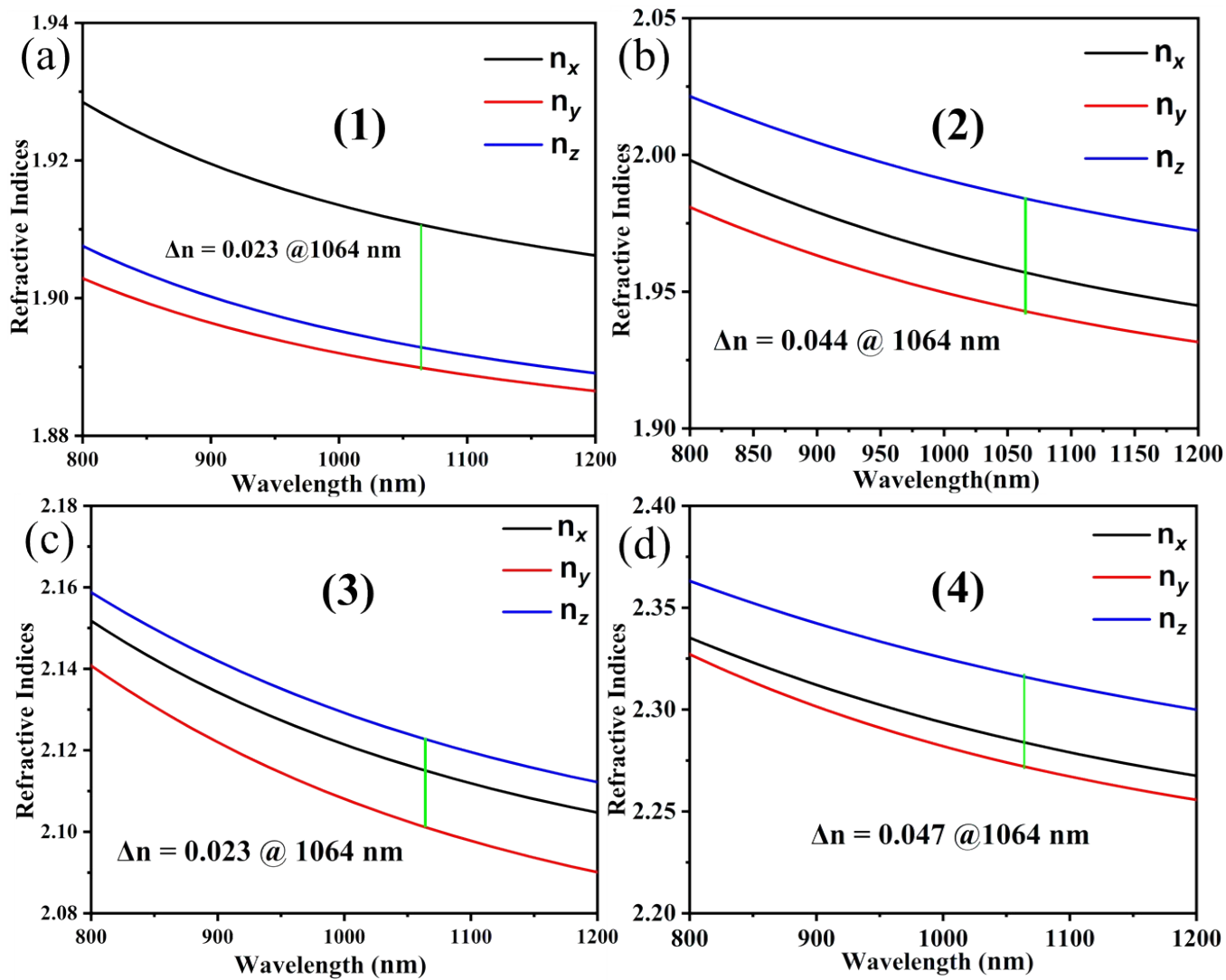
**Figure S6.** (a) 2D structure of **(2)** along the *ab* plane, (b) 12-MR channel, (c) 20-MR channel, and (d) 16-MR channel.



**Figure S7.** (a) 2D structure of **(3)** along the *ab* plane, (b) 12-MR channel, (c) 20-MR channel, and (d) 16-MR channel.



**Figure S8.** The calculated refractive indices of (1), (2), (3) and (4).



## References:

- 1 Brachtel, G. Jansen, M. Silber(I)-metaborat,  $\text{AgBO}_2$ , *Z. anorg. allg. Chem.* **1981**, 478, 13—19.
- 2 Cerqueira, T. F. T. Lin, S. Amsler, M. Goedecker, S. Botti, S. Identification of Novel Cu, Ag, and Au Ternary Oxides from Global Structural Prediction, *Chem. Mater.* **2015**, 27, 4562—4573.
- 3 Krogh-Moe, J. The crystal structure of silver tetraborate  $\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ , *Acta Cryst.* **1965**, 18, 77—81.
- 4 Jansen, M. Scheld, W. Silber(I)-orthoborat, *Z. anorg. allg. Chem.* **1981**, 477, 85—89.
- 5 Jansen, M. Brachtel, G.  $\text{Ag}_3\text{BO}_3$ -II, eine neue Form von Silber(I)-orthoborat, *Z. anorg. allg. Chem.* **1982**, 489, 42—46.
- 6 Skakibaie-Moghadam, M. Heller, G. Timper, U. Die Kristallstruktur von  $\text{Ag}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\cdot 3\text{H}_2\text{O}$ , einem neuen Dodekaborat, *Z. Krist. Cryst. Mater.* **1990**, 190, 85—96.
- 7 Penin, N. Touboul, M. Nowogrocki, G. Crystal structure of the second form of silver octoborate  $\beta\text{-Ag}_2\text{B}_8\text{O}_{13}$ , *Solid State Sci.* **2003**, 5, 559—564.
- 8 Sohr, G. Falkowski, V. Schauperl, M. L. Liedl, K. R. Huppertz, H. Structure, Thermal Behavior, and Vibrational Spectroscopy of the Silver Borate  $\text{AgB}_3\text{O}_5$ , *Eur. J. Inorg. Chem.* **2015**, 3, 527—533.
- 9 Sohr, G. Falkowski, V. Huppertz, H. The new silver borate  $\text{Ag}_3\text{B}_5\text{O}_9$ , *J. Solid State Chem.* **2015**, 225, 114—119.
- 10 Ziegler, R. Purtscher, F. R. S. Hofer, T. S. Huppertz, H. High-pressure Synthesis, Structure, IR Spectroscopy, and Theoretical Calculations of the New Silver Tetraborate  $\text{Ag}_2\text{B}_4\text{O}_7$  with a Unique Crystal Structure, *Eur. J. Inorg. Chem.* **2023**, e202300120 (1 of 9).
- 11 Krogh-Moe, J. The crystal structure of silver tetraborate  $\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ , *Acta Cryst.* **1965**, 18, 77—81.
- 12 Penin, N. Touboul, M. Nowogrocki, G. Crystal structure of the second form of silver octoborate  $\beta\text{-Ag}_2\text{B}_8\text{O}_{13}$ , *Solid State Sci.* **2003**, 5, 559—564.
- 13 Vegas, A. Jenkins, H. D. B. A re-interpretation of the structure of the silver borate,  $\text{Ag}_{16}\text{B}_4\text{O}_{10}$ , in the light of the extended Zintl–Klemm concept, *Acta Cryst. B*, **2020**. B76, 865—874.
- 14 Du, Z. P. Zhou, Y. Zhao. S. G. Synthesis, Crystal Structure and Birefringence Properties of Silver Cluster Compound  $\text{Ag}_3\text{B}_6\text{O}_{10}\text{I}$ . *Chin. J. of Appl. Chem.* **2023**, 40, 229—235.
- 15 Volkov, S. N. Charkin, D. O. Firsova, V. A. Manelis, L. S. Banaru, A. M. Povolotskiy, A. V. Yuhkno, V. A. Arsent'ev, M. Y. Savchenko, Y. Ugolkov, V. L. Krzhizhanovskaya, M. G. Bubnova, R. S. Aksenov, S. M.  $\text{Ag}_4\text{B}_7\text{O}_{12}\text{X}$  (X = Cl, Br, I) Heptaborate Family: Comprehensive Crystal Chemistry, Thermal Stability Trends, Topology, and Vibrational Anharmonicity, *Inorg. Chem.* **2023**, 62, 30—34.
- 16 Volkov, S. N. Charkin, D. O. Arsent'ev, Y. M. Povolotskiy, A. V. Stefanovich, S. Y. Ugolkov, V. L. Krzhizhanovskaya M. G. Shilovskikh, V. V. Bubnova, R. S. Bridging the Salt-Inclusion and Open-Framework Structures: The Case of Acentric  $\text{Ag}_4\text{B}_4\text{O}_7\text{X}_2$  (X = Br, I) Borate Halides, *Inorg. Chem.* **2020**, 59, 2655—2658.
- 17 Volkov, S. N. Charkin, D. O. Kireev, V. E. Ugolkov, V. L. Krzhizhanovskaya, M. G. Tsvetov, N. S. Vaitieva, Y. A. Aksenov, S. M. Bubnova, R. S. A novel contribution to the  $M_3\text{B}_6\text{O}_{10}\text{X}$  hexaborate family: The new silver compound  $\text{Ag}_3\text{B}_6\text{O}_{10}\text{Br}$  and thermal behavior of  $\text{Ag}_3\text{B}_6\text{O}_{10}(\text{NO}_3)$  and  $\text{Na}_3\text{B}_6\text{O}_{10}\text{I}$ , *Solid State Sci.* **2023**, 145, 107311—107317.
- 18 Wiesch, A. Bluhm, K.  $\text{Ag}_2\text{Cs}[\text{B}_{15}\text{O}_{24}]$ : An Anhydrous Quaternary Silver(I)-Borate with a New Helical Borate Anion. *Z. Naturforsch., B: J. Chem. Sci.* **1998**, 53, 157—160.
- 19 Wiesch, A. Bluhm, K.  $\text{AgSr}(\text{B}_7\text{O}_{12})$ : Das erste wasserfreie quaternäre Silber(I)-Borat mit vierfach koordiniertem Silberion und einem neuartigen Boratanion, *Z. Naturforschung B.* **1997**, 52b, 227—230.
- 20 Volkov, S. N. Aksenov, S. M. Charkin, D. O. Banaru, A. M. Banaru, D. A. Vaitieva, Y. A. Krzhizhanovskaya, M. G. Yamnova, N. A. Kireev, V. E. Gosteva, A. N. Tsvetov, N. S. Savchenko, Y. E. Bubnova, R. S. Preparation of novel silver borates by soft hydrothermal synthesis in sealed tubes: New representatives of larderellite and veatchite families, *Solid State Sci.* **2024**, 148, 107414—107425.