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# Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub>: A new bismuth oxo-selenite bromide

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stability were studied. The new compound is stable up to 400 °C.

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## ARTICLE INFO

# ABSTRACT

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# 1. Introduction

The family of complex selenite halides attracts growing attention in the last decades due to the specifics of their crystal chemistry governed by stereochemical effect of Se(IV) lone electron pair [1–4]. These pairs are considered to be similar in size to oxygen anions [5] and do not participate in the chemical bonding, usually segregating in the channels or in inter-layer gaps. The presence of the halogen ions alongside with a lone-pair element enhances the probability of formation of open-framework or layered structures [6–8]. Not only the polyhedrons with asymmetric coordination, but also the lone-pair atoms themselves may be the reason for noncentrosymmetric structures which lead to new potential piezoelectric and non-linear optic materials.

The rare-earth (REE) complex selenite halides are probably the most numerous and well-studies part of the family under discussion. The most common compositions are  $M_3O_2(SeO_3)_2Cl$  (M=Tb, Dy, Er),  $M_4O_3(SeO_3)_2Cl_2$  (M=Er, Yb),  $Tb_5O_4(SeO_3)_2Cl_3$  and  $Gd_5O_4(-SeO_3)_2Br_3$ ,  $M_9O_8(SeO_3)_4Cl_3$  (M=Pr, Nd, Sm, Gd),  $M_9O_8(SeO_3)_4Br_3$  (M=La, Pr) [4,9,10], and  $Nd_7O_5(SeO_3)_4Cl_3$  [11]. The simplest composition MSeO\_3Cl is described for M=Sm-Lu [12]. Compounds with similar compositions have also been observed for trivalent bismuth but their structures may be different. For instance, the structures of both BiSeO\_3Cl polymorphs [1,13] differ

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from those of MSeO<sub>3</sub>Cl (M=Ln) while all Cu<sub>3</sub>M(SeO<sub>3</sub>)<sub>2</sub>O<sub>2</sub>X (X=Cl, Br, I) compounds (M=Bi; M=all Ln in case of X=Cl) adopt the same francisite structure [2,14]. However, the bismuth selenite-halides are relatively scarce. Besides BiSeO<sub>3</sub>Cl, only two selenite-bromides are hitherto known: BiSeO<sub>3</sub>Br and Bi<sub>10.67</sub>(SeO<sub>3</sub>)<sub>12</sub>Br<sub>8</sub>, the former observed upon investigation of the BiOBr–SeO<sub>2</sub> system

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A new bismuth oxo-selenite bromide Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub> was synthesized and structurally characterized.

The crystal structure belongs to the triclinic system (space group  $P\bar{1}$ , Z=2, a=7.1253(7)Å,

b=10.972(1) Å, c=12.117(1) Å,  $\alpha=67.765(7)^{\circ}$ ,  $\beta=82.188(8)^{\circ}$ ,  $\gamma=78.445(7)^{\circ}$ ) and is unrelated to those

of other known oxo-selenite halides. It can be considered as an open framework composed of BiO<sub>x</sub> or

 $BiO_{\nu}Br_{z}$  polyhedrons forming channels running along [100] direction which contain the selenium

atoms in pyramidal shape oxygen coordination (SeO<sub>3</sub>E). The spectroscopic properties and thermal

from BiOBr to  $SeO_2$  in a temperature gradient [3]. For a long time, our group had performed a systematical search and study of selenite halogenides in order to establish the correlation between their chemical composition and crystal structures. In the present work, we report on the synthesis, crystal structure, thermal and spectroscopic properties of a yet new bismuth oxo-selenite bromide,  $Bi_6(SeO_3)_3O_5Br_2$ .

[15], and the latter synthesized by chemical transport reaction

## 2. Experimental

# 2.1. Synthesis

Our original attempts were aimed at the preparation of  $Bi_8(SeO_3)_4O_8X_3$  (*X*=Cl, Br) by analogy to similar compounds of early rare-earths [4,9]. Chemically pure  $Bi_2O_3$ , BiOX (*X*=Cl, Br) were used as starting materials as received.  $SeO_2$  was obtained by dehydratation of pure selenous acid under vacuum at 70–80 °C followed by sublimation of product in a flow of dry air/NO<sub>2</sub> mixture. The mixtures of starting materials (~0.5 g total weight) were weighted in an argon-filled glovebox in the desired ratios, vacuum-sealed in quartz tubes, preheated at 300 °C for 24 h and

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then annealed at 475 °C for 60 h. Small crystals were found in the sample aimed at Bi<sub>9</sub>(SeO<sub>3</sub>)<sub>4</sub>O<sub>8</sub>Br<sub>3</sub> composition. Powder X-ray diffraction (XRD) analysis was performed on STOE STADI/P instrument (Cu $K_{\alpha 1}$  radiation, transmission geometry, linear PSD detector). The XRD patterns of chloride and bromide samples were different from each other. In the former, only BiOCl could be identified; all other lines belong to yet unknown compound(s). Further attempts identify them were not successful. In the bromide sample, only Bi<sub>2</sub>O<sub>3</sub> could be identified; the unidentified reflexions in the Cl and Br samples are not similar to each other or those for known rare-earth compounds [4.9]. A small crystal taken from the 'Bi<sub>9</sub>(SeO<sub>3</sub>)<sub>4</sub>O<sub>8</sub>Br<sub>3</sub>' sample was selected for structure investigation which revealed a different composition of the novel compound, Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub>. The composition was confirmed by a successful synthesis from a mixture of 2BiOBr, 2Bi<sub>2</sub>O<sub>3</sub>, and 3SeO<sub>2</sub> at 475 °C for 60 h. The observed XRD pattern agreed well with that simulated from single crystal data. All attempts to prepare analogous chloride at different synthesis temperatures and annealing times were unsuccessful.

# 2.2. Crystal structure determination

A suitable single crystal was mounted on an IPDS II (STOE) goniometer head. The X-ray data were collected at room temperature and indexed based on a triclinic unit cell parameters with a=7.1253(7) Å, b=10.972(1) Å, c=12.117(1) Å,  $\alpha=67.765(7)^{\circ}$ ,  $\beta=82.188(8)^{\circ}$ , and  $\gamma=78.445(7)^{\circ}$ . The intensities of reflections were integrated using the X-area STOE software. Numerical absorption correction was performed with the programs X-red and X-shape implemented in X-Area package. The structure was solved in the centrosymmetric space group  $P\overline{1}$  (No 2) by Direct methods (SHELXS 97) [16] and refined by full matrix least squares against  $F^2$  (SHELXL 97) [16]. The final anisotropic refinement led to R1=0.066, and wR2=0.160 and composition Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub>. The data collection and structure refinement parameters are listed in Table 1.

Further details of the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany, on quoting the depository number CSD-423997.

 Table 1

 Crystal data and structure refinement for Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub>.

Space group	<i>P</i> 1̄ (N 2)			
Cell parameters				
A, Å	7.1253(7)			
B, Å	10.972(1)			
c, Å	12.117(2)			
α, deg.	67.765(7)			
β, deg.	82.188(8)			
γ, deg.	78.445(7)			
V, Å <sup>3</sup>	858.2(1)			
Ζ	2			
Density (calc.), g cm <sup>-3</sup>	7.263			
Radiation, λ, Å	0.71073			
μ, mm <sup>-1</sup>	72.466			
Data collection range, deg.	1.82 to 29.22			
Reflections collected	9796			
Independent reflections	4587 $[R_{(int)}=0.1426]$			
Parameters refined	227			
$R_1$ , w $R_2$ ( $F_0 > 4\sigma F_0$ )	0.0669, 0.1606			
$R_1$ , w $R_2$ (all data)	0.1141, 0.1926			
Largest diff. peak and hole, e/Å <sup>3</sup>	4.614 and -4.371			
$G-O-f.$ on $F^2$	0.972			
ICSD number	423997			

#### 2.3. Thermal and IR characterization

The thermal behavior of  $Bi_6(SeO_3)_3O_5Br_2$  was studied using a NETZSCH STA 409 PC instrument in air and argon atmosphere. The samples (ca. 10 mg) were heated from room temperature to 1000 °C with a rate of 10 °C/min. The results are presented in the supplement (Figs. S1 and S2).

The thermal decomposition process of Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub> is not sensitive to atmosphere, so oxidation processes may be ruled out. Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub> is stable up to 400 °C There are at least two plateaus in the 400–900 °C range with loss of about 4% and 19–20% sample mass.

The IR transmission spectrum collected on a PerkinElmer FT-IR spectrometer Spectrum One in 450–4000 cm<sup>-1</sup> range is given in supplement Fig. S3. The examined sample of  $Bi_6(SeO_3)_3O_5Br_2$  was pressed into thick pellet in KBr matrix (Aldrich, for FTIR analysis) with sample content about 0.2–0.5 mass%. In the range 1700–4000 cm<sup>-1</sup> the sample is transparent. The range 450–1800 cm<sup>-1</sup> is presented in the supplement (Fig. S3 in supplement).

## 3. Results

According to the crystal structure determination, the title oxoselenite bromide of bismuth possesses composition that has not been known among oxo-selenite halides of REEs. The compound is stable in air up to 400 °C and decomposes at higher temperatures. The first plateau on the TG curve in 400–900 °C range is in good agreement with the loss of first molecule of SeO<sub>2</sub> (which should correspond to the mass loss of 6%). The loss of three SeO<sub>2</sub> molecules corresponds to 17.7% loss. Therefore, the second plateau at 800 °C corresponds to a mixture of bismuth oxide or oxybromides. The small disagreement with suggested model of decomposition and observed values of mass loss may be caused by a complex decomposition mechanism wherein several processes may run simultaneously.

 $Bi_6(SeO_3)_3O_5Br_2$  crystallizes in the centrosymmetric space group  $P\overline{1}$  (Table 1). There are six bismuth, two bromine, three selenium and 14 oxygen atoms per one unit cell (Fig. 1).

The bismuth atoms reside in irregular coordination polyhedrons comprised of oxygen and bromine atoms, or oxygen atoms only (Table 2). The bond valence sum (BVS) calculations [17,18] using constants from [19] lead to Bi(1)O<sub>6</sub>, Bi(2)O<sub>7</sub>, Bi(3)O<sub>8</sub>, Bi(4)O<sub>8</sub>Br, Bi(5)O<sub>5</sub>Br<sub>2</sub> and Bi(6)O<sub>6</sub>Br six-to-nine-vertex polyhedrons (Table 2). The BVS for Bi(5) atom somewhat exceeds 3 if two bromide ions are included in consideration. However, the difference in bond lengths for Bi(5)–Br(1) and Bi(5)–Br(2) is negligible (Table 24). Hence, we suggest both bromide ions should be considered in the Bi(5) environment. A general feature of all Bi polyhedrons is their asymmetry, which manifests the effect of the stereochemically active lone E-pair of the Bi<sup>3+</sup>.

All three selenium atoms exhibit pyramidal oxygen coordination usual for selenite groups with lone electron pair. The Se–O distances in the SeO<sub>3</sub> E groups vary from 1.66 to 1.72 Å. The BVS value equals 4.09 for Se1, taking into account O11, O10 and O6, 4.31 for Se2 with O12, O13 and O14, and 4.20 for Se3 with O1, O8 and O9.

The Bi(4)O<sub>8</sub>Br polyhedrons are connected via O(6)–O(6) and O(3)–O(3) edges in zigzag chains propagating along [1 0 0] direction (Fig. S4 in supplement). The seven-vertex Bi(2)O<sub>7</sub> and Bi(5)O<sub>5</sub>Br<sub>2</sub> polyhedrons are connected to zigzag Bi(4)O<sub>8</sub>Br chains by shared O(10)–O(3) and O(3)–O(11) edges or O(3)–O(8)–Br plane and O(3)–O(6) and O(6)–O(9) edges, respectively. The Bi(1)O<sub>6</sub> and Bi(3)O<sub>8</sub> polyhedrons are linked together into Bi(4)O<sub>8</sub>Br, Bi(2)O<sub>7</sub> and Bi(5)O<sub>5</sub>Br<sub>2</sub> columns in layers (Fig. S5 in supplement).



Fig. 1. The view on unite cell of Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub>.

Table 2Bond lengths [Á] for  $Bi_6(SeO_3)_3O_5Br_2$ .

Bond	Length	Bond	Length
Bi(1)-O(7)	2.15(2)	Bi(4)-O(11)	2.61(2)
Bi(1)-O(5)	2.17(2)	Bi(4)-O(6)	2.90(2)
Bi(1)-O(5)	2.29(2)	Bi(4)-O(8)	2.95(2)
Bi(1)-O(2)	2.36(2)	Bi(4)-O(9)	2.99(2)
Bi(1)-O(1)	2.67(2)	Bi(4)-Br(2)	3.011(3)
Bi(1)-O(9)	2.83(2)	Bi(5)-O(2)	2.173(17)
Bi(1)-O(10)	3.02(3)	Bi(5)-O(3)	2.23(2)
Bi(1)-O(4)	3.15(2)	Bi(5)-O(8)	2.42(2)
Bi(2)-O(4)	2.19(2)	Bi(5)-O(9)	2.44(2)
Bi(2)-O(2)	2.21(2)	Bi(5)-O(6)	2.48(2)
Bi(2)-O(7)	2.213(16)	Bi(5)-Br(1)	3.211(4)
Bi(2)-O(12)	2.66(2)	Bi(5)-Br(2)	3.218(3)
Bi(2)-O(11)	2.70(2)	Bi(6)-O(7)	2.142(16)
Bi(2)-O(10)	2.74(2)	Bi(6)-O(13)	2.26(2)
Bi(2)-O(3)	2.80(2)	Bi(6)-O(14)	2.35(3)
Bi(3)-O(5)	2.18(2)	Bi(6)-O(1)	2.49(2)
Bi(3)-O(4)	2.204(19)	Bi(6)-O(12)	2.50(2)
Bi(3)-O(4)	2.26(2)	Bi(6)-O(5)	2.92(3)
Bi(3)-O(2)	2.56(2)	Bi(6)-Br(2)	3.210(3)
Bi(3)-O(1)	2.81(2)	Se(1)-O(11)	1.66(2)
Bi(3)-O(14)	2.83(3)	Se(1)-O(10)	1.71(2)
Bi(3)-O(12)	3.00(2)	Se(1)-O(6)	1.72(2)
Bi(3)-O(8)	3.06(3)	Se(2)-O(13)	1.67(2)
Bi(4)-O(3)	2.21(2)	Se(2)-O(14)	1.67(3)
Bi(4)-O(3)	2.25(2)	Se(2)-O(12)	1.69(2)
Bi(4)-O(6)	2.47(2)	Se(3)-O(8)	1.66(2)
Bi(4)-O(10)	2.52(2)	Se(3)-O(9)	1.68(2)
		Se(3)-O(1)	1.72(2)

 $Bi(6)O_6Br$  polyhedrons share common O(7)-O(12) edges with  $Bi(2)O_7$  and O(1) vertex with  $Bi(1)O_6$  from one layer and Br(2) vertex with another  $Bi(6)O_6Br$  from the other layer forming an open-framework structure (Fig. 2).

In the bismuth-oxygen framework, there are channels running along [1 0 0] direction of the structure. In the corners of the channels, the selenium atoms are situated. All of them are bonded to oxygen atoms from the Bi polyhedrons (Fig. 2). The lone electron pairs of Se(IV) are thus located inside the channels. Some of the oxygen atoms are bound only to Bi atoms which permits to consider the new compound  $Bi_6(SeO_3)_3O_5Br_2$  as a member of oxoselenite halide family.

In general, the crystal structure of  $Bi_6(SeO_3)_3O_5Br_2$  may be described as a 3D framework composed of bismuth-oxygenbromine polyhedrons additionally decorated by  $SeO_3^{2-}$  groups situated close to framework voids.

Besides the new compound, there are two known compositions of bismuth selenite halogenides,  $BiSeO_3X$  (X=Cl, Br) [1,13,15] and  $Bi_8(SeO_3)_9Br_6$  [3]. The list of related REE compounds longer. The known compositions of Bi and/or REE selenite halides are schematically represented in Fig. 3 [1,3,4,9–13,15,20–23]. As yet,  $Bi_6(SeO_3)_3O_5Br_2$  has no analogues among REEs derivatives and can be considered as a new structure type.

The MSeO<sub>3</sub>X family is the most numerous among those given in Fig. 3. The chloride family consists of the bismuth compound [1,13] and analogs formed by almost all REEs [12]. Other compositions (Fig. 3) include only several or even one REE compounds.

The compositions  $M_4(SeO_3)_2O_3Cl_2$  (M=Er, Yb [4,9]),  $M_9(SeO_3)_4O_8X_3$  (M=Pr, Nd, Sm, Gd, X=Cl; M=La, Pr, X=Br [4,9]) and Nd<sub>7</sub>(SeO<sub>3</sub>)\_4O<sub>5</sub>Cl<sub>3</sub> [11] are situated quite close to the Bi<sub>6</sub>(SeO<sub>3</sub>)\_3O<sub>5</sub>Br<sub>2</sub> composition in the M<sub>2</sub>O<sub>3</sub>-MCl<sub>3</sub>-SeO<sub>2</sub> 'triangle' (Fig. 3). We can now compare the structure of Bi<sub>6</sub>(SeO<sub>3</sub>)\_3O<sub>5</sub>Br<sub>2</sub> with some others. The cell constants for related compounds are presented in Table 3.

Similarly to  $Bi_6(SeO_3)_3O_5Br_2$ , the compositionally closest compounds crystallize in triclinic system (space group  $P\overline{1}$ ) and have similar cell constants (Table 3). The common structural feature for these compounds is the pure-oxygen and mixed oxygen-halogen environment of REEs ions, as also observed for  $Bi_6(SeO_3)_3O_5Br_2$ . The most comon environment among these structures is a distorted cube or a square antiprism with different ratio of oxygen and halogen vertexes. In addition, seven-and nine-vertex polyhedrons may exist in the structures. In Table 4 we compare similar polyhedrons in bismuth and REE compounds. The REE polyhedrons are generally less distorted compared to the bismuth ones. This trend may be illustrated by the differences between the longest and shortest M–O distances, by their ratio, or by the



Fig. 2. Polyhedron representation of Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub> crystal structure.



Fig. 3. The known compositions of Bi or REE selenite halides. M=Bi or REE. X=Cl, Br.

difference between the mean and the shortest distance in the  $MO_8$  polyhedron (Table 4).

The  $MO_x$  and  $MO_yHal_z$  polyhedrons are linked in frameworks in individual manner in case of different Bi or REE compounds. However, all these structures contain channels, as in the case of Bi<sub>6</sub>(SeO<sub>3</sub>)<sub>3</sub>O<sub>5</sub>Br<sub>2</sub> which home the selenium atoms coordinated by three oxygen atoms with pyramidal shape [SeO<sub>3</sub>E]. The Se–O distances vary in a narrow range of 1.65–1.75 Å.

The crystal structures of complex REE selenite halides may be represented in terms of oxygen polyhedrons-tetrahedrons  $OM_4$  [4,9]. In  $Bi_6(SeO_3)_3O_5Br_2$  the  $OBi_4$  polyhedrons are formed by O(2)-O(5) atoms and all Bi atoms. These tetrahedrons share edges with each other to form 2D nets. The key elements of these nets are junctions between  $O(2)Bi_4$ ,  $O(5)Bi_4$  and  $O(4)Bi_4$  tetrahedrons (Fig. 4.). The groups of six tetrahedrons (Fig. 4b) are "stitched" by pairs of  $O(3)Bi_4$  tetrahedrons (Fig. 4c) connected by common Bi(4)-Bi(4) edges.

The selenium atoms are situated between the  $OBi_4$  nets. All these are bonded to oxygen atoms not contributing to the into  $OBi_4$  nets, to form SeO<sub>3</sub> pyramids (Fig. 4d). At the same time, the oxygen atoms of SeO<sub>3</sub> pyramids are bridged by Bi atoms.

The bromine atoms reside in the space between Bi–Se–O layers. The Br(1) atoms are connected with Bi atoms from one layer. Br(2) are  $\Psi$ -connected with Bi atoms from two different layers and complete the formation of the open framework (Fig. 4d).

Description of the crystal structure, given in terms of  $OM_4$  tetrahedrons, shows common features between  $Bi_6(SeO_3)_3O_5Br_2$  and related REE derivatives, described in [4,9]. However, the framework in each case is individual.

The synthesis of new bismuth containing selenite bromide confirmed the purpose of this work to find new open framework structures among selenite halides. The crystal structure of  $Bi_6(SeO_3)_3O_5Br_2$  is related to those of REEs selenite halides, but it has, as yet, no complete analogues among them and demonstrate a unique structural type.

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**Fig. 4.** The 2D net formed by  $OBi_4$  tetrahedrons in the structure of  $Bi_6(SeO_3)_3O_5Br_2$ : (a) edge connected  $O(5)Bi_4$  group, (b) the junction of  $O(2)Bi_4$ ,  $O(5)Bi_4$  and  $O(4)Bi_4$  tetrahedrons (c) final net, and (d)  $OBi_4$  presentation of the  $Bi_6(SeO_3)_3O_5Br_2$  crystal structure.

#### Table 3 Crystallographic data for known selenate(IV) halides of REEs and Bi expect MSeO<sub>3</sub>X composition.

Composition	Space group	Ζ	<i>a</i> , Å	b, Å	<i>c</i> , Å	α, °	β, °	γ, °	Reference
Bi <sub>10.666</sub> (SeO <sub>3</sub> ) <sub>12</sub> Br <sub>8</sub>	B bab	4	15.884(5)	15.884(5)	18.305(5)				[3]
Bi <sub>6</sub> (SeO <sub>3</sub> ) <sub>3</sub> O <sub>5</sub> Br <sub>2</sub>	<b>P</b> 1	2	7.1253(7)	10.972(1)	12.117(2)	67.765(7)	82.188(8)	78.445(7)	This study
Tb <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> Cl	P nma	4	5.3516(4))	15.3051(9)	10.8272(7)				[4,9,10]
Dy <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> Cl	P nma	4	5.3381(2)	15.2104(7)	10.7656(4)				[4,9]
$Y_3(SeO_3)_2O_2Cl$	P nma	4	5.4824(4)	14.5792(9)	11.0283(7)				[20]
Er <sub>3</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>2</sub> Cl	C 2/c	4	14.9823(6)	11.0203(5)	5.4795(3)		105.515(2)		[4,9]
$Er_4(SeO_3)_2O_3Cl_2$	$\bar{P}1$	4	8.6164(2)	11.7056(3)	12.0842(3)	67.666(1)	77.833(1)	85.270(1)	[9]
Yb <sub>4</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>3</sub> Cl <sub>2</sub>	$\bar{P}1$	4	8.5387(6)	11.4592(8)	11.9546(9)	68.132(7)	78.113(7)	85.748(7)	[4,9]
$Nd_7(SeO_3)_4O_5Cl_3$	$\bar{P}1$	2	6.9446(4)	9.4453(5)	15.6792(9)	87.821(3)	81.649(3)	84.852(3)	[11]
Gd <sub>5</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>4</sub> Br <sub>3</sub>	C 2 m	2	12.4370(10)	5.4991(4)	10.0529(9)		91.869(3)		[9]
Tb <sub>5</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>4</sub> Cl <sub>3</sub>	C 2 m	2	12.2913(4)	5.4617(4)	9.7879(7)		90.485(6)		[9,10]
La <sub>9</sub> (SeO <sub>3</sub> ) <sub>4</sub> O <sub>8</sub> Br <sub>3</sub>	$\bar{P}1$	1	7.1172(3)	9.1956(4)	9.9658(5)	99.658(2)	94.938(2)	95.840(2)	[9]
$Pr_9(SeO_3)_4O_8Br_3$	$\bar{P}1$	1	7.0035(4)	9.0609(6)	9.8591(7)	99.623(3)	95.076(3)	95.874(3)	[9]
$Pr_9(SeO_3)_4O_8Cl_3$	ΡĪ	1	7.0012(1)	9.0163(2)	9.6688(2)	99.787(1)	94.979(1)	95.901(1)	[9]
Nd <sub>9</sub> (SeO <sub>3</sub> ) <sub>4</sub> O <sub>8</sub> Cl <sub>3</sub>	ΡĪ	1	6.9630(2)	8.9680(3)	9.6387(4)	99.528(2)	95.176(2)	95.893(2)	[9]
Sm9(SeO3)4O8Cl3	ΡĪ	1	6.8870(1)	8.8879(2)	9.5909(2)	98.647(1)	95.419(1)	96.031(1)	[9]
$Gd_9(SeO_3)_4O_8Cl_3$	ΡĪ	1	6.8017(5)	8.8286(7)	9.6018(8)	97.241(6)	95.539(6)	96.265(6)	[4,9]

Table 4

Comparison of some characteristics of the  $[MO_8]$  polihedrons (M=Bi, Ln) for  $Bi_6(SeO_3)_3O_5Br_2$  and related compounds.

Compound	Yb <sub>4</sub> (SeO <sub>3</sub> ) <sub>2</sub> O <sub>3</sub> Cl	2		Gd <sub>9</sub> (SeO <sub>3</sub> ) <sub>4</sub> O <sub>8</sub> Cl <sub>3</sub>		Nd7(SeO3)4O5Cl3		Bi <sub>6</sub> (SeO <sub>3</sub> ) <sub>3</sub> O <sub>5</sub> Br <sub>2</sub>
Reference Polyhedron L <sub>sh</sub> *, Å	[4,9] Yb(1)O <sub>8</sub> 2.19	Yb(2)O <sub>8</sub> 2.20	Yb(3)O <sub>8</sub> 2.23	[4,9] Gd(1)O <sub>8</sub> 2.03	Gd(2)O <sub>8</sub> 2.08	[11] Nd(3)O <sub>8</sub> 2.04	Nd(4)O <sub>8</sub> 2.03	This study Bi(3)O <sub>8</sub> 2.15
L 1**, Å	2.53	2.59	2.98	2.34	2.48	2.46	2.48	3.15
$L_{\rm l}$ – $L_{\rm sh}$ , Å	0.34	0.39	0.75	0.31	0.40	0.42	0.45	1.00
L <sub>l</sub> /L <sub>sh</sub> L <sub>av</sub> *≈≈ -L <sub>sh</sub> , Å	1.15 0.14	1.17 0.16	1.34 0.20	1.15 0.18	1.19 0.16	1.20 0.26	1.22 0.27	1.46 0.43

\* — $L_{sh}$  shortest M–O distance in polyhedron.

\*\*  $-L_1$  longest M–O distance in polyhedron.

\*\*\* —  $L_{av}$  average M–O distance in polyhedron  $L_{av} = \frac{\sum_{i=1}^{8} L_i}{8}$ .

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2012.06.020.

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