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Hydrothermal synthesis and crystal structure of ErSeO_3Cl

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Abstract

A new erbium–selenium oxychloride, ErSeO_3Cl , has been synthesized hydrothermally starting from $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ and SeO_2 in LiCl aqueous solution, and its crystal structure solved from single-crystal X-ray diffraction data. ErSeO_3Cl crystallizes in the HoTeO_3Cl structure type in the orthorhombic system, space group $Pnma$ (No. 62), with the cell parameters $a = 7.185(1) \text{ \AA}$, $b = 6.890(1) \text{ \AA}$, $c = 8.720(2) \text{ \AA}$, $V = 431.7(1) \text{ \AA}^3$, $Z = 4$. The structure was refined to $R1 = 0.0259$, $wR2 = 0.0648$ for 35 variables and 508 unique reflections. The 3D structure of ErSeO_3Cl is formed from linked ErO_5Cl_2 polyhedra and SeO_3E (E—lone electron pair) polyhedra. We compare the crystal structure of ErSeO_3Cl with the structures of other known rare-earth (Bi)—Se(Te) oxyhalides of the common formula $M\text{ChO}_3X$ ($M = \text{Ln}(\text{Bi})$, $\text{Ch} = \text{Se, Te}$, $X = \text{Cl, Br, I}$).

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1. Introduction

The family of layered rare-earth or bismuth (III) and tellurium (IV) oxyhalides is rich with Sillen-type compounds and exhibits anomalously high percentage of non-centrosymmetric structures [1–7]. The Sillen-type structure is an ordered sequence of fluorite-derived metal–oxygen layers and sheets of halide ions. It is believed that Bi–Te (or Ln–Te) cation ordering, as well as displacement of oxygen and halide ions from their ideal positions, are the driving force for occurrence of non-centrosymmetry so frequent in the class of Bi–Te and Ln–Te oxyhalides.

Thus, we supposed that related compounds of Se (IV), which is an electronic analog of Te (IV), might exhibit similar behavior. The first representative of the selenium series, BiSeO_3Cl , demonstrates several different crystal structures [8,9]; however, its α -modification exhibits strong non-linear optical activity. Hence, the search for other Bi or Ln–Se(IV) oxide halogenides is likely to produce new interesting and promising materials.

The synthesis and X-ray powder characterization of a new family of rare-earth-selenium (IV) oxyhalides with composition LnSeO_3Cl revealed two isostructural groups of compounds [10]. The compounds of La–Eu are tetragonal and possibly similar to BiTeO_3Br [3], while their analogs with smaller lanthanides and Y belong to a novel orthorhombic structure type.

The aim of the present investigation is the determination of the crystal structure of ErSeO_3Cl as the representative of the LnSeO_3Cl ($\text{Ln} = \text{Tb–Yb}$, Y) type. It should be mentioned that last year the crystal structure of a 3D Ho–Te oxychloride HoTeO_3Cl was reported [11]. This fact indicates that crystal chemistry of Ln–Te(Se) oxyhalides is not completely clear.

2. Experimental

2.1. Synthesis

Single crystals of ErSeO_3Cl were obtained by the hydrothermal method. The starting materials and solvents used are given in Table 1. SeO_2 was prepared according to Ref. [12] by oxidizing selenium (>99.9999

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Table 1
Starting compositions for hydrothermal synthesis

Sample	Mass SeO ₂ (g)	Mass ErCl ₃ ·6H ₂ O (g)	Mass Er ₂ O ₃ (g)	SeO ₂ /second component molar ratio	Solution (ml)
1	0.6634	2.2816		1/1	NH ₄ Cl 7% 8.0
2	0.7453	2.5608		1/1	LiOH 10% 7.7
3	0.7199	2.4688		1/1	LiCl 20% 8.0
4	0.8519		2.9382	1/1	NH ₄ Cl 7% 8.2
5	0.9074		3.1240	1/1	LiCl 30% 8.7

purity) by O₂–NO₂ mixture. The rest of the components were obtained commercially and were of reagent grade.

The hydrothermal syntheses were performed in sealed Teflon bombs of 11 cm³ volume. The filling ratio of the solution was 70% of the bomb volume. The bombs were placed in steel autoclaves with ~160–170 cm³ volume, and the synthesis was conducted at 280°C for 10 days. For the pressure balancing in the autoclaves, the calculated amounts of distilled water were added to autoclaves up to the 70% filling ratio. Pink precipitates and solutions were found as the reaction products. The solutions were decanted and the precipitates were washed with water, and dried first at 90°C in air, then at 150–180°C under dynamic vacuum (~10⁻¹ Torr).

2.2. Sample characterization

The crystalline products obtained were identified with X-ray phase analysis (STOE STADI/P diffractometer, CuKα₁ radiation). The X-ray data from Ref. [10] and JCPDS database were used as references. We were unable to identify the products of the experiments 1, 4 and 5. The target compound ErSeO₃Cl was observed as a fine powder in experiment 2 (with small amount of an admixture phase) and as perfect pink crystals of hexagonal bipyramidal shape in experiment 3 (Table 1). The X-ray diffraction pattern of the crushed crystals proved to be identical to that given in Ref. [10], thus indexed as orthorhombic system with the cell parameters $a = 7.173(2)$ Å, $b = 6.883(2)$ Å, $c = 8.710(2)$ Å, $F(30) = 22.3$.

The absence of the bands typical for chemically bound and adsorbed water in the IR spectra (PE 1600 FTIR Fourier spectrometer, the samples were ground crystals suspended in Vaseline oil) allowed us to conclude that the compound did not contain crystallization water.

2.3. Structure determination

The selected single crystal was mounted on a CAD-4 (Nonius) goniometer head for structure determination. Orthorhombic unit-cell parameters ($a = 7.185(1)$ Å, $b = 6.890(1)$ Å, $c = 8.720(2)$ Å) were refined based on

24 well-centered reflections in the angular range $14.3^\circ < \theta < 15.7^\circ$. The data set was collected at ambient temperature in ω - 2θ mode with the data-collection parameters listed in Table 2. A semiempirical absorption correction was applied to the data based on ψ -scans of seven reflections having their χ angles close to 90°. Analysis of the systematic extinctions revealed two possible space groups $Pna2_1$ (No. 33) and $Pnma$ (No. 62). The crystal structure was successfully refined in the centrosymmetric space group $Pnma$. Positions of erbium and selenium atoms were found by means of direct methods (SHELXS-97) [13]. Chlorine and oxygen atoms were localized by a sequence of least-square cycles and $\Delta\rho(xyz)$ synthesis. Final anisotropic refinement on F^2 (SHELXL-97) [14] led to $R1 = 0.0259$, and $wR2 = 0.0648$.

Data-collection parameters are given in Table 2. Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666, E-mail: crysdata@fiz-karlsruhe.de) on quoting the deposited number CSD-412861). Final positional and thermal atomic parameters for ErSeO₃Cl are shown in Table 3, and main bond distances are collected in Table 4.

Table 2
Crystal data and structure refinement for ErSeO₃Cl

Empirical formula	ErSeO ₃ Cl
Formula weight	329.67
Temperature	293(2) K
Wavelength	0.71073 Å
Space group	$Pnma$ (No. 62)
Unit-cell dimensions	$a = 7.185(1)$ Å $b = 6.890(1)$ Å $c = 8.720(2)$ Å
Volume	431.68(13) Å ³
Z	4
Calculated density	5.073 g/cm ³
Absorption coefficient	28.341 mm ⁻¹
Crystal size	0.10 × 0.15 × 0.15 mm ³
Theta range for data collection	3.67–26.94°
Reflections collected/unique	1083/508 [$R(\text{int}) = 0.0332$]
Data/parameters	508/35
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0259$, $wR2 = 0.0648$
R indices (all data)	$R1 = 0.0278$, $wR2 = 0.0659$
Extinction coefficient	0.0034(5)
Largest diff. peak and hole	2.521 and $-2.919e$ Å ⁻³
Depository no.	CSD 412861

Table 3
Atomic and thermal parameters for ErSeO₃Cl

Atom	x	y	z	$U(\text{eq})$ (Å ² × 10 ³)
Er(1)	0.3948(1)	0.25	0.9601(1)	6(1)
Se(2)	0.7901(1)	0.25	0.11338(1)	8(1)
Cl(4)	0.0592(3)	0.25	0.8169(2)	19(1)
O(1)	0.3578(6)	0.9263(6)	0.9314(5)	13(1)
O(2)	0.2494(9)	0.25	0.11808(7)	15(1)

2.4. Results and discussion

In the structure of ErSeO_3Cl , the Er is seven-coordinated, and its polyhedron can be described as a pentagonal bipyramid with a somewhat distorted base formed by one Cl and four O1 atoms and with O2 and Cl atoms in the apical positions (Fig. 1). The ErO_5Cl_2 polyhedra are linked via common O1–O1 edges forming zigzag chains along the *b*-axis. The parallel chains are

Table 4
Interatomic distances in ErSeO_3Cl

Bond		Bond length (Å)
Er(1)–O(2)	× 1	2.190(6)
Er(1)–O(1)	× 2	2.260(4)
Er(1)–O(1)	× 2	2.352(4)
Er(1)–Cl(4)	× 1	2.689(2)
Er(1)–Cl(4)	× 1	2.715(2)
Er(1)–Se(2)	× 1	3.219(1)
Er(1)–Er(1)	× 2	3.8259(5)
Se(2)–O(2)	× 1	1.642(6)
Se(2)–O(1)	× 2	1.711(4)

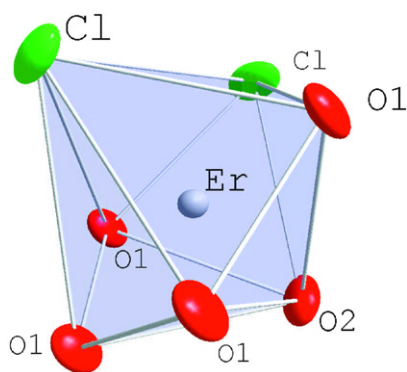


Fig. 1. Er polyhedron in the ErSeO_3Cl structure.

connected through common Cl atoms. Each Cl atom is equatorial in one chain and apical in the other (Fig. 2).

The Se atoms form open polyhedra typical for Se^{IV} compound [8,15] with two O1 and one O2 atoms. Usually, such a polyhedron is described as a trigonal SeO_3E pyramid with oxygen atoms in the base and lone electron pair (E) at the top. The selenium polyhedra are linked with the base of an ErO_5Cl_2 bipyramid in one chain via O1–O1 edge and with the apex of an Er polyhedron of the other chain via O2 atom (Fig. 3).

The 3D crystal structure of ErSeO_3Cl is isotypic to that of HoTeO_3Cl (*Pnma*, $a = 7.3025 \text{ \AA}$, $b = 6.9654 \text{ \AA}$, $c = 9.0518 \text{ \AA}$) [11]. The latter is built of pentagonal bipyramids, HoO_5Cl_2 linked via common oxygen edges, chlorine vertices and TeO_3E pyramids in a way similar to that described above in the structure of ErSeO_3Cl . Thus, HoTeO_3Cl and ErSeO_3Cl can be considered as progenitors of a new structure type, which comprises all LnSeO_3Cl compounds with Ln^{3+} ionic radii smaller than that of Gd^{3+} .

It should be mentioned that one of the BiSeO_3Cl modifications [9] has a structure related to HoTeO_3Cl and ErSeO_3Cl . The difference is that in the BiO_5Cl_2 pentagonal bipyramid, both chlorine atoms are basal, and the polyhedra are connected in zigzag chains via common O–Cl edges; the chains in turn are connected via apical oxygen atoms.

Up to now, HoTeO_3Cl was the only one representative of LnTeO_3X ($\text{Ln} = \text{REE}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) phases with the described structure. It is known that when passing along the lanthanide series, the symmetry of LnTeO_3Cl compounds turns from orthorhombic ($\text{Ln} = \text{La}, \text{Nd}$) to tetragonal ($\text{Ln} = \text{Sm}, \text{Gd}, \text{Er}, \text{Lu}$) [16] in contrast to their bromide and iodide analogues, all of which are tetragonal. Still, judging from the structural model of the NdTeO_3Cl structure [7] and the unit-cell parameters of the mentioned oxychlorides [16], all of them belong to the Sillen-type layered structures, well determined for

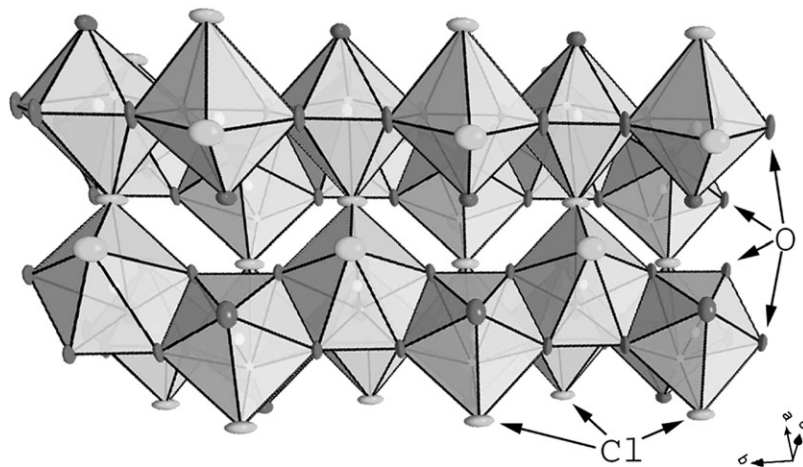


Fig. 2. The chains of ErO_5Cl_2 polyhedra in the ErSeO_3Cl structure.

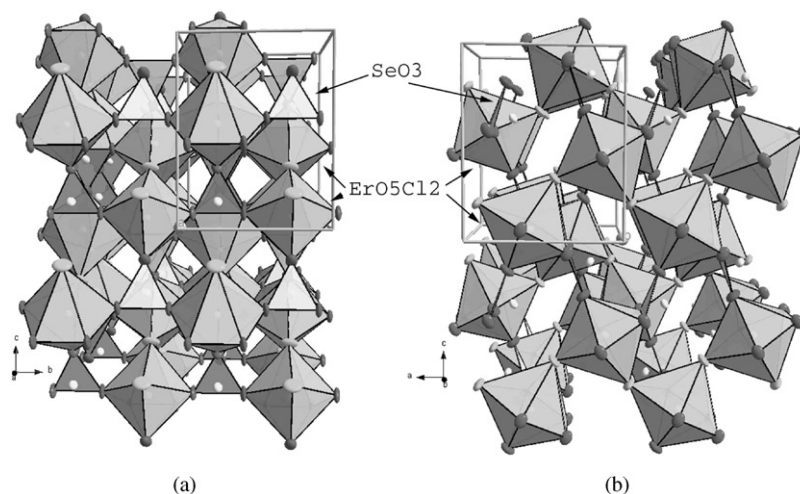


Fig. 3. ErSeO_3Cl crystal structure in polyhedra. *a*—along the *a*-axis of the unit cell, *b*—along the *b*-axis.

Table 5
Structure types of $MChO_3X$ ($M = \text{Bi, REE; Ch} = \text{Te, Se; X} = \text{Cl, Br, I}$) phases

<i>M</i>	<i>Ch</i>	<i>X</i>	Symmetry	Structure type	Reference
La, Nd	Te	Cl	Orthorhombic		[7]
Sm, Gd, Er, Lu			Tetragonal		[16]
Bi, Nd, Sm, Er, Lu	Te	Br	Tetragonal	Layered Sillen	[3,7,1,2]
Bi, La, Nd, Sm, Gd	Te	I	Tetragonal		[7,18]
La, Pr, Nd, Sm, Eu, Gd	Se	Cl	Tetragonal		[10]
Ho	Te	Cl	Orthorhombic	HoTeO_3Cl	[11]
Gd, Dy, Ho, Er, Yb, Y	Se	Cl	Orthorhombic		[10] and this work
Bi	Se	Cl	Orthorhombic	$\alpha\text{-BiSeO}_3\text{Cl}$	[8]
Bi	Se	Cl	Orthorhombic	$\gamma\text{-BiSeO}_3\text{Cl}$	[9]
Bi	Te	I	Monoclinic	$\beta\text{-BiTeO}_3\text{I}$	[17]

several oxybromides [7]. The latter are built of fluorite-like Ln_2O_2 layers, separated with a single halogen layer from two fluorite-like LnTe_2O_5 layers separated by a double halogen layer. LnSeO_3Cl where $\text{Ln} = \text{La–Gd}$ also possibly belong to the same structure type [10].

All LnTeO_3X compounds have crystal structure derived from layered BiTeO_3Br type (Table 5). They were prepared at 500°C [16]. HoTeO_3Cl is an exception (3D structure); however, its single crystals were prepared at high temperature (800°C), and the compound is likely to be dimorphous. This may be the case for some other LnTeO_3X and LnSeO_3Cl , as well.

Hence, most of the oxyhalides known by now, $MChO_3X$ ($M = \text{Bi, REE; Ch} = \text{Te, Se; X} = \text{Cl, Br, I}$) belong to one of the two different structural families (Table 5). Only BiTeO_3I [7,17] and BiSeO_3Cl polymorphs [8,9] are the only representatives of their own structure types. While the percentage of tellurium-containing phases which do not belong to the Sillen family is relatively small, the selenium-containing oxychlorides form two sets of equal number. From this point of view, the search and determination of structures

of LnSeO_3X compounds with other halogens is promising. This problem is under investigation at the moment.

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References

- [1] M.B. Novikova, V.A. Dolgikh, L.N. Kholodkovskaya, S.Yu. Stefanovitch, A.E. Baron, *MSU Bull. Chem.* 45 (1) (1990) 59–61.
- [2] I.V. Tarasov, V.A. Dolgikh, B.A. Popovkin, A.E. Baron, *Russ. J. Inorg. Chem.* 40 (1) (1995) 145–149.
- [3] L.N. Kholodkovskaya, V.A. Dolgikh, B.A. Popovkin, *Russ. J. Inorg. Chem.* 36 (1991) 1244.
- [4] L.N. Kholodkovskaya, V.A. Dolgikh, B.A. Popovkin, *J. Solid State Chem.* 116 (1995) 406.
- [5] V.A. Dolgikh, L.N. Kholodkovskaya, B.A. Popovkin, *Russ. J. Inorg. Chem.* 41 (1996) 932.

- [6] G.B. Nikiforov, A.M. Kusainova, P.S. Berdonosov, V.A. Dolgikh, P. Lightfoot, *J. Solid State Chem.* 146 (1999) 473–477.
- [7] P.S. Berdonosov, D.O. Charkin, A.M. Kusainova, Ch.H. Hervoches, V.A. Dolgikh, P. Lightfoot, *Solid State Sci.* 2 (2000) 553–562.
- [8] P.S. Berdonosov, S.Yu. Stefanovitch, V.A. Dolgikh, *J. Solid State Chem.* 149 (2000) 236–241.
- [9] S.A. Ibragimov, P.S. Berdonosov, V.A. Dolgikh, D.C. Huong, H. Oppermann, *Inorg. Mater.* 38 (12) (2002) 1291–1296.
- [10] D.G. Shabalin, P.S. Berdonosov, V.A. Dolgikh, H. Oppermann, P. Schmidt, B.A. Popovkin, *Russ. Chem. Bull.* 1 (2003) 93–96.
- [11] S.F. Meier, T. Schleid, *Z. Anorg. Allerg. Chem.* 628 (2002) 526–528.
- [12] Yu.V. Karyakin, I.I. Angelov, *The Pure Chemical Reagents, The Handbook for Inorganic Reagents and Preparates Preparation in Laboratory*, 4th Edition, Khimiya, Moscow, pp. 56 (in Russian).
- [13] M. Sheldrik, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [14] M. Sheldrik, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [15] J.D. McCullough, *J. Am. Chem. Soc.* 59 (1937) 789–794.
- [16] G.B. Nikiforov, P.S. Berdonosov, V.A. Dolgikh, B.A. Popovkin, *Russ. J. Inorg. Chem.* 42 (11) (1997) 1785–1789.
- [17] P. Wilk, H.-L. Keller, L. Wimbirt, *Z. Kristallogr.* 15 (Suppl.) (1998) 64.
- [18] M.B. Novikova, V.A. Dolgikh, L.N. Kholodkovskaya, S.Yu. Stefanovich, V.M. Shorikov, *Izv. Akad. Nauk SSSR (Russ.) Inorg. Mater.* 27 (2) (1991) 388–391.