Synthesis and powder X-ray diffraction analysis of new mixed rare-earth and selenium oxychlorides with composition $LnSeO_3Cl$

D. G. Shabalin,[a] *P. S. Berdonosov,*[b]★ *V. A. Dolgikh,*[b] *H. Oppermann,*[c]
P. Schmidt,[c] *and B. A. Popovkin*[b]

[a]*Department of Materials Science, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119992 Moscow, Russian Federation.
E-mail: shabalin@r450.inorg.chem.msu.ru
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 0998. E-mail: psberd@inorg.chem.msu.ru; dolgikh@inorg.chem.msu.ru
[c]*Institute of Inorganic Chemistry, Technical University of Dresden,*
*Mommsenstraße 13, D-01069, Dresden, Germany.**
Fax: +49 (351) 4633 7287. E-mail: peer.schmidt@chemie.tu-dresden.de

A series of new mixed rare-earth and selenium oxychlorides with composition $LnSeO_3Cl$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, or Y) were prepared by annealing together LnOCl and SeO_2 in sealed silica tubes. The resulting compounds were characterized by powder X-ray diffraction. The unit cell parameters of the phases were determined. Lanthanum—europium oxychlorides crystallized in the tetragonal system to give the Sillen phases analogously to tellurium compounds with the similar formula, whereas Tb—Yb and Y oxychlorides crystallized in the orthorhombic system. It is likely that the latter oxychlorides are not layered compounds.

Key words: Sillen phases, rare-earth and selenium oxychlorides, powder X-ray diffraction characteristics.

Earlier,[1] we have synthesized a large series of bismuth—tellurium and rare-earth metal (REM)—tellurium oxyhalides. Many of these compounds have non-centrosymmetrical structures. The most common composition of the compounds, which was found in all M_2O_3—MOHal—TeO_2 systems, corresponds to the formula $MTeO_3Hal$, where M = Bi or any REM and Hal = Cl, Br, or I. All phases with this composition have layered structures of the Sillen phases,[1] which are built by alternating double (M_2O_2) and triple (MTe_2O_5) fluorite-like layers separated by the single and double layers of halide anions (Fig. 1).

Rather recently, bismuth—selenium oxyhalides with analogous stoichiometry $BiSeO_3Hal$ (Hal = Cl or Br) have been synthesized.[2—4] However, their structures differ from those found for the tellurium derivatives. In addition, we have prepared[5] the $SmSeO_3Cl$ phase.

The present study was aimed at synthesizing the $LnSeO_3Cl$ phases (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, or Y) and performing their X-ray diagnostics. The data on these phases are lacking in the literature.

Results and Discussion

The samples synthesized in the present study occur as pale powders (in the case of Nd and Er, as pinkish powders). The powder X-ray diffraction patterns of all annealed samples have no lines of the starting phases or known phases in the Ln_2O_3—$LnCl_3$—SeO_2 systems. According to the character of arrangement and intensities of reflections in the powder diffraction patterns, the compounds under consideration can be classified into two groups: 1) derivatives of Ln = La—Eu and 2) derivatives of Ln = Tb—Yb and Y. Figure 2 shows the powder diffraction patterns of the samples with compositions $SmSeO_3Cl$ and $HoSeO_3Cl$ as typical examples. The gadolinium-containing sample boundary to both families of oxychlorides gives a diffraction pattern, which is similar in the arrangement of lines to the family of light REMs and still has noticeable differences (see Fig. 2). The diffraction pattern

---

* Technishe Universität Dresden, Institut für Anorganische Chemie, Mommsenstraße 13, D-01069, Dresden, Germany.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 93—96, January, 2003.

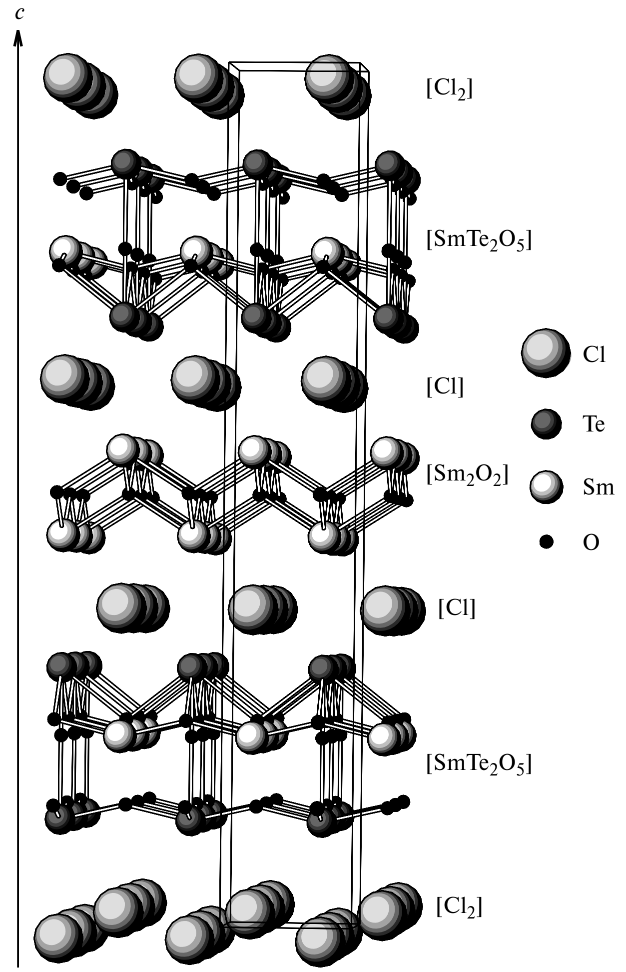

Fig. 1. Fragment of the $SmTeO_3Cl$ structure.

of the sample with composition $GdSeO_3Cl$, which was annealed at 600 °C for 72 h, appeared to be similar to the diffraction patterns of the samples containing heavy REMs or Y (see Fig. 2). The $GdSeO_3Cl$ sample was prepared in connection with the fact that the heating curve, which was obtained in the differential thermal study (evacuated Stepanov's vessels, heating from room temperature to 600 °C, rate 10 deg min^{-1}, Al_2O_3 reference) of the $GdSeO_3Cl$ sample annealed at 300 °C, showed an exothermic effect at 565±5 °C, and this effect was not reproduced on cooling.

The IR spectra of the samples belonging to the same family are also very similar to each other and differ noticeably from the IR spectra of compounds belonging to another family. The typical IR spectra of the samples with compositions $SmSeO_3Cl$ and $HoSeO_3Cl$ are shown in Fig. 3.

The powder diffraction patterns of the La—Eu-containing compounds were indexed based on their similarity to the diffraction patterns of the known $MTeO_3Hal$ compounds assuming the tetragonal symmetry of the unit cells and the space group *P*4/*nmm* (Table 1). Table 2 gives the results of indexing of the diffraction pattern of the $PrSeO_3Cl$ sample as a typical example.

Table 1. Unit cell parameters (Å) of the $LnSeO_3Cl$ compounds belonging to the tetragonal (space group *P*4/*nmm*) and orthorhombic (*Pnma*) systems

Ln	*a*	*b*	*c*
		*P*4/*nmm*	
La	4.026(2)	—	26.56(2)
Pr	3.9805(6)	—	26.346(9)
Nd	3.9627(7)	—	26.30(2)
Sm	3.931(2)	—	26.14(2)
Eu	3.906(1)	—	26.09(1)
		Pnma	
Gd	7.253(2)	7.031(2)	8.871(4)
Tb	7.244(8)	6.980(6)	8.73(1)
Dy	7.177(4)	6.910(3)	8.721(7)
Ho	7.233(6)	6.943(5)	8.795(6)
Er	7.201(4)	6.909(4)	8.750(4)
Yb	7.140(8)	6.818(8)	8.65(1)
Y	7.185(6)	6.896(5)	8.73(2)

A series of lines in the diffraction pattern of the $GdSeO_3Cl$ sample annealed at 300 °C can also be indexed within an analogous unit cell. Apparently, the structure of this compound corresponds to a distorted structure of lighter REM oxychlorides. We failed to index all reflections in the diffraction pattern of this sample.

The diffraction patterns of the $LnSeO_3Cl$ compounds, where Ln = Gd, Tb, Dy, Ho, Yb, or Y, were indexed under the assumption of the orthorhombic system and the

Table 2. Results of indexing of the powder diffraction pattern of $PrSeO_3Cl$*

Line	*d*/Å		*h*	*k*	*l*	I/I_0
	Experiment	Calculation				
1	8.81	8.78	0	0	3	60
2	3.626	3.626	1	0	3	60
3	2.9501	2.9491	1	0	6	100
4	2.8138	2.8146	1	1	0	80
5	2.5905	2.5881	1	1	4	10
6	2.3693	2.3696	1	1	6	10
7	2.1926	2.1955	0	0	12	10
8	2.0284	2.0289	1	1	9	20
9	1.9905	1.9902	2	0	0	40
10	1.9419	1.9410	2	0	3	10
11	1.9231	1.9224	1	0	12	10
12	1.7448	1.7446	2	1	3	10
13	1.7321	1.7311	1	1	12	10
14	1.6509	1.6497	2	1	6	30
15	1.4743	1.4745	2	0	12	10
16	1.4065	1.4073	2	2	0	10
17	1.2701	1.2701	3	0	6	10

* The figure of merit F(17) = 7.9.

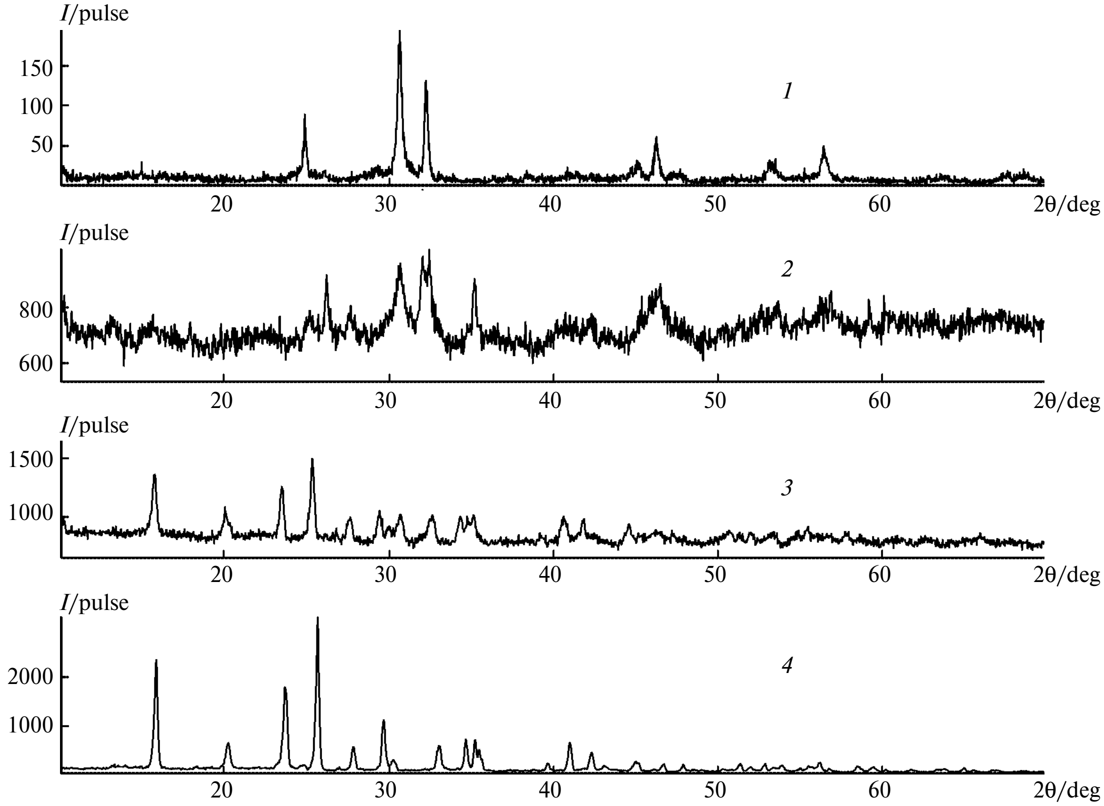

Fig. 2. X-ray diffraction patterns of $SmSeO_3Cl$ (*1*), $GdSeO_3Cl$ (*2*, *3*), and $HoSeO_3Cl$ (*4*) annealed at 300 (*1*, *2*, *4*) and 600 °C (*3*).

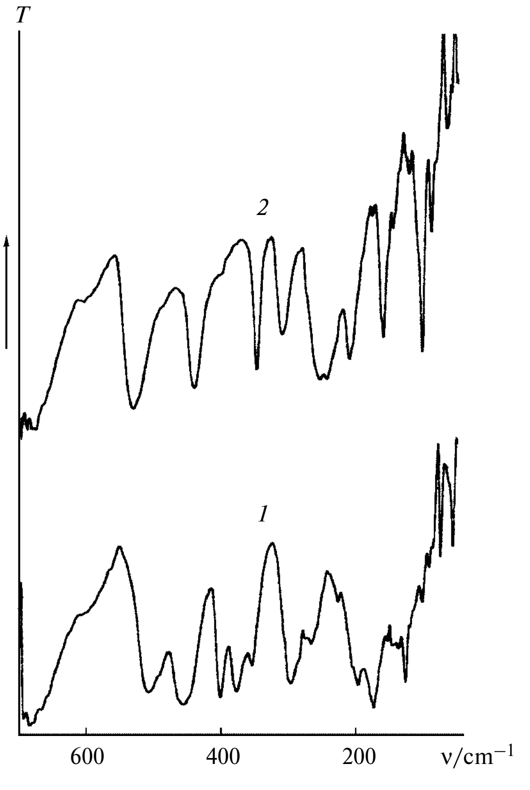

Fig. 3. IR absorption spectra of $SmSeO_3Cl$ (*1*) and $HoSeO_3Cl$ (*2*).

space group *Pnma* (see Table 1). Table 3 gives the results of indexing of the diffraction pattern of the $HoSeO_3Cl$ sample as an example. It should be noted that the reflection with $2\theta = 30.667°$, $d = 2.9130$ Å, $I/I_0 = 63.3$, which was observed in the diffraction pattern of the $GdSeO_3Cl$ compound annealed at 600 °C, could not be indexed within the unit cell parameters given in Table 1.

The results obtained in the present study provide evidence that all rare-earth metals under consideration form compounds with composition $LnSeO_3Cl$. Most likely, the structure type of these phases depends on the size of the Ln^{3+} ion. Oxychlorides $LnSeO_3Cl$ containing lanthanides with large ionic radii have the $Bi_{0.97}TeO_3Br_{0.9}$ structures (see Fig. 1). The parameter *a* monotonically decreases on going from La to Eu. In the structures of this type, the parameter *a* is numerically equal to the Ln—Ln distance (see Fig. 1). Hence, its change in the series under consideration can be explained in the context of the phenomenon of lanthanide contraction. The parameter *c* also decreases on going from La to Eu. This parameter for the $Bi_{0.97}TeO_3Br_{0.9}$ structures would be determined primarily by the thicknesses of the fluorite-like $[Ln_2O_2]$ and $[LnSe_2O_5]$ packets (see Fig. 1), which decrease with decreasing ionic radius of Ln^{3+} due to a decrease in the Ln—O distance. This change in the parameter *c* can also be accounted for by the lanthanide contraction.

Table 3. Results of indexing of the powder diffraction pattern of $HoSeO_3Cl$*

Line	d/Å		h	k	l	I/I_0
	Experiment	Calculation				
1	5.6290	5.5863	1	0	1	73.5
2	4.4123	4.3975	0	0	2	18.3
3	3.7685	3.7575	1	0	2	59.1
4	3.6073	3.6163	2	0	0	2.3
5	3.4830	3.4713	0	2	0	100.0
6	3.2137	3.2073	2	1	0	17.3
7	3.0175	3.0132	2	1	1	36.2
8	2.9597	2.9485	1	2	1	7.0
9	2.7166	2.7247	0	2	2	18.2
		2.7170	1	0	3	
10	2.5917	2.5913	2	1	2	21.2
11	2.5439	2.5498	1	2	2	15.3
12	2.2758	2.2773	2	0	3	5.6
13	2.2046	2.2048	3	1	1	20.9
		2.1988	0	0	4	
14	2.1394	2.1395	1	2	3	13.4
		2.1380	1	3	1	
15	2.0989	2.1037	1	0	4	3.1
16	2.0161	2.0133	1	1	4	7.0
17	1.9489	1.9493	2	3	0	5.1
18	1.9013	1.9042	2	2	3	4.3
		1.9031	2	3	1	
19	1.7818	1.7820	2	3	2	5.1
20	1.7606	1.7618	1	3	3	2.7
21	1.7345	1.7357	0	4	0	4.8
22	1.7077	1.7092	1	0	5	3.0
		1.7051	0	1	5	
23	1.6707	1.6723	4	0	2	2.0
24	1.6537	1.6523	2	2	4	3.2
25	1.6385	1.6409	3	2	3	5.9
		1.6402	3	3	1	
26	1.5780	1.5776	4	2	1	3.7
		1.5757	1	4	2	
27	1.5562	1.5567	1	3	4	2.9
28	1.5379	1.5406	2	4	1	1.3
		1.5390	4	0	3	
29	1.5028	1.5025	4	1	3	1.2
30	1.4625	1.4627	1	4	3	1.6
31	1.4364	1.4366	1	0	6	2.5

* The figure of merit F(31) = 7.8.

We believe that this factor is also responsible for a decrease in the unit cell parameters of the orthorhombic phases $LnSeO_3Cl$ on going from Gd to Yb.

Apparently, gadolinium—selenium oxychloride exists on the boundary of stability of two structure types and can occur as two modifications. The orthorhombic modification is stable at high temperatures (600 °C), whereas the phase with the distorted $MTeO_3Hal$ structure is formed under the conditions of low-temperature annealing (300 °C). Apparently, the latter phase can be assigned to the layered Sillen phases.

The above-mentioned change in the structure type in the $LnSeO_3Cl$ series at Ln = Gd agrees with the general tendency for a change in the properties of REM derivatives, *viz.*, with the existence of the so-called "gadolinium break."

When this study was being prepared for publication, the structure of the holmium—tellurium oxychloride $HoTeO_3Cl$ was established (orthorhombic system, space group *Pnma*; a = 7.3025(5), b = 6.9654(5), c = 9.0518(7) Å; Z = 4) and reported.[6] The unit cell parameters published in the cited study[6] are very close to those determined in our study for the $LnSeO_3Cl$ compounds with end members of the REM series taking into consideration that the radius of Se is smaller than that of Te. Hence, it can be assumed that the structures of the compounds under consideration are similar to the $HoTeO_3Cl$ structure.

Experimental

The present study was carried out with the use of the oxychlorides LnOCl (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Yb, or Y) and selenium dioxide.

Oxychlorides of the above-mentioned REMs were prepared according to a procedure described earlier[7] by pyrohydrolysis of the corresponding REM trichloride hexahydrates at 400—500 °C for 2—4 h. Some rare-earth trichloride hexahydrates were commercially available reagents (high-purity grade) and the remaining reagents were prepared by dissolution of oxides of the corresponding lanthanides in concentrated HCl followed by concentration of the solutions on a sand bath until crystallization started.

Selenium dioxide was synthesized according to a known procedure[8] by oxidation on heating of powdered selenium (high-purity grade) in a flow reactor under a stream of air and nitrogen oxides, which were generated by thermal decomposition of $Pb(NO_3)_2$ at 400—450 °C. White SeO_2 crystals, which were condensed in the cold zone of the reactor, were transferred into a tube. The tube was sealed and placed in a dry box, where all subsequent operations with SeO_2 were carried out.

The products thus obtained were identified by powder X-ray diffraction analysis (Stoe diffractometer, Stadi-p, Cu-Kα_1 radiation) based on the data from the JCPDS PDF-2 database.

The $LnSeO_3Cl$ sample was synthesized by solid-phase annealing (300±5 °C, 240 h) of carefully ground equimolar mixtures of REM oxychlorides and SeO_2 in evacuated (residual pressure was $1 \cdot 10^{-2}$ Pa) silica tubes.

X-ray diffraction and IR spectroscopic diagnostics. X-ray diffraction diagnostics of the annealing products was carried out on a Stoe diffractometer (Stadi-p, Cu-Kα_1 radiation) and a Guinier camera (Enraf—Nonius, Delft) using the photographic method (germanium as the internal standard). The X-ray diffraction patterns were processed with the use of the WinX^{POW} program package (Stoe&CIE GmbH computer software). The Guinier patterns were measured on an IZA-2 comparator and processed with the use of the Powder2 program package.

The IR spectra were recorded on a Perkin—Elmer FTIR-1720 instrument (as Nujol mulls).

We thank L. N. Reshetova for help in recording the IR spectra.

This study was financially supported by the Russian Foundation for Basic Research and the German Research Foundation (DFG, Deutsche Forschungsgemeinschaft; RFBR-DFG Project No. 01-03-04002).

References

1. P. S. Berdonosov, D. O. Charkin, A. M. Kusainova, C. H. Hervoches, V. A. Dolgikh, and P. Lightfoot, *Solid State Sciences*, 2000, **2**, 553.
2. P. S. Berdonosov, S. Yu. Stefanovitch, and V. A. Dolgikh, *J. Solid State Chem.*, 2000, **149**, 236.
3. H. Oppermann, Dao Quoc Huong, M. Zhang, P. Schmidt, B. A. Popovkin, S. A. Ibragimov, P. S. Berdonosov, and V. A. Dolgikh, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1347.
4. H. Oppermann, P. Schmidt, M. Zhang-Preβe, Dao Quoc Huong, R. Kucharkowski, B. A. Popovkin, S. A. Ibragimov, and V. A. Dolgikh, *Z. Anorg. Allg. Chem.*, 2002, **628**, 91.
5. H. Oppermann, Dao Quoc Huong, M. Zhang-Preβe, P. Schmidt, B. A. Popovkin, P. S. Berdonosov, and V. A. Dolgikh, *Z. Anorg. Allg. Chem.*, 2002, **628**, 891.
6. S. F. Meier and Th. Schleid, *Z. Anorg. Allg. Chem.*, 2002, **628**, 526.
7. G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart, 1975.
8. Yu. V. Karyakin and I. I. Angelov, *Chistye khimicheskie reaktivy. Rukovodstvo po prigotovleniyu neorganicheskikh reaktivov i preparatov v laboratornykh usloviyakh* [*Pure Chemical Reagents. Laboratory Manual on Preparation of Inorganic Reagents*], Khimiya, Moscow, 1974, 56 (in Russian).

Received May 14, 2002;
in revised form October 4, 2002