

The synthesis and crystal structures of the first rare-earth alkaline-earth selenite chlorides $MNd_{10}(SeO_3)_{12}Cl_8$ ($M = Ca$ and Sr)

P.S. Berdonosov^{a,*}, A.V. Olenev^a, V.A. Dolgikh^a, P. Lightfoot^b

^aDepartment of Chemistry, Moscow State University, Leninskie Gory, Moscow 119992, Russia

^bEaStChem, School of Chemistry, St. Andrews University, St. Andrews, KY16 9ST, UK

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Abstract

Two new alkaline-earth Nd selenite chlorides $MNd_{10}(SeO_3)_{12}Cl_8$ ($M = Ca, Sr$) were obtained using crystal growth from alkaline-earth chloride melts in quartz tubes. These new compounds crystallize in the orthorhombic system in space group $Ccca$ (#68). The compounds were studied by energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction. It was shown that both compounds adopt the same structure type, constructed by complex $[M_{11}(SeO_3)_{12}]^{8+}$ slabs separated by chloride anion layers perpendicular to the longest cell parameter. The SeO_3 groups show a pyramidal shape and may be described as SeO_3E tetrahedra. Such SeO_3 groups decorate the Nd–O skeletons forming the $[M_{11}(SeO_3)_{12}]^{8+}$ slabs.

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Keywords: Selenite chloride; Rare earth compound; Crystal structure

1. Introduction

Compounds which contain ions with lone electron pairs such as Se(IV), Te(IV), Sb(III), Bi(III) and others together with halide ions attract attention due to their possibility to form low dimensional structures and to possess unusual physical properties such as quantum spin systems or non linear optical phenomena [1–3].

A rare earth (REE)-Cu compound with composition $Cu_3Er(SeO_3)_2O_2Cl$ with the mineral francisite structure type was known from 1996 [4] but the first selenite-halogenides of REE were synthesized and characterized in 2002 [5,6]. Just after that, numerous more complex compositions of selenite-halogenides with REEs were described: $M Ln(SeO_3)_2Cl$ [7], $CsSm_{21}(SeO_3)_{24}Br_{16}$ and $Bi_{10.67}(SeO_3)_{12}Br_8$ [8], $CsTmSeO_3Cl_2$ [9]. Later, the family of alkali metal-REE selenite chlorides was extended by $CsEu_4O_3(SeO_3)_2Cl_3$ [10], $Rb_6LiLn_{11}(SeO_3)_{12}Cl_{12}$ [11,12], $Cs_3La_{11}(SeO_3)_{12}Cl_{16}$ [13], $K_7Sm_{11}(SeO_3)_{12}Cl_{16}$ and $Cs_7Pr_{11}(SeO_3)_{12}Cl_{16}$ [14] and one other compound with composition $CoNd_{10}(SeO_3)_{12}Cl_8$ was described [15]. As

may be seen, during the last 5 years a new family of compounds—complex selenite-halogenides of REE has begun to form. Up to now this family was presented by alkaline metals-REE and d-metals-REE compounds only.

In the present study we describe the synthesis and crystal structure of two new alkaline earth and neodymium selenite chlorides, which are the first representatives of alkaline-earth inclusion in such compounds.

2. Experimental

2.1. Synthesis and preliminary characterization

Single crystals of the title compounds were obtained by the common technique described in [13] and [14]. $NdOCl$ was obtained by pyrohydrolysis of $NdCl_3 \cdot 6H_2O$ (chemically pure) in a tube furnace in air flow at 823 K. Selenium dioxide was obtained by dehydration of H_2SeO_3 (98%) under vacuum at 333 K and product sublimation in a flow of dried air with addition of NO_2 followed by dehydration. The purity of samples was confirmed by powder X-ray diffraction testing (Stoe STADI-P system, $CuK\alpha_1$ radiation, Ge monochromator) and using PDF2 [16]. A double

*Corresponding author. Fax: +7495 939 0998.

E-mail address: psberd@inorg.chem.msu.ru (P.S. Berdonosov).

weight excess of anhydrous MCl_2 ($M = Ca, Sr$) (both chemically pure) was added to the mixture of $NdOCl$ and SeO_2 in molar ratio 1:1 under a dried argon atmosphere. Mixtures, total weight about 0.3–0.4 g, were placed in quartz tubes and sealed under vacuum. Tubes were loaded into electronically controlled furnaces and preheated at 573 K for 24 h. After that the temperature was raised up to 1073 K (for $CaCl_2$) and 1173 K (for $SrCl_2$). After 15 min at high temperature the furnaces were cooled at $2 K h^{-1}$ down to 673 K and then were switched off. After cooling to room temperature, the reaction products were washed out by water to remove excess of MCl_2 and dried in air. In both cases well-shaped plate-like crystals were observed. The final yield of product was about 80–85% based on the original amount of $NdOCl$.

The obtained crystals were analyzed by X-ray powder diffraction after grinding and by energy dispersive X-ray spectroscopy (EDX) using a JEOL JEM 2011 HRTEM microscope with an Oxford Instruments ISIS EDX Analysis System and Supra 50 VP (LEO) equipped with INCA energy+ (Oxford) analyzing unit. According to EDX data the compounds consist from Nd, Se and Cl as the main part, plus a small amount of calcium or strontium. For example, for Ca compound the following data were obtained in atomic%: Nd 14.47(0.23), Se 16.07(0.19), Ca 1.88(0.06) and Cl 11.94(0.23) (calculated % from finally obtained formula Nd 14.92, Se 17.91, Ca 1.49, Cl 11.94). X-ray powder pattern analysis showed the

absence of known compounds and starting materials and the similarity of structures of Ca and Sr containing samples.

2.2. Single crystal study

Suitable crystals were studied on Rigaku mercury CCD diffractometer. Some crystallographic data and experimental details are summarized in Table 1.

The initial structural model was obtained in space group $Ccca$ (68) using direct methods (Shelxs-86). Final refinement was performed using Shelxl-97 [17] software package. Atomic coordinates and isotropic displacement parameters are summarized in Table 2. We have tried to refine the site occupancy of the metal atoms in order to obtain the alkaline earth metal distribution at the metal positions. It was shown that the distribution of alkaline earth metal is different at the different crystallographic sites. In both compounds alkaline earth metal is mostly located in the Nd2 positions (site occupancy about 17–25% of Ca or Sr). According to the X-ray site occupation accuracy determination the composition (Table 2) of the compound is $MNd_{10}(SeO_3)_{12}Cl_8$, $M = Ca, Sr$. In the header of Table 2 the compositions of the compounds are presented with errors according to the X-ray solution. These formulae correlate with EDX data and charge balance of the substances.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum

Table 1
Crystal data and structure refinement for $CaNd_{10}(SeO_3)_{12}Cl_8$ and $SrNd_{10}(SeO_3)_{12}Cl_8$

	$CaNd_{10}(SeO_3)_{12}Cl_8$		$SrNd_{10}(SeO_3)_{12}Cl_8$
Diffractometer		Rigaku mercury CCD	
Temperature, K	93(2)		93(2)
Crystal system		Orthorhombic	
Space group		$Ccca$ (68)	
Cell parameters, Å			
<i>a</i>	15.588(3)		15.773(4)
<i>b</i>	17.419(4)		17.622(4)
<i>c</i>	15.681(3)		15.836(4)
Cell volume, Å ³	4257.7(14)		4401.4(19)
<i>Z</i>		4	
Calculated density, g cm ⁻³	5.132		5.053
Absorption coefficient, mm ⁻¹	22.942		23.426
Wavelength		MoK α	
F(000)	5808		5899
Limiting indices	$-20 \leq h \leq 19$ $-20 \leq k \leq 14$ $-20 \leq l \leq 20$		$-17 \leq h \leq 18$ $-17 \leq k \leq 21$ $-17 \leq l \leq 19$
Crystal size, mm	$0.10 \times 0.03 \times 0.03$		$0.10 \times 0.03 \times 0.01$
Theta range for data collection, deg	2.18–28.14		2.16–25.36
Reflections collected	12474		12493
Reflections unique	2221 [R(int) = 0.0426]		2013 [R(int) = 0.0717]
Data / restraints / parameters	2221/1/153		2013/31/159
Goodness-of-fit on F^2	1.241		1.074
Final <i>R</i> indices [$I > 2\sigma(I)$]	R1 = 0.0383 wR2 = 0.0976		R1 = 0.0430 wR2 = 0.1092
<i>R</i> indices (all data)	R1 = 0.0426 wR2 = 0.0999		R1 = 0.0443 wR2 = 0.1108
Largest diff. peak and hole eÅ ⁻³	5.026 and -1.593		5.099 and -2.812
ICSD number	418190		418191

Table 2

Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{CaNd}_{10}(\text{SeO}_3)_{12}\text{Cl}_8$ and $\text{SrNd}_{10}(\text{SeO}_3)_{12}\text{Cl}_8$

Atom	Parameter	$\text{Ca}_{1\pm 0.14}\text{Nd}_{9.97\pm 0.14}(\text{SeO}_3)_{12}\text{Cl}_8$ 93 K	$\text{Sr}_{1\pm 0.01}\text{Nd}_{10\pm 0.01}(\text{SeO}_3)_{12}\text{Cl}_8$ 93K
Nd1	<i>x</i>	1/2	1/2
	<i>y</i>	1/4	1/4
	<i>z</i>	1/4	1/4
	<i>U</i> (eq)	3(1)	3(1)
Nd2	<i>x</i>	0.1194(1)	0.1190(1)
	<i>y</i>	0.0730(1)	0.0727(1)
	<i>z</i>	0.1303(1)	0.1305(1)
	Site occ.	Nd 0.805(2) Ca 0.194(2)	Nd 0.7499(6) Sr 0.2500(6)
	<i>U</i> (eq)	4(1)	5(1)
Nd3	<i>x</i>	0.2379(1)	0.2376(1)
	<i>y</i>	1/4	1/4
	<i>z</i>	1/4	1/4
	Site occ.	Nd 0.976(2)	
	<i>U</i> (eq)	4(1)	4(1)
Nd4	<i>x</i>	0	0
	<i>y</i>	1/4	1/4
	<i>z</i>	0.0120(1)	0.0122(1)
	Site occ.	Nd 0.958(2) Ca 0.042(2)	
	<i>U</i> (eq)	4(1)	4(1)
Nd5	<i>x</i>	1/4	1/4
	<i>y</i>	1/4	1/4
	<i>z</i>	0	0
	Site occ.	Nd 0.930(2) Ca 0.062(2)	
	<i>U</i> (eq)	4(1)	4(1)
Nd6	<i>x</i>	0	
	<i>y</i>	1/4	
	<i>z</i>	1/4	
	Site occ.	0.025(4)	
	<i>U</i> (eq)	4(1)	
Se1	<i>x</i>	0.1105(1)	0.1109(1)
	<i>y</i>	0.3631(1)	0.3628(1)
	<i>z</i>	0.1396(1)	0.1392(1)
	<i>U</i> (eq)	4(1)	5(1)
Se2	<i>x</i>	0.3777(1)	0.3777(1)
	<i>y</i>	0.3770(1)	0.3761(1)
	<i>z</i>	0.1011(1)	0.1012(1)
	<i>U</i> (eq)	4(1)	4(1)
Se3	<i>x</i>	0.6490(1)	0.6492(1)
	<i>y</i>	0.3740(1)	0.3733(1)
	<i>z</i>	0.1277(1)	0.1277(1)
	<i>U</i> (eq)	4(1)	4(1)
Cl1	<i>x</i>	0	0
	<i>y</i>	−0.0029(2)	−0.0037(2)
	<i>z</i>	1/4	1/4
	<i>U</i> (eq)	12(1)	17(1)
Cl2	<i>x</i>	0	0
	<i>y</i>	0	0
	<i>z</i>	0	0
	<i>U</i> (eq)	20(1)	23(1)
Cl3	<i>x</i>	1/4	1/4
	<i>y</i>	0	0
	<i>z</i>	0.2370(2)	0.2373(2)
	<i>U</i> (eq)	9(1)	14(1)
Cl4	<i>x</i>	1/4	1/4
	<i>y</i>	0	0
	<i>z</i>	0.0172(2)	0.0168(2)
	<i>U</i> (eq)	11(1)	15(1)
O1	<i>x</i>	0.0042(4)	0.1381(3)
	<i>y</i>	0.3503(3)	0.2720(3)
	<i>z</i>	0.1235(3)	0.1115(3)
	<i>U</i> (eq)	5(1)	7(1)
O2	<i>x</i>	0.1373(4)	0.6205(3)
	<i>y</i>	0.2713(3)	0.3208(3)

Table 2 (continued)

Atom	Parameter	Ca _{1±0.14} Nd _{9.97±0.14} (SeO ₃) ₁₂ Cl ₈ 93 K	Sr _{1±0.01} Nd _{10±0.01} (SeO ₃) ₁₂ Cl ₈ 93K
O3	<i>z</i>	0.1119(4)	0.0429(3)
	<i>U</i> (eq)	5(1)	6(1)
	<i>x</i>	0.6210(3)	0.1273(3)
	<i>y</i>	0.3212(3)	0.3503(4)
	<i>z</i>	0.0422(3)	0.2446(3)
O4	<i>U</i> (eq)	4(1)	7(1)
	<i>x</i>	0.3752(3)	0.4620(3)
	<i>y</i>	0.3490(3)	0.3220(3)
	<i>z</i>	−0.0041(3)	0.1257(3)
	<i>U</i> (eq)	5(1)	7(1)
O5	<i>x</i>	0.1267(3)	0.3754(3)
	<i>y</i>	0.3508(4)	0.3480(4)
	<i>z</i>	0.2449(4)	−0.0035(3)
	<i>U</i> (eq)	7(1)	7(1)
	<i>x</i>	0.7541(4)	0.2928(3)
O6	<i>y</i>	0.3464(3)	0.3227(3)
	<i>z</i>	0.1255(3)	0.1291(3)
	<i>U</i> (eq)	4(1)	5(1)
	<i>x</i>	0.6243(3)	0.6246(3)
	<i>y</i>	0.3205(3)	0.3199(3)
O7	<i>z</i>	0.2126(4)	0.2122(3)
	<i>U</i> (eq)	5(1)	6(1)
	<i>x</i>	0.4623(4)	0.7535(3)
	<i>y</i>	0.3220(3)	0.3451(4)
	<i>z</i>	0.1254(3)	0.1254(2)
O8	<i>U</i> (eq)	6(1)	7(1)
	<i>x</i>	0.2926(4)	0.0057(3)
	<i>y</i>	0.3230(3)	0.3498(4)
	<i>z</i>	0.1288(3)	0.1231(3)
	<i>U</i> (eq)	5(1)	8(1)

Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247 808 666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD numbers 418190 for CaNd₁₀(SeO₃)₁₂Cl₈, and 418191 for SrNd₁₀(SeO₃)₁₂Cl₈.

Some important interatomic distances for the studied compounds are presented in Table 3.

3. Results and discussion

Our experiments show that CaNd₁₀(SeO₃)₁₂Cl₈ and SrNd₁₀(SeO₃)₁₂Cl₈ have the same structure (Tables 1–3). The unit cell for CaNd₁₀(SeO₃)₁₂Cl₈ is presented in Fig. 1.

There are five Nd positions in the structures. Alkaline earth atoms are distributed on the Nd sites in an ordered manner. In the Sr compound all Sr ions are in the Nd2 position, where they are about 1/4 of full occupancy. In the Ca compound most of the calcium ions are in the Nd2 site too, but some of them are in sites of Nd4 and Nd5. The explanation of this phenomenon may be in the difference in ionic radii of Nd³⁺ (1.109 Å), Ca²⁺ (1.12 Å) and Sr²⁺ (1.26 Å) [18]. From this point of view Ca²⁺ may more satisfactorily substitute Nd³⁺, as was observed for CaNd₁₀(SeO₃)₁₂Cl₈. Another possible reason for the agglomeration of Ca/Sr on the Nd2 site could be the

Nd2–Cl bonds. The only Nd site which forms Nd–Cl bonds is the Nd2 site, where the majority of the Ca/Sr ions are located. It should be noted that in the compounds under discussion the O^{2−} is a rather strong Lewis base (*S_b-norm* = 0.50 v.u.) compared to weaker halides (*S_b-norm* = 0.17 for Cl[−] and 0.05 for Br[−]) [19]. In accordance with Brown's valence matching principle RE cations which are the stronger Lewis acids (for example, *S_a* = 0.4 v.u. for Nd³⁺) will tend to bond to the O^{2−} anions, and alkali and AE metals as the weaker Lewis acids (*S_a* = 0.27 and 0.24 for Ca²⁺ and Sr²⁺ accordingly) will tend to bond with halides.

The neodymium atoms in positions Nd1, Nd3–Nd5 have only oxygen neighbors (Table 3). Coordination surroundings for Nd1 and Nd3 are square antiprisms. In the cases of Nd1 and Nd3 such antiprisms are capped by two additional oxygen atoms. [Nd3O₈] and [Nd5O₁₀] polyhedra share their O2–O6–O9 sides and form infinite chains along the *c*-axis. In the perpendicular direction these chains are connected by [Nd1O₈] antiprisms via O7–O7 edges and by [Nd4O₁₀] polyhedra via a common O2–O3–O4 face. As the result of such polyhedral linkage a friable metal-oxygen slab is formed (Fig. 2) perpendicular to the [010] direction of structure. Inside this slab, in case of CaNd₁₀(SeO₃)₁₂Cl₈, one additional, partly occupied (about 2.5%) site

Table 3
Bond lengths (Å) for $MNd_{10}(SeO_3)_{12}Cl_8$ ($M = Ca, Sr$)

$CaNd_{10}(SeO_3)_{12}Cl_8$ bond	93 K distance	$SrNd_{10}(SeO_3)_{12}Cl_8$ bond	93 K distance
Nd1–O7 × 4	2.368(5)	Nd1–O7 × 4	2.396(5)
Nd1–O8 × 4	2.394(5)	Nd1–O4 × 4	2.418(5)
Nd2–O1	2.347(6)	Nd2–O9	2.397(6)
Nd2–O5	2.368(6)	Nd2–O3	2.403(6)
Nd2–O4	2.404(6)	Nd2–O5	2.451(6)
Nd2–O6	2.422(6)	Nd2–O8	2.481(6)
Nd2–Cl3	2.9262(17)	Nd2–Cl3	2.9620(18)
Nd2–Cl1	2.9550(15)	Nd2–Cl1	2.9859(17)
Nd2–Cl4	2.9853(19)	Nd2–Cl4	3.025(2)
Nd2–Cl2	3.0422(6)	Nd2–Cl2	3.0707(6)
Nd3–O9 × 2	2.442(5)	Nd3–O6 × 2	2.463(5)
Nd3–O5 × 2	2.468(6)	Nd3–O3 × 2	2.481(6)
Nd3–O7 × 2	2.544(5)	Nd3–O7 × 2	2.569(5)
Nd3–O6 × 2	2.578(5)	Nd3–O8 × 2	2.592(5)
Nd3–O2 × 2	2.699(5)	Nd3–O1 × 2	2.724(5)
Nd4–O3 × 2	2.412(5)	Nd4–O2 × 2	2.436(5)
Nd4–O1 × 2	2.471(6)	Nd4–O9 × 2	2.487(6)
Nd4–O8 × 2	2.563(5)	Nd4–O4 × 2	2.595(5)
Nd4–O4 × 2	2.603(5)	Nd4–O5 × 2	2.619(5)
Nd4–O2 × 2	2.678(6)	Nd4–O1 × 2	2.714(5)
Nd5–O3 × 2	2.453(5)	Nd5–O2 × 2	2.487(5)
Nd5–O9 × 2	2.478(5)	Nd5–O6 × 2	2.506(5)
Nd5–O2 × 2	2.510(6)	Nd5–O1 × 2	2.526(5)
Nd5–O6 × 2	2.588(5)	Nd5–O8 × 2	2.598(5)
Nd5–O4 × 2	2.605(5)	Nd5–O5 × 2	2.626(5)
Nd6–O1 × 4	2.644(5)		
Nd6–O5 × 2	2.644(4)		
Nd6–O5 × 2	2.644(5)		
Se1–O5	1.684(6)	Se1–O9	1.695(5)
Se1–O1	1.691(6)	Se1–O3	1.703(5)
Se1–O2	1.709(6)	Se1–O1	1.714(6)
Se2–O8	1.674(6)	Se2–O4	1.681(6)
Se2–O9	1.682(6)	Se2–O6	1.695(5)
Se2–O4	1.719(6)	Se2–O5	1.731(5)
Se3–O7	1.671(6)	Se3–O7	1.681(5)
Se3–O3	1.684(6)	Se3–O2	1.692(5)
Se3–O6	1.708(6)	Se3–O8	1.720(6)

exists, Nd6. The Nd6 environment is a cube constructed by eight oxygen atoms (4 O5 and 4 O1 at distances about 2.64 Å (Table 3)). The selenium atoms are situated in the hollows of this metal–oxygen slab and connected with three oxygens of it (Fig. 2). The SeO_3 pyramids may be described as classical SeO_3E ψ -tetrahedron with E-lone electron pair. As may be seen from Fig. 2 the SeO_3E groups are situated in such a way that E pairs should be directed into the interlayer space. The Se–O bonds play a role as additional linkage of metal–oxygen slabs (Fig. 1). Finally Ca(Sr)–Nd–Se–O form layers with composition $[M_{11}(SeO_3)_{12}]^{8+}$ between which layers of chloride anions are situated. Nd2 is situated at the border of the $[M_{11}(SeO_3)_{12}]^{8+}$ block and has a distorted square antiprismatic environment, with Cl atoms in one bigger base and oxygen in another smaller one (Table. 3). Each $Nd_2O_4Cl_4$ antiprism shares one Cl–Cl edge with another antiprism from a different $[M_{11}(SeO_3)_{12}]^{8+}$ block. Thus the structure

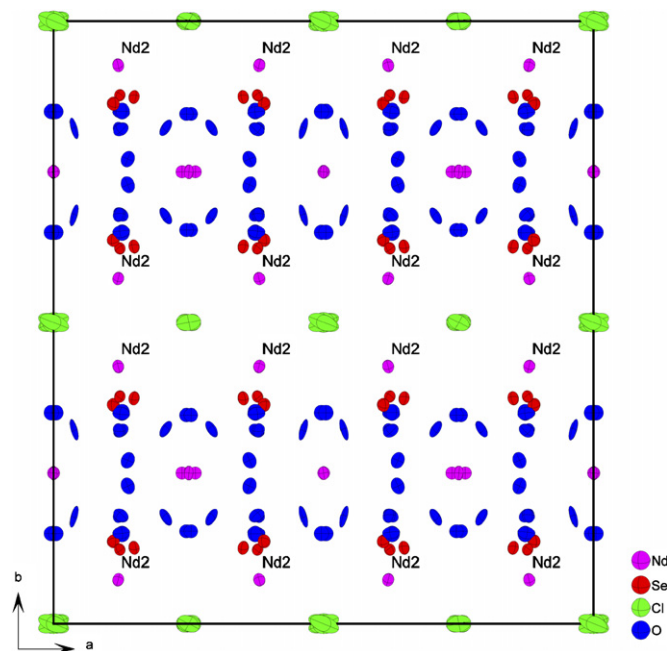


Fig. 1. Unit cell for $CaNd_{10}(SeO_3)_{12}Cl_8$. Nd2 positions are marked. Thermal ellipsoids are drawn with 95% probability.

of $MNd_{10}(SeO_3)_{12}Cl_8$ ($M = Ca, Sr$) may be considered as a 3D-structure with an open framework (Fig. 3).

It is easy to see that the crystal structures of the new compounds described above are close to the known phases $CsSm_{21}(SeO_3)_{24}Br_{16}$ ($Z = 2$) or $Bi_{10.67}(SeO_3)_{12}Br_8$ ($Z = 4$) [8]. In the crystal structure of $CsSm_{21}(SeO_3)_{24}Br_{16}$ cesium atoms are distributed in one of the Sm sites (Sm5). As in the Ca(Sr) compounds the basis of the $CsSm_{21}(SeO_3)_{24}Br_{16}$ structure is a samarium–oxygen layer formed by Sm1–Sm4 and linked by SeO_3E groups. Sm5 atoms (positions of which are 1/8 filled by Cs) have $4O+4Cl$ antiprismatic surrounding. These $Sm_5O_4Cl_4$ polyhedra connect different Sm–O layers by sharing oxygen and chloride vertices.

Another example of a related structure is the compound $CoNd_{10}(SeO_3)_{12}Cl_8$ [15]. Cobalt has a smaller coordination number 6 (CoO_4Cl_2) in this compound and occupies a different site from neodymium. For this reason the crystal structure of $CoNd_{10}(SeO_3)_{12}Cl_8$ is more distorted (to monoclinic) ($P2/c$, $a = 15.699(2)$, $b = 15.700(2)$, $c = 19.171(2)$, $\beta = 113.995(5)^\circ$).

The variety of alkali metal REE selenite-halogenides ($Cs_3La_{11}(SeO_3)_{12}Cl_{12}$ [13], $K_7Sm_{11}(SeO_3)_{12}Cl_{16}$ and $Cs_7Pr_{11}(SeO_3)_{12}Cl_{16}$ [14]) shows the trend that increasing the alkali metal content in these compounds leads to formation of ordering in the metal and REE crystallographic sites. The geometry of the unit cell may differ, but the principle of structural architecture is the same. Metal–oxygen layers with composition $[M_{11}(SeO_3)_{12}]^{n+}$ are separated by different layers of halogenide anions or ‘CsCl’-like type. The difference is only in the linkage of

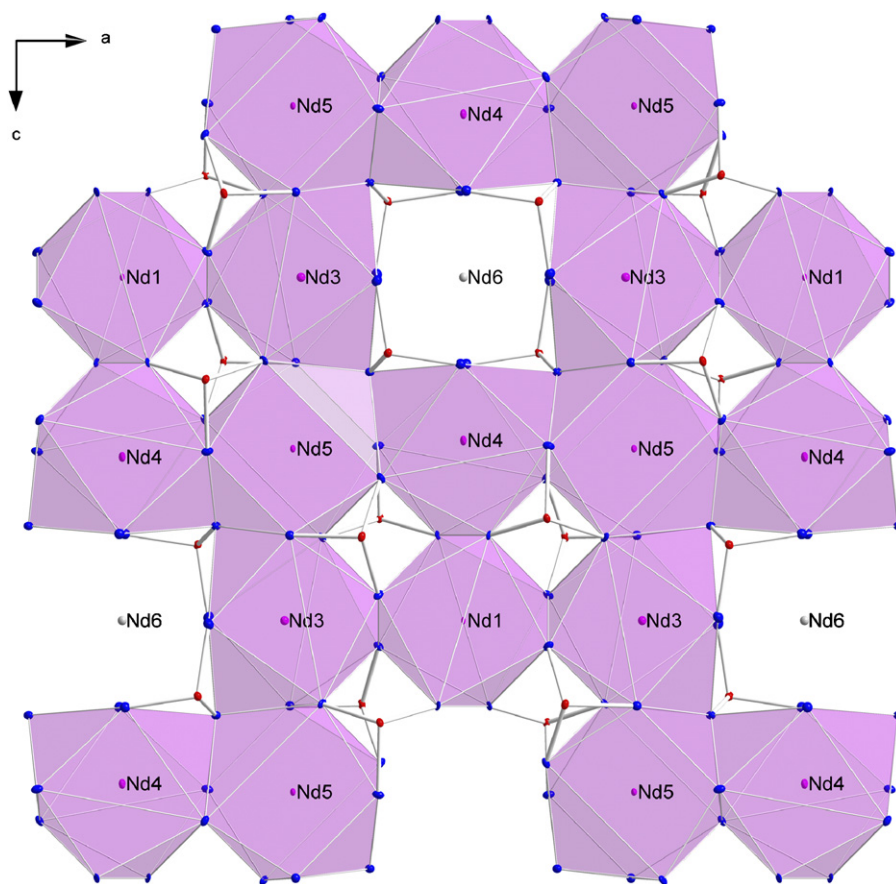


Fig. 2. Neodymium polyhedral layer with SeO_3 groups in the structure of $\text{CaNd}_{10}(\text{SeO}_3)_{12}\text{Cl}_8$. Nd6 sites are marked as gray balls.

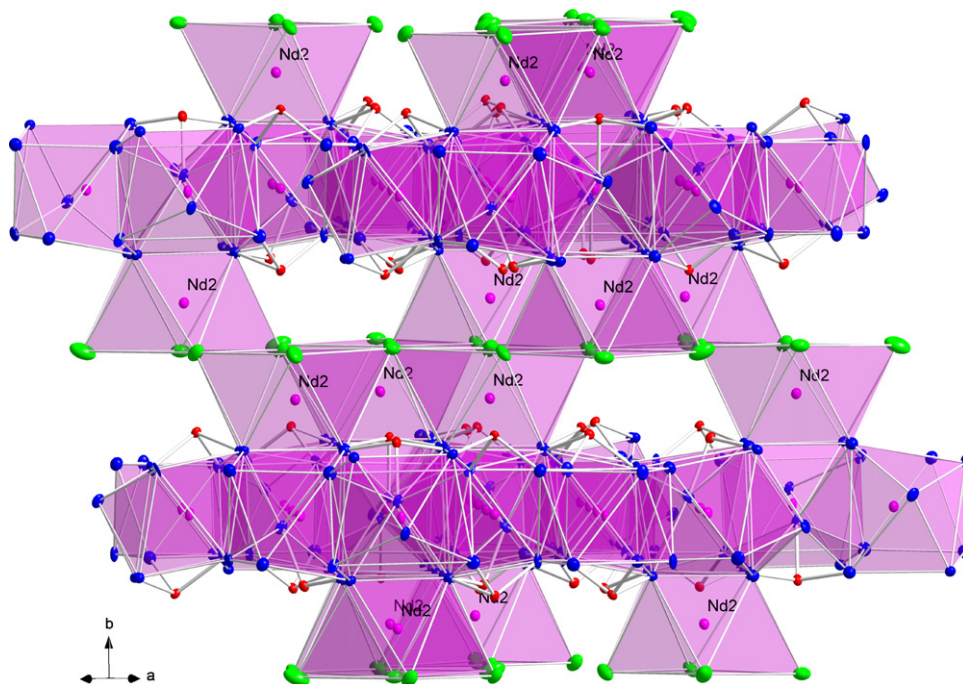


Fig. 3. Representation of the crystal structure of $\text{CaNd}_{10}(\text{SeO}_3)_{12}\text{Cl}_8$ with Nd-polyhedra revealing the 3D-framework.

such structure blocks into a 3D-framework. Several examples of $[\text{M}_{11}(\text{SeO}_3)_{12}]^{n+}$ block linkage are presented in Fig. 4.

The observations listed above prompt us to suggest that alkaline-earth metal REE selenite-halogenides may form phases with much bigger alkaline-earth content and with

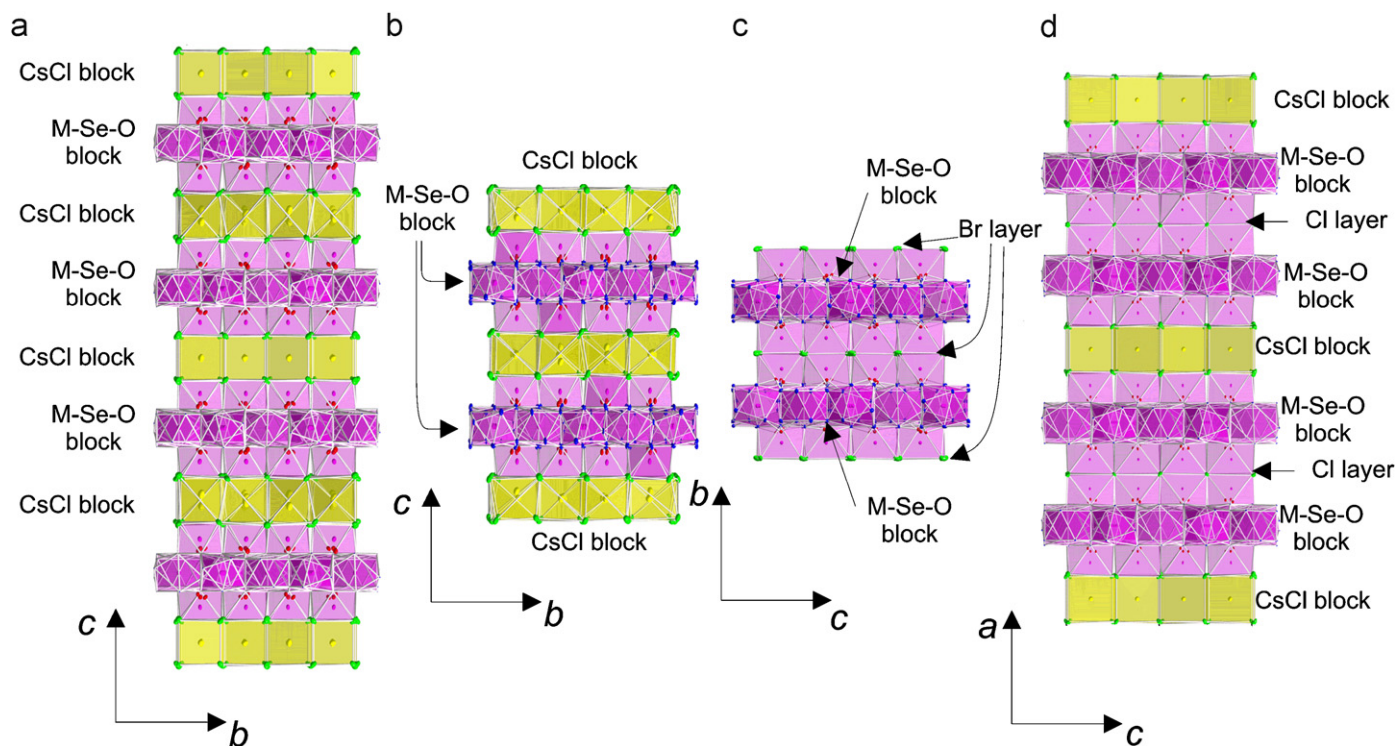


Fig. 4. Different type of $[M_{11}(\text{SeO}_3)_{12}]^{n+}$ block linkage in (a) $\text{Cs}_7\text{Pr}_{11}(\text{SeO}_3)_{12}\text{Cl}_{16}$ [14], (b) $\text{K}_7\text{Sm}_{11}(\text{SeO}_3)_{12}\text{Cl}_{16}$ [14], $\text{Rb}_6\text{LiLn}_{11}(\text{SeO}_3)_{12}\text{Cl}_{12}$ [11,12], (c) $\text{MNd}_{10}(\text{SeO}_3)_{12}\text{Cl}_8$ ($M = \text{Ca}, \text{Sr}$), $\text{CsSm}_{21}(\text{SeO}_3)_{24}\text{Br}_{16}$, $\text{Bi}_{10.67}(\text{SeO}_3)_{12}\text{Br}_8$ [8], (d) $\text{Cs}_3\text{La}_{11}(\text{SeO}_3)_{12}\text{Cl}_{16}$ [13] All unit cells are shown in a direction perpendicular the longest cell parameter.

ordering in metal sites. The search for such compounds is now in progress.

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