Litharge-derived compounds structurally based on layers of Cl⁻ and Br⁻-centered tetrahedra: Synthesis and structures of the new representatives of *MX*(ReO₄) family (*M*=Ba, Pb; *X*=Cl, Br)

Dmitri O. Charkin [a], Oleg I. Siidra [b,c], Igor V. Plokhikh [a,*], Artem S. Borisov [b,d], Mishel R. Markovski [b]

[a] *Department of Chemistry, Moscow State University, Leninskie Gory 1, Moscow, 119991, Russia*
[b] *Department of Crystallography, St. Petersburg State University, University Emb. 7/9, St. Petersburg, 199034, Russia*
[c] *Kola Science Center, RAS, Fersmana Str. 14, 184209, Apatity, Russia*
[d] *Institute of Silicate Chemistry, Russian Academy of Sciences, Adm. Makarova emb. 2, 199034, St. Petersburg, Russia*

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ABSTRACT

Two new layered barium perrhenate halides, Ba*X*(ReO₄) (*X* = Cl and Br), were prepared and their structures were refined from single-crystal and powder data, respectively. Both compounds are isostructural to the previously reported BaCl(MnO₄), exhibiting a matlockite (PbFCl)-derived motif. The structure of previously reported PbBr(ReO₄) was also refined, in order to obtain a complete data set; it is similar to PbCl(ReO₄). The structures of Ba and Pb compounds correspond to the centro- and non-centrosymmetric versions (pseudo-polymorphs) of the same motif corresponding to the alternation of $[M_2X_2]^{2+}$ litharge-derived slabs and double sheets of perrhenate anions. Strong relationships exist to the structures of Ln*X*(*T*O₄) (*X* = Cl, Br; *T* = Mo, W) which are monoclinically distorted versions of the orthorhombic permanganates and perrhenates. Crystal chemistry and further perspectives of the compounds with litharge slabs constructed of Cl, Br, and I-centered tetrahedra are discussed.

1. Introduction

Variable in chemical and structural details, litharge-type layers are particularly widespread among inorganic structures. Apart from the mineral world [1], they are observed in the structures of various materials including ferroelectrics [2], catalysts [3], thermoelectrics [4], and superconductors [5,6]. In the latter cases, these building blocks were considered mostly as charge reservoirs which prompted investigators to look at various possible chemical compositions. While in the overwhelming majority these layers are formed by edge-sharing oxygen-centered tetrahedra [1], data are rapidly accumulating that similar architectures can be constructed, sometimes with enhanced properties, using litharge-derived layers comprised of tetrahedra centered by other anions close in size to O²⁻, namely N³⁻, F⁻, and H⁻ [7]. Crystal structures based on tetrahedra centered by larger anions such as S²⁻ [8,9], Cl⁻ [10–24] Br⁻ [20,25,26], or even I⁻ [27–29] are scarce to date while some representatives exhibit promising properties, *e.g.* optical non-linearity [20,23,24].

Compared to the tetrahedra centered by H⁻, F⁻, O²⁻ or N³⁻ which

set the dimensions of the corresponding tetragonal net in the range of 3.8–4.2 Å [7], centering by larger anions leads to essential increase of the metrics towards 4.8–6.2 Å. Therefore, their positive charge can hardly be compensated by small monoatomic species which would form too loose nets but rather by either essentially larger molecular anions [13–20,23,24,28,29] or 1D or 2D polymeric species [11,12,19,21,26, 27]. The former case is observed in *MXY* compounds where *X* is a halogen, *M* = Pb, Ba, or early *Ln* while *Y* is a molecular anion [13–17,20, 22,24,27,28]. These structures can be considered as derivatives of matlockite PbFCl structure (Fig. 1a).

Apart from linear N₃⁻ [16,17], NCO⁻ [15,28], NCS⁻ [13,18] and CN₂²⁻ [14,29] (Fig. 1b and c), the interlayer space can be filled by tetrahedral anions like BF₄⁻ [24], ClO₄⁻ [23], MnO₄⁻ [22], and ReO₄⁻ [20] (Fig. 1, d-f). In two cases, these structures also contain additional water molecules [18,23]. The halide perrhenates Pb*X*(ReO₄) (*X* = Cl and Br) were among the first representatives of the small and rather unusual family comprising tetrahedral anions [20]. Both compounds were assumed to be isostructural but good quality crystals could be prepared only for the chloride using a melt technique. This compound was found

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* Corresponding author.
 E-mail address: ig.plohih@yandex.ru (I.V. Plokhikh).

to be non-centrosymmetric and exhibit a noticeable SHG activity [20]. Later, a chemically and structurally related BaCl(MnO$_4$) compound was discovered as a by-product in preparation of Ba(MnO$_4$)$_2$ [22]; its structure is centrosymmetric. In an attempt to obtain its perchlorate analogue, we succeeded in preparation of non-centrosymmetric BaCl (ClO$_4$)(H$_2$O) [23]. The best NLO activity is exhibited by a recently found BaCl(BF$_4$) compound [24] which is isostructural to PbCl(ReO$_4$). To date, no relationships can be traced between the structural details and the size of M, X, and Y. The formal analogs, $LnX(TO_4)$ with $X =$ Cl and Br and $T =$ Mo and W, exhibit slightly different structures with polymerized tetrahedral units [19,21,26]. Surprisingly, no strontium compound has been reported though Sr^{2+} ($r = 1.26$ Å) is similar in size to early Ln^{3+} ($r = 1.16$–1.06 Å) and Pb^{2+} ($r = 1.29$ Å [30]).

In the current study, we attempted to expand the family of the MX (ReO$_4$) compounds and to review crystal chemical relationships in this family. As a result, two new BaX(ReO$_4$) ($X =$ Cl, Br) compounds were prepared; structural data were also obtained for PbBr(ReO$_4$) in order to obtain a complete data set.

2. Experimental

2.1. Synthesis

The starting compounds were rhenium powder (>99.5% according to EDX analysis), lead oxide (spectroscopic grade), lead, strontium and barium halides (chemically pure), as well as strontium and barium carbonate (spectroscopic grade). The phase content of all target and intermediate products was controlled using a Rigaku Miniflex II powder diffractometer utilizing CuKα radiation. Perrhenic acid was prepared by slowly adding rhenium powder to a 15% solution of hydrogen peroxide. Alkaline earth perrhenates were prepared by dissolving the corresponding carbonates in the acidic solution thus obtained. The solutions were filtered from excess MCO$_3$, evaporated and solid residues dried at 140 °C. At higher temperatures, their color changes to yellow which

should be avoided. Lead perrhenate was prepared in two steps. First, ammonium perrhenate was prepared by neutralizing the HReO$_4$ solution by excess ammonia; large transparent crystals formed upon evaporation to dryness at room temperature. Next, PbO and NH$_4$ReO$_4$ were mixed in 1:2 ratio and heated first at 400 °C (ramp 20 °C/h, soak 48 h) and then, after grinding, at 550 °C for 24 h. The off-while crystallized melt corresponded to pure Pb(ReO$_4$)$_2$.

Two approaches were followed to prepare the corresponding MX (ReO$_4$) compounds. In the solution-based procedure, the corresponding halide and perrhenate were dissolved in water (heating was necessary to dissolve the lead compounds) and solution was evaporated at room temperature. Acceptable quality brick-shaped colorless crystals of PbX (ReO$_4$) were produced within days while only hydrates of MX_2 and M (ReO$_4$)$_2$ were observed for alkaline earths. Therefore, the latter experiments were repeated at 100 °C. They produced colorless tabular crystals which piled readily at the final evaporation stages. Good quality crystals could be picked out only for BaCl(ReO$_4$). According to PXRD data, formation of an isostructural compound took place for the BaBr$_2$ – Ba (ReO$_4$)$_2$ sample. In all other cases, the PXRD patterns were unrelated. In addition, oxidation of iodides (yellow coloring) was observed. Attempts to prepare BaBr(MnO$_4$) starting from BaBr$_2$ and AgMnO$_4$ yielded dark solutions which turned deep green before any crystallization started, due to reduction of MnO$_4^-$ to MnO$_4^{2-}$.

The solid-state procedure was utilized in preparation of single-phase BaCl(ReO$_4$) and search for its possible analogs. The alkaline earth halides were dehydrated at 400 °C (in dynamic vacuum in case of iodides), while the perrhenates, at 140 °C. The anhydrous salts were taken in 1:1 M ratio, quickly ground, placed in silica-jacketed alumina crucibles, evacuated to 10^{-1} Torr, flame-sealed, and annealed at 550 °C for 48 h. The samples were then re-ground and annealed once more under the same conditions. The powder samples had a brownish tint, probably due to slight reduction of Re^{VII}. PXRD indicated presence of two phase-pure compounds BaCl(ReO$_4$) and BaBr(ReO$_4$); in other cases (involving BaI$_2$ and all Sr-containing samples), the patterns could not be interpreted in

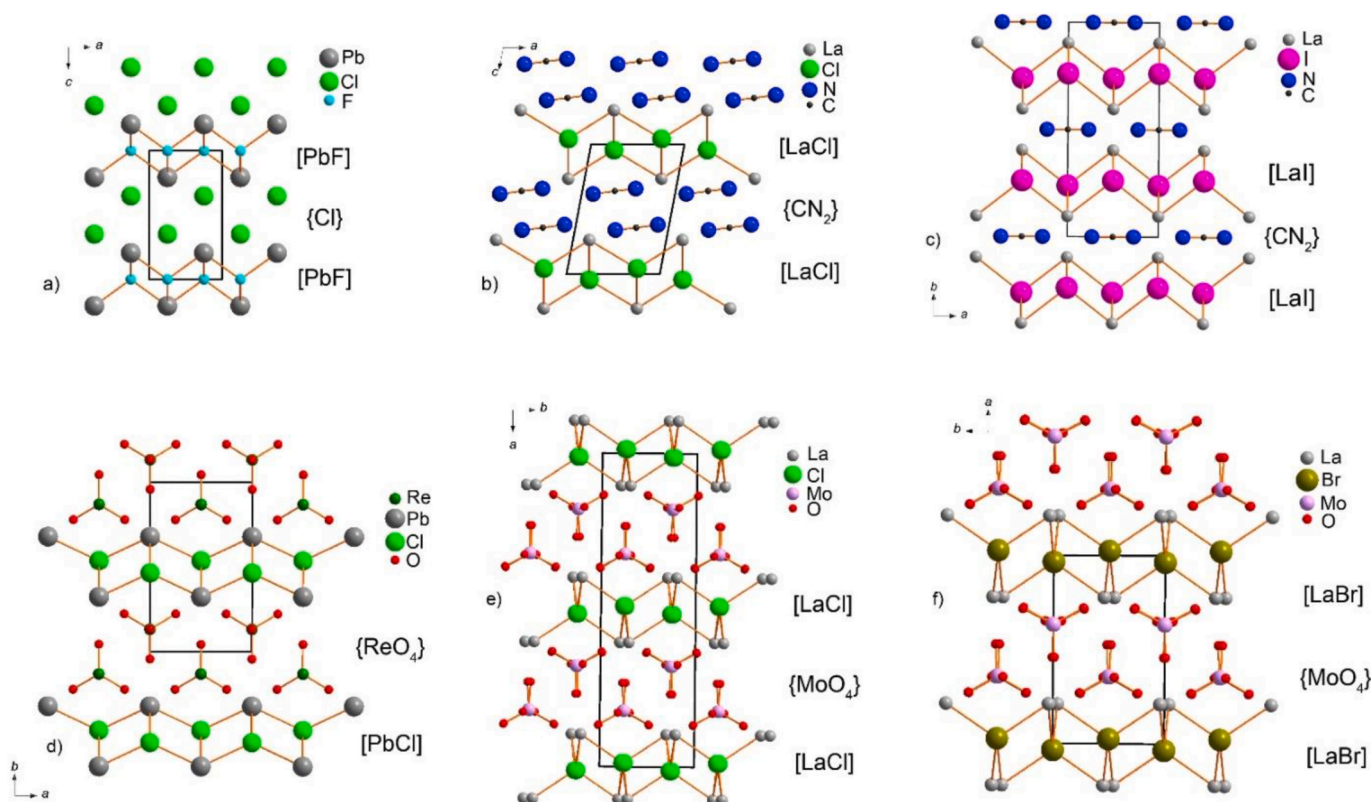**Fig. 1.** The PbFCl structure (*a*) and its derivatives: LaCl(CN$_2$) [14] (*b*), LaI(CN$_2$) [28] (*c*), PbCl(ReO$_4$) [20] (*d*), LaCl(MoO$_4$) [21] (*e*), and LaBr(MoO$_4$) [26] (*f*).

favor of isostructural compounds.

2.2. Single-crystal XRD studies

Selected single crystals taken from $PbBr_2$ – $Pb(ReO_4)_2$ – H_2O and $BaCl_2$ – $Ba(ReO_4)_2$ – H_2O systems were mounted on glass fibers using an epoxy resin and mounted on a Bruker SMART APEX II DUO diffractometer equipped with a micro-focus X-ray tube utilizing $MoK\alpha$ radiation. The experimental data sets were collected at 150 K. Unit cell parameters were calculated using least-squares fits. Structure factors were derived using APEX 2 after introducing the required corrections [31] details on data collection are presented in Table 2. The structures were solved using direct methods and refined in SHELXL [32]. Special attention was paid to the possible symmetry lowering keeping in mind the monoclinic structures of rare-earth halide molybdates and tungstates [19,21,26]; no improvement was observed.

2.3. Powder XRD studies

The PXRD patterns of $BaX(ReO_4)$ (X = Cl and Br) are very similar. The data for the chloride were fully indexed using the unit cell obtained during single-crystal study, and those for $BaBr(ReO_4)$ were indexed by analogy. High-quality data for the latter were collected on a PANalytical – X'pert diffractometer utilizing $CuK\alpha_{1,2}$ radiation. Rietveld refinement was performed using the JANA2006 program suite [33] using the structure of $BaCl(ReO_4)$ as a starting model. The refinement proceeded smoothly yet the precision of distances to oxygen atoms, as weakest scatterers, was about ± 0.02 Å. We note that similar problems were observed in test refinements of $PbBr(ReO_4)$ and $BaCl(ReO_4)$ from powder data (of similar quality) which did not occur in single-crystal refinements. Final Rietveld refinement plot for $BaBr(ReO_4)$ is given in Fig. 2, and refinement details, in Table 1. Selected bond distances for the $MX(ReO_4)$ compounds are collected in Table 2.

3. Results and discussion

The crystal structures of $PbCl(ReO_4)$ and $BaCl(ReO_4)$ are shown in Fig. 3; the bromides are complete structural analogs of the chlorides. The difference between the Pb and Ba halide perrhenates is that in the former case, all terminal oxygen atoms of ReO_4^- tetrahedra, are pointing in the same direction, yielding a non-centrosymmetric structure while in barium compounds, they point in opposite directions in two consecutive
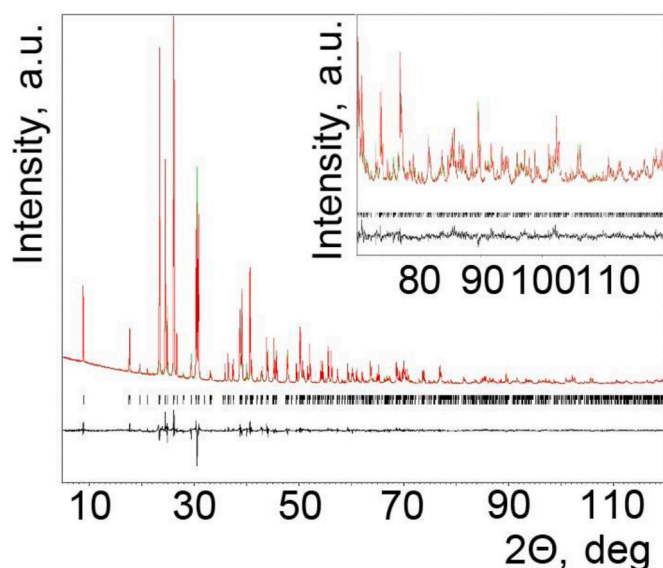

Fig. 2. Final Rietveld refinement plot for $BaBr(ReO_4)$.

Table 1
Data for the single-crystal and powder data experiments.

	Single-crystal XRD		Powder XRD	
	$PbBr(ReO_4)$	$BaCl(ReO_4)$		$BaBr(ReO_4)$
Space Group	$Pmn2_1$	$Pnma$	Space Group	$Pnma$
$a(\text{Å})$	5.769(3)	19.484(4)	$a(\text{Å})$	20.0406(1)
$b(\text{Å})$	9.684(5)	5.7260(16)	$b(\text{Å})$	5.84559(4)
$c(\text{Å})$	4.541(2)	4.6081(11)	$c(\text{Å})$	4.65124(3)
$V(\text{Å}^3)$	253.7(2)	514.1(2)	$V(\text{Å}^3)$	544.889(6)
D_x, g/cm^3	7.034	5.465	D_x, g/cm^3	5.698
θ range (°).	2.103–27.962	2.090–27.993	2θ range (°).	5–120
R_{int}	0.060	0.026	R_P	0.034
R_1	0.034	0.013	R_{WP}	0.035
Gof	1.079	1.050	R_F	0.036
CCDC	2039265	2039266		2039388

Table 2
Selected bond distances for the $MX(ReO_4)$ compounds.

Compound	$PbCl(ReO_4)$ [a]	$PbBr(ReO_4)$ [b]	$BaCl(ReO_4)$ [b]	$BaBr(ReO_4)$ [a]
$d(MX)$	2.834(6) × 1	2.987(3) × 1	3.147(1) × 1	3.298(3) × 1
	3.147(2) × 2	3.235(2) × 2	3.163(1) × 1	3.312(1) × 2
	3.186(6) × 1	3.305(3) × 1	3.193(1) × 2	3.318(3) × 1
$d(MO)$	2.54(1) × 2	2.57(1) × 2	2.749(4) × 1	2.669(11) × 1
	2.66(2) × 1	2.63(2) × 1	2.818(2) × 2	2.834(11) × 2
	3.08(1) × 1	3.16(1) × 1	2.940(2) × 2	2.996(11) × 2
	3.38(1) × 2	3.42(1) × 2	3.387(2) × 2	3.402(5) × 2
$d(ReO)$	1.67(2) × 1	1.72(2) × 1;	1.712(4) × 1	1.717(12) × 1
	1.74(1) × 2	1.74(1) × 2;	1.713(3) × 1	1.784(14) × 1
	1.72(2) × 1	1.76(2) × 1	1.732(2) × 2	1.716(9) × 2

[a] Ref. [20].
[b] This work.

slabs, as indicated by the arrows in Fig. 3. The structural relationship between these structures is exactly the same as that between LnCl (MoO_4) [21] and $LnBr(MoO_4)$ [26]. It is also very similar to those between polytypes though does not fully obey the exact definition of polytypism.

For both lead and barium compounds, bromides are full structural analogs of chlorides which differs these compounds from $PbX(N_3)$, where the chloride and bromide are not isostructural [17], and BaX $(ClO_4)(H_2O)$ where the possible bromide analog is unknown to date [23]. Note also that among rare-earth halide molybdates, the formation of centric/acentric pseudo-polytype is determined by the nature of halide anion, not the rare-earth cation [21,26].

$BaCl(ReO_4)$ is isostructural to $BaCl(MnO_4)$ [22] which suggests that analogous pertechnate compounds should exist and adopt the same arrangement. The same probably applies to the suggested $PbX(TcO_4)$ keeping in mind the very slight size difference between Tc^{VII} and Re^{VII} [30]. In fact, the separation of $MX(TO_4)$ structures into the $[M_2X_2]^{2+}$ litharge layers and sheets of tetrahedral anions is essentially artificial but useful for comparison to other related structures and their classification. The Ba^{2+} cations reside in slightly distorted tricapped BaO_5Cl_4 Archimedean antiprisms (Fig. 4) where the smaller O_4 lid is capped by oxygen atoms coming from the perrhenate groups. Slightly distorted ReO_4^- tetrahedra share three vertices with the BaO_7Cl_4 polyhedra. This differs the structure of $BaCl(ReO_4)$ from that of $BaCl(ClO_4)(H_2O)$ where the capping is provided by the water molecules and ClO_4^- tetrahedra share three vertices with the $BaCl_4O_6(H_2O)$ polyhedra from the same $[Ba_2Cl_2]^{2+}$ layer [23]. In $PbX(ReO_4)$, the coordination number of Pb^{2+} also equals nine but the environment is less regular, most likely due to the stereochemical activity of the lone electron pair.

A slightly different coordination pattern is observed in $BaCl(BF_4)$ which is formally isostructural to $PbX(ReO_4)$. The smaller BF_4^- anions cluster around Ba^{2+} so that its coordination polyhedron is rather regular and similar to that one observed in $BaCl(ClO_4)(H_2O)$ [23]. The Ba–F distances are shorter compared to Ba–O as contributions from F^- to the
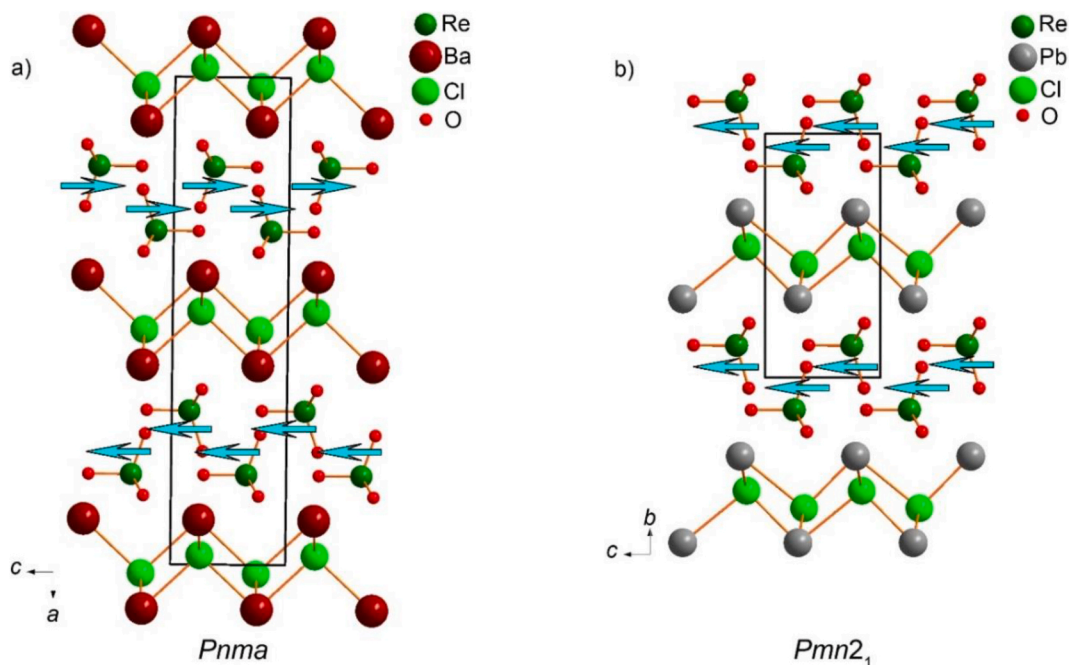
Fig. 3. Projections of centrosymmetric BaCl(ReO$_4$) (a) and non-centrosymmetric PbCl(ReO$_4$) (b). Arrows illustrate the alignment of the perrhenate anions.
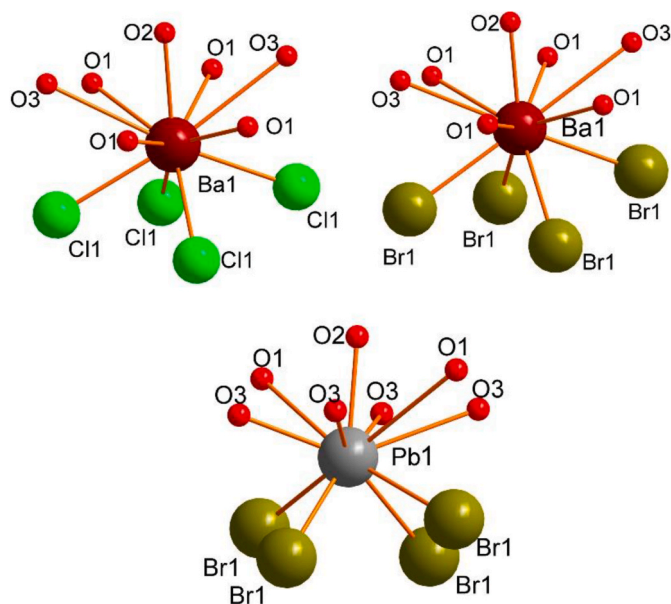

Fig. 4. Environment of Ba^{2+} (upper) and Pb^{2+} (lower) in the structures of the new MX(ReO$_4$) halide perrhenates. The radius of the coordination spheres is taken as 3.55 Å.

BVS of Ba^{2+} are smaller compared to O^{2-} upon the same distances. The crystals of BaCl(BF$_4$) were prepared hydrothermally under relatively high temperatures which seem to disfavor formation of hydrates; one can speculate that the use of lower-temperature solution synthesis (between 25 and 100 °C) could possibly lead to a BaCl(ClO$_4$)(H$_2$O)-type compound.[1]

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[1] Hojo et al. [34] reported precipitation of a barium perchlorate chloride from acetonitrile which they identified as BaCl(ClO$_4$). However, the reported IR spectrum clearly shows the presence of water and the provided XRD pattern contains most lines of BaCl(ClO$_4$)(H$_2$O), except the weakest.

As expected, the ionic XM_4 tetrahedra (X = Cl, Br; M = Pb, Ba) forming the [X_2M_2]$^{2+}$ layers exhibit essential distortions which are more pronounced in the lead compounds. Table 3 lists the known structures comprising Cl, Br, or I-based litharge layers and the X – M (M = Pb, Ba, Sr, early Ln) distances therein. The X–Pb distances lie in an essentially wider range compared to X–Ba; the same is true for the other iso-structural MCl(N$_3$) group (Cl–Pb: 2.950–3.212 Å [17]; Cl–Ba: 3.113–3.161 Å [16]). These structural elements seem to be essentially less stable compared to [Ba$_2X_2$]$^{2+}$ which are more common as illustrated by Table 3; there we also observe relatively narrow distribution of Ba–Cl distances (Table 3). The largest differences are observed in the perite-type compounds BaSbO$_2$Cl [36] and BaBiO$_2$Cl [37] This structure is commonly considered as alternation of oxocentred litharge-based [M^{II}PnO$_2$]$^+$ slabs (M^{II} = Sr, Ba, Pb; Pn = Sb, Bi) and halide anions; yet, in can alternatively be considered as alternations of [$M^{II}_2X_2$] slabs and [Pn$_2$O$_4$]$^{2-}$ chain anions. As noted above, both ways of separating layers are artificial and used here only for the sake of comparisons. The cases involving [Sr$_2X_2$]$^{2+}$ layers are less common and found almost entirely in Ba$_2$Cu$_3$O$_4$Cl$_2$-type compounds [12,25,27] with a yet only "outside" case of SrI(OCN) [28]. Attempts to prepare Sr analog of barium chloride perchlorate (actually a hydrate [23]) were unsuccessful to date [34]. In a similar vein, preparation of SrX(ReO$_4$) using the solution or high-temperature solid-state techniques has not been fruitful as yet. There exists a compound SrCl(BH$_4$) [42] with a composition formally related to that of BaCl(BF$_4$) but its structure is three-dimensional and bears some relationship to PbCl$_2$ (note a similar pattern of PbFCl-derived PbCl(N$_3$) and PbCl$_2$-related PbBr(N$_3$) [17], as well as α- and β-polymorphs of BaI(OCN) [28]). The balance between the PbCl$_2$ and PbFCl structures is rather delicate and more data are necessary for its elucidation.

The ionic radii of early Ln^{3+} cations are of the same order as that of Sr^{2+} and Pb^{2+} [30] and four families structurally based on [Ln$_2X_2$]$^{4+}$ layers are known: LnCl(CN$_2$) (Ln = La – Pr) [14] and LaI(CN$_2$) [29], LnCl(MoO$_4$) (Ln = La – Pr) [21], LnBr(MoO$_4$) (Ln = La and Ce) [26] and LnCl(WO$_4$) (Ln = La – Sm) [19]. The LaCl(CN$_2$), isostructural to BaCl(N$_3$), exhibits a relatively broad range in the La–Cl distances (3.039–3.172 Å) which is much more pronounced in the case of LnX(MoO$_4$) (La–Cl: 3.015–3.672 Å [21]; La–Br: 3.153–3.633 Å [26]). Note that $M^{II}X$(OCN) (M^{II} = Sr, Ba, Pb, Eu) and $Ln^{III}X$(CN$_2$) form two isostructural groups, one

Table 3
Known structures containing litharge layers of Cl, Br, or I-centered tetrahedra.

Compound	Sp. Gr.	a, Å	b, Å/β, °	c, Å	V, Å³	d(M − X)	Ref.
1. Structures with uniatomic interlayer anions							
PbFCl (matlockite)	P4/nmm	4.1062(2)		7.2264(9)	121.84	Pb–F 2.539 Pb–Cl 3.089–3.216	[35]
LnClTe (Ln = La–Nd)	P4/nmm	4.517(1)-4.416(1)		8.274(2)-8.122(1)	168.9–158.5	3.018 (La) 2.955 (Nd)	[10]
2. Structures with linear interlayer anions							
BaCl(OCN)	P21/m	5.5716(5)	4.4938(4) 102.410(6)	7.8489(7)	191.93	3.130–3.160	[15]
BaCl(SCN)	P2₁/m	5.886(1)	4.658(1) 100.20(3)	8.644(2)	233.25	3.160–3.218	[13]
PbCl(N₃)	P2₁/m	5.5039(11)	4.3270(9) 101.28(3)	7.658(2)	178.85	2.950–3.212	[17]
BaCl(N₃)	P2₁/m	5.5746(5)	4.5207(4) 101.835(6)	7.8081(7)	192.59	3.113–3.161	[16]
LnCl(CN₂) (Ln = La – Pr)	P2₁/m	5.330(1) – 5.296(2)	4.0305(8) – 3.934(1) 100.75(2) – 100.43(1)	7.545(1) – 7.460(2)	159.24–152.8	3.039–3.172 (La)	[14]
β-BaI(OCN)	Cmcm	5.6928(2)	13.1937(1)	6.6502(1)	499.49	3.530–3.658	[28]
LaI(CN₂)	Cmcm	5.3408(3)	12.6432(7)	6.3659(3)	429.86	3.657–3.388	[29]
BaCl(SCN)(H₂O)	Pnma	5.863(2)	4.762(1)	20.246(6)	565.26	3.175–3.192	[18]
3. Structures with tetrahedral interlayer anions							
PbCl(ReO₄)	Pmn2₁	5.6800(3)	9.4389(5)	4.4656(2)	239.41	2.834–3.186	[20]
PbBr(ReO₄)	Pmn2₁	5.769(3)	9.684(5)	4.541(2)	253.7	2.987–3.305	This work
BaCl(ReO₄)	Pnma	19.484(4)	5.7260(16)	4.6081(11)	514.1	3.147–3.193	This work
BaBr(ReO₄)	Pnma	20.0406(1)	5.84559(4)	4.65124(3)	544.89	3.298–3.318	This work
BaCl(MnO₄)	Pnma	19.2318(9)	5.5024(3)	4.7231(2)	499.80	3.150–3.170	[22]
BaCl(BF₄)	Pmn2₁	5.228(3)	9.351(5)	4.734(3)	231.4	3.114–3.165	[24]
LnCl(MoO₄) (Ln = La – Pr)	P2₁/c	19.206(2) – 19.063(2)	5.8046(5) – 5.7968(6) 90.040(6) – 90.036(6)	8.0382(7) – 7.8886(7)	896.1–871.73	3.010 - 3.672 (La) 2.957–3.720 (Pr)	[21]
LnBr(MoO₄) (Ln = La and Ce)	Pc	9.8197(4)/9.7691(4)	5.8183(2)/5.8146(2) 90.039(3)/90.004(3)	8.1051(3)/8.0259(3)	463.08–455.9	3.153–3.633 (La) 3.123–3.653 (Ce)	[26]
LnCl(WO₄) (Ln = La – Sm)	Pbcm or Pbc2₁	5.893(3)	7.856(4)	19.270(9)	892.11	2.972–3.434 (La)	[19]
BaCl(ClO₄)(H₂O)	Cmc2₁	5.2933(9)	22.550(4)	4.7722(8)	569.62	3.125–3.177	[23]
4. Structures with square-planar anionic sheets							
Ba₂Cu₃O₄Cl₂ (tetr.)	I4/mmm	5.517		13.808	420.28	3.182	[11]
Ba₂Cu₃O₄Cl₂ (orth.)	Pmma	6.553	6.000	10.563	415.32	3.170–3.185	[11]
Ba₂Cu₃O₄Br₂	I4/mmm	5.5386(2)		14.624(1)	448.61	3.272	[25]
Sr₂Cu₃O₄Cl₂	I4/mmm	5.462		12.591	375.63	3.07	[12]
Sr₂Cu₃O₄Br₂	I4/mmm	5.4840(2)		13.297(1)	399.9	3.168	[25]
Sr₂Cu₃O₄I₂	I4/mmm	5.54505(5)		14.2716(3)	438.82	3.339	[27]
5. Perite-like structures							
BaClSbO₂	Cmcm	5.849(3)	12.793(6)	5.514(2)	412.59	3.143–3.329	[36]
BaClBiO₂	Cmcm	5.880(4)	12.945(18)	5.677(3)	432.11	3.271–3.407	[37]
PbClSbO₂	Cmcm	5.603(5)	12.245(8)	5.448(7)	373.78	3.137–3.256	[38]
PbClBiO₂	Cmcm	5.593(2)	12.428(8)	5.558(2)	386.34	3.246–3.261	[39]
SrClBiO₂	Cmcm	5.7109(2)	12.4081(5)	5.5888(2)	396.03	3.491–3.527	[40]
BaIBiO₂	Cmcm	6.0492(1)	14.0224(2)	5.8212(1)	493.78	3.881–3.931	[41]

for $X = $ Cl and the other for $X = $ I; their structural motifs are related but far from being identical. The bromides, unknown to date, are expected to shed more light on the structure-driving factor of the halide size in this family. The $LnX(MoO_4)$ halide molybdates exhibit two closely related structures, one for $X = $ Cl and the other for $X = $ Br, which can be considered as monoclinically distorted versions of $BaCl(ReO_4)$ and $PbCl(ReO_4)$, respectively. These distortions may arise due to association of the MoO_4^{2-} and WO_4^{2-} into weak chains [21,26] which is not possible for MnO_4^- and unlikely for ReO_4^-. The structure of $LaCl(WO_4)$ was refined in the same orthorhombic space group $Pbcm$ as $BaCl(MnO_4)$ with a hint that the correct symmetry is monoclinic as found later for $LaCl(MoO_4)$ [19]. Apart from these unresolved details, the overall structural motifs for the two polymorphs (all TO_4 tetrahedra point into one direction, or to opposite directions in consecutive interlayers) are essentially the same. In the case of Ba and Pb perrhenate halides, the chlorides and bromides are isostructural.

Apart from the tetragonal (or pseudo-tetragonal) $[M_2X_2][Cu_3O_4]$ and $[MX][PnO_2]$ (Pn = Sb or Bi), the structures of overwhelming majority of the $[M_2X_2]^{2+}$-based compounds exhibit severe orthorhombic (or pseudo-orthorhombic) distortions of the ideally tetragonal litharge layers which are caused by the alignment of molecular anions in the interlayer space. There exists the only family of LnClTe compounds

wherein the interlayer is filled by monoatomic Te^{2-} anions [10]. Of the analogous chloride iodides of divalent cations, only PbClI is known which again exhibits an anion-ordered $PbCl_2$ motif [43] adopted by $PbBr(N_3)$ [17] and $PbCl(SCN)$ [44]. There exists also a handful of structures bearing isoelectronic $[Ln_2S_2]^{2+}$ layers, e.g. NdSBr [8] and CeSI [9] wherein the SLn_4 tetrahedra are severely distorted. No examples of $LnS(TX_4)$ compounds have been reported to date. It is also worth noting that while single-charged tetrahedral anions contribute willingly to this family, no matter centered by both transition and non-transition elements (B^{III} in the fluoroborate, Mn^{VII}, Re^{VII}, Cl^{VII} in oxoanions), tetrahedral dianions contribute more selectively (only MoO_4^{2-} and WO_4^{2-} are found to date). The crystal structures of formal sulfate analogs. $LnCl(SO_4)$, are totally different and correspond to 3D arrangements [45,46] while halide selenates and chromates are hitherto unknown.

4. Conclusions

To sum up, the litharge-derived $[M^{II}_2X_2]^{2+}$ and $[Ln_2X_2]^{4+}$ have been observed mostly in combination with linear (N_3^-, CN_2^{2-}, OCN^-, and SCN^-) and tetrahedral (BF_4^-, ClO_4^-, MnO_4^-, ReO_4^-, MoO_4^{2-}, and WO_4^{2-}) anions to yield matlockite-derived structures. With the latter, two polytype-related modifications (centrosymmetric and non-

centrosymmetric) are observed though "selection rules" for their formation are yet obscure. From structural and chemical data, we suggest that this family could be extended introducing some other linear (*e.g.* CNO^- or $SeCN^-$) and tetrahedral (TcO_4^-, BrO_4^-, IO_4^-, RuO_4^-, $OsNO_3^-$, CrO_3F^-, *etc.*) anions. It could then help formulating the conditions when these rare and possibly unstable structural fragments can form and what differs them from the very common metal-fluoride litharge slabs. Of particular interest are the relatively sparse bromides and iodides where a change of structural motif may be anticipated, by analogy to the structures containing linear anions.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solidstatesciences.2021.106576.

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