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Litharge-derived compounds structurally based on layers of Cl^- and Br^- centered tetrahedra: Synthesis and structures of the new representatives of $MX(ReO_4)$ family (M=Ba, Pb; X=Cl, Br)

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ABSTRACT

Two new layered barium perrhenate halides, BaX(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 LnX(TO₄) (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 O^{2-} , namely N^{3-} , 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^- , O^{2-} or N^{3-} 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 CN_2^{2-} [14,29] (Fig. 1b and c), the interlayer space can be filled by tetrahedral anions like BF₄⁻ [24], ClO_4^- [23], MnO_4^- [22], and ReO_4^- [20] (Fig. 1, d-f). In two cases, these structures also contain additional water molecules [18,23]. The halide perrhenates PbX(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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to be non-centrosymmetric and exhibit a noticeable SHG activity [20]. Later, a chemically and structurally related BaCl(MnO₄) compound was discovered as a by-product in preparation of Ba(MnO₄)₂ [22]; its structure is centrosymmetric. In an attempt to obtain its perchlorate analogue, we succeeded in preparation of non-centrosymmetric BaCl (ClO₄)(H₂O) [23]. The best NLO activity is exhibited by a recently found BaCl(BF₄) compound [24] which is isostructural to PbCl(ReO₄). 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 Sr²⁺ (*r* = 1.26 Å) is similar in size to early Ln³⁺ (*r* = 1.16–1.06 Å) and Pb²⁺ (*r* = 1.29 Å [30]).

In the current study, we attempted to expand the family of the MX (ReO₄) compounds and to review crystal chemical relationships in this family. As a result, two new BaX(ReO₄) (X = Cl, Br) compounds were prepared; structural data were also obtained for PbBr(ReO₄) 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 CuK α 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 HReO₄ solution by excess ammonia; large transparent crystals formed upon evaporation to dryness at room temperature. Next, PbO and NH₄ReO₄ 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(ReO₄)₂.

Two approaches were followed to prepare the corresponding MX (ReO₄) 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 (ReO₄) were produced within days while only hydrates of MX_2 and M(ReO₄)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(ReO₄). According to PXRD data, formation of an isostructural compound took place for the BaBr₂ - Ba $(\text{ReO}_4)_2$ sample. In all other cases, the PXRD patterns were unrelated. In addition, oxidation of iodides (vellow coloring) was observed. Attempts to prepare BaBr(MnO₄) starting from BaBr₂ and AgMnO₄ vielded 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(ReO₄) 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(ReO₄) and BaBr(ReO₄); in other cases (involving BaI₂ and all Sr-containing samples), the patterns could not be interpreted in



Fig. 1. The PbFCl structure (a) and its derivatives: LaCl(CN₂) [14] (b), LaI(CN₂) [28] (c), PbCl(ReO₄) [20] (d), LaCl(MoO₄) [21] (e), and LaBr(MoO₄) [26] (f).

favor of isostructural compounds.

2.2. Single-crystal XRD studies

Selected single crystals taken from PbBr₂ – Pb(ReO₄)₂ – H₂O and BaCl₂ – Ba(ReO₄)₂ – H₂O 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 α 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(ReO₄) (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(ReO₄) 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(ReO₄) 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(ReO₄) and BaCl(ReO₄) from powder data (of similar quality) which did not occur in single-crystal refinements. Final Rietveld refinement plot for BaBr(ReO₄) is given in Fig. 2, and refinement details, in Table 1. Selected bond distances for the *MX*(ReO₄) compounds are collected in Table 2.

3. Results and discussion

The crystal structures of PbCl(ReO₄) and BaCl(ReO₄) 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(ReO₄).

Table 1

Data i	or t	he si	ngle-	crystal	and	powd	er c	lata	experim	ents.
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Single-crystal X	RD	Powder XRD			
	PbBr(ReO ₄)	BaCl(ReO ₄)		BaBr(ReO ₄)	
Space Group $a(\mathring{A})$ $b(\mathring{A})$ $c(\mathring{A})$ $V(\mathring{A}^3)$ $D_{xo} g/cm^3$ θ range (°). R_{int} R_1 Gof	Pmn2 ₁ 5.769(3) 9.684(5) 4.541(2) 253.7(2) 7.034 2.103–27.962 0.060 0.034 1.079	Pnma 19.484(4) 5.7260(16) 4.6081(11) 514.1(2) 5.465 2.090–27.993 0.026 0.013 1.050	Space Group a(Å) b(Å) c(Å) $V(Å^3)$ $D_x, g/cm^3$ 2θ range (°). R_P R_WP R_r	Pnma 20.0406(1) 5.84559(4) 4.65124(3) 544.889(6) 5.698 5–120 0.034 0.035 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) imes 1	3.193(1) × 2	3.318(3) × 1
d(MO)	$2.54(1) \times 2$	$2.57(1) \times 2$	2.749(4) imes 1	$2.669(11) \times 1$
	$2.66(2) \times 1$	$2.63(2) \times 1$	2.818(2) × 2	$2.834(11) \times 2$
	$3.08(1) \times 1$	$3.16(1) \times 1$	2.940(2) × 2	$2.996(11) \times 2$
	3.38(1) × 2	3.42(1) × 2	3.387(2) × 2	3.402(5) × 2
d(ReO)	$1.67(2) \times 1$	$1.72(2) \times 1;$	1.712(4) × 1	$1.717(12) \times 1$
	$1.74(1) \times 2$	$1.74(1) \times 2;$	1.713(3) × 1	$1.784(14) \times 1$
	$1.72(2) \times 1$	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 (ClO₄)(H₂O) 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(ReO₄) is isostructural to BaCl(MnO₄) [22] which suggests that analogous pertechnate compounds should exist and adopt the same arrangement. The same probably applies to the suggested PbX(TcO₄) 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 Ba²⁺ cations reside in slightly distorted tricapped BaO₅Cl₄ Archimedean antiprisms (Fig. 4) where the smaller O_4 lid is capped by oxygen atoms coming from the perrhenate groups. Slightly distorted ReO₄⁻ tetrahedra share three vertices with the BaO₇Cl₄ polyhedra. This differs the structure of BaCl(ReO₄) from that of BaCl(ClO₄)(H₂O) where the capping is provided by the water molecules and ClO₄⁻ tetrahedra share three vertices with the BaCl₄O₆(H₂O) polyhedra from the same $[Ba_2Cl_2]^{2+}$ layer [23]. In PbX(ReO₄), the coordination number of Pb²⁺ 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(BF₄) which is formally isostructural to PbX(ReO₄). The smaller BF₄⁻ anions cluster around Ba²⁺ so that its coordination polyhedron is rather regular and similar to that one observed in BaCl(ClO₄)(H₂O) [23]. The Ba–F distances are shorter compared to Ba–O as contributions from F⁻ to the



Fig. 3. Projections of centrosymmetric BaCl(ReO₄) (a) and non-centrosymmetric PbCl(ReO₄) (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 $MX(\text{ReO}_4)$ halide perrhenates. The radius of the coordination spheres is taken as 3.55 Å.

BVS of Ba²⁺ are smaller compared to O²⁻ upon the same distances. The crystals of BaCl(BF₄) 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(ClO₄)(H₂O)-type compound.¹

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 isostructural MCl(N₃) 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 BaSbO₂Cl [36] and BaBiO₂Cl [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 $[M^{II}_{2}X_{2}]$ slabs and $[Pn_2O_4]^{2-}$ 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 $Ba_2Cu_3O_4Cl_2$ -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(ReO₄) using the solution or high-temperature solid-state techniques has not been fruitful as yet. There exists a compound SrCl(BH₄) [42] with a composition formally related to that of BaCl(BF₄) but its structure is three-dimensional and bears some relationship to PbCl₂ (note a similar pattern of PbFCl-derived PbCl(N₃) and PbCl₂-related PbBr(N₃) [17], as well as α - and β -polymorphs of BaI(OCN) [28]). The balance between the PbCl₂ 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 [Ln₂X₂]⁴⁺ layers are known: LnCl(CN₂) (Ln = La – Pr) [14] and LaI(CN₂) [29], LnCl (MoO₄) (Ln = La – Pr) [21], LnBr(MoO₄) (Ln = La and Ce) [26] and LnCl (WO₄) (Ln = La – Sm) [19]. The LaCl(CN₂), isostructural to BaCl(N₃), 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(MOO₄) (La–Cl: 3.015–3.672 Å [21]; La–Br: 3.153–3.633 Å [26]). Note that $M^{II}X(\text{CCN})$ ($M^{II} = \text{Sr}$, Ba, Pb, Eu) and $Ln^{III}X(\text{CN}_2)$ form two isostructural groups, one

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 $BaCl(ClO_4)(H_2O)$, except the weakest.

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Table 3

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

leml	Compound	Sp. Gr.	a, A	b, Α/β, °	с, А	V, A^3	d(M - X)	Ref.
<table-container>PerformationAlong2)ProgramProgram Program<</table-container>	1. Structures with uniate	omic interlayer ani	ons					
LaCTre (La = La-Nd)P4/mm4.517(1)-4.416(1)B.27(2)-8.122(1)16.89-15.8.3.018 ()1102. Structures with lines:5.571 (6.5)4.4938(1)7.4849(7)91.933.130 - 3.161.5BaC(ICON)P21/m5.571 (6.5)4.658 (1)8.644(2)32.3253.160 - 3.2181.5BaC(ISCN)P21/m5.5039(11)4.327 (0)7.658(2)7.8852.950 - 3.2121.7Pd(IN)P21/m5.573 (6.5)4.327 (0)7.658(2)7.8853.09 - 3.12 (1.6)1.6BaC(ISCN)P21/m5.573 (6.5)4.327 (0)7.658(2)7.8853.039 - 3.12 (1.6)1.6BaC(ICON)P21/m5.573 (6.5)4.327 (0)7.555 (1.6)7.856 (1.6)7.856 (1.6)7.856 (1.6)7.856 (1.6)7.856 (1.6)7.856 (1.6)7.857 (1	PbFCl (matlockite)	P4/nmm	4.1062(2)		7.2264(9)	121.84	Pb-F 2.539 Pb-Cl 3 089-3 216	[35]
1. Section in the section of the sect	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]
<table-container>JACIONP21/mS-716(5)A989(4)7.8499(4)7.849(7)19.191.9.19.191.5.19JACIONP2.4/mS-86(1)G-86(1)S-46(2)S-32.12[]JPC(A)P2.4/mS-503(1)A2070(7)7.58(2)J.7.85J.50-3.12[]JPC(A)P2.4/mS-503(1)A2070(7)7.85(1)J.8.15J.5.15(1)[]JBA(A)P2.4/mS-503(1)A2070(7)J.801(7)J.5.15(1)J.1.3.16[]JPLJ2.4/mS-301(7)A301(7)J.5.15(1)J.0.15(1)J.3.13(1)[]J.1.1JPL(A)P2.4/mS-301(7)A301(7)J.5.15(1)J.0.15(1)J.3.13(1)[]J.1.1JPL(A)P2.4/mS-301(7)A301(7)J.5.15(1)J.0.15(1)J.3.13(1)J.1.1<</table-container>	2. Structures with linear	interlayer anions						
Bed(SCN)P21/m5.886(1)4.587(1)6.844(2)2.3.2123.1.60-3.212[.]Pb(M_3)P21/m5.039(1)4.327(9)7.658(2)17.852.50-3.212[.]Bed(M_3)P21/m5.746(3)4.327(9)7.801(7)19.2503.133-3.161[.]Bed(M_3)P21/m5.746(3)4.308(3)7.545(1)-7.460(2)19.24-1523.039-3.172 (m. 10.100-100)1.007(2)-100-430	BaCl(OCN)	P21/m	5.5716(5)	4.4938(4) 102.410(6)	7.8489(7)	191.93	3.130-3.160	[15]
Pb(lx)Pa1/m5,039(1)4,320°97,658(2)17,8582,950-3.212[1]Ba(lx)Pa1/m5,574(5)4,500(4)7,808(7)19.2583,113-3.161[5]La(lx)11.835(6)11.835(6)11.835(6)11.835(7)15.92,4152.83,039-3,172 (10.81)La(lxO)Corra5,030(1) 5,26(2)13.930(1)6,562(1)49.943.03-3,578[2]Ja(lxO)Corra5,042(2)13.197 (10.6502(1)49.943.03-3,588[2]Ja(lxO)Corra5,042(3)12.642(7)6,569(3)29.863.63-3,388[2]Ja(lxO)Corra5,692(3)12.642(7)6.369(3)29.863.63-3,388[2]Ja(lxO)Pina5,693(3)4.641(2)23.72.97-3,30511.81 withJa(lxO)Pina19.484(4)5,7260(16)4.6512(3)4.9413.14-3.19311.81 withBa(lkO_0)Pina19.218(9)5.504(3)4.2512(3)49.813.19-3.170[2]Ba(lkO_0)Pina19.228(3)9.31(4)4.734(3)21.43.14-3.193[1]Ba(lkO_0)Pina19.228(3)9.31(4)4.734(3)21.43.14-3.193[2]Ba(lkO_0)Pina19.228(3)9.31(4)4.734(3)21.43.14-3.193[2]Ba(lxO_0)Pina19.228(3)9.31(4)4.734(3)21.43.14-3.193[3][3]Ba(lxO_0)Pina5.92(3)9.31(4)4.734(3)21.43.14-3.193 <td< td=""><td>BaCl(SCN)</td><td>$P2_1/m$</td><td>5.886(1)</td><td>4.658(1)</td><td>8.644(2)</td><td>233.25</td><td>3.160-3.218</td><td>[13]</td></td<>	BaCl(SCN)	$P2_1/m$	5.886(1)	4.658(1)	8.644(2)	233.25	3.160-3.218	[13]
BackIN, P P P 5.5746(5) 4.507(4) 10.1835(6) 7.808(17) P P 9.113-3.161 [16] LnCI(CN) P.1/m 5.330(1) - 5.296(2) 4.035(6) - 9.39(4) 7.545(1) - 7.460(2) 159.24-152.8 3.039-3.172 (1a) [14] (n = 1a - PT) - 100.75(2) - 100.43(1) 1.592(2) 1.5137(1) 6.552(1) 49.940 3.530-3.658 [28] Lal(CN) Cmm 5.498(3) 12.6432(7) 0.305(3) 429.86 3.657-3.388 [29] BaC(ISCN)(M) Pmma 5.680(3) 12.6432(7) 0.246(6) 562.6 3.175-3.192 [18] 3.507-508(7) Pmma 5.680(3) 9.489(5) 4.465(2) 239.41 3.417-3.192 This work BaB(R6O,) Pmma 5.790(3) 9.520(16) 4.612(1) 514.1 3.147-3.192 This work BaB(R6O,) Pmma 19.248(9) 5.502(1) 4.512(3) 544.1 3.147-3.192 This work BaC(R6A) Pmma 19.248(3) 5.502(1) 4.512(PbCl(N ₃)	$P2_1/m$	5.5039(11)	4.3270(9)	7.658(2)	178.85	2.950-3.212	[17]
LnCl(CN) P1/m 5.330(1) - 5.296(2) Ln0.330(1) 7.545(1) - 7.460(2) 159.24-152.8 3.039-3.172 (La) [14] LnCl(CN) Cmcm 5.6528(2) 13.030(1) C.65502(1) 99.49 3.530-3.658 28 Lal(CN) Cmcm 5.4928(2) 13.037(1) 6.65502(1) 99.49 3.530-3.658 29 BaC(SN)(H ₂ O) Pma 5.863(2) 4.762(1) 20.246(6) 56.526 3.175-3.192 [18] Structures with termbertal Intergeneration 4.665(2) 29.41 2.834-3.166 [20] Structures with termbertal Intergeneration 4.665(2) 29.44 2.834-3.166 [20] Structures with termbertal Intergeneration 4.665(2) 29.44 2.834-3.168 [20] BaC(MO ₄) Pmm2 5.680(3) 9.484(3) 5.7260(16) 4.65124(3) 54.412 3.114-3.165 [21] BaC(MO ₄) Pmm2 5.228(3) 9.351(5) 4.721(2) 9.81-871.73 3.100-3.572(10) [21] Ind(MO ₄) Pm	BaCl(N ₃)	$P2_1/m$	5.5746(5)	4.5207(4)	7.8081(7)	192.59	3.113–3.161	[16]
Line La – Pf) 100.75(2) = 100.43(1) (P-BaI(CON) Cmcm 5.6928(2) 13037(1) 6.6502(1) 499.49 3.530-3.658 [28] Lal (CN ₂) Cmcm 5.4908(3) 12.6432(7) 6.3650(3) 429.66 3.577-3.382 [29] 3. Structures with tetral-ter and tetral interlay S.683(2) 4.762(1) 20.246(6) 552.66 3.175-3.192 [31] 9 Cd(RCN(A) Pmm2 5.680(3) 9.4389(5) 4.465(2) 239.41 2.834-3.186 [20] 9 DBG(ReO,A) Pmm2 5.769(3) 9.648(5) 4.465(2) 239.41 2.834-3.186 [21] Bad(ReO,A) Pmm2 10.484(4) 5.7260(1) 4.6612(3) 544.89 3.298-3.318 This work Bad(ReO,A) Pmm2 10.200(2) 5.804(5) - 5.7968(6) 8.038(2) - 7.888(7) 896.1-871.73 3.010-3.672 (1) [21] LaC(MOA,A) P/2 9.8197(4)/9.7961(4) 5.804(5) - 5.7968(6) 8.0382/7-7.888(7) 896.1-871.73 3.010-3.672 (1) [21] LnCf(WOA, Pem or Pbc2	LnCl(CN ₂)	$P2_1/m$	5.330(1) – 5.296(2)	4.0305(8) - 3.934(1)	7.545(1) – 7.460(2)	159.24–152.8	3.039–3.172 (La)	[14]
pBallOCN Child 5.692(2) 15.193(1) 6.502(1) 499.49 3.530-5.658 [28] Lal(CN) Pmma 5.408(3) 12.6432(7) 6.3505(3) 429.86 3.575-3.192 [18] BaC(ISCN)(H ₂ O) Pmma 5.660(3) 9.4389(5) 4.4656(2) 239.41 2.834-3.186 [20] Structures with tetra-tetrate minuter Fmma 19.484(4) 5.7260(16) 4.6051(10) 514.1 3.147-3.193 This work BaC(IReO,) Pmma 19.431(4) 5.7260(16) 4.6051(2) 29.80 3.150-3.170 [22] BaC(IRGA,) Pmma 19.431(8) 5.024(3) 4.7231(2) 499.80 3.150-3.170 [22] BaC(IRGA,) Pmm2, 5.228(3) 9.351(5) 4.731(2) 201.4 3.114-3.165 [24] LnC(MoO,) Pm2,1/c 19.205(2)-5.7968(6) 8.0382(7)-7.886(7) 89.1-871.73 3.010-3.672 (1) [24] LnC(MoO,) Pc 9.8197(1).9690(3) 5.8146(2) 8.1051(3)/8.0259(3) 463.08-455.9 3.153-3.633 (1,a	(Ln = La - Pr)	<i>.</i>	5 (000(0))	100.75(2) - 100.43(1)	((500(1))	100.10	0.500.0.650	5003
Lal (Csy) Oricin 5.349(3) 12.443(7) 6.365(3) 42.98b 3.557–3.388 [24] BaCl (SCN)(H_0) Pma 5.863(2) 4.762(1) 20.246(6) 565.26 3.175–3.192 [18] 3. Structures with tetral-itertal interlay: arrives Filterlay: arrives 239.41 2.834–3.186 [20] PbG(ReO_4) Pma2, 5.769(3) 9.684(5) 4.665(2) 239.41 2.834–3.186 [20] BaC(MRO_4) Pmaa 19.484(4) 5.7260(16) 4.6081(11) 514.13 3.147–3.193 This work BaC(MRO_4) Pmaa 19.2318(9) 5.5024(3) 4.7231(2) 499.80 3.150–3.170 [21] BaC(MRO_4) Pmaa 19.206(2) - 19.063(2) 5.804(6) 5.7368(6) 8.0382(7) 896.1–871.73 3.010–3.672 (a) [21] LnC(MO_4) P Pana 5.893(3) 7.856(4) 8.1051(3).8.025(3) 463.08–455.9 3.153–3.633 (a) [21] LnC(MO_4) P S.933(3) 7.856(4) 1.9270(9) 892.11 2.972-3.43	β-Bal(OCN)	Cmcm	5.6928(2)	13.1937(1)	6.6502(1)	499.49	3.530-3.658	[28]
BaCl(SN)(H2O)Puma5.863(2)4.762(1)2.02426(6)565.263.175-3.192[18]3.Structures with tetral-erial interlayer and interlay	Lal(CN ₂)	Cmcm	5.3408(3)	12.6432(7)	6.3659(3)	429.86	3.657-3.388	[29]
3. Structures with terretrier interretrier 3. Structures with terretrier 3. Structures with terretretrier 3. Structures with	BaCl(SCN)(H ₂ O)	Pnma	5.863(2)	4.762(1)	20.246(6)	565.26	3.175–3.192	[18]
PbCl(ReQ.)Pmm215.6800(3)9.4389(5)4.4656(2)239.412.834.3.186[20]PbBr(ReQ.)Pmm25.769(3)9.684(5)4.541(2)25.72.987-3.305This workBabl(ReQ.)Pmma19.484(4)5.7260(16)4.6081(11)514.13.147-3.193This workBabl(ReQ.)Pmma19.2316(9)5.5024(3)4.65124(3)544.893.298-3.318This workBaCl(MoQ.)Pmm25.2024(3)9.351(5)4.7231(2)49.003.150-3.170[2]BaCl(MoQ.)Pmm25.2024(3)9.351(5)4.7231(2)9.061-871.33.010-3.672 (1a)[2]LnCl(MoQ.)P2,/c19.206(2)-19.062(5)9.036(6)0.0386(7) -7.886(7)8.01-871.33.010-3.672 (1a)[2]LnE(MoQ.)Pc9.8197(4)/9.7691(4)5.8183(2)/5.8146(2)8.1051(3)/8.0259(3)463.08-455.93.153-3.633 (1a)[2]LnCl(WoA)Pc9.8197(4)/9.7691(4)5.8183(2)/5.8146(2)8.1051(3)/8.0259(3)463.08-455.93.153-3.7633 (1a)[2]LnCl(WoA)Pc9.8197(4)/9.7691(4)5.8183(2)/5.8146(2)8.1051(3)/8.0259(3)463.08-455.93.153-3.7633 (1a)[3][3]LnCl(WoA)Pc9.8197(4)/9.7691(4)5.8183(2)/5.8146(2)19.270(9)82.113.123-3.1633 (1a)[4]LnCl(WoA)Pc5.933(3)2.550(4)19.270(9)82.113.123-3.1633 (1a)[1]LnCl(WoA)Pmma5.51713.808420.283.18211.1BagCuS(QAC	Structures with tetrah	edral interlayer an	ions					
PbR(Re0.)PmR2,5.769(3)9.684(5)4.541(2)253.72.987-3.305This workBaC(Re0.)Pma19.484(4)5.7260(16)4.6081(11)514.13.147-3.193This workBaC(Re0.)Pmma19.2318(9)5.5024(3)4.65124(3)544.893.298-3.318This workBaC(Re7.)Pmm25.238(3)9.515(5)4.7231(2)499.803.116-3.170[24]BaC(Re7.)Pm25.238(3)9.515(5)4.734(3)231.43.114-3.165[24]LnC(MoO.)P2./c19.206(2)-19.063(2)5.8046(5) - 5.7968(6)8.0382(7) - 7.888(7)896.1-871.733.010 - 3.672 (La)[24]LnB(MoO.)P2.9.8197(4).9.7691(4)5.8183(2).5.8146(2)8.1051(3).8.0259(3)463.08-455.93.153-3.630 (La)[26]LnB(MoO.)Pc9.8197(4).9.7691(4)5.8183(2).5.8146(2)8.1051(3).8.0259(3)463.08-455.93.153-3.630 (La)[26]LnB(MOO.)Pc9.8197(4).9.7691(4)5.8183(2).5.8146(2)8.1051(3).8.0259(3)40.308-455.93.123-3.653 (Ca)[26]LnB(MOO.)Pc9.8197(4).9.7691(4)5.8183(2).5.8146(2)19.270(9)892.113.124-3.631 (La)[21]LnC(WO.)Phm or Pbc2.5.293(9)2.550(4)1.927(8)56.9623.125-3.177[23]LnC(WO.)Imma5.1713.890415.203.126-3.175[21]Ba_2UsQ.ACL (tert.)H/mm35.5713.69011.23.114-3.321[11]Ba_2UsQ.ACL (tert.)	PbCl(ReO ₄)	$Pmn2_1$	5.6800(3)	9.4389(5)	4.4656(2)	239.41	2.834-3.186	[20]
BaC(ReQ_a)Pmma19.484(4)5.7260(16)4.608(11)514.13.147-3.193This workBaBr(ReQ_a)Pmma19.201(9)5.54559(4)4.65124(3)544.893.298-318This workBaC(MOQ_b)Pmma19.2318(9)5.5024(3)4.7231(2)499.803.150-3.170[22]BaC(MOQ_b)Pmn25.228(3)9.351(5)4.734(3)896.1-871.33.010-3.672 (1a)[24]LnC(MOQ_b)P2_1/c19.206(2)-19.063(2)5.8046(5)-5.5768(6)8.0382(7)-7.888(7)896.1-871.33.010-3.672 (1a)[24]LnC(MOQ_b)P2_1/c19.206(2)-19.063(2)5.804(6)-9.036(6)8.0382(7)-7.888(7)896.1-871.33.010-3.672 (1a)[24]LnE(MOQ_b)P2_1/c9.8197(4)/9.7691(4)5.8183(2)/5.8146(2)8.1051(3)/8.0259(3)463.08-455.93.153-3.633 (1a)[26]LnC(WO_b)Pccn or Pbc2_15.893(3)7.856(4)19.270(9)892.112.927-3.434 (1a)[19]LnC(WO_b)Pccn or Pbc2_15.893(3)2.550(4)4.7728(8)569.623.182-3.177[23]LnC(WO_b)Pccn or Pbc2_15.93(3)2.550(4)4.7728(8)569.623.182-3.177[24]BaC(LQ_0)(Lg_0)Mcc1_1S.5171.8201.626(1)4.15.323.170-3.185[11]Ba2(U_0,QL_2)I/mmm5.5171.8308415.323.170-3.185[12]Ba2(U_0,QL_2)I/mmm5.540(2)1.426(1)448.613.272[25]Sr_2(U_0,QL_2)I/mmm5.5405(5)<	PbBr(ReO ₄)	$Pmn2_1$	5.769(3)	9.684(5)	4.541(2)	253.7	2.987-3.305	This work
BaR(ReQ.) Pmma 20.040(c) 5.84559(A) 4.6512(A) 544.89 3.298-3.18 This work BaC(IRA) Pmma 19.2318(9) 5.5024(A) 4.7231(A) 499.80 3.150-3.170 [2] BaC(IRF.) Pmma2 5.228(3) 9.515(5) 4.734(3) 231.4 3.114-3.165 [2] LnC(MoO_4) P2_1/c 19.206(2)-19.063(2) 5.8046(5)-5.57968(6) 8.0382(7)-7.8886(7) 896.1-871.73 3.010-3.672 (La) [2] LnC(MoO_4) P2 9.8197(4)/9.7691(4) 5.838(2)/5.8146(2) 8.105(3)/8.0259(3) 453.083 (La) [6] LnBr(MoO_4) Pc 9.8197(4)/9.7691(4) 5.838(2)/5.8146(2) 8.105(3)/8.0259(3) 853.043 (La) [6] LnBr(MOO_4) Pc 9.8197(4)/9.7691(4) 5.838(2)/5.814(2) 8.105(3)/8.0259(3) 853.043 (La) [7] LnBr(MOO_4) Pc 9.8197(4)/9.7691(4) 5.838(2)/5.814(2) 8.105(3)/8.0259(3) 853.043 (La) [7] LnBr(MOO_4) Pc 9.8197(4)/9.7691(4) 5.838(2)/5.814(2) 1.217 3.123.516(2)	BaCl(ReO ₄)	Pnma	19.484(4)	5.7260(16)	4.6081(11)	514.1	3.147-3.193	This work
lacl(MnO_4)Pma19.2318(9)5.5024(3)4.7231(2)99.98.03.150-3.170[22]BaC(BF_4)Pma2,5.228(3)9.351(5)4.734(3)231.43.110-3.672 (a)[24]LnC(MOO_4)P2_1/c5.208(2)-19.063(2)5.804(5) 5.5796(8)8.032(7) 7.888(67)89.1-871.33.101-3.672 (a)[21] $(Ln = La - Pr)$ 90.404(5) - 5.7968(6)8.032(7) 7.888(67)89.1-871.33.101-3.672 (a)[21] $(Ln = La - Pr)$ 9.8197(4)/9.7991(4)5.8183(2)/5.814(2)8.1051(3).8.0259(3)463.08-455.93.153-3.633 (a)[2] $(Ln = La - Rr)$ 5.893(3)7.856(4)19.270(9)892.112.972-3.434 (La)[1] $(Ln = La - Sm)$ 5.939(9)2.550(4)4.7722(8)569.623.125-3.177[2] $BaC(CO_4)(H_2)$ Mmam5.5172.550(4)4.7722(8)569.623.125-3.177[2] $BaC(CO_4)(L_2)$ Mmam5.5176.00010.56315.323.170-3.185[1] $Ba_2Cu_5Q_4C_2$ H/mmm5.5171.82011.662(1)448.613.272[2] $Sr_2Cu_5Q_4Br_2$ I/mmm5.462(5)1.4216(3)48.613.272[2] $Sr_2Cu_5Q_4L_2$ I/mmm5.460(5)1.4216(3)3.99.93.168[2] $Sr_2Cu_5Q_4L_2$ I/mmm5.4505(5)1.4216(3)3.8123.391[2] $Sr_2Cu_5Q_4L_2$ I/mmm5.4505(5)1.4216(3)3.8123.137-3.256[3] $Sr_2Cu_5Q_4L_2$ I/mmm5.4505(5)	BaBr(ReO ₄)	Pnma	20.0406(1)	5.84559(4)	4.65124(3)	544.89	3.298-3.318	This work
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BaCl(MnO ₄)	Pnma	19.2318(9)	5.5024(3)	4.7231(2)	499.80	3.150-3.170	[22]
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	BaCl(BF ₄)	$Pmn2_1$	5.228(3)	9.351(5)	4.734(3)	231.4	3.114-3.165	[24]
$ \begin{array}{ c c c c c c } (ln = La - Pr) & 90.040(6) - 90.036(6) & 2.957-3.720 (Pr) & 2.957-3.657 (Pr) & 2.957-3.657 (Pr) & 2.957-3.657 (Pr) & 2.957-3.720 (Pr) & 2.957-3.720 (Pr) & 2.957-3.720 (Pr) & 2.957-3.657 (Pr) & 2.957-3.757 (Pr) & 2.957-3.7$	LnCl(MoO ₄)	$P2_1/c$	19.206(2) - 19.063(2)	5.8046(5) - 5.7968(6)	8.0382(7) - 7.8886(7)	896.1-871.73	3.010 - 3.672 (La)	[21]
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	(Ln = La - Pr)			90.040(6) - 90.036(6)			2.957-3.720 (Pr)	
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	LnBr(MoO ₄)	Рс	9.8197(4)/9.7691(4)	5.8183(2)/5.8146(2)	8.1051(3)/8.0259(3)	463.08-455.9	3.153–3.633 (La)	[26]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	(Ln = La and Ce)			90.039(3)/90.004(3)			3.123-3.653 (Ce)	
$\begin{array}{ c c c c c c } (Ln = La - Sm) & 22.550(4) & 4.7722(8) & 569.62 & 3.125 - 3.177 & [23] \\ \hline BaCl(ClO_4)(H_2O) & Cmc_1 & 5.2933(9) & 22.550(4) & 4.7722(8) & 569.62 & 3.125 - 3.177 & [23] \\ \hline A. Structures with square-planar anionic shere reasonable of the structures with square shows a single of the structure shows a structure shows a single of the structure shows a structure shows a structure shows a structure sh$	LnCl(WO ₄)	Pbcm or $Pbc2_1$	5.893(3)	7.856(4)	19.270(9)	892.11	2.972-3.434 (La)	[19]
BaCl(ClO_4)(H_2O) $Cnc2_1$ $5.2933(9)$ $22.550(4)$ $4.7722(8)$ 569.62 $3.125-3.177$ $[23]$ $4.$ Structures with square-plane anionic short $4.$	(Ln = La - Sm)							
4. Structures with square-planar anionic sheet11 $Ba_2Cu_3O_4Cl_2$ (tetr.) $I4/mmm$ 5.517 13.808 420.28 3.182 [11] $Ba_2Cu_3O_4Cl_2$ (orth.) $Pmma$ 6.553 6.000 10.563 415.32 $3.170-3.185$ [11] $Ba_2Cu_3O_4Br_2$ $I4/mmm$ $5.5386(2)$ $14.624(1)$ 448.61 3.272 [25] $Sr_2Cu_3O_4Br_2$ $I4/mmm$ 5.462 12.591 375.63 3.07 [12] $Sr_2Cu_3O_4Br_2$ $I4/mmm$ $5.448(2)$ $3.1297(1)$ 399.9 3.168 [25] $Sr_2Cu_3O_4I_2$ $I4/mmm$ $5.54505(5)$ $14.2716(3)$ 438.82 3.339 [27] $S.$ Perite-like structures $S.849(3)$ $12.793(6)$ $5.514(2)$ 412.599 $3.143-3.329$ [36] $BaClBiO_2$ $Cmcm$ $5.880(4)$ $12.2945(18)$ $5.677(3)$ 432.11 $3.271-3.407$ [37] $PbClSbO_2$ $Cmcm$ $5.603(5)$ $12.245(8)$ $5.448(7)$ 373.78 $3.137-3.256$ [38] $PbClBiO_2$ $Cmcm$ $5.593(2)$ $12.428(8)$ $5.558(2)$ 386.34 $3.246-3.261$ [39] $SrClBiO_2$ $Cmcm$ $5.7109(2)$ $12.4081(5)$ $5.588(2)$ 396.03 $3.491-3.527$ [40] $BalBiO_2$ $Cmcm$ $6.0492(1)$ $14.0224(2)$ $5.8212(1)$ 493.78 $3.881-3.931$ [41]	$BaCl(ClO_4)(H_2O)$	$Cmc2_1$	5.2933(9)	22.550(4)	4.7722(8)	569.62	3.125-3.177	[23]
Ba2cUa3O4Cl2 (tetr.)I4/mmm5.51713.808420.283.182[11]Ba2Cu3O4Cl2 (orth.)Pmma6.5536.00010.563415.323.170-3.185[11]Ba2Cu3O4Br2I4/mmm5.5386(2)14.624(1)448.613.272[25]Sr2Cu3O4Cl2I4/mmm5.46212.591375.633.07[12]Sr2Cu3O4Br2I4/mmm5.4840(2)13.297(1)399.93.168[25]Sr2Cu3O4Br2I4/mmm5.4840(2)13.297(1)399.93.168[25]Sr2Cu3O4I2I4/mmm5.4840(2)12.916(3)438.823.339[27]S.Perite-like structures5.593(2)12.793(6)5.514(2)412.593.143-3.329[36]BaClBiO2Cmcm5.880(4)12.945(18)5.677(3)432.113.271-3.407[37]PbClSbO2Cmcm5.603(5)12.245(8)5.448(7)373.783.137-3.256[38]PbClBiO2Cmcm5.593(2)12.428(8)5.558(2)386.343.246-3.261[39]SrClBiO2Cmcm5.7109(2)12.4081(5)5.888(2)396.033.491-3.527[40]BalBiO2Cmcm6.0492(1)14.0224(2)5.8212(1)493.783.881-3.931[41]	4. Structures with square	e-planar anionic sh	eets					
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ba ₂ Cu ₃ O ₄ Cl ₂ (tetr.)	I4/mmm	5.517		13.808	420.28	3.182	[11]
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$Ba_2Cu_3O_4Cl_2$ (orth.)	Pmma	6.553	6.000	10.563	415.32	3.170-3.185	[11]
Tr_2Cu_3O_4Cl_2 I//mm 5.462 12.591 375.63 3.07 [12] Sr_2Cu_3O_4Br_2 I//mm 5.4840(2) 13.297(1) 399.9 3.168 [25] Sr_2Cu_3O_4L_2 I//mm 5.54505(5) 14.2716(3) 438.82 3.339 [27] 5. Perite-like structures	Ba ₂ Cu ₂ O ₄ Br ₂	I4/mmm	5.5386(2)		14.624(1)	448.61	3.272	[25]
Sr2Cu3O4Br2 14/mm 5.4840(2) 13.097(1) 399.9 3.168 [25] Sr2Cu3O4I2 14/mm 5.54505(5) 14.2716(3) 438.82 3.339 [27] 5. Perite-like structures	Sr ₂ Cu ₂ O ₄ Cl ₂	I4/mmm	5 462		12.591	375.63	3.07	[12]
Sh2ugoqh2 14/mm 5.460(2) 10.27(1) 59.5 5.100 [23] Sr_2Cu_3O_4L2 14/mm 5.5400(2) 14.2716(3) 438.82 3.339 [27] S. Perite-like structures	Sr ₂ Cu ₂ O ₄ Br ₂	IA/mmm	5 4840(2)		13 297(1)	300.0	3 168	[25]
Shipering and structures Friending Frieding Frie Frieding Fri	Sr. Cu. O. L	IA /mmm	5 54505(5)		14.2716(2)	139.92	3 220	[27]
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POLIDIO2 Chttm 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] BalBiO2 Cmcm 6.0492(1) 14.0224(2) 5.8212(1) 493.78 3.881-3.931 [41]	PUCIOU2	Gillen	5.003(5)	12.243(8)	0.448(/) E EE8(2)	3/3./8	3.13/-3.230	[30]
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BalBiO ₂ Cmcm 6.0492(1) 14.0224(2) 5.8212(1) 493.78 3.881-3.931 [41]	SICIBIO2	Cmcm	5.7109(2)	12.4081(5)	5.5888(2)	396.03	3.491-3.527	[40]
	BaiBiO ₂	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(MoO₄) 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(ReO₄) and PbCl (ReO₄), 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 MnO₄⁻ and unlikely for ReO₄⁻. The structure of LaCl(WO₄) was refined in the same orthorhombic space group Pbcm as BaCl(MnO₄) with a hint that the correct symmetry is monoclinic as found later for LaCl(MoO₄) [19]. Apart from these unresolved details, the overall structural motifs for the two polymorphs (all TO₄ 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) $[M_2X_2]$ [Cu₃O₄] 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 LnCITe 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 PbCl₂ motif [43] adopted by PbBr(N₃) [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 SLn₄ 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 MOQ₄^{2–} and WO₄^{2–} are found to date). The crystal structures of formal sulfate analogs. *Ln*Cl (SO₄), 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 $(BF_4^-, CIO_4^-, MnO_4^-, ReO_4^-, MoO_4^{2-}, and WO_4^{2-})$ 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.

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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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