

Layer Perovskite-Like Crystals with CsCl-Type Blocks

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Abstract—The crystal chemistry of layer perovskite-like structures with CsCl-type blocks have been analyzed. Some characteristic features of their formation are described and new praphases are derived. Possible oxyhalides and oxides are indicated. © 2001 MAIK “Nauka/Interperiodica”.

INTRODUCTION

All the numerous praphases of layer perovskite-like structures¹ can be represented as combinations of stacks (formed by layers of octahedra, pyramids, or squares inherited from perovskite-like structures) alternating with several dozens of different types of intermediate blocks [1–3]. According to [4], a *praphase* is a hypothetical phase with a symmetric structure from which the structure of a real crystal can be obtained with the aid of small atomic displacements. The arrangement of the atoms in intermediate blocks is similar to those in the elements of the well-known NaCl, CsCl, CaF₂, BiF₃, etc., structures. Below, we consider the parental phases (praphases) which include CsCl-type blocks.

The principle of the geometric construction of praphases of perovskite-like layer structure, which are in fact intergrowth structures, is rather simple. This principle provides the determination of general and coordination formulas, symmetry, undistorted space groups, approximate unit-cell parameters, and sometimes even relative atomic coordinates along the principal axis.

Most of praphases of layer perovskite-like structures belong to the tetragonal system (sp. gr. *I4/mmm* or *P4/mmm*). However, real the symmetry of crystals may be lower depending on their chemical composition or thermodynamic conditions of their growth. The structural phase transitions in all families of layer perovskite-like crystals are most often associated with the soft lattice modes corresponding to small rotations of bound octahedral groups. By analyzing layer perovskite-like crystals with the sp. gr. *I4/mmm* and *P4/mmm* [5], one can construct models of distorted phases, in which one can determine the directions not only of all the anionic displacements but, in many cases, also the displace-

ments of bulky cations. These data with due regard for the unit-cell parameters and the systematic absences of rejections can be used in structure determinations.

The method for combining stacks and blocks enables one to derive not only all the known structures of this type but, more importantly, also hundreds of new praphases [6–9]. The close correspondence of the praphases thus obtained to real structures confirms the reliability of this method for prediction of new structures.

POSSIBLE PRAPHASES

Structures of the CsCl type (*Pm3m*, $Z = 1$) are formed by monovalent metals with large halide anions (Cl⁻, Br⁻, or I⁻). Two types of blocks with the structure similar to that of CsCl are the well-known layer perovskite-type structures.

Block Cs1. A Cl or Br anion is located in the block center and has the cationic environment close to cubic one.

It was shown [2] that all the known stacks can be divided into four types (*A*, *B*, *C*, and *D*). Type *A* consists of n layers of octahedra. If $n \rightarrow \infty$, this type becomes similar to cubic perovskite. Type *B* has anionic vacancies in the stack. The *C* and *D* types have vacancies in the positions of apical anions of the octahedra. When constructing praphases, the Cs1 block is matched to the *C* and *D* stacks (Fig. 1) with anionic vacancies in the shared planes. Layer perovskite-like structures involving the *C1* stack are formed with the participation of two types of blocks. The unit cell of this stack has one anionic vacancy. The Cs1 block can grow from the side of this vacancy. The opposite face of the *C1* stack containing an anion in the center can grow into the blocks, whose outer planes are formed by anions. A series of blocks used to construct praphases are shown in Fig. 2. The notation of these blocks corresponds to the conventional notation, namely, *R* (from rock salt), *F* (from fluorite), etc. Since the only known

¹ The term *praphase*, which can be translated as *forephase* or *parental phase*, is widely used in Russian literature and, in particular, in this paper. Therefore, we decided to retain it here (Translator's note).

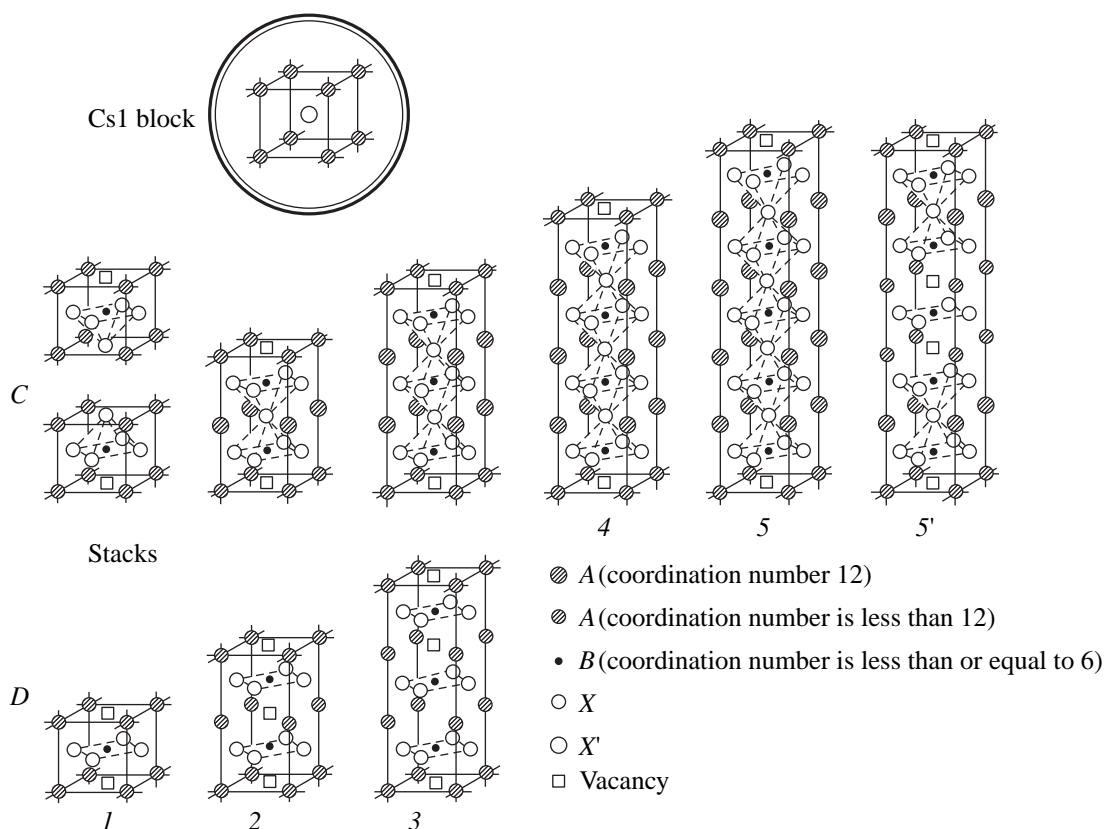


Fig. 1. Block of the Cs1 type and the corresponding stacks.

P-type blocks include lead, we retained the symbol of this element in the labelling atoms in Fig. 2 and in the coordination formulas of the praphases obtained (see below). In praphases with *P2*, *P4*, and *P6* blocks, the latter can have two orientations without any change of the crystal symmetry. Therefore, we added symbols (1) and (2) to the notation of these blocks in Fig. 2. The praphases obtained by combining the Cs1 block with the *C* and *D* stacks are indicated in Table 1.

Block Cs'1. The block center is occupied by a cation in an pseudocubic (eight vertices) anionic environment. This block is an "antipode" of the Cs1 block and can be formed only in the presence of cationic vacancies in the boundary layer of the stack. Consequently, the stack structure at the site of its junction with the block should be similar to the ReO_3 structure. The junction of these stacks obtained from the *A* and *B* types (denoted *A** and *B**) with the Cs'1 block is shown in Fig. 3. In fact, *A**-type stacks are combined from two structures—perovskite (inner layers) and ReO_3 (layers adjacent to the block). The *B** stacks, similar to the *B* stacks, have anionic vacancies.

Nine possible praphases with Cs'1 blocks are indicated in Table 2; the corresponding figures can be found elsewhere [8, 9].

PREREQUISITES FOR CRYSTALLOCHEMICAL CONSTRUCTION OF PRAPHASES

(1) A necessary condition for the formation of layer perovskite-like structures with Cs1 blocks is the presence of one large monovalent anion (Cl, Br, or I) per formula unit.

(2) Only monovalent *A* cations can be included into structures with a Cs'1 block, because at higher cation valences, the repulsion between the cations in the adjacent unit cells considerably increases.

(3) The *B* cation in these structures should have a valence equal to or higher than three, because a monovalent *A* cation requires a good "assistant." The anionic environment of the *A* cation is close to cubic, but it is also surrounded by eight additional anions from the second coordination sphere which provide the connection of octahedra into layers. This anionic construction (8 + 8) can be held only by the joint effect of the *A* and *B* cations.

The experience gained in the studies of other layer structures [7, 9] allows for the formulation of the following rules:

(4) If the coordination number is equal to 4 or 5 (a square or a square pyramid), the *B* cation in the stack can only have valence 2+ or 3+.

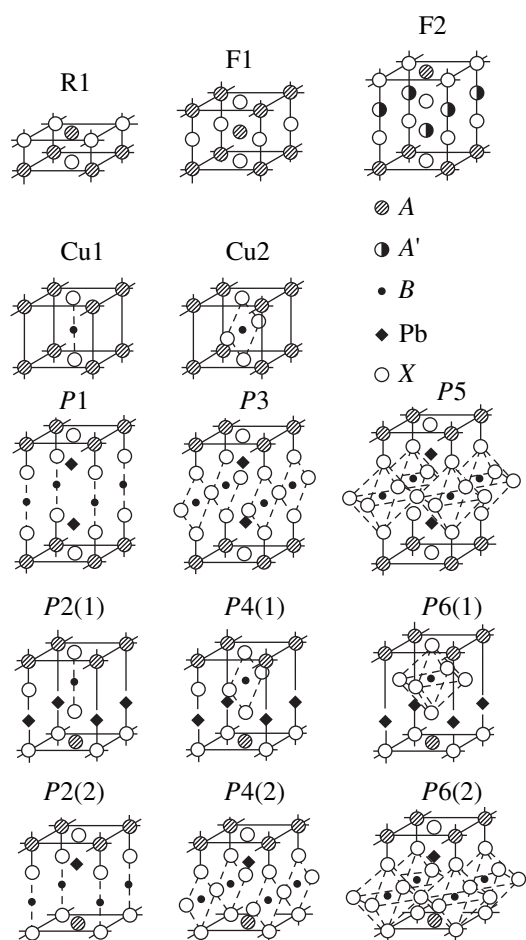


Fig. 2. Blocks matching the C1 stack.

(5) If the coordination number is equal to 6 (an octahedron), the B cation in a multilayer stack can be multicharged.

KNOWN CRYSTAL STRUCTURES

Altogether, about twenty crystals with the perovskite-like layered structure have been studied. The $\text{Pb}_4\text{Fe}_3\text{O}_8\text{Cl}$ [10] and $\text{Sr}_2\text{Pb}_2\text{Cu}_2\text{TaO}_8\text{Cl}$ [11] structures belong to the sp. gr. $P4/mmm$, $Z = 1$ and consist of three-layer stacks and Cs1-type blocks slightly “compressed” along the principal axis. A number of other oxyhalides were considered in [11, 12].

Several compounds with layer structures containing Cs1 and P1 blocks and C1 stacks were also reported in [13]: $\text{Sr}_3\text{Pb}_3\text{Cu}_3\text{O}_8\text{Cl}$, $\text{Ba}_3\text{Pb}_3\text{Cu}_3\text{O}_8\text{Cl}$, and $\text{Ba}_2\text{SrPb}_3\text{Cu}_3\text{O}_8\text{Cl}$. These structures are distorted (sp. gr. $Cmmm$, $Z = 2$) in comparison with their praphase ($P4/mmm$, $Z = 4$).

Until recently, only one-layer structures (mainly fluorides) with Cs'1 blocks have been known. The “fatter” of this family is a TlAlF_4 crystal (Fig. 4).

The structures of the TlAlF_4 type with the general formula ABX_4 consist of square octahedral networks perpendicular to the z -axis. These networks are linked by alkali metal or complex organic cations forming a Cs'1-type block. The structures of the TlAlF_4 type are high-temperature phases stable only at high temperatures. About one hundred of the known crystalline phases belong to this family, with most of them being considered as the structures formed upon distortion of the praphase caused by rotation of the BX_6 octahedra.

Recently, two compounds have been synthesized— $\text{RbLaTa}_2\text{O}_7$ with a Cs'1 block and a double layer of octahedra in the stack [14] and $\text{RbCa}_2\text{Ta}_3\text{O}_{10}$ with the same block and a triple layer of octahedra [15] (Fig. 4). We believe that other multilayer crystals of this family of oxides may also be synthesized.

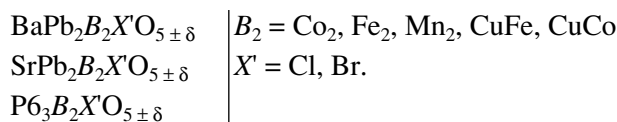
Thus, the existence of the above structures with Cs1 and Cs'1 blocks gives grounds to expect the synthesis of other praphases indicated in Tables 1 and 2.

PREDICTION OF NEW COMPOUNDS

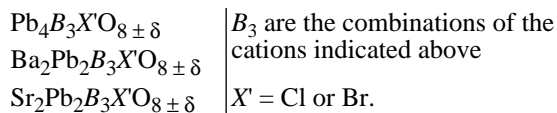
Compound with Cs1 blocks. Consider probable compounds with blocks involving Pb^{2+} cations. The B cations in the stacks were chosen proceeding from the known chemical compounds. In the general formulas, A and B are cations and X and X' are anions.

Possible Cs1\C2 compounds with the general formula $A_3B_2X_6$. To our knowledge, the following combinations of the B cations can exist in C2 stacks: Fe_2 , Co_2 , CuFe , CuCo , and $\text{Mn}^{2+}\text{Mn}^{3+}$. The total valence of two B cations in the stack should range from five to six.

The following compounds are probable:



Possible Cs1\C3 compounds with the general formula $A_4B_3X_9$. The following combinations of B cations are known for C3 stacks: Fe_3 , Cu_2Nb , Cu_2Ta , Cu_2Pb , and Cu_2Fe . The total valence of three B cations is 9+. One of A cations should provide the formation of the block, whereas the remaining three A cations should form the stack. Two A cations have the coordination number 12 and two other A cations have the coordination number 8. Thus, the following compounds are possible:



The compositions of the known compounds, show that the following substances may be synthesized: $\text{Sr}_4\text{Fe}_3\text{O}_8\text{Cl}$, $\text{Sr}_4\text{Fe}_3\text{O}_8\text{Br}$, $\text{Sr}_4\text{Cu}_2\text{TaO}_8\text{Cl}$,

Table 1. Possible praphases of layer perovskite-like structures with a Cs1 block

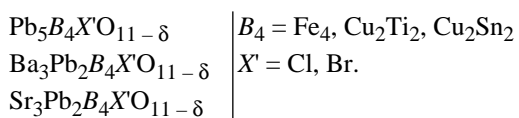
Block\stack	Sp. gr.	Z	General formula	Coordination formula
Cs1\C2	<i>P4/mmm</i>	1	$A_3B_2X_6$	$A^{XII} A_2^{VIII} B_2^V X_5X'$
Cs1\C3*	<i>P4/mmm</i>	1	$A_4B_3X_9$	$A_2^{XII} A_2^{VIII} B^{VI} B^V X_8X'$
Cs1\C4	<i>P4/mmm</i>	1	$A_5B_4X_{12}$	$A_3^{XII} A_2^{VIII} B_2^{VI} B_2^V X_{11}X'$
Cs1\C5	<i>P4/mmm</i>	1	$A_6B_5X_{15}$	$A_4^{XII} A_2^{VIII} B_3^{VI} B_2^V X_{14}X'$
Cs1\C5'	<i>P4/mmm</i>	1	$A_6B_5X_{13}$	$A_2^{XII} A_2^{VIII} A_2^{VIII} B_4^V B^{IV} X_{12}X'$
Cs1\D1	<i>P4/mmm</i>	1	A_2BX_3	$A_2^{VIII} B^{IV} X_2X'$
Cs1\D2	<i>P4/mmm</i>	1	$A_3B_2X_5$	$A_2^{VIII} A^{VIII} B_2^{IV} X_4X'$
Cs1\D3	<i>P4/mmm</i>	1	$A_4B_3X_7$	$A_2^{VIII} A_2^{VIII} B_3^{IV} X_6X'$
R1\C1\Cs1	<i>I4/mmm</i>	2	$A_4B_2X_7$	$A_2^{IX} A_2^{VIII} B_2^V X_6X'$
Cu1\C1\Cs1	<i>P4/mmm</i>	1	$A_4B_3X_7$	$A_2^{VIII} A_2^{VIII} B_2^V B^{II} X_6X'$
Cu2\C1\Cs1	<i>Pmmm</i>	1	$A_4B_3X_8$	$A_2^{VIII} A_2^{VIII+II} B_2^V B^{IV} X_7X'$
F1\C1\Cs1	<i>P4/mmm</i>	1	$A_5B_2X_8$	$A_2^{IX} A_2^{VIII} A^{VI} B_2^V X_7X'$
F2\C1\Cs1	<i>I4/mmm</i>	2	$A_6B_2X_9$	$A_2^{IX} A_2^{VIII} A_2^{VI} B_2^V X_8X'$
P1\C1\Cs1*	<i>P4/mmm</i>	1	$A_6B_3X_9$	$A_2^{IX} A_2^{VIII} Pb_2^V B_2^V B^{II} X_8X'$
P3\C1\Cs1	<i>Pmmm</i>	1	$A_6B_3X_{10}$	$A_2^{IX} A_2^{VIII} Pb_2^{VII} B_2^V B^{IV} X_9X'$
P5\C1\Cs1	<i>P4/mmm</i>	1	$A_6B_3X_{11}$	$A_2^{IX} A_2^{VIII} Pb_2^{IX} B^{VI} B_2^V X_{10}X'$
P2\C1\Cs1	<i>I4/mmm</i>	2	$A_5B_3X_8$	$A^{IX} A_2^{VIII} A^{VIII} Pb^V B_2^V B^{II} X_7X'$
P4\C1\Cs1	<i>P2/mmm</i>	2	$A_5B_3X_9$	$A^{IX} A_2^{VIII} A^{VIII+II} Pb^{VII} B_2^V B^{II} X_8X'$
P6\C1\Cs1	<i>P4/mmm</i>	2	$A_5B_3X_{10}$	$A^{XII} A_2^{VIII} A^{IX} Pb^{IX} B^{VI} B_2^V X_9X'$

Note: In general formulas, *A* and *B* are cations and *X* and *X'* are anions; *Z* is the number of formula units per unit cell. The superscripts signify the coordination numbers of the cations.

* Praphases corresponding to the already synthesized compounds, are primed; however, real crystals may be more distorted than the praphases.

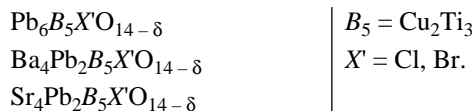
$Sr_4Cu_2NbO_8Cl$, $Sr_4Cu_2TaO_8Br$, $Sr_4Cu_2NbO_8Br$,
 $Ba_3Pb_3Cu_3O_8Br$, and $Ba_2SrPb_3Cu_3O_8Br$.

Possible Cs1\C4 compounds with the general formula $A_5B_4X_{12}$:



Possible Cs1\C5 compounds with the general for-

mula $A_6B_5X_{15}$:



Possible Cs1\D1 compounds with the general formula $A_3B_2X_5$:



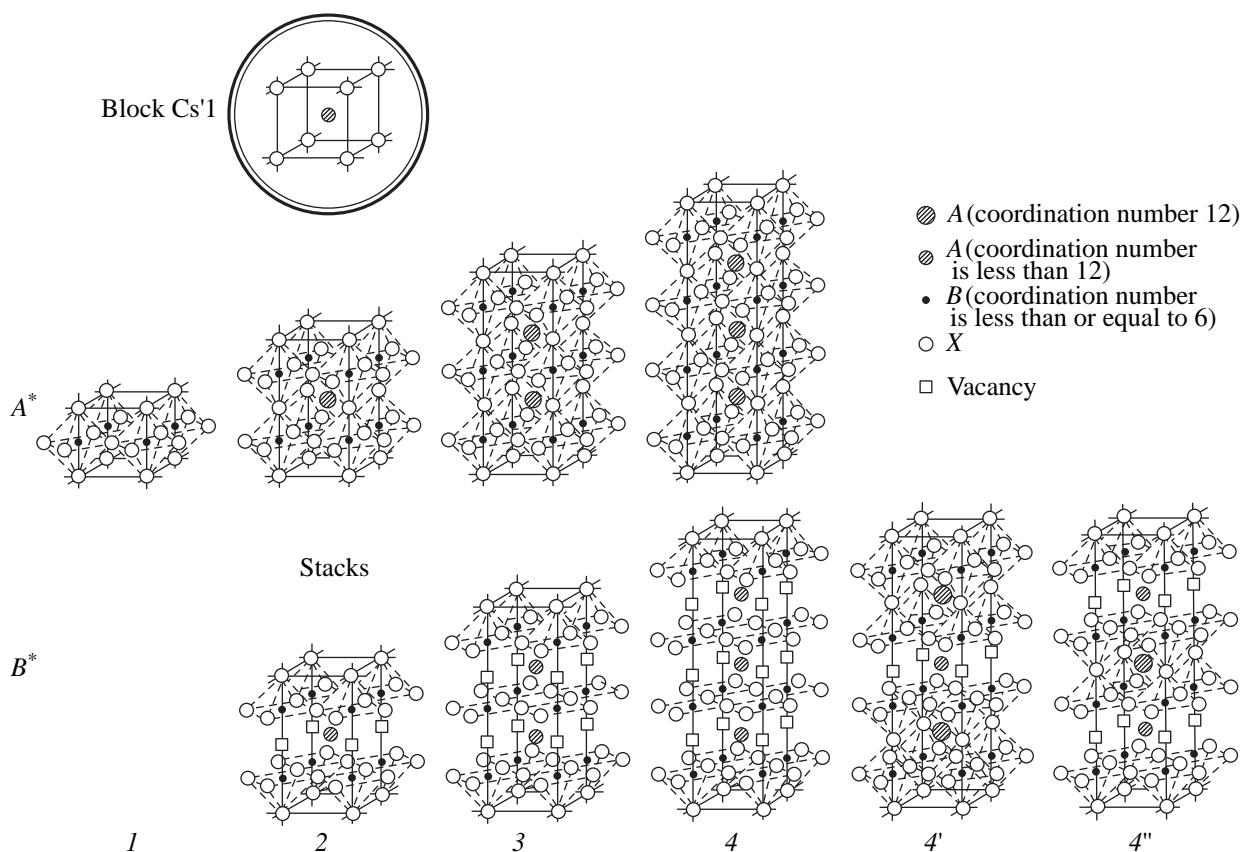


Fig. 3. Cs'1-type block and corresponding stacks.

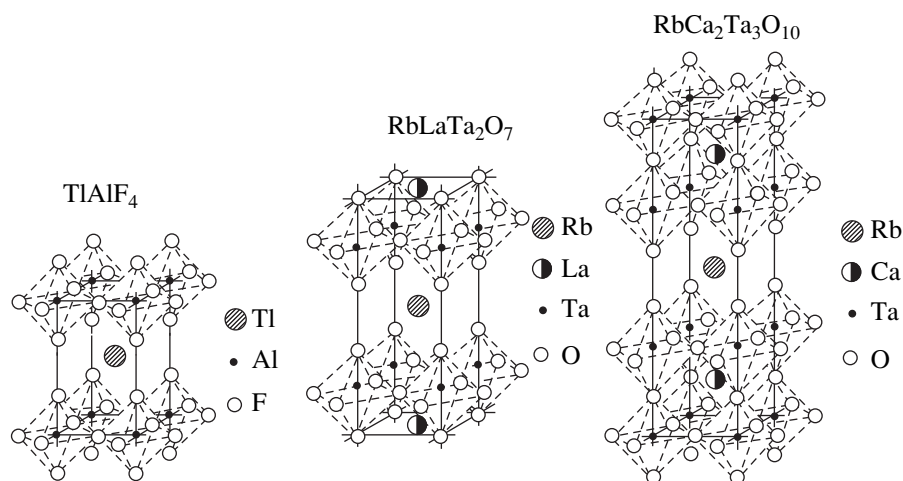
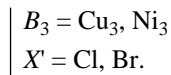
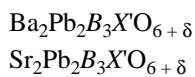


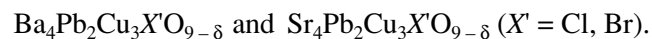
Fig. 4. Well-known structures containing the Cs'1 block.

Possible Cs1\D3 compounds with the general formula $A_4B_3X_7$:



For the Cs1\C1\P3 praphases, the following

compounds are possible:



The synthesis of Cs1\C1\P5 praphases is more difficult. To provide their electroneutrality, one has to introduce into the crystal trivalent cations, but unfortunately

Table 2. Possible praphases of layer perovskite-like structures with Cs'1 blocks

Block\stack	Sp. gr.	Z	General formula	Coordination formula
Cs'1\A*1**	<i>P4/mmm</i>	1	ABX_4	$A^{VIII}B^{VI}X_4$
Cs'1\A*2**	<i>P4/mmm</i>	1	$A_2B_2X_7$	$A^{XII}A^{VIII}B_2^{VI}X_7$
Cs'1\A*3**	<i>P4/mmm</i>	1	$A_3B_3X_{10}$	$A_2^{XII}A^{VIII}B_3^{VI}X_{10}$
Cs'1\A*4	<i>P4/mmm</i>	1	$A_4B_4X_{13}$	$A_3^{XII}A^{VIII}B_4^{VI}X_{13}$
Cs'1\B*2	<i>P4/mmm</i>	1	$A_2B_2X_6$	$A^{VIII}A^{VIII}B_2^V X_6$
Cs'1\B*3	<i>P4/mmm</i>	1	$A_3B_3X_8$	$A^{VIII}A_2^{VIII}B_2^V B^{IV} X_8$
Cs'1\B*4	<i>P4/mmm</i>	1	$A_4B_4X_{10}$	$A^{VIII}A_3^{VIII}B_2^V B_2^{IV} X_{10}$
Cs'1\B*4'	<i>P4/mmm</i>	1	$A_4B_4X_{12}$	$A_2^{XII}A^{VIII}A^{VIII}B_2^{VI}B_2^V X_{12}$
Cs'1\B*4''	<i>P4/mmm</i>	1	$A_4B_4X_{11}$	$A^{XII}A^{VIII}A_2^{VIII}B_4^V X_{11}$

Note: For hole and notation see Table 1.

they are too small. Here, the following compounds are probable: $La_4Pb_2Cu_3X'O_{10+\delta}$ ($X' = Cl$ or Br).

Altogether, we obtained 105 possible chemical compounds with Cs1-type blocks that have layer perovskite-like structures.

The blocks in both well known and predicted crystals include divalent lead. The number of such compounds can be increased by using blocks with Sr^{2+} , Eu^{2+} , Sm^{2+} , Nd^{2+} , or Sn^{2+} cations with the size close to that of lead. Thus, the number of the probable compounds amounts 600.

Compounds with Cs'1 blocks. In 1986, new fluoride-containing compounds were predicted [16]. In subsequent years, about 14 new crystalline fluoride compounds were synthesized, in full accord with the prediction made.

In oxide systems, the structures of the $TlAlF_4$ type have not been revealed, and, apparently, they are difficult to synthesize. This brings up the question as to the types of new oxide compounds with possible multilayer structures. Proceeding from the sizes of the A and B cations in the known compounds with $n = 2$ or 3 , the probable compounds should lie in the existence range of structures with $n = 1$. It may be that the ranges of existence of these structures would be the same, as is the case of Ruddlesden–Popper-type layer phases [6]. In order to be able to predict new multilayer phases with Cs'1 blocks, one has to use the geometric conditions of existence of the structures which belong to the $TlAlF_4$ family. The problem of possible formation of structures with $n > 3$ is still open. Therefore, in the present study we restricted ourselves only to compounds with $n = 2$ and 3 .

Proceeding from the known compositions $RbLaTa_2O_7$ and $RbCa_2Ta_3O_{10}$, one can obtain some modified compounds by replacing the Ta^{5+} ions by the Nb^{5+} cations. Indeed, such compounds have been reported (for example, $RbLaNb_2O_7$ [17]). A Rb^+ cation can be replaced by a Cs^+ or Tl^+ cation, a Ca^{2+} cation can be replaced by a Sr^{2+} , and a La^{3+} cation can be replaced by another (more appropriate) trivalent cation. These modified compounds have A^* -type stacks.

The question arises about the types of layered perovskite-like structures, formed with the participation of Cs'1 blocks and B^* -type stacks. The structures with B^*4' blocks are most probable because octahedra in these blocks can have highly charged cations, whereas the second A cation (in the cuboctahedron) would stabilize the stack.

We considered only some possible new compounds with Cs1 and Cs'1 blocks. The synthesis of other praphases depends on the requirements of physicists, skill of chemists, and the available technical facilities.

CONCLUSIONS

The number of new compounds with CsCl-type blocks can be multiply increased.

In layered perovskite-like crystals, the stacks and blocks produce an effect similar to that of high pressure. Hence, some cations in the layers may exist in an unusual crystallochemical state. This phenomenon may be of great importance when studying physical properties of such crystals.

If some oxygen atoms in a layer perovskite-like structure are replaced by halogen atoms, the latter atoms are usually incorporated by the blocks. There-

fore, halides (or other anions) can be used to obtain new blocks, to change the block composition, and thus increase the anisotropy of various physical properties.

The results obtained give grounds to expect the discovery of new unique properties (other than the high- T_c superconductivity) in layer crystals.

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