

Possible new phases in layered perovskite-like crystals (crystal-chemical prognosis)

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1. Introduction

The broad group of crystals containing in their structures octahedral BX_6 groups (B – small cation, X – anion) which linked by vertices and form three-dimensional frames or two-dimensional slabs is widely studied in the modern solid state physics.

Among octahedral structures, of special importance are perovskites ABX_3 and related structures, including layered perovskite-like structures built by two-dimensional single, double, etc. layers of octahedra-sharing vertices. Perovskite-like (PL) structures are often cation- or anion-deficient. In some instances, octahedra degenerate into pyramids, plane square BX_4 networks, and even X–B–X dumbbells, alternating along one or two directions. Hereafter, A and B denote cations and X denotes anions.

During the last few years, the authors tried to analyze the published structural data concerning perovskites, their deficient versions, PL-polytypes and layered PL-structures. The main aims of the work have been an effort to find the general scheme of architecture for the stoichiometric, anion- and cation-deficient PL-crystals and to determine the interrelations between different types of PL-structures. It was shown recently [1, 2] that the structures of the all known PL-crystals can be considered as the systems of *slabs* containing n layers ($n = 1, 2, \dots, \infty$) vertice-linked octahedra BX_6 (O), pyramids BX_5 (P) and/or square nets

BX_4 (Q) intergrowing by their outer surfaces with *blocks* of different types when the layered PL-structures are formed.

In Fig. 1 four rows of two-dimensional PL-slabs are shown. The row A corresponds to octahedral slabs: O, O–O, O–O–O, ...; perovskite frame is formed when $n = \infty$. These slabs can be cation-deficient and the vacancies can be disordered or ordered in different ways. Row B begins from single octahedral layer O and then $P^+ - P^-$, $P^+ - Q - P^-$, $P^+ - Q - Q - P^-$, ... Signs “+” and “–” correspond to vertices of tetrahedra “up” and “down” respectively. Row C contains as the first member ($n = 1$) single layers of P^+ or P^- pyramids and then $P^- - P^+$, $P^- - O - P^+$, $P^- - O - O - P^+$.

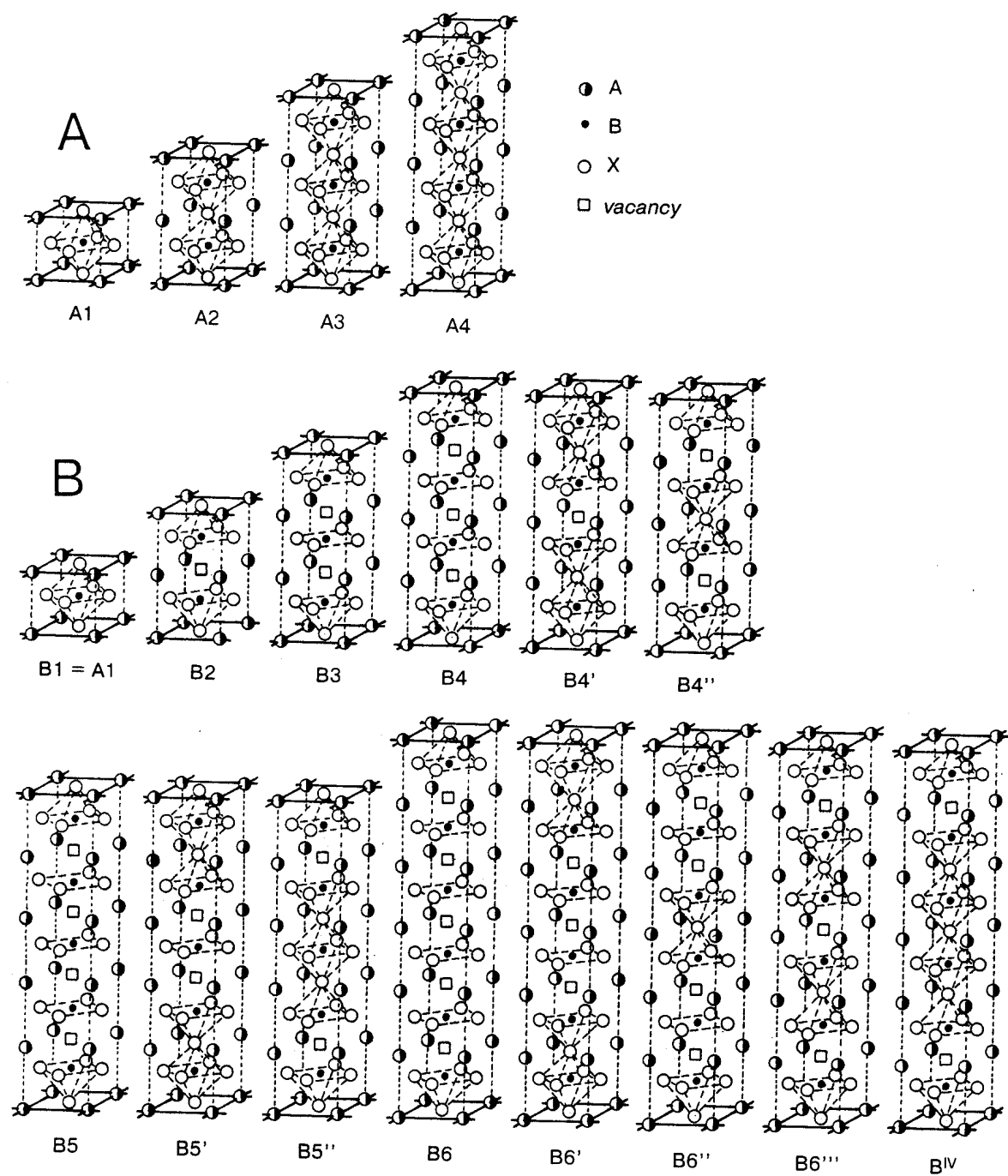


Fig. 1a. Types of provskite-like slabs

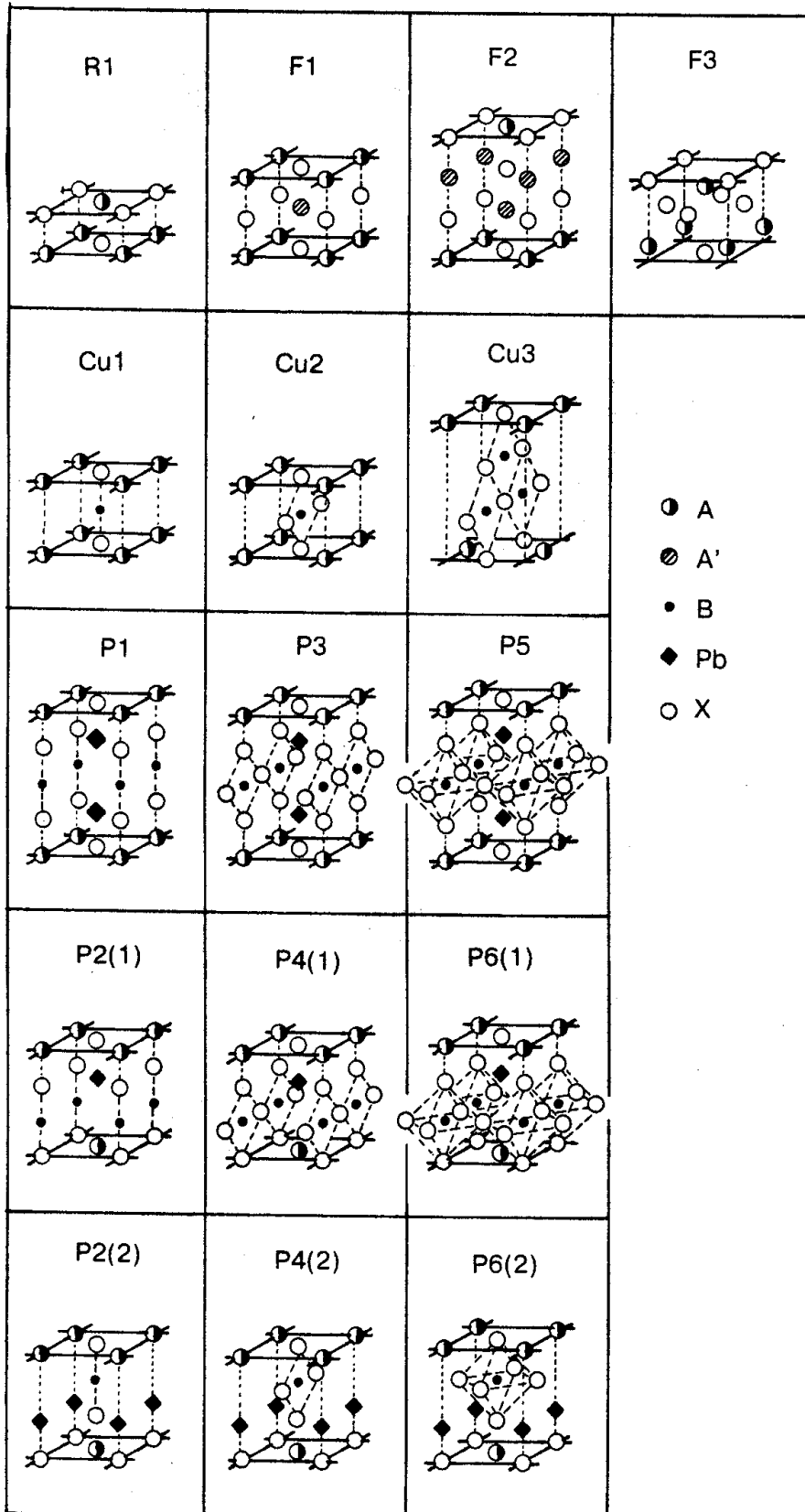


Fig. 1b. Types of blocks known in the layered perovskite-like structures

Last row consists of square nets: Q, Q – Q, Q – Q – Q. Structures with $n = 4$ are unknown in row D. It should be mentioned that slab $O - P^+$ or $P^- - O$ exists in some structures.

Variants of intermediate blocks found in different PL-crystals are shown in Fig. 2. We use here scheme proposed by Tokura and Arima [3].

We will use below the short notations of slabs (A1, A2, ..., B1, B2, ...) and blocks from Figs. 1 and 2

The main aim of the paper is the prognosis of new possible PL-crystals. In course of the study we have used the laws of the PL-structures construction [1, 4, 5] and the known structural data for PL-crystals. Simple compounds like NaCl, CsCl, CaF₂, BiF₃ are similar to the structures of many blocks. These structural data were used for selection of the block content in order to fit the unit cell parameters between outer surfaces of slab and block. In some cases we were obliged to make corrections in chemical composition of possible compounds.

It allowed to present not only all known PL-structures but hundreds of new praphases, to determine their space groups, general chemical formulas [6]. New compounds can be distorted due to many different reasons, but the layered PL-crystals in their praphases belong usually to two tetragonal space groups : *P4/mmm* or *I4/mmm*.

In Tables below we have divided possible structures into four classes:

1. Praphases having no vacancies on the outer planes of slabs and blocks.
2. Praphases having the anionic vacancies on the outer planes of slabs and blocks.
3. Praphases with cationic vacancies on the outer planes of slabs and blocks.
4. Praphases having two different blocks in their structures.

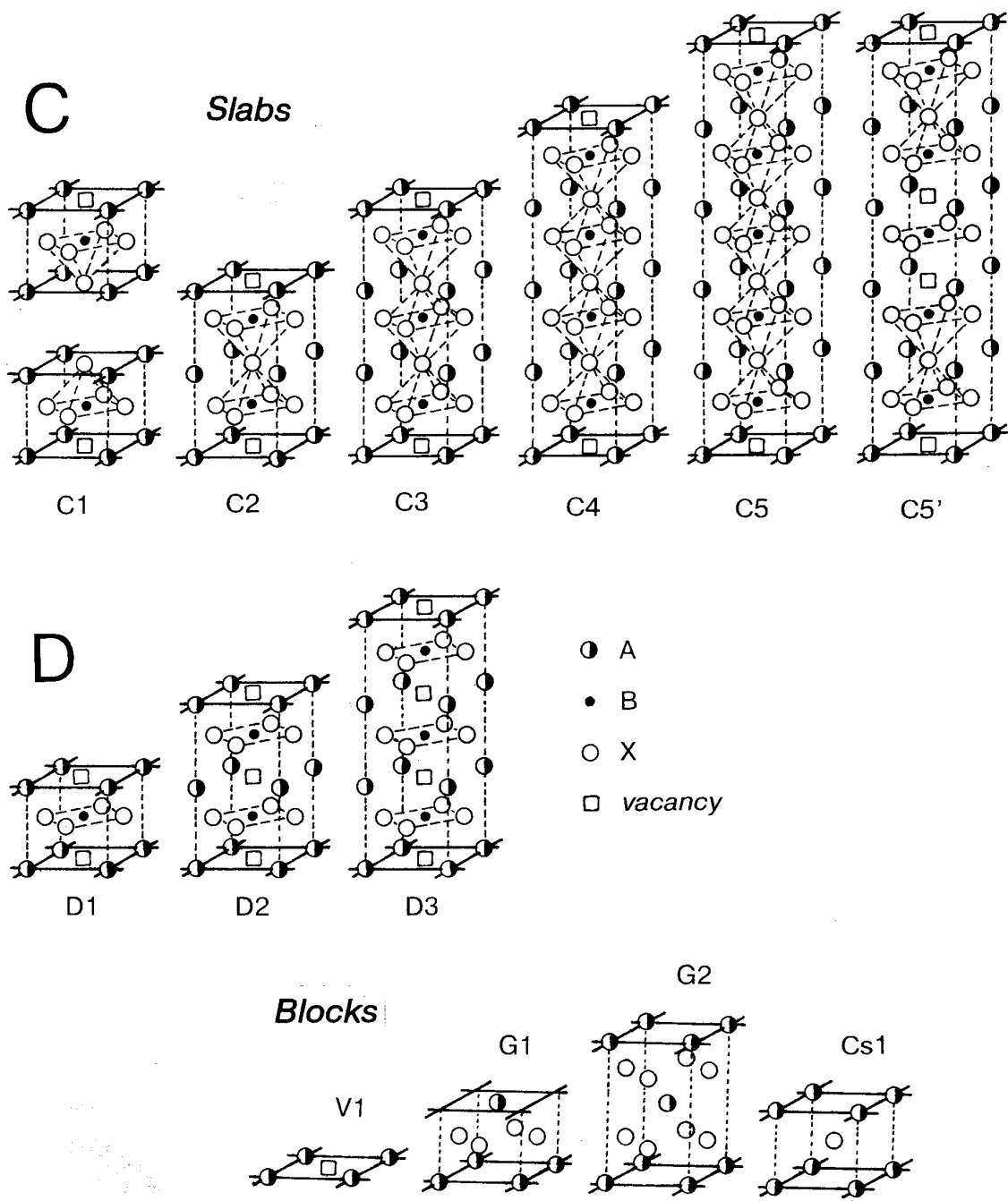


Fig. 2. Perovskite-like slabs C, D and intermediate blocks

2. Results of prognosis

2.1. Praphases having no vacancies on the outer surfaces of slabs and blocks.

These structure can be formed with A- and B-slabs and corresponding blocks from Fig. 2. Crystallographical data for 208 possible PL-compound are presented in Table 1. It is seen that only 36 crystals have been synthesized up to now. It is useful to mention here that in the well known Ruddlesden-Popper's series the bulk crystals containing 1, 2 and 3 layered A-slabs have been grown up to now. But in thin layers studied by electron microscope there were found the single crystal parts having up to eight octahedral layers as for example in $\text{Sr}_{n-1}\text{Ti}_n\text{O}_{3n+1}$ [7], and $\text{La}_{n-1}\text{Ni}_n\text{O}_{3n+1}$ [8]. Ruddlesden-Popper's series was restricted in Table 1 by the four layered A-slab [9, 10]. In Aurivillius's phases $\text{A}_2\text{X}_2(\text{A}'_{n-1}\text{B}_n\text{X}_{3n+1})$ F3-block and A-slabs are intergrow and the crystals with $n \leq 8$ were found [11]. The same number of the octahedral layers exist in series M-12(n-1)n and M-22(n-1)n where F1- and F2-blocks intergrow with B_n -slabs. The known crystals of these and other series have been collected in [1].

In Table 1 are presented space groups, general and coordination formulas of proposed praphases with one tipe of block intregrowind with A- and B-slabs.

1. The known praphases are denoted by sign ✓.
2. Coordination numbers (CN):
 - CN = 12 (XII) – cubooctahedron.
 - CN = 10 (X) – two opposite anions in the basal plane of cubooctahedron are absent.
 - CN = 8 (VIII-1) – half of cubooctahedron, orthogonal to main axis.
 - CN = 9 (IX) – tetragonal prism added to previons halt of cubooctahedron.
 - CN = 8 (VIII-2) – coordination close to cube.
 - CN = 6 (VI-1) – octahedron.
 - CN = 6 (VI-2) – octahedron with increased basic plane.
 - CN = 5 (V-1) – half of octahedron or tetrahonal prism.
 - CN = 5 (V-2) – half of octahedron with in increased basic.
 - CN = 7 (VII) = 5 + 2 – tetragonal prism plus two anions on the side of the basis.

CN = 4 (IV) – anionic square

CN = 2 (II) – dumb-bell.

Z – number of the formula units in unit cell.

Table 1
Possible layered PL-compounds due to intergrowth of A- and B-slabs
with corresponding blocks

General formula	Block/slab	Space group	Z	Coordination atoms
A_2BX_4	R1\A1 ✓	<i>I4/mmm</i>	2	$A^{\text{IX}}_2B^{\text{VI-1}}X_4$
$A_3B_2X_7$	R1\A2 ✓	<i>I4/mmm</i>	2	$A^{\text{XII}}A^{\text{IX}}_2B^{\text{VI-1}}_2X_7$
$A_4B_3X_{10}$	R1\A3 ✓	<i>I4/mmm</i>	2	$A^{\text{XII}}_2A^{\text{IX}}_2B^{\text{VI-1}}_3X_{10}$
$A_5B_4X_{13}$	R1\A4	<i>I4/mmm</i>	2	$A^{\text{XII}}_3A^{\text{IX}}_2B^{\text{VI-1}}_4X_{13}$
$A_3B_2X_6$	R1\B2 ✓	<i>I4/mmm</i>	2	$A^{\text{IX}}_2A^{\text{VIII-2}}B^{\text{V-1}}_2X_6$
$A_4B_3X_8$	R1\B3 ✓	<i>I4/mmm</i>	2	$A^{\text{IX}}_2A^{\text{VIII-2}}_2B^{\text{V-1}}_2B^{\text{IV-1}}X_8$
$A_5B_4X_{10}$	R1\B4	<i>I4/mmm</i>	2	$A^{\text{IX}}_2A^{\text{VIII-2}}_3B^{\text{V-1}}_2B^{\text{IV-1}}_2X_{10}$
$A_5B_4X_{12}$	R1\B4'	<i>I4/mmm</i>	2	$A^{\text{XII}}_2A^{\text{IX}}_2A^{\text{VIII-2}}_2B^{\text{VI-1}}_2B^{\text{V-1}}_2X_{12}$
$A_5B_4X_{11}$	R1\B4''	<i>I4/mmm</i>	2	$A^{\text{XII}}A^{\text{IX}}_2A^{\text{VIII-2}}B^{\text{V-1}}_4X_{11}$
$A_2B_2X_4$	Cu1\A1 ✓	<i>P4/mmm</i>	1	$A^{\text{VIII-1}}_2B^{\text{VI-1}}B^{\text{II}}X_4$
$A_3B_3X_7$	Cu1\A2 ✓	<i>P4/mmm</i>	1	$A^{\text{XII}}A^{\text{VIII-1}}_2B^{\text{VI-1}}_2B^{\text{II}}X_7$
$A_4B_4X_{10}$	Cu1\A3	<i>P4/mmm</i>	1	$A^{\text{XII}}_2A^{\text{VIII-1}}_2B^{\text{VI-1}}_3B^{\text{II}}X_{10}$
$A_5B_5X_{13}$	Cu1\A4	<i>P4/mmm</i>	1	$A^{\text{XII}}_3A^{\text{VIII-1}}_2B^{\text{VI-1}}_4B^{\text{II}}X_{13}$
$A_3B_3X_6$	Cu1\B2 ✓	<i>P4/mmm</i>	1	$A^{\text{VIII}}A^{\text{VIII-2}}_2B^{\text{V-1}}_2B^{\text{II}}X_6$
$A_4B_4X_8$	Cu1\B3	<i>P4/mmm</i>	1	$A^{\text{VIII-1}}_2A^{\text{VIII-2}}_2B^{\text{V-1}}_2B^{\text{IV-1}}B^{\text{II}}X_8$
$A_5B_5X_{10}$	Cu1\B4	<i>P4/mmm</i>	1	$A^{\text{VIII-2}}_3A^{\text{VIII-1}}_2B^{\text{V-1}}_2B^{\text{IV-1}}_2B^{\text{II}}X_{10}$
$A_5B_5X_{12}$	Cu1\B4'	<i>P4/mmm</i>	1	$A^{\text{XII}}_2A^{\text{VIII-2}}A^{\text{VIII-1}}_2B^{\text{VI-1}}_2B^{\text{V-1}}_2B^{\text{II}}X_{12}$
$A_5B_5X_{11}$	Cu1\B4''	<i>P4/mmm</i>	1	$A^{\text{XII}}A^{\text{VIII-2}}_2A^{\text{VIII-1}}_2B^{\text{V-1}}_4B^{\text{II}}X_{11}$
$A_2B_2X_5$	Cu2\A1 ✓	<i>Pmmm</i>	1	$A^{\text{X}}_2B^{\text{VI-1}}B^{\text{IV-1}}X_5$
$A_3B_3X_8$	Cu2\A2 ✓	<i>Pmmm</i>	1	$A^{\text{XII}}A^{\text{X}}_2B^{\text{VI-1}}_2B^{\text{IV-1}}X_8$
$A_4B_4X_{11}$	Cu2\A3	<i>Pmmm</i>	1	$A^{\text{XII}}_2A^{\text{X}}_2B^{\text{VI-1}}_3B^{\text{IV-1}}X_{11}$
$A_5B_5X_{14}$	Cu2\A4	<i>Pmmm</i>	1	$A^{\text{XII}}_3A^{\text{X}}_2B^{\text{VI-1}}_4B^{\text{IV-1}}X_{14}$
$A_3B_3X_7$	Cu2\B2 ✓	<i>Pmmm</i>	1	$A^{\text{X}}_2A^{\text{VIII-2}}B^{\text{V-1}}_2B^{\text{IV-1}}X_7$
$A_4B_4X_9$	Cu2\B3	<i>Pmmm</i>	1	$A^{\text{X}}_2A^{\text{VIII-2}}_2B^{\text{V-1}}_2B^{\text{IV-1}}B^{\text{IV-1}}X_9$
$A_5B_5X_{11}$	Cu2\B4	<i>Pmmm</i>	1	$A^{\text{X}}_2A^{\text{VIII-2}}_3B^{\text{V-1}}_2B^{\text{IV-1}}B^{\text{IV-1}}_2X_{11}$
$A_5B_5X_{13}$	Cu2\B4'	<i>Pmmm</i>	1	$A^{\text{XII}}_2A^{\text{X}}_2A^{\text{VIII-2}}B^{\text{VI-1}}_2B^{\text{V-1}}_2B^{\text{IV-1}}X_{13}$
$A_5B_5X_{12}$	Cu2\B4''	<i>Pmmm</i>	1	$A^{\text{XII}}A^{\text{X}}_2A^{\text{VIII-2}}_2B^{\text{V-1}}_4B^{\text{IV-1}}X_{12}$
$A_2B_3X_6$	Cu3\A1	<i>Ammm</i>	2	$A^{\text{X}}_2B^{\text{VI-1}}B^{\text{IV-1}}_2X_6$
$A_3B_4X_9$	Cu3\A2	<i>Ammm</i>	2	$A^{\text{XII}}A^{\text{X}}_2B^{\text{VI-1}}_2B^{\text{IV-1}}_2X_9$
$A_4B_5X_{12}$	Cu3\A3	<i>Ammm</i>	2	$A^{\text{XII}}_2A^{\text{X}}_2B^{\text{VI-1}}_3B^{\text{IV-1}}_2X_{12}$
$A_3B_4X_8$	Cu3\B2 ✓	<i>Ammm</i>	2	$A^{\text{X}}_2A^{\text{VIII-2}}B^{\text{V-1}}_2B^{\text{IV-1}}_2X_8$
$A_4B_5X_{10}$	Cu3\B3	<i>Ammm</i>	2	$A^{\text{X}}_2A^{\text{VIII-2}}_2B^{\text{V-1}}_2B^{\text{IV-1}}_3X_{10}$
$A_5B_6X_{12}$	Cu3\B4	<i>Ammm</i>	2	$A^{\text{X}}_2A^{\text{VIII-2}}_3B^{\text{V-1}}_2B^{\text{IV-1}}_4X_{12}$

General formula	Block/slab	Space group	Z	Coordination atoms
A ₅ B ₆ X ₁₄	Cu3\B4'	<i>Ammm</i>	2	A ^{XII} ₂ A ^X ₂ A ^{VIII-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₄
A ₅ B ₆ X ₁₃	Cu3\B4''	<i>Ammm</i>	2	A ^{XII} ₂ A ^X ₂ A ^{VIII-2} ₂ B ^{V-1} ₄ B ^{IV-1} ₂ X ₁₃
A ₃ BX ₅	F1\A1 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ X ₅
A ₄ B ₂ X ₈	F1\A2 ✓	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ X ₈
A ₅ B ₃ X ₁₁	F1\A3	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₃ X ₁₁
A ₆ B ₄ X ₁₄	F1\A4	<i>P4/mmm</i>	1	A ^{XII} ₃ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₄ X ₁₄
A ₈ B ₆ X ₁₇	F1\B 6'''	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{V-1} ₆ X ₁₇
A ₄ B ₂ X ₇	F1\B2 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ X ₇
A ₅ B ₃ X ₉	F1\B3 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₉
A ₆ B ₄ X ₁₁	F1\B4 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₁
A ₆ B ₄ X ₁₃	F1\B4'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₃
A ₆ B ₄ X ₁₂	F1\B4''	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₄ X ₁₂
A ₇ B ₅ X ₁₃	F1\B5 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₄ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₃ X ₁₃
A ₇ B ₅ X ₁₅	F1\B5'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₅
A ₈ B ₆ X ₁₅	F1\B6 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₅ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₄ X ₁₅
A ₈ B ₆ X ₁₇	F1\B6'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₇
A ₈ B ₆ X ₁₆	F1\B6''	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₄ A ^{VI-2} ₂ B ^{V-1} ₄ B ^{IV-1} ₂ X ₁₆
A ₄ BX ₆	F2\A1 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ X ₆
A ₅ B ₂ X ₉	F2\A2 ✓	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ X ₉
A ₆ B ₃ X ₁₂	F2\A3 ✓	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₃ X ₁₂
A ₇ B ₄ X ₁₅	F2\A4	<i>I4/mmm</i>	2	A ^{XII} ₃ A ^{IX} ₂ A ^{VI-2} ₂ B ^{VI-1} ₄ X ₁₅
A ₅ B ₂ X ₈	F2\B2 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ X ₈
A ₆ B ₃ X ₁₀	F2\B3 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₀
A ₇ B ₄ X ₁₂	F2\B4 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₂
A ₇ B ₄ X ₁₄	F2\B4'	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₄
A ₇ B ₄ X ₁₃	F2\B4''	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₄ X ₁₃
A ₂ BX ₆	F3\A1 ✓	<i>I4/mmm</i>	2	A ^{XII} ₂ B ^{VI-1} ₂ X ₆
A ₃ B ₂ X ₉	F3\A2 ✓	<i>I4/mmm</i>	2	A ^{XII} ₃ B ^{VI-1} ₂ X ₉
A ₄ B ₃ X ₁₂	F3\A3 ✓	<i>I4/mmm</i>	2	A ^{XII} ₄ B ^{VI-1} ₃ X ₁₂
A ₅ B ₄ X ₁₅	F3\A4 ✓	<i>I4/mmm</i>	2	A ^{XII} ₅ B ^{VI-1} ₄ X ₁₅
A ₃ B ₂ X ₈	F3\B2	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{VIII-2} ₂ B ^{V-1} ₂ X ₈
A ₄ B ₃ X ₁₀	F3\B3	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{VIII-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₀
A ₅ B ₄ X ₁₂	F3\B4	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{VIII-2} ₃ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₂
A ₅ B ₄ X ₁₄	F3\B4'	<i>I4/mmm</i>	2	A ^{XII} ₄ A ^{VIII-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₄
A ₅ B ₄ X ₁₃	F3\B4''	<i>I4/mmm</i>	2	A ^{XII} ₃ A ^{VIII-2} ₂ B ^{V-1} ₄ X ₁₃
A ₄ B ₂ X ₆	P1\A1 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ Pb ^{V-2} ₂ B ^{VI-1} ₂ B ^{II} ₂ X ₆
A ₅ B ₃ X ₉	P1\A2	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ Pb ^{V-2} ₂ B ^{VI-2} ₂ B ^{II} ₂ X ₉
A ₆ B ₄ X ₁₂	P1\A3	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ Pb ^{V-2} ₂ B ^{VI-1} ₃ B ^{II} ₂ X ₁₂
A ₇ B ₅ X ₁₅	P1\A4	<i>P4/mmm</i>	1	A ^{XII} ₃ A ^{IX} ₂ Pb ^{V-2} ₂ B ^{VI-1} ₄ B ^{II} ₂ X ₁₅
A ₅ B ₃ X ₈	P1\B2 ✓	<i>I4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{V-1} ₂ B ^{II} ₂ X ₈
A ₆ B ₄ X ₁₀	P1\B3	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ B ^{II} ₂ X ₁₀
A ₇ B ₅ X ₁₂	P1\B4	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₃ Pb ^V ₂ B ^V ₂ B ^{IV-1} ₂ B ^{II} ₂ X ₁₂
A ₇ B ₅ X ₁₄	P1\B4'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} ₂ X ₁₄

General formula	Block/slab	Space group	Z	Coordination atoms
A ₇ B ₅ X ₁₃	P1\B4''	<i>P4/mmm</i>	1	A ^{XII} A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{V-1} ₄ B ^{II} X ₁₃
A ₃ B ₂ X ₅	P2\A1	<i>P4/mmm</i>	2	A ^{IX} A ^{VIII-1} Pb ^{V-2} B ^{VI-1} B ^{II} X ₅
A ₄ B ₃ X ₈	P2\A2	<i>P4/mmm</i>	2	A ^{XII} A ^{IX} A ^{VIII-1} Pb ^V B ^{VI-1} ₂ B ^{II} X ₈
A ₅ B ₄ X ₁₁	P2\A3	<i>P4/mmm</i>	2	A ^{XII} ₂ A ^{IX} A ^{VIII-1} Pb ^{V-2} B ^{VI-1} ₃ B ^{II} X ₁₁
A ₆ B ₅ X ₁₄	P2\A4	<i>P4/mmm</i>	2	A ^{XII} ₃ A ^{IX} A ^{VIII-1} Pb ^{V-2} B ^{VI-1} ₄ B ^{II} X ₁₄
A ₄ B ₃ X ₇	P2\B2 ✓	<i>P4/mmm</i>	2	A ^{IX} A ^{VIII-2} A ^{VIII-1} Pb ^{V-2} B ^{V-1} ₂ B ^{II} X ₇
A ₅ B ₄ X ₉	P2\B3	<i>P4/mmm</i>	2	A ^{IX} A ^{VIII-2} ₂ A ^{VIII-1} Pb ^{V-2} B ^{V-1} ₂ B ^{IV-1} B ^{II} X ₉
A ₆ B ₅ X ₁₁	P2\B4	<i>P4/mmm</i>	2	A ^{IX} A ^{VIII-2} ₃ A ^{VIII-1} Pb ^{V-2} B ^{V-1} B ^{IV-1} ₂ B ^{II} X ₁₁
A ₆ B ₅ X ₁₃	P2\B4'	<i>P4/mmm</i>	2	A ^{XII} ₂ A ^{IX} A ^{VIII-1} A ^{VIII-2} Pb ^{V-2} B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₃
A ₆ B ₅ X ₁₂	P2\B4''	<i>P4/mmm</i>	2	A ^{XII} A ^{IX} A ^{VIII-2} ₂ A ^{VIII-1} Pb ^{V-2} B ^{V-1} ₄ B ^{II} X ₁₂
A ₄ B ₂ X ₇	P3\A1	<i>Pmmm</i>	1	A ^{IX} Pb ^{VII} ₂ B ^{VI-1} B ^{IV-1} X ₇
A ₅ B ₃ X ₁₀	P3\A2	<i>Pmmm</i>	1	A ^{XII} A ^{IX} ₂ Pb ^{VII} ₂ B ^{VI-1} ₂ B ^{IV-1} X ₁₀
A ₆ B ₄ X ₁₃	P3\A3	<i>Pmmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ Pb ^{VII} ₂ B ^{VI-1} ₃ B ^{IV-1} X ₁₃
A ₇ B ₅ X ₁₆	P3\A4	<i>Pmmm</i>	1	A ^{XII} ₃ A ^{IX} ₂ Pb ^{VII} ₂ B ^{VI-1} ₄ B ^{IV-1} X ₁₆
A ₅ B ₃ X ₉	P3\B2 ✓	<i>Pmmm</i>	1	A ^{IX} ₂ A ^{VIII-2} Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} X ₉
A ₆ B ₄ X ₁₁	P3\B3	<i>Pmmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} B ^{IV-1} X ₁₁
A ₇ B ₅ X ₁₃	P3\B4	<i>Pmmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₃ Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ B ^{IV-1} X ₁₃
A ₇ B ₅ X ₁₅	P3\B4'	<i>Pmmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} Pb ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₅
A ₇ B ₅ X ₁₄	P3\B4''	<i>Pmmm</i>	1	A ^{XII} A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{VII} ₂ B ^{V-1} ₄ B ^{IV-1} X ₁₄
A ₃ B ₂ X ₆	P4\A1	<i>Pmmm</i>	2	A ^{IX} A ^X Pb ^{IX} B ^{VI-1} B ^{IV-1} X ₆
A ₄ B ₃ X ₉	P4\A2	<i>Pmmm</i>	2	A ^{XII} A ^{IX} A ^X Pb ^{VII} B ^{VI-1} ₂ B ^{IV-1} X ₉
A ₅ B ₄ X ₁₂	P4\A3	<i>Pmmm</i>	2	A ^{XII} ₂ A ^{IX} A ^X Pb ^{VII} B ^{VI-1} ₃ B ^{IV-1} X ₁₂
A ₆ B ₅ X ₁₅	P4\A4	<i>Pmmm</i>	2	A ^{XII} ₃ A ^{IX} A ^{VIII-1} Pb ^{VII} B ^{VI-1} ₄ B ^{IV-1} X ₁₅
A ₄ B ₃ X ₈	P4\B2	<i>Pmmm</i>	2	A ^{IX} A ^X A ^{VIII-2} Pb ^{VII} B ^{V-1} ₂ B ^{IV-1} X ₈
A ₅ B ₄ X ₁₀	P4\B3	<i>Pmmm</i>	2	A ^{IX} A ^{VIII-2} ₂ A ^X Pb ^{VII} B ^{V-1} ₂ B ^{IV-1} B ^{IV-1} X ₁₀
A ₆ B ₅ X ₁₂	P4\B4	<i>Pmmm</i>	2	A ^{IX} A ^{VIII-2} ₃ A ^X Pb ^{VII} B ^{V-1} ₃ B ^{IV-1} X ₁₂
A ₆ B ₅ X ₁₄	P4\B4'	<i>Pmmm</i>	2	A ^{XII} ₂ A ^{IX} A ^{VIII-2} A ^X Pb ^{VII} B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₄
A ₆ B ₅ X ₁₃	P4\B4''	<i>Pmmm</i>	2	A ^{XII} A ^{IX} A ^{VIII-2} ₂ A ^X Pb ^{VII} B ^{V-1} ₄ B ^{IV-1} X ₁₃
A ₄ B ₂ X ₈	P5\A1	<i>P4/mmm</i>	1	A ^{IX} ₂ Pb ^{IX} ₂ B ^{VI-1} ₂ X ₈
A ₅ B ₃ X ₁₁	P5\A2	<i>P4/mmm</i>	1	A ^{XII} A ^{IX} ₂ Pb ^{IX} ₂ B ^{VI-1} ₃ X ₁₁
A ₆ B ₄ X ₁₄	P5\A3	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ Pb ^{IX} ₂ B ^{VI-1} ₄ X ₁₄
A ₇ B ₅ X ₁₇	P5\A4	<i>P4/mmm</i>	1	A ^{XII} ₃ A ^{IX} ₂ Pb ^{IX} ₂ B ^{VI-1} ₅ X ₁₇
A ₅ B ₃ X ₁₀	P5\B2 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} Pb ^{IX} ₂ B ^{VI-1} B ^{V-1} ₂ X ₁₀
A ₆ B ₄ X ₁₂	P5\B3	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{IX} ₂ B ^{VI-1} B ^{V-1} ₂ B ^{IV-1} X ₁₂
A ₇ B ₅ X ₁₄	P5\B4	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₃ Pb ^{IX} ₂ B ^{VI-1} B ^{V-1} ₂ B ^{IV-1} X ₁₄
A ₇ B ₅ X ₁₆	P5\B4'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ Pb ^{IX} ₂ A ^{VIII-2} B ^{VI-1} ₃ B ^{V-1} ₂ X ₁₆
A ₇ B ₅ X ₁₅	P5\B4''	<i>P4/mmm</i>	1	A ^{XII} A ^{IX} ₂ Pb ^{IX} ₂ A ^{VIII-2} ₂ B ^{VI-1} B ^{V-1} ₄ X ₁₅
A ₃ B ₂ X ₇	P6\A1	<i>P4/mmm</i>	2	A ^{XII} A ^{IX} Pb ^{IX} B ^{VI-1} ₂ X ₇
A ₄ B ₃ X ₁₀	P6\A2	<i>P4/mmm</i>	2	A ^{XII} ₂ A ^{IX} Pb ^{IX} B ^{VI-1} ₃ X ₁₀
A ₅ B ₄ X ₁₃	P6\A3	<i>P4/mmm</i>	2	A ^{XII} ₃ A ^{IX} Pb ^{IX} B ^{VI-1} ₄ X ₁₃
A ₆ B ₅ X ₁₆	P6\A4	<i>P4/mmm</i>	2	A ^{XII} ₄ A ^{IX} Pb ^{IX} B ^{VI-1} ₅ X ₁₆
A ₄ B ₃ X ₉	P6\B2	<i>P4/mmm</i>	2	A ^{XII} A ^{IX} Pb ^{IX} A ^{VIII-2} B ^{VI-1} B ^{V-1} ₂ X ₉
A ₅ B ₄ X ₁₁	P6\B3	<i>P4/mmm</i>	2	A ^{XII} A ^{IX} Pb ^{IX} A ^{VIII-2} ₂ B ^{VI-1} ₂ B ^{V-1} B ^{IV-1} X ₁₁

General formula	Block/slab	Space group	Z	Coordination atoms
$A_6B_5X_{13}$	P6\B4	$P4/mmm$	2	$A^{XII}A^{IX}Pb^{IX}A^{VIII-2}{}_3B^{VI-1}{}_2B^{IV-1}{}_2X_{13}$
$A_6B_5X_{15}$	P6\B4'	$P4/mmm$	2	$A^{XII}{}_3A^{IX}Pb^{IX}A^{VIII-2}{}_3B^{VI-1}{}_3B^{V-1}{}_2X_{15}$
$A_6B_5X_{14}$	P6\B4''	$P4/mmm$	2	$A^{XII}{}_2A^{IX}Pb^{IX}A^{VIII-2}{}_2B^{VI-1}{}_3B^{V-1}{}_4X_4$

2.2. Praphases with anionic vacancies on the outer surfaces of slabs and blocks.

Anionic vacancies on outer surfaces exist in C- and D-slabs in the places of apical anions in BX_6 -octahedra. Four types of blocks can intergrowth with these slabs: V1- is the layer $\square A$, \square - is vacancy, block Cs1 is similar to CsCl-structure; G1 and G2-blocks are parts of the known fluorite structure.

Crystallographic data for possible combinations of these slabs and blocks are presented in Table 2. It is seen that the number of new possible PL-compound is much less in respect to Table 1. The most probable to obtain new compound similar to $La_3Sr_2Cu_3O_{12}$ [11] but with two and four layered B2 and B3 slabs and G2-blocks.

Table 2
Possible praphases of layered PL-crystals due to intergrowth of C- and D-slabs and corresponding blocks

General formula	Block/slab	Space group	Z	Coordination Atoms
$A_3B_2X_6$	Cs1\C2	$P4/mmm$	1	$A^{XII}A^{VIII-3}{}_2B^{V-1}{}_2X_5X'$
$A_4B_3X_9$	Cs1\C3 ✓	$P4/mmm$	1	$A^{XII}{}_2A^{VIII-3}{}_2B^{VI-1}{}_2B^{V-1}{}_2X_8X'$
$A_5B_4X_{12}$	Cs1\C4	$P4/mmm$	1	$A^{XII}{}_3A^{VIII-3}{}_2B^{VI-1}{}_2B^{V-1}{}_2X_{11}X'$
$A_6B_5X_{15}$	Cs1\C5	$P4/mmm$	1	$A^{XII}{}_4A^{VIII-3}{}_2B^{VI-1}{}_3B^{V-1}{}_2X_{14}X'$
$A_6B_5X_{13}$	Cs1\C5'	$P4/mmm$	1	$A^{XII}{}_2A^{VIII-3}{}_2A^{VIII-2}{}_2B^{VI-1}{}_4B^{IV-1}{}_2X_{12}X'$
A_2BX_3	Cs1\D1	$P4/mmm$	1	$A^{VIII-3}{}_2B^{IV-1}{}_2X_2X'$
$A_3B_2X_5$	Cs1\D2	$P4/mmm$	1	$A^{VIII-3}{}_2A^{VIII-2}{}_2B^{IV-1}{}_2X_4X'$
$A_4B_3X_7$	Cs1\D3	$P4/mmm$	1	$A^{VIII-3}{}_2A^{VIII-2}{}_2B^{IV-1}{}_3X_6X'$
$A_3B_2X_7$	G1\C2 ✓	$I4/mmm$	2	$A^{XII}A^{VIII-2}{}_2B^{V-1}{}_2X_7$
$A_4B_3X_{10}$	G1\C3 ✓	$I4/mmm$	2	$A^{XII}{}_2A^{VIII-2}{}_2B^{VI-1}{}_2B^{V-1}{}_2X_{10}$
$A_5B_4X_{13}$	G1\C4 ✓	$I4/mmm$	2	$A^{XII}{}_3A^{VIII-2}{}_2B^{VI-1}{}_2B^{V-1}{}_2X_{13}$
$A_6B_5X_{16}$	G1\C5 ✓	$I4/mmm$	2	$A^{XII}{}_4A^{VIII-2}{}_2B^{VI-1}{}_3B^{V-1}{}_2X_{16}$
$A_6B_5X_{14}$	G1\C5'	$I4/mmm$	2	$A^{XII}{}_2A^{VIII-2}{}_4B^{V-1}{}_4B^{IV-1}{}_2X_{14}$

General formula	Block/slab	Space group	Z	Coordination Atoms
A_2BX_4	G1\ D1 ✓	<i>I4/mmm</i>	2	$A^{VIII-2}_2B^{IV-1}X_4$
$A_3B_2X_6$	G1\ D2	<i>I4/mmm</i>	2	$A^{VIII-2}_3B^{IV-1}_2X_6$
$A_4B_3X_8$	G1\ D3 ✓	<i>I4/mmm</i>	2	$A^{VIII-2}_4B^{IV-1}_3X_8$
$A_7B_5X_{16}$	G2 \ C5'	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-2}_5B^{V-1}_4B^{IV-1}X_{16}$
$A_4B_2X_9$	G2\ C2	<i>P4/mmm</i>	1	$A^{XII}A^{VIII-2}_3B^{V-1}_2X_9$
$A_5B_3X_{12}$	G2\ C3 ✓	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-2}_3B^{VI-1}B^{V-1}_2X_{12}$
$A_6B_4X_{15}$	G2\ C4	<i>P4/mmm</i>	1	$A^{XII}_3A^{VIII-2}_3B^{VI-1}_2B^{V-1}_2X_{15}$
$A_7B_5X_{18}$	G2\ C5	<i>P4/mmm</i>	1	$A^{XII}_4A^{VIII-2}_3B^{VI-1}_3B^{V-1}_2X_{18}$
A_3BX_6	G2\ D1	<i>P4/mmm</i>	1	$A^{VIII-2}_3B^{IV-1}X_6$
$A_4B_2X_8$	G2\ D2	<i>P4/mmm</i>	1	$A^{VIII-2}_4B^{IV-1}_2X_8$
$A_5B_3X_{10}$	G2\ D3	<i>P4/mmm</i>	1	$A^{VIII-2}_5B^{IV-1}_3X_{10}$
$A_2B_2X_5$	V1\ C2 ✓	<i>P4/mmm</i>	1	$A^{XII}A^{VIII-2}B^{V-1}_2X_5$
$A_3B_3X_8$	V1\ C3 ✓	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-2}B^{VI-1}B^{V-1}_2X_8$
$A_4B_4X_{11}$	V1\ C4 ✓	<i>P4/mmm</i>	1	$A^{XII}_3A^{VIII-2}B^{VI-1}_2B^{V-1}_2X_{11}$
$A_5B_5X_{14}$	V1\ C5 ✓	<i>P4/mmm</i>	1	$A^{XII}_4A^{VIII-2}B^{VI-1}_3B^{V-1}_2X_{14}$
$A_5B_5X_{12}$	V1\ C5'	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-2}_3B^{V-1}_4B^{IV-1}X_{12}$
ABX_2	V1\ D1 ✓	<i>P4/mmm</i>	1	$A^{VIII-2}B^{IV-1}X_2$
$A_2B_2X_4$	V1\ D2	<i>P4/mmm</i>	1	$A^{VIII-2}_2B^{IV-1}_2X_4$
$A_3B_3X_6$	V1\ D3 ✓	<i>P4/mmm</i>	1	$A^{VIII-2}_3B^{IV-1}_3X_6$

2.3. Praphases having cationic vacancies on the outer surfaces of slabs and blocks.

These praphases can be formed using modified slabs A^* and B^* which contain cationic vacancies on the outer planes (Fig. 3). The slabs can intergrow with blocks $Cs'1$ which is similar to $CsCl$ -structure but contain cation in the center of cube. Two other blocks $G'1$ and $G'2$ (hypothetical) are fragments antiferite structure.

In combinations $Cs'1\|A^*$ three first members were known ABX_4 , $A_2B_2X_7$ and $A_3B_3X_{10}$. Recently the fourth member of the series was found [13]. Two substances with $G'1\|A^*$ intergrowth are known, but some other combinations can be found in future. Results of the prognosis are presented in Table 3.

Table 3
Praphases appearing due to intergrowth
of slabs hawing cationic vacancies on outer planes and proper blocks

General formula	Block/slab	Space group	Z	Coordination atoms
ABX ₄	Cs'1\A*1 ✓	<i>P4/mmm</i>	1	A ^{VIII} B ^{VI-1} X ₄
A ₂ B ₂ X ₇	Cs'1\A*2 ✓	<i>P4/mmm</i>	1	A ^{XII} A ^{VIII} B ^{VI-1} ₂ X ₇
A ₃ B ₃ X ₁₀	Cs'1\A*3 ✓	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{VIII} B ^{VI-1} ₃ X ₁₀
A ₄ B ₄ X ₁₃	Cs'1\A*4 ✓	<i>P4/mmm</i>	1	A ^{XII} ₃ A ^{VIII} B ^{VI-1} ₄ X ₁₃
A ₂ B ₂ X ₆	Cs'1\B*2	<i>P4/mmm</i>	1	A ^{VIII-2} A ^{VIII} B ^{V-1} ₂ X ₆
A ₃ B ₃ X ₈	Cs'1\B*3	<i>P4/mmm</i>	1	A ^{VIII-2} ₂ A ^{VIII} B ^{V-1} ₂ B ^{IV-1} X ₈
A ₄ B ₄ X ₁₀	Cs'1\B*4	<i>P4/mmm</i>	1	A ^{VIII-2} ₃ A ^{VIII} B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₀
A ₄ B ₄ X ₁₂	Cs'1\B*4'	<i>P4/mmm</i>	1	A ^{VIII-2} ₃ A ^{VIII} B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₂
A ₄ B ₄ X ₁₁	Cs'1\B*4''	<i>P4/mmm</i>	1	A ^{VIII-2} ₃ A ^{VIII} B ^{IV-1} ₄ X ₁₁
A ₂ BX ₄	G'1\A*1	<i>I4/mmm</i>	2	Less possible
A ₃ B ₂ X ₇	G'1\A*2 ✓	<i>I4/mmm</i>	2	A ^{XII} A ^{IV-2} ₂ B ^{VI-1} ₂ X ₇
A ₄ B ₃ X ₁₀	G'1\A*3 ✓	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IV-2} ₂ B ^{VI-1} ₃ X ₁₀
A ₅ B ₄ X ₁₃	G'1\A*4	<i>I4/mmm</i>	2	A ^{XII} ₃ A ^{IV-1} ₂ B ^{VI-1} ₄ X ₁₃
A ₃ B ₂ X ₆	G'1\B*2	<i>I4/mmm</i>	2	A ^{VIII-2} A ^{IV-2} ₂ B ^{V-1} ₂ X ₆
A ₄ B ₃ X ₈	G'1\B*3	<i>I4/mmm</i>	2	A ^{VIII-2} ₂ A ^{IV-2} ₂ B ^{V-1} ₂ B ^{IV-1} X ₈
A ₅ B ₄ X ₁₀	G'1\B*4	<i>I4/mmm</i>	2	A ^{VIII-2} ₃ A ^{IV-2} ₂ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₀
A ₅ B ₄ X ₁₂	G'1\B*4'	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{VIII-2} A ^{IV-1} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₂
A ₅ B ₄ X ₁₁	G'1\B*4''	<i>I4/mmm</i>	2	A ^{XII} A ^{VIII-2} ₂ A ^{IV-1} ₂ B ^{V-1} ₄ X ₁₁
A ₄ BX ₅	G'2\A*1	<i>P4/mmm</i>	1	Less possible
A ₅ B ₂ X ₈	G'2\A*2	<i>P4/mmm</i>	1	A ^{XII} A ^{IV-2} ₄ B ^{VI-1} ₂ X ₈
A ₆ B ₃ X ₁₁	G'2\A*3	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IV-2} ₄ B ^{VI-1} ₃ X ₁₁
A ₇ B ₄ X ₁₄	G'2\A*4	<i>P4/mmm</i>	1	A ^{XII} ₃ A ^{IV-2} ₄ B ^{VI-1} ₄ X ₁₄
A ₅ B ₂ X ₇	G'2\B*2	<i>P4/mmm</i>	1	A ^{VIII} A ^{IV-2} ₄ B ^{V-1} ₂ X ₇
A ₆ B ₃ X ₉	G'2\B*3	<i>P4/mmm</i>	1	A ^{VIII} ₂ A ^{IV-2} ₄ B ^{V-1} ₂ B ^{IV-1} X ₉
A ₇ B ₄ X ₁₁	G'2\B*4	<i>P4/mmm</i>	1	A ^{VIII} ₃ A ^{IV-2} ₄ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₁
A ₇ B ₄ X ₁₃	G'2\B*4'	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{VIII-2} A ^{IV-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₃
A ₇ B ₄ X ₁₂	G'2\B*4''	<i>P4/mmm</i>	1	A ^{XII} A ^{VIII-2} ₂ A ^{IV-2} ₄ B ^{V-1} ₂ B ^{IV-1} ₂ X ₁₂

2.4. Praphases containing two types blocks.

Many crystals containing two types of blocks have been found. Two groups of such compounds can be described. In the first group appearance of new compounds are the most probable when slabs have different outer surfaces, C1 as example, Fig. 1. Another slab can be considered as a result of appearing one cationic vacancy on a outer plane of

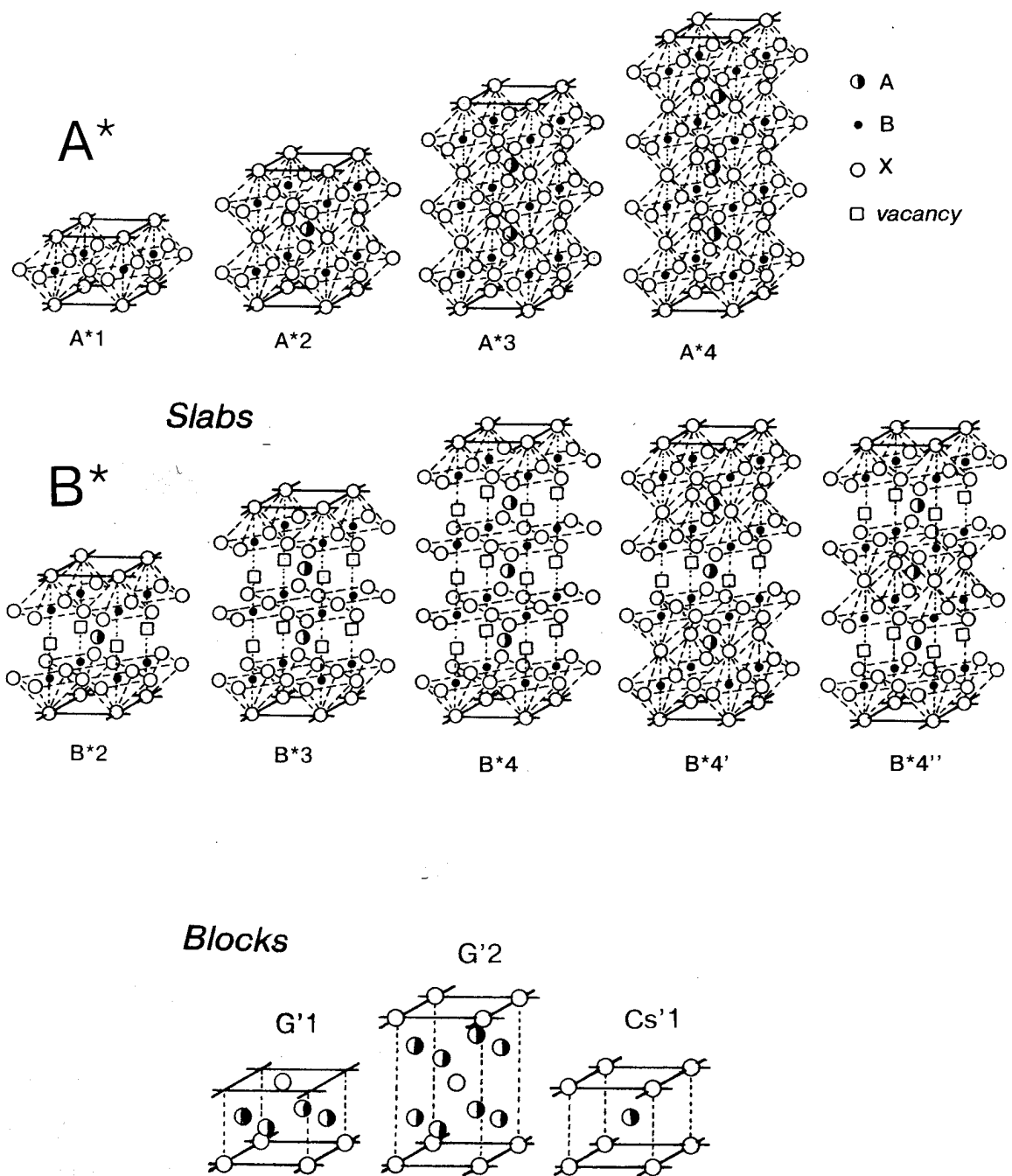


Fig. 3. Perovskite-like slabs A*, B* and intermediate blocks

the double A2 slab, or it can be considered as one half of B4-slab (see Fig. 1). It will be marked below as (A1+C1). On the surface with a cationic vacancy these two types of slabs can intergrow with V1, G1, G2 and Cs1 blocks. The opposite surfaces of the slabs can intergrow with many types of blocks: R1, Cu1, F1, F2 etc. As it is shown in Table 4 more than hundred combinations of compounds with these slabs and two blocks are possible but only 15 crystals have been synthesized up to now.

Table 4
Possible praphases containing two different types of blocks

General Formula	Block/slab/block	Space group	Z	Coordination atoms
$A_6B_3X_{10}$	Cs1\C1\ P3	<i>Pmmm</i>	1	$A^{IX}_2A^{VIII-3}_2Pb^{VII}_2B^{V-1}_2B^{IV-1}X_9X'$
$A_4B_3X_7$	Cs1\C1\Cu1	<i>P4/mmm</i>	1	$A^{VIII-3}_2A^{VIII-1}_2B^{V-1}_2B^{II}X_6X'$
$A_4B_3X_8$	Cs1\C1\Cu2	<i>Pmmm</i>	1	$A^{VIII-3}_2A^X_2B^{V-1}_2B^{IV-1}X_7X'$
$A_5B_2X_8$	Cs1\C1\F1	<i>P4/mmm</i>	1	$A^{IX}_2A^{VIII-3}_2A^{VI-2}B^{V-1}_2X_7X'$
$A_6B_2X_9$	Cs1\C1\F2	<i>I4/mmm</i>	2	$A^{IX}_2A^{VIII-3}_2A^{VI-2}B^{V-1}_2X_8X'$
$A_4B_2X_9$	Cs1\C1\F3	<i>I4/mmm</i>	2	$A^{XII}_2A^{VIII-3}_2B^{V-1}_2X_8X' \text{ ???}$
$A_6B_3X_9$	Cs1\C1\P1 ✓	<i>P4/mmm</i>	1	$A^{IX}_2A^{VIII-3}_2Pb^{V-2}B^{V-1}_2B^{II}X_8X'$
$A_5B_3X_8$	Cs1\C1\P2	<i>I4/mmm</i>	2	$A^{IX}_2A^{VIII-3}_2A^{VIII-1}Pb^{V-2}B^{V-1}_2B^{II}X_7X'$
$A_5B_3X_9$	Cs1\C1\P4	<i>P2/mmm</i>	2	$A^{IX}_2A^{VIII-3}_2A^XPb^{VII}B^{V-1}_2B^{II}X_8X'$
$A_6B_3X_{11}$	Cs1\C1\P5	<i>P4/mmm</i>	1	$A^{IX}_2A^{VIII-3}_2Pb^{IX}_2B^{VI-1}B^{V-1}_2X_{10}X'$
$A_5B_3X_{10}$	Cs1\C1\P6	<i>P4/mmm</i>	2	$A^{XII}_2A^{VIII-3}_2A^{IX}Pb^{IX}B^{VI-1}B^{V-1}_2X_9X'$
$A_4B_2X_7$	Cs1\C1\R1	<i>I4/mmm</i>	2	$A^{IX}_2A^{VIII-3}_2B^{V-1}_2X_6X'$
$A_6B_5X_{12}X'$	Cu1\A1+C1\Cs1	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-1}_2A^{VIII-3}_2B^{VI-1}_2B^{V-1}_2B^{II}X_{12}X'$
$A_6B_5X_{14}$	Cu1\A1+C1\G1	<i>I4/mmm</i>	2	$A^{XII}_2A^{VIII}_2A^{VIII-2}_2B^{VI-1}_2B^{V-1}_2B^{II}X_{14}$
$A_7B_5X_{16}$	Cu1\A1+C1\G2	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-1}_2A^{VIII-2}_3B^{VI-1}_2B^{V-1}_2B^{II}X_{16}$
$A_5B_5X_{12}$	Cu1\A1+C1\V1	<i>P4/mmm</i>	1	$A^{XII}_2A^{VIII-1}_2A^{VIII-2}B^{VI-1}_2B^{V-1}_2B^{II}X_{12}$
$A_4B_3X_8$	Cu1\C1\G1	<i>I4/mmm</i>	2	$A^{VIII-1}_2A^{VIII-2}_2B^{V-1}_2B^{II}X_8$
$A_5B_3X_{10}$	Cu1\C1\G2	<i>P4/mmm</i>	1	$A^{VIII-1}_2A^{VIII-2}_3B^{V-1}_2B^{II}X_{10}$
$A_6B_5X_{13}X'$	Cu2\A1+C1\Cs1	<i>Pmmm</i>	1	$A^{XII}_2A^X_2A^{VIII-3}_2B^{VI-1}_2B^{V-1}_2B^{IV-1}X_{13}X'$
$A_6B_5X_{15}$	Cu2\A1+C1\G1	<i>Pmmm</i>	2	$A^{XII}_2A^X_2A^{VIII-2}_2B^{VI-1}_2B^{V-1}_2B^{IV-1}X_{15}$
$A_7B_5X_{17}$	Cu2\A1+C1\G2	<i>Pmmm</i>	1	$A^{XII}_2A^X_2A^{VIII-2}_3B^{VI-1}_2B^{V-1}_2B^{IV}X_{17}$
$A_5B_5X_{13}$	Cu2\A1+C1\V1	<i>Pmmm</i>	1	$A^{XII}_2A^X_2A^{VIII-2}B^{VI-1}_2B^{V-1}_2B^{IV-1}X_{13}$
$A_4B_3X_9$	Cu2\C1\G1	<i>Pmmm</i>	2	$A^X_2A^{VIII-2}_2B^{V-1}_2B^{IV-1}X_9$

General Formula	Block/slab/block	Space group	Z	Coordination atoms
A ₅ B ₃ X ₁₁	Cu2\C1\G2	<i>Pmmm</i>	1	A ^X ₂ A ^{VIII-2} ₃ B ^{V-1} ₂ B ^{IV-1} X ₁₁
A ₆ B ₇ X ₁₄	Cu3\B2\Cu1 ✓	<i>Ammm</i>	2	A ^X ₂ A ^{VIII} ₂ A ^{VIII-2} ₃ B ^{V-1} ₄ B ^{IV-1} ₂ B ^{II} X ₁₄
A ₆ B ₇ X ₁₅	Cu3\B2\Cu2 ✓	<i>Ammm</i>	2	A ^X ₄ A ^{VIII-2} ₂ B ^{V-1} ₄ B ^{IV-1} ₃ X ₁₅
A ₇ B ₄ X ₁₃ X'	F1\A1+C1\Cs1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-3} ₂ A ^{VI-2} ₂ B ^{VI-2} ₂ B ^{V-1} ₂ X ₁₃ X'
A ₇ B ₄ X ₁₅	F1\A1+C1\G1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₅
A ₈ B ₄ X ₁₇	F1\A1+C1\G2	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₇
A ₆ B ₄ X ₁₃	F1\A1+C1\V1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₃
A ₅ B ₂ X ₉	F1\C1\G1 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ X ₉
A ₆ B ₂ X ₁₁	F1\C1\G2 ✓	<i>P4/mmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{V-1} ₂ X ₁₁
A ₈ B ₄ X ₁₄ X'	F2\A1+C1\Cs1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-3} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₄ X'
A ₈ B ₄ X ₁₆	F2\A1+C1\G1	<i>P4/nmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₆
A ₉ B ₄ X ₁₈	F2\A1+C1\G2	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₈
A ₇ B ₄ X ₁₄	F2\A1+C1\V1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₄
A ₆ B ₂ X ₁₀	F2\C1\G1 ✓	<i>P4/nmm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{V-1} ₂ X ₁₀
A ₈ B ₅ X ₁₄ X'	P1\A1+C1\Cs1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-3} ₂ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₄ X'
A ₈ B ₅ X ₁₆	P1\A1+C1\G1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₆
A ₉ B ₅ X ₁₈	P1\A1+C1\G2	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₈
A ₇ B ₅ X ₁₄	P1\A1+C1\V1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₄
A ₆ B ₃ X ₁₀	P1\C1\G1 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{V-1} ₂ B ^{II} X ₁₀
A ₇ B ₅ X ₁₃ X'	P2\A1+C1\Cs1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-1} ₂ A ^{VIII-3} ₂ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₃ X'
A ₇ B ₅ X ₁₅	P2\A1+C1\G1	<i>P4mm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-1} ₂ A ^{VIII-2} ₂ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₅
A ₈ B ₅ X ₁₇	P2\A1+C1\G2	<i>P4mm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-1} ₂ A ^{VIII-2} ₃ A ^{V-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₇
A ₆ B ₅ X ₁₃	P2\A1+C1\V1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-1} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{II} X ₁₃
A ₅ B ₃ X ₉	P2\C1\G1 ✓	<i>P4mm</i>	1	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{V-2} ₂ B ^{V-1} ₃ X ₉
A ₆ B ₃ X ₁₁	P2\C1\G2	<i>P4mm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VIII-1} ₂ Pb ^{V-2} ₂ B ^{V-1} ₂ B ^{II} X ₁₁
A ₈ B ₅ X ₁₅ X'	P3\A1+C1\Cs1	<i>Pmmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-3} ₂ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₅ X'
A ₈ B ₅ X ₁₇	P3\A1+C1\G1	<i>P2mm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₇
A ₉ B ₅ X ₁₉	P3\A1+C1\G2	<i>Pmmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₉
A ₇ B ₅ X ₁₅	P3\A1+C1\V1	<i>Pmmm</i>	1	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₅
A ₆ B ₃ X ₁₁	P3\C1\G1	<i>P2mm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₁
A ₇ B ₅ X ₁₄ X'	P4\A1+C1\Cs1	<i>P2mm</i>	2	A ^{XII} ₂ A ^X ₂ A ^{IX} ₂ A ^{VIII-3} ₂ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₄ X'
A ₇ B ₅ X ₁₆	P4\A1+C1\G1	<i>P2mm</i>	1	A ^{XII} ₂ A ^X ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₆
A ₈ B ₅ X ₁₈	P4\A1+C1\G2	<i>Pmm2</i>	2	A ^{XII} ₂ A ^X ₂ A ^{IX} ₂ A ^{VIII-2} ₃ A ^{VII} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₈
A ₆ B ₅ X ₁₄	P4\A1+C1\V1	<i>Pmm2</i>	2	A ^{XII} ₂ A ^X ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^{VI-2} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₄
A ₅ B ₃ X ₁₀	P4\C1\G1	<i>P2mm</i>	1	A ^{IX} ₂ A ^X ₂ A ^{VIII-2} ₂ Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₀
A ₆ B ₃ X ₁₂	P4\C1\G2	<i>Pmm2</i>	2	A ^X ₂ A ^{IX} ₂ A ^{VIII-2} ₃ Pb ^{VII} ₂ B ^{V-1} ₂ B ^{IV-1} X ₁₂
A ₈ B ₅ X ₁₆ X'	P5\A1+C1\Cs1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₄ A ^{VIII-3} ₂ B ^{VI-1} ₃ B ^{V-1} ₂ X ₁₆ X'
A ₈ B ₅ X ₁₈	P5\A1+C1\G1	<i>I4/mmm</i>	2	A ^{XII} ₂ A ^{IX} ₂ A ^{VIII-2} ₂ A ^V ₂ B ^{VI} ₃ B ^V ₂ X ₁₈
A ₉ B ₅ X ₂₀	P5\A1+C1\G2	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₄ A ^{VIII-2} ₃ B ^{VI-1} ₃ B ^{V-1} ₂ X ₂₀
A ₇ B ₅ X ₁₆	P5\A1+C1\V1	<i>P4/mmm</i>	1	A ^{XII} ₂ A ^{IX} ₄ A ^{VIII-2} ₂ B ^{VI-1} ₃ B ^{V-1} ₂ X ₁₆
A ₆ B ₃ X ₁₂	P5\C1\G1 ✓	<i>I4/mmm</i>	2	A ^{IX} ₂ A ^{VIII-2} ₂ Pb ^{IX} ₂ B ^{VI-1} ₂ B ^{V-1} ₂ X ₁₂
A ₇ B ₅ X ₁₅ X'	P6\A1+C1\Cs1	<i>I4/mmm</i>	2	A ^{XII} ₃ A ^{IX} ₂ A ^{VIII-3} ₂ B ^{VI-1} ₃ B ^{V-1} ₂ X ₁₅ X'
A ₇ B ₅ X ₁₇	P6\A1+C1\G1	<i>P4mm</i>	1	A ^{XII} ₃ A ^{IX} ₂ A ^{VIII-2} ₂ B ^{VI-1} ₃ B ^{V-1} ₂ X ₁₇

General Formula	Block/slab/block	Space group	Z	Coordination atoms
$A_8B_5X_{19}$	P6\A1+C1\G2	$P4mm$	2	$A^{XII}_3A^{IX}_2A^{VIII-2}_3B^{VI-1}_3B^{V-1}_2X_{19}$
$A_6B_5X_{15}$	P6\A1+C1\V1	$P4mm$	2	$A^{XII}_3A^{IX}_2A^{VIII-2}_2A^{VI-2}_2B^{VI-1}_3B^{V-1}_2X_{15}$
$A_5B_3X_{11}$	P6\C1\G1	$P4mm$	1	$A^{XII}_2A^{IX}_2A^{VIII-2}_2Pb^{IX}_2B^{VI-1}_2B^{V-1}_2X_{11}$
$A_6B_3X_{13}$	P6\C1\G2	$P4mm$	2	$A^{XII}_2A^{IX}_2A^{VIII-2}_3Pb^{IX}_2B^{VI-1}_2B^{V-1}_2X_{13}$
$A_6B_4X_{12}X'$	R1\A1+C1\Cs1	$I4/mmm$	2	$A^{XII}_2A^{IX}_2A^{VIII-3}_2B^{VI-1}_2B^{V-1}_2X_{12}X'$
$A_6B_4X_{14}$	R1\A1+C1\G1 ✓	$P4/nmm$	1	$A^{XII}_2A^{IX}_2A^{VIII-2}_2B^{VI-1}_2B^{V-1}_2X_{14}$
$A_7B_4X_{16}$	R1\A1+C1\G2	$I4/mmm$	2	$A^{XII}_2A^{IX}_2A^{VIII-2}_3B^{VI-1}_2B^{V-1}_2X_{16}$
$A_5B_4X_{12}$	R1\A1+C1\V1 ✓	$I4/mmm$	2	$A^{XII}_2A^{IX}_2A^{VIII-2}_2B^{VI-1}_2B^{V-1}_2X_{12}$
A_2BX_4	R1\C1\V1 ✓	$P4/nmm$	2	$A^{IX}_2A^{VIII-2}_2B^{V-1}_2X_4$
$A_5B_2X_{10}$	R1\C1\G2 ✓	$I4/mmm$	2	$A^{IX}_2A^{VIII-2}_3B^{V-1}_2X_{10}$

Much more possibilities exist in the second group where A- and B-slabs (Fig. 1) are intergrow with two types of blocks R1, F1, Cu1, F2 etc. But experimental data are extremely pure. Few examples are known up to now. Combination R1\A1\F1 is realized in the structure $Sr_{1,4}La_{2,6}TiNi_2O_9$ ($I4/mmm$, $Z = 2$) [14], where Ti-ion is located in F1-block and statistically fills the center of the block. Another example is $Ba_4HgTl_2Cu_2O_{10+\delta}$ ($I4/mmm$, $Z = 2$). Structure of the crystal has been considered as intergrow of Hg-1201 and Tl-2201 ones [15]. But it can be considered as F1\A1\F2 where Tl-positions in F2-block are partially filled. Combinations Cu3\B2\Cu1 [16, 17] and Cu3\B2\Cu2 [18] are also known. In both cases these structures belong to $Ammm$ space group with $Z = 2$.

Total number possible combinations with A- and B-slabs and two blocks is estimated by value more than four thousands. That is why we have restricted ourselves by the most probable praphases. F1-block was selected for the purpose. It is similar to one unit cell of NaCl type and contains two cations as well as F2-block and admits to partial disordering of anions in the basal plane, as it have been found in structures of $Sr_4PbFe_2O_9$ [19] and $(Sr_{0,87}Eu_{0,19})(Eu_{0,75}Ce_{0,25})_2Pb_{0,5}Cu_{0,5}Cu_2O_9$ [20]. Anion vacancies are often exist in F1-block, as it have been met in structures $BaCa_4HgCu_3O_{12+\delta}$ and $Ba_2Ca_5HgCu_5O_{14+\delta}$ [21].

In Table 5 are enumerated possible praphases with A- and B-slabs and F1-block. The number of layers in slabs was restricted by three and four ones in A- and B-slabs respectively and hypothetical blocks were excluded.

Table 5

Praphases containing A- and B-slabs and two types of intermediate blocks

General formula	Block/slab/block	Space group	Z	Coordination atoms
$A_7B_2X_{11}$	F1\A1\F2✓	<i>I4/mmm</i>	2	$A^{IX}_4A^{VI-2}_3B^{VI-1}_2X_{17}$
$A_9B_4X_{17}$	F1\A2\F2	<i>I4/mmm</i>	2	$A^{XII}_2A^{IX}_4A^{VI-2}_3B^{VI-1}_4X_{17}$
$A_{11}B_6X_{23}$	F1\A3\F2	<i>I4/mmm</i>	2	$A^{XII}_4A^{IX}_4A^{VI-2}_3B^{VI-1}_6X_{23}$
$A_5B_2X_9$	F1\A1\R1✓	<i>I4/mmm</i>	2	$A^{IX}_4A^{VI-2}B^{VI-1}_2X_9$
$A_7B_4X_{15}$	F1\A2\R1	<i>I4/mmm</i>	2	$A^{XII}_2A^{IX}_4A^{VI-2}B^{VI-1}_4X_{15}$
$A_9B_6X_{21}$	F1\A3\R1	<i>I4/mmm</i>	2	$A^{XII}_4A^{IX}_4A^{VI-2}B^{VI-1}_6X_{21}$
$A_5B_3X_9$	F1\A1\Cu1	<i>P4/mmm</i>	2	$A^{IX}_2A^{VIII-1}_2A^{VI-2}B^{VI-1}_2B^{II}X_9$
$A_7B_5X_{15}$	F1\A2\Cu1	<i>P4/mmm</i>	2	$A^{XII}_2A^{IX}_2A^{VIII-1}_2A^{VI-2}B^{VI-1}_4B^{II}X_{15}$
$A_9B_7X_{21}$	F1\A3\Cu1	<i>P4/mmm</i>	2	$A^{XII}_4A^{IX}_2A^{VIII-1}_2A^{VI-2}B^{VI-1}_6B^{II}X_{21}$
$A_5B_3X_{10}$	F1\A1\Cu2	<i>Pmmm</i>	2	$A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_2B^{IV-1}X_{10}$
$A_7B_5X_{16}$	F1\A2\Cu2	<i>Pmmm</i>	2	$A^{XII}_2A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_4B^{IV-1}X_{16}$
$A_9B_7X_{22}$	F1\A3\Cu2	<i>Pmmm</i>	2	$A^{XII}_4A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_6B^{IV-1}X_{22}$
$A_5B_4X_{11}$	F1\A1\Cu3	<i>Ammm</i>	2	$A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_2B^{IV-1}_2X_{11}$
$A_7B_6X_{17}$	F1\A2\Cu3	<i>Ammm</i>	2	$A^{XII}_2A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_4B^{IV-1}_2X_{17}$
$A_9B_8X_{23}$	F1\A3\Cu3	<i>Ammm</i>	2	$A^{XII}_4A^X_2A^{IX}_2A^{VI-2}B^{VI-1}_6B^{IV-1}_2X_{23}$
$A_7B_3X_{11}$	F1\A1\P1	<i>P4/mmm</i>	2	$A^{IX}_4A^{VI-2}Pb^{V-2}_2B^{VI-1}_2B^{II}X_{11}$
$A_9B_5Z_{17}$	F1\A2\P1	<i>P4/mmm</i>	2	$A^{XII}_2A^{IX}_4A^{VI-2}Pb^{V-2}_2B^{VI-1}_4B^{II}X_{17}$
$A_{11}B_7X_{23}$	F1\A3\P1	<i>P4/mmm</i>	2	$A^{XII}_4A^{IX}_4A^{VI-2}Pb^{V-2}_2B^{VI-1}_6B^{II}X_{23}$
$A_6B_3X_{10}$	F1\A1\P2	<i>P4/mmm</i>	2	$A^{IX}_3A^{VIII-1}A^{VI-2}Pb^{V-2}B^{VI-1}_2B^{II}X_{10}$
$A_8B_5X_{16}$	F1\A2\P2	<i>P4/mmm</i>	2	$A^{XII}_2A^{IX}_3A^{VIII-1}A^{VI-2}Pb^{V-2}B^{VI-1}_4B^{II}X_{16}$
$A_{10}B_7X_{22}$	F1\A3\P2	<i>P4/mmm</i>	2	$A^{XII}_4A^{IX}_3A^{VIII-1}A^{VI-2}Pb^{V-2}B^{VI-1}_6B^{II}X_{22}$
$A_7B_3X_{12}$	F1\A1\P3	<i>Pmmm</i>	2	$A^{IX}_4Pb^{VII}_2A^{VI-2}B^{VI-1}_2B^{IV-1}X_{12}$
$A_9B_5X_{18}$	F1\A1\P3	<i>Pmmm</i>	2	$A^{XII}_2A^{IX}_4Pb^{VII}_2A^{VI-2}B^{VI-1}_4B^{IV-1}X_{18}$
$A_{11}B_7X_{24}$	F1\A1\P3	<i>Pmmm</i>	2	$A^{XII}_4A^{IX}_4Pb^{VII}_2A^{VI-2}B^{VI-1}_6B^{IV-1}X_{24}$
$A_7B_3X_{13}$	F1\A1\P5	<i>P4/mmm</i>	2	$A^{IX}_4Pb^{IX}_2A^{VI-2}B^{VI-1}_3X_{13}$
$A_9B_5X_{19}$	F1\A2\P5	<i>P4/mmm</i>	2	$A^{XII}_2A^{IX}_4Pb^{IX}_2A^{VI-2}B^{VI-1}_5X_{19}$
$A_{11}B_7X_{25}$	F1\A3\P5	<i>P4/mmm</i>	2	$A^{XII}_4A^{IX}_4Pb^{IX}_2A^{VI-2}B^{VI-1}_7X_{25}$
$A_9B_4X_{15}$	F1\B2\F2	<i>I4/mmm</i>	2	$A^{IX}_4A^{VIII-2}_2A^{VI-2}_3B^{V-1}_4X_{15}$
$A_{11}B_6X_{19}$	F1\B3\F2	<i>I4/mmm</i>	2	$A^{IX}_4A^{VIII-2}_4A^{VI-2}_3B^{V-1}_4B^{IV-1}_2X_{19}$
$A_{13}B_8X_{23}$	F1\B4\F2	<i>I4/mmm</i>	2	$A^{IX}_4A^{VIII-2}_6A^{VI-2}_3B^{V-1}_4B^{IV-1}_4X_{23}$
$A_7B_4X_{13}$	F1\B2\R1	<i>P4/mmm</i>	2	$A^{IX}_4A^{VIII-2}_2A^{VI-2}B^{V-1}_4X_{13}$

General formula	Block/slab/block	Space group	Z	Coordination atoms
$A_9B_6X_{17}$	F1\B3\R1	$P4/mmm$	2	$A_{4A}^{IX}A_{4A}^{VIII-2}A_{2A}^{VI-2}B_{4B}^{V-1}B_{2B}^{IV-2}X_{17}$
$A_{11}B_8X_{21}$	F1\B4\R1	$P4/mmm$	2	$A_{4A}^{IX}A_{6A}^{VIII-2}A_{2A}^{VI-2}B_{4B}^{V-1}B_{4B}^{IV-2}X_{21}$
$A_7B_5X_{13}$	F1\B2\Cu1	$P4/mmm$	2	$A_{2A}^{IX}A_{2A}^{VIII-1}A_{3A}^{VIII-2}A_{2A}^{VI-2}B_{4B}^{V-1}B_{2B}^{II}X_{13}$
$A_9B_7X_{17}$	F1\B2\Cu1	$P4/mmm$	2	$A_{2A}^{IX}A_{2A}^{VIII-1}A_{2A}^{VIII-2}A_{4A}^{VI-2}B_{4B}^{V-1}B_{2B}^{IV-1}B_{2B}^{II}X_{17}$
$A_{11}B_9X_{21}$	F1\B2\Cu1	$P4/mmm$	2	$A_{2A}^{IX}A_{2A}^{VIII-1}A_{2A}^{VIII-2}A_{6A}^{VI-2}B_{4B}^{V-1}B_{4B}^{IV-1}B_{4B}^{II}X_{21}$
$A_7B_5X_{14}$	F1\B2\Cu2	$Pmmm$	2	$A_{2A}^XA_{2A}^{IX}A_{2A}^{VIII-2}A_{2A}^{VI-2}B_{4B}^{V-1}B_{4B}^{IV-1}X_{14}$
$A_9B_7X_{18}$	F1\B3\Cu2	$Pmmm$	2	$A_{2A}^XA_{2A}^{IX}A_{4A}^{VIII-2}A_{4A}^{VI-2}B_{4B}^{V-1}B_{3B}^{IV-1}X_{18}$
$A_{11}B_9X_{22}$	F1\B4\Cu2	$Pmmm$	2	$A_{2A}^XA_{2A}^{IX}A_{6A}^{VIII-2}A_{6A}^{VI-2}B_{4B}^{V-1}B_{5B}^{IV-1}X_{22}$
$A_7B_6X_{15}$	F1\B2\Cu3	$Ammm$	2	$A_{2A}^XA_{2A}^{IX}A_{2A}^{VIII-2}A_{2A}^{VI-2}B_{4B}^{V-1}B_{2B}^{IV-1}X_{15}$
$A_9B_8X_{19}$	F1\B3\Cu3	$Ammm$	2	$A_{2A}^XA_{2A}^{IX}A_{4A}^{VIII-2}A_{4A}^{VI-2}B_{4B}^{V-1}B_{4B}^{IV-1}X_{19}$
$A_{11}B_{10}X_{23}$	F1\B4\Cu3	$Ammm$	2	$A_{2A}^XA_{2A}^{IX}A_{6A}^{VIII-2}A_{6A}^{VI-2}B_{4B}^{V-1}B_{6B}^{IV-1}X_{23}$
$A_9B_5X_{15}$	F1\B2\P1	$P4/mmm$	2	$A_{4A}^{IX}A_{2A}^{VIII-2}A_{2A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{4B}^{II}X_{15}$
$A_{11}B_7X_{19}$	F1\B3\P1	$P4/mmm$	2	$A_{4A}^{IX}A_{4A}^{VIII-2}A_{4A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{2B}^{IV-1}B_{2B}^{II}X_{19}$
$A_{13}B_9X_{23}$	F1\B4\P1	$P4/mmm$	2	$A_{4A}^{IX}A_{6A}^{VIII-2}A_{6A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{4B}^{IV-1}B_{4B}^{II}X_{23}$
$A_8B_5X_{14}$	F1\B2\P2	$P4/mmm$	2	$A_{3A}^{IX}A_{2A}^{VIII-2}A_{2A}^{VIII-1}A_{2A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{4B}^{II}X_{14}$
$A_{10}B_7X_{18}$	F1\B3\P2	$P4/mmm$	2	$A_{3A}^{IX}A_{4A}^{VIII-2}A_{4A}^{VIII-1}A_{2A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{2B}^{IV-1}B_{2B}^{II}X_{18}$
$A_{12}B_9X_{22}$	F1\B4\P2	$P4/mmm$	2	$A_{3A}^{IX}A_{6A}^{VIII-2}A_{6A}^{VIII-1}A_{2A}^{VI-2}Pb_{2B}^{V-2}B_{4B}^{V-1}B_{4B}^{IV-1}B_{4B}^{II}X_{22}$
$A_9B_5X_{16}$	F1\B2\P3	$Pmmm$	2	$A_{4A}^{IX}A_{2A}^{VIII-2}Pb_{2A}^{VII}A_{2A}^{VI-2}B_{4B}^{V-1}B_{4B}^{IV-1}X_{16}$
$A_{11}B_7X_{20}$	F1\B3\P3	$Pmmm$	2	$A_{4A}^{IX}A_{4A}^{VIII-2}Pb_{2A}^{VII}A_{2A}^{VI-2}B_{4B}^{V-1}B_{3B}^{IV-1}X_{20}$
$A_{13}B_9X_{24}$	F1\B4\P3	$Pmmm$	2	$A_{4A}^{IX}A_{6A}^{VIII-2}Pb_{2A}^{VII}A_{2A}^{VI-2}B_{4B}^{V-1}B_{5B}^{IV-1}X_{24}$
$A_9B_5X_{17}$	F1\B2\P5	$P4/mmm$	2	$A_{4A}^{IX}A_{2A}^{VIII-2}Pb_{2A}^{IX}A_{2A}^{VI-2}B_{4B}^{VI-1}B_{4B}^{V-1}X_{17}$
$A_{11}B_7X_{21}$	F1\B3\P5	$P4/mmm$	2	$A_{4A}^{IX}A_{4A}^{VIII-2}Pb_{2A}^{IX}A_{2A}^{VI-2}B_{4B}^{VI-1}B_{4B}^{V-1}B_{2B}^{IV-1}X_{21}$
$A_{13}B_9X_{25}$	F1\B4\P5	$P4/mmm$	2	$A_{4A}^{IX}A_{6A}^{VIII-2}Pb_{2A}^{IX}A_{2A}^{VI-2}B_{4B}^{VI-1}B_{4B}^{V-1}B_{4B}^{IV-1}X_{25}$

3. Conclusion

Preparing this publication the authors would like to propose to specialits a rather rich possibilities for future search of many new layered perovskite-like crystals which can exhibit interesting physical properties such as ferro- and antiferromagnetism, ferro- and antiferroelectricity, superconductivity and others.

Praphases of new layered compounds in Tables 1-5 belong to two tetragonal space groups: $P4/mmm$ and $I4/mmm$. Real crystals can have

distorted structures depending on thermodynamical conditions and deficiency of anions or cations.

Assortment of proposed praphases can be widely enriched, but it has to be taken into account that our prognosis has been made on the crystal chemical basis and it should be considered as a first approximation.

In order to construct theoretically a new structure it is necessary to provide both electroneutrality of its composition and proper values of charges and ionic radii in order to minimize mismatch of the intergrowing surface nets.

Authors hope that content of the paper will stimulate search of new crystals and would be grateful to international community for any remarks, criticism and information about results of the search. We are ready to send our preprints (in Russian) if somebody will be interested in pictures of proposed structures and other details.

The work was partially supported by INTAS 99–10177 and RFBR 00–15–96790 grants.

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