

Perovskite-Like Crystals of the Ruddlesden–Popper Series¹

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Abstract—The layer perovskite-like structures of the so-called Ruddlesden–Popper phases have been analyzed in terms of crystal chemistry. The geometrical boundaries of the existence ranges of these compounds with multilayer stacks are determined and new phases of this type are predicted. The possible variants of related structures are also considered. © 2000 MAIK “Nauka/Interperiodica”.

INTRODUCTION

The analysis of the structural data [2–4] shows that all the variety of the well-known perovskite-like structures can be represented as combinations of four series of stacks formed by layers of octahedra, pyramids, and squares and twenty variants of the intermediate block layers. Thus, using the principle of combination of such stacks and block layers, one can obtain several hundreds of hypothetical tetragonal phases and consider the conditions of their formation in the concrete crystals of various chemical compositions.

We begin the analysis with the family of the phases in which the intermediate block layer is denoted as $R1$ [2], which can be represented by an element of the NaCl-type structure. Such structures are usually named after their first researchers [5, 6] the Ruddlesden–Popper (RP) phases. Earlier [7–10], we performed the crystallochemical analysis of one-layer (or the K_2MgF_4 - or K_2NiF_4 -type) structures and predicted new phases of this type. The present study is aimed to predict new multilayer structures of such type.¹

STRUCTURAL CHARACTERISTICS OF RUDDLESDEN–POPPER PHASES

The general formula of the Ruddlesden–Popper phases can be written as $A_{n-1}A'_2B_nX_{3n+1}$, where A , A' , and B are cations, X is an anion, and n is the number of the layers of octahedra in the perovskite-like stack. The hypothetical tetragonal phases and possible related structures are shown in Fig. 1. There exist stoichiometric compounds with $n = 1–3$. The A cations are characterized by cuboctahedral anionic coordination with the coordination number c.n. = 12 and are included into the

perovskite-like stack. The A' cations (c.n. = 9) are located at the stack boundaries with an intermediate block layer. The B cations are located inside the anionic octahedra, pyramids, and squares.

These phases are the “closest successors” of the perovskite structure. Therefore, numerous crystal lattices with the stacks containing octahedra show some perovskite features (Figs. 1a–1d), whereas those with the anion-deficient compositions, show some Ruddlesden–Popper phase features (Figs. 1e–1i).

Five hypothetical phases shown in Figs. 1e–1i are the combinations of the perovskite-like stacks of type B with the block layer $R1$ [2], of them three types of the structures were found in real compounds with the compositions $AA'_2B_2X_6$, $A_2A'_2B_3X_8$, and $A_3A'_2B_4X_{12}$. As far as we know, no representatives of the four-layer hypothetical phases of the compositions $A_3A'_2B_4X_{10}$ and $A_3A'_2B_4X_{11}$ have been found.

In one-layer RP-phases, the A cations occupy one crystallographic position at the boundary between the perovskite-like stack and the block layer. Therefore, the general formula of the compounds with $n = 1$ can be written in a more convenient form as A'_2BX_4 or A_2BX_4 .

The most symmetric tetragonal RP-phases (sp. gr. $I4/mmm$) contain two formula units per unit cell ($Z = 2$). The coordination formula of one-layer compounds is written as $A_2^{IX}B^{VI}X_4$. Some compositions are characterized by less symmetric structures. In some crystals, where the cation size R_B exceeds the size of the anionic vacancy ($R_B > 0.41R_X$), the decrease of the temperature can give rise to the rotational structural phase transitions. However, the number of such crystals is still rather small.

The sites of layer contacts in the K_2MgF_4 -type structures and their multilayer analogues are square networks with A , A' , and X anions at the lattice sites, which are displaced with respect to one another by a

¹ A more detailed consideration of the results obtained is given in our preprint [1], which can be sent to all those interested by requesting to the following address: Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia.

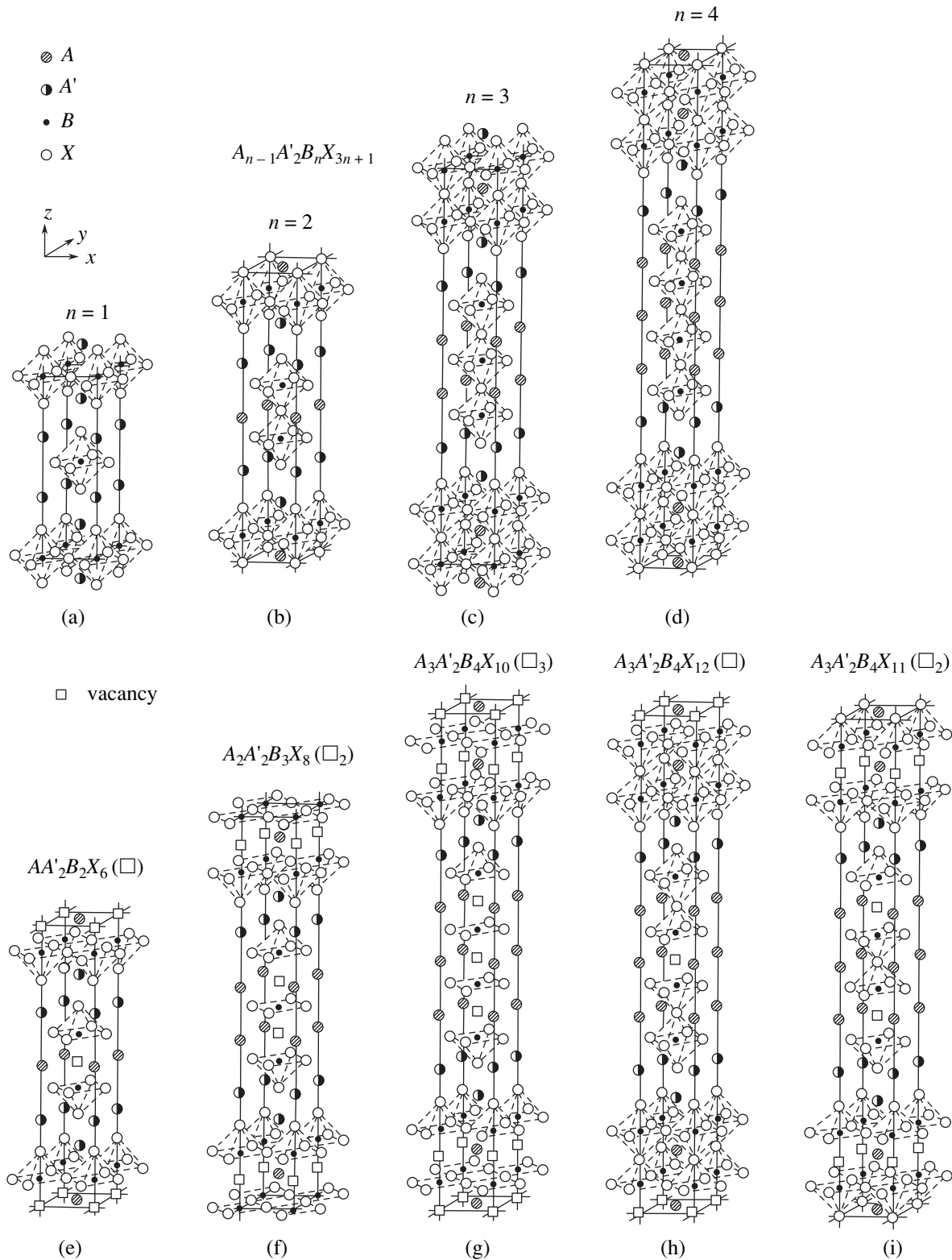


Fig. 1. (a–d) Ruddlesden–Popper phases and (e–i) possible related tetragonal structures.

half-diagonal of the unit cell. These stacks always have matching dimensions, which, probably, can explain the widespread occurrence of one-layer RP-phases. There

exists a variant of the K_2MgF_4 antiphase, the Na_4OI_2 structure [11], where the stack is formed according to the antiperovskite principle ($IONa_3$).

In order to establish the laws of RP-phase formation, we used the bond strengths calculated by the Fesenko method [12]. The bond length in a crystal is compared with the sum of ionic radii with due regard for the cation coordination. If the calculated ratio exceeds unity, the bond is extended, if it is less than unity, it is shortened.

The calculation of bond lengths and strengths for a nine-vertex polyhedron showed that most of the tetragonal phases can "solve their internal problems" not only with the aid of rotation of octahedra, but also with the aid of their deformation. The octahedron deformation within certain limits does not change the total symmetry of the crystal lattice.

There exist some Nd_2CuO_4 -type structures (sp. gr. $I4/mmm$, $Z=2$) [13] well known for cuprates. In these compounds, copper is located in the anionic squares. The A -cations are usually trivalent and form an interlayer as in the CaF_2 -type structures.

Thus, the Ruddlesden–Popper phases in oxides are most probable if the cation valence is $A = 1+$ or $2+$. If the cation valence is equal to $3+$ or exceeds $3+$, the structure of the Nd_2CuO_4 type with the square coordination of the B cations is formed.

Two-layer structures differ from the one-layer structures in the following. The A cation in A_2BX_4 has the c.n. = 9 and has only one position for all the A cations, whereas in $A_3B_2X_7$, the A cation has two different positions in the unit cell—one with the c.n. _{A} = 9 (i.e., the same as in the one-layer unit cell) filled with cations located at the boundary between the stack and the block layer, whereas the second position with the coordination number c.n. _{A} = 12 is located in the perovskite-like stack. This signifies that in such structures, the positions with coordination number c.n. _{A} can be filled only with larger cations and that the structure can contain two different A -cations. Therefore, the general formula of the two-layer compound should be written as

$A A'_2 B_2 X_7 = [A^{\text{XII}} A_2^{\text{IX}} B_2^{\text{VI}} X_7]$. In the one-layer structures, the anions can fill two crystallographic positions with (c.n.) _{X} = 6, but with different sets of surrounding cations. In the two-layer structures, there are three anionic positions with six surrounding cations, but their sets are also different. This provides the prerequisites for the formation of these structures in crystals with mixed anions, e.g., oxyhalides, or in crystals with a deficiency in anions.

At $n = 3$, A -cations also have two possible positions with c.n. = 12 and 9. The coordination formula has the form $[A_2^{\text{XII}} A_2^{\text{IX}} B_3^{\text{VI}} X_{10}]$. B -cations have two octahedral positions and the anions have four positions, so there exist wider possibilities for composition variation.

The RP phases are formed if the A positions are occupied with larger cations. This signifies that these cations should again have the valences $1+$ and $2+$.

RANGES OF EXISTENCE OF THE RUDDLESDEN–POPPER-PHASES

The geometrical limits of existence of the K -type structures depend on the cationic coordination. They were established in our earlier study [9] as $0.41R_X \leq R_B \leq 0.73R_X$ and $R_A \leq 0.73R_X$. All the known compounds with such a structure exist within these ranges. However, in oxides, the Sr_2PbO_4 -type structures also exist in the same composition range [14, 15], with their isolated octahedra forming no stacks at all. Therefore, it was necessary to refine the existence ranges of one-layer structures and determine the existence ranges for multilayer RP-phases. With this aim, we calculated bond strengths for the compositions $A_{n+1}^{2+} B_n^{4+} O_{3n+1}^{2-}$ and the unit-cell parameters, and also the lengths and strengths of the bonds for hypothetical compounds with different combinations of the cationic A and B radii using the formulas obtained for such compositions by averaging the structural data [16] and modifying them in a way to take into account the multilayer nature of the phases under consideration. We used the values of the free parameters for the atomic coordinates determined for the compositions $\text{Sr}_{n-1}\text{Ti}_n\text{O}_{3n+1}$. The formulas for the unit-cell parameters of the tetragonal phases are:

$$a = 0.166 \times 2R_A^{\text{IX}} + 1.705R_B + 2.418 \quad (n = 1),$$

$$a = 0.166(R_A^{\text{XII}} + R_A^{\text{IX}}) + 1.705R_B + 2.418 \quad (n = 2, 3).$$

The a parameters for $n = 1$ –3 have close values and are almost independent of the number of perovskite-like stacks:

$$c = 2.158(R_A^{\text{XII}} + R_A^{\text{IX}}) + 0.396R_B + 6.752 + 2(n-1) \times a,$$

where R_A and R_B are the Shannon cationic radii [17]. The Roman superscripts of A and B ions show their coordination.

The formation of the RP-phases was assumed to be possible if the bond lengths A – X and B – X were elongated or shortened by not more than 10%.

Proceeding from the number of the known RP-phases, it seemed that two- and also three-layered structures should be less common. The range of phase existence should decrease with an increase of the number of layers in the structure.

However, analysis showed that the existence ranges of RP phases with $n = 1$ –3 almost coincide (within the accuracy of the calculation) (Fig. 2). With an increase of the cationic radii, the existence range of these phases becomes narrower and then is tampered at the hypothetical point with the approximate coordinates $R_A = 4$ and $R_B = 2.5 \text{ \AA}$.

According to the minimum cationic radius B , the range of the structure existence is written as $R_B > 0.50 \text{ \AA}$, which is close to the boundary of existence of

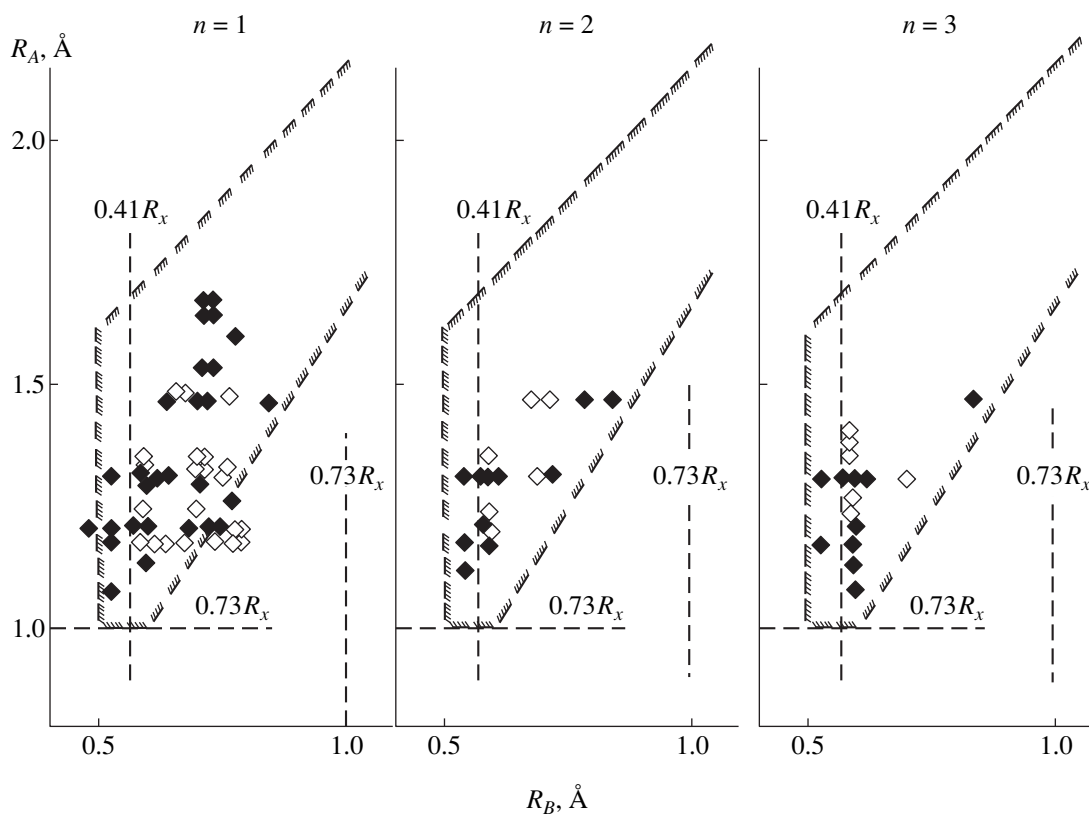


Fig. 2. (◆) Known and (◇) predicted Ruddlesden-Popper phases and possible ranges of their existence.

Sn oxygen octahedron. The approximate existence range for oxides can be written as $1.6R_B < R_A < 1.24R_B + 0.9 \text{ \AA}$. The values of the ionic radii F^- and O^{2-} are close and therefore, the existence ranges of the fluoride-based RP-phases should be approximately the same.

Although the geometric ranges of the phase existence are independent of the number of layers in the stack, the structures become less strong with an increase in n , and their formation can be limited because of the following. In the K_2MgF_4 -type structures, the intermediate block layer stabilizes the octahedral part of the stack, which is similar to an increase of the number cubic densely filled layers AX_3 in halide polytypes, ABX_3 , under high pressures. With an increase of the number of layers in these stacks, the stabilizing effect of the block layer is diminished. Therefore, the number of layers in stacks would also be limited. Numerous perovskite-like oxides ABX_3 possess cubic lattices at high temperatures, and distorted lattices at room temperature. This “heredity” can also affect the stack stability. Thus, some constraints are imposed on the formation of multilayer RD-phases.

Since the existence ranges of RP phases with $n = 1-3$ coincide, two important conclusions can be drawn:

1. In the composition providing no formation of one-layer structures or in the compositions where no

such structures can be predicted, no multilayer structures can form. This considerably reduces the number of possible compositions.

2. The formation of the compounds with $n = 3$ is the most probable for the compositions, where the compound with $n = 1, 2$ are known.

PREDICTION OF NEW COMPOUNDS

The following cations are appropriate for synthesis of new oxides: $A^{2+} = Ba, Sr, \text{ and } Ca$, then $A^{2+} = Nd, Sm, Eu, \text{ and } Dy$ and $B^{4+} = Cr, V, Fe, Sn, Ru, \text{ and } Zr$.

The probable compositions are: $Sr_4Cr_3O_{10}$, $Ca_4V_3O_{10}$, $Ca_3V_2O_7$, $Sr_4Ru_3O_{10}$, $Eu_4Ti_3O_{10}$, and $Sm_4Ti_3O_{10}$ (see table). Since the compounds $K_2Gd_2Ti_3O_{10}$ and $K_2La_2Ti_3O_{10}$ exist [18], one can expect the formation of a three-layer structure within the compositions with intermediate RE cations, namely, $K_2Pr_2Ti_3O_{10}$, $K_2Eu_2Ti_3O_{10}$, and $K_2Ce_2Ti_3O_{10}$. The size of Bi-cation is comparable with the sizes of RE cations, and therefore, the synthesis of $K_2Bi_2Ti_3O_{10}$ is possible. The structure of the $Na_2Nd_2Ti_3O_{10}$ compound is solved up to the determination of atomic coordinates [19]. In this structure, Nd is surrounded with 12 anions, whereas Na is surrounded with 9 anions. Therefore, the formula of this compound should rather

Predicted Ruddlesden–Popper Phases with the composition $(ABX_3)_nAX$, $n = 1-3$

B^{4+} -oxides												
A^{2+}	Ti	Zr	Cr	Mn	V	Fe	Sn	Pb	Hf	Tb	Rh	Ru
Ba		123					123	123	123	123		123
Sr	123	123	123	123	123	123	123		123	123	123	123
Ca	1'2'3'			123	123							
Nd	123	123			123	123			123	123		
Sm	123	123			123	123			123			
Eu	123	123			123	123			123			
Dy	123				123	123			123			

B^{2+} -fluorides												
A^+	Ni	Co	Fe	V	Mn	Ti	Cu	Cr	Zn	Cd	Hg	Mg
Cs			123	123	123	123	123	123		123	123	123
Rb	123	123	123	123	123	123	123	123	123	123	123	123
Tl	123	123	123	123	123	123	123	123	123	123		123
NH ₄	123	123	123	123	123	123	123	123	123	123	123	123
K	123	123	123	123	123		123		123			123

B^{2+} -chlorides														
A^+	Ni	Co	Fe	V	Mn	Ti	Cu	Cr	Zn	Cd	Hg	Yb	Mg	Ca
Cs					123	123		123		123		123		123
Rb				123	123	123		123		123	123		123	2
Tl				123	123	123		123						
NH ₄				123		123		123						
K					123	123							123	

Notation

Compounds	Known	Predicted	Composition
$n = 1$	1	1	A_2BX_4
$n = 2$	2	2	$A_3B_2X_7$
$n = 3$	3	3	$A_4B_3X_{10}$
	1', 2', 3'	1'	Distorted phases
	RD-phases are low probable		

be written as $Nd_2Na_2Ti_3O_{10}$. The size of the A_2^{XII} -cation in this compound can still be increased and, therefore, it might be possible to synthesize the compounds $Pr_2Na_2Ti_3O_{10}$, $Ce_2Na_2Ti_3O_{10}$, $La_2Na_2Ti_3O_{10}$, and $Bi_2Na_2Ti_3O_{10}$.

In the compositions $A_2A'_2B_3X_{10}^{2-}$ with the odd valence of B -cations (3+ or 5+), only nonstoichiometric compounds can be synthesized. The stoichiometric compositions can be formed only by cations with the even valence. The most often encountered compositions are formed by B -cations with valence 4+. Theoretically, the cations with the valence 2+ (B^{2+}) can form the composition $A_2^{3+}A_2^{4+}B_3^{2+}X_{10}^{2-}$, but, in practice, it is hardly probable, because it is difficult to find the cat-

ions with such valences that would simultaneously satisfy the geometric conditions for the existence of this structure type.

Since Bi is often present in many layer structures (especially in the Aurivillius phases), the new com-

pounds of the $Bi_2^{3+}M^{2+}O_4$ type with $M^{2+} = Ni, Co, Fe, V, Mn, Ti, Cr, Zn, Mg, Cd$, and Ca are of great interest from the standpoint of their physical properties. One can expect the formation of the K_2MgF_4 -type structures in these compounds.

However, the synthesis of new compounds and especially the growth of single crystals from melts encounter some specific difficulties. The compounds with such structures (even one-layer compounds) melted

incongruently, and, therefore, no such structures (especially of two- and three-layered structures) were revealed in the studies of the phase diagrams of the multicomponent compositions of many of these phases. They were synthesized only recently by solid-phase synthesis at high temperatures and, sometimes, also under high pressures.

Is the synthesis of RP phases with $n > 3$ possible at all? For simple compositions, it is hardly probable. In the compositions with complicated combinations of cations, such structures are possible.

Is it possible to synthesize the compound of the composition Ca_2TiO_4 ? We know the compounds $\text{Ca}_3\text{Ti}_2\text{O}_7$ (sp. gr. $Ccm2_1$) and $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ (sp. gr. $Pcab$). Even at room temperature, their structures have the characteristic orthorhombic distortion, more pronounced for the two-layer structure than for the three-layer one. This signifies that the one-layer Ca_2TiO_4 compound can also be distorted or it can exist only at elevated temperatures.

RELATED STRUCTURES

Numerous compounds show some similarity to the RP-phases. Structurally, the compounds closest to the RP-phases are oxyhalides [20] containing no anionic vacancies at all. However, since the cation-halogen bond in octahedron is much weaker than the corresponding bond with oxygen, the cation is displaced from the octahedron center, and acquires the coordination number five (the coordination polyhedron is four-faced pyramid).

In one-layer oxyhalides of the compositions $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Br}_2$ [21], the copper coordination can still be considered as octahedral, because the elongation of the copper-halogen bond does not exceed 10% (in $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, it equals 7.7%, and in $\text{Ca}_2\text{CuO}_2\text{Br}_2$ 9.6%). In oxychlorides of the compositions $\text{Ba}_3\text{In}_2\text{O}_5\text{Cl}_2$ [22] and $\text{Ba}_3\text{Ti}_2\text{O}_5\text{Cl}_2$ [23], despite their structural similarity to two-layer RP-phases, the cation displacement in the octahedron is much more pronounced. In the first compound, the metal-halogen bond is elongated by 17.6%, in the second, by 30%. The coordination numbers of In^{3+} and Ti^{3+} ions are equal to five. Comparing these structures with their prototype, $\text{Sr}_3\text{Ti}_2\text{O}_7$, we see that despite the same structure type, the B -cations in these structures have different coordinations.

A similar situation is also characteristic of the $\text{Nd}_2\text{Na}_2\text{Ti}_3\text{O}_{10}$ [19, 24] structure. Titanium atoms of the outer octahedral layers are displaced by 0.4 Å toward block layers. This increases the coordination number of Ti^{4+} up to five (the four-faced pyramid). The bond to the sixth anion of the octahedron is elongated by 17.3%. Assuming the titanium coordination to be $(5 + 1)$, we can relate this structure to the RP-phases with $n = 3$.

These structures have the following characteristic features:

In oxyhalides, the coordination of the central cation in the outer octahedral layers in the stacks increases to five, and the cation itself is displaced toward the stack.

At different valences of cations in the A positions, the B cation is displaced toward the block layer.

The $\text{La}_2\text{Sr}_4\text{Cu}_2\text{Ti}_2\text{O}_{13}$ structure [25], which is the closest to the RP-phases with $n = 2$, acquires some vacancies. The lattice has about 30% of disordered anionic vacancies located at the centers of the stacks. This signifies that the stack has up to 30% of semioctahedra. Thus, the bonds inside the stack are weakened due to formation of such vacancies.

A bright example of the anion-deficient structures are the Sr_2CuO_3 and Ca_2CuO_3 crystals with the formal copper valence $2+$. The structure has no octahedra anymore; they are degenerated into squares. The tetragonal $\text{Sr}_2\text{CuO}_{3+\delta}$ crystal is a closer analogue of the K_2MgF_4 structure, but its basal planes formed by the octahedral layers contain oxygen vacancies ($g = 1/2$). The structures of the compounds $\text{LnSr}_5\text{Ni}_3\text{O}_8$ ($\text{Ln} = \text{Y, Dy, Ho, Er, and Tm}$) [26] are close to the Sr_2CuO_3 -type, nickel has the formal valence $1+$ and is coordinated with a square of oxygen atoms.

Among the related RP-phases, one can find the compounds with the number of perovskite-like layers exceeding three. An example here is the $\text{Ba}_2\text{CaGd}_2\text{Ti}_2\text{Cu}_2\text{O}_{12}$ structure [27].

The ion sizes in all the known nonstoichiometric compounds range within the limits $R_A = (1.05-1.47)$ and $R_B = (0.58-0.80)$ Å. Therefore, similar to the stoichiometric phases, all the nonstoichiometric compounds exist within the range shown in Fig. 2 in the R_B-R_A coordinates. Proceeding from this fact and knowing the cationic dimensions [17] for each concrete chemical composition, one can change these cations in the A and B positions and, thus, synthesize new crystals. It is also possible to synthesize the $A_2\text{BO}_3$ compounds using the cations $A^{2+} = \text{Ba, Sr, Nd, Sm, Eu}$ and $B^{2+} = \text{Ni, Co, Fe, V, Cr, Mn, Cu}$. Within the compositions $A_3^{2+} B_2^{3+} O_{7\pm\delta}$, one can synthesize the compounds $\text{Ba}_3\text{Ti}_2\text{O}_{7\pm\delta}$ and $\text{Sr}_3\text{In}_2\text{O}_{7\pm\delta}$.

CONCLUSION

The existence ranges of all the tetragonal Ruddlesden-Popper phases with $n = 1-3$ in the R_B-R_A coordinates are the same.

With an increase of R_A and R_B , the existence ranges become narrower and are tapered at the hypothetical point with the coordinates $R_A = 4$ and $R_B = 2.5$ Å (for oxides and fluorides).

The calculation of bond strengths shows that the similar tapering of the cubic phases is also characteristic of perovskites. The existence range of cubic fluo-

rides-perovskites in the R_B - R_A coordinates almost coincides with the existence range of the corresponding RP phases.

The apical anion in the octahedron of all the tetragonal phases is strongly sterically hindered, which can give rise to the formation of rotational RP-phases at lower temperatures. However, four anions of their octahedra lying in the layer plane cannot be displaced, which seems to explain the fact that only a small number of rotational RP-phases is known in these systems.

The stoichiometric (with respect to anion) RP phases can be formed only at $n = 1-3$, however the related nonstoichiometric phases can have a larger number of perovskite-like layers.

The prediction of one-layered RP phases showed that the possible number of such phases can attain about 2400. Since the existence ranges of two- and three-layer phases coincide with the existence range of one-layer ones, one can predict the synthesis of a quite a large number of new crystals with $n = 2, 3$.

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