Ferroelectrics

ISSN: 0015-0193 (Print) 1563-5112 (Online) Journal homepage: https://www.tandfonline.com/loi/gfer20

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To cite this article: K. S. Aleksandrov & B. V. Beznosikov (1999) Architecture and properties of perovskite-like crystals, Ferroelectrics, 226:1, 1-9, DOI: 10.1080/00150199908230285

To link to this article: https://doi.org/10.1080/00150199908230285

Published online: 26 Oct 2011.

Ferroelectrics, 1999, Vol. 226, pp. 1–9
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ARCHITECTURE AND PROPERTIES OF PEROVSKITE-LIKE CRYSTALS

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(Received in final form 17 July 1998)

A variety of the known structures of perovskite-like crystals including cation- and anion-deficient phases were considered as the intergrowth systems of slabs containing n-layers ($n = 1, 2, 3, \ldots \infty$) of corner-linked octahedra BX_6, pyramids BX_5 or square-planar nets BX_4 (B–cation, X–anion) linked by intermediate blocks of different types.[1–3] Some new structural types and new representatives of ferroelectrics, ferroelastics and HTSC's can be constructed on this basis. The prognosis of new possible representatives in Ruddlesden–Popper's family is discussed.

Keywords: Perovskites; perovskite-like crystals; new representatives of Ruddlesden–Popper's phases

1. INTRODUCTION

The numerous inorganic and metallorganic compounds with perovskite-like structures form an extensive group of crystals with interesting electric, magnetic, elastic and superconducting properties. The well known family of ABX_3 crystals (A, B–cations, X–anion) with perovskite-type structure are characterized by a three-dimensional frame of the corner-linked BX_6 octahedra and A-ions located in dodecahedral cavities. The ideal perovskite structure belongs to cubic space group $Pm3m$, $Z = 1$, but there are many structures, slightly distorted due to the polar or antipolar displacements of B-ions, Jahn-Teller distortions and octahedral tilts. The nearest related

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structures are elpasolites, $A_2BB'X_6$ with the ordered B, B'-ions (space group $Fm3m$, $Z = 4$), $\square BX_3$ and $\square_2BB'X_6$ ($\square$ – vacancy) and crystals of $K_2\square PtCl_6$ type with ordered vacancies at A or B positions.

In general crystals are attributed to the perovskite-like family if the main feature of the perovskite structure is preserved, namely slabs or layers of the corner-linked octahedra BX_6, pyramids BX_5 or square BX_4 nets. This group includes polytypes ABX_3 with different sequences of h- and c-packing of planar AX_3 layers. During the last decades many new types of the layered structures have been studied in course of search for new superconductors and ferroelectrics.

The main purpose of this paper is a general consideration of these structural types on a common basis and a demonstration of many new possibilities for the search of new representatives among the known families of perovskite-like crystals and preparation of new types of structures, unknown yet.[1-3]

2. FAMILIES OF PEROVSKITE-LIKE CRYSTALS

The whole variety of perovskite-like (PL) crystals can be divided into nine groups, Table I.

The first group includes ABX_3 cubic and distorted perovskites and more complex compounds with two or more A- and/or B-cations disordered in the lattice (disordered solid solutions). We attribute the ordered compounds $(A_{1-x}A'_x)(B_{1-y}B'_y)X_3$ to the same group also. They belong to different space groups, and have different unit cell dimensions depending on x and y values. Elpasolites $A_2BB'X_6$ ($x = 0$, $y = 1/2$), $AB_{1/3}B'_{2/3}X_3$ ($x = 0$, $y = 2/3$) and many other crystals belong to the group.

TABLE I Families of perovskite-like crystals

1	Perovskites ABX_3 and more complex disordered structures, c-sequence of AX_3 layers
2	$(A_{1-x}B_{1-y}X_3)_n$, cation-deficient structures
3	$(A_{1-x}A'_x)(B_{1-y}B'_y)X_{3-z}$, anion-deficient ordered structures
4	$(ABX_3)_n$, polytypes with h: hhc; hc; hcc... sequences of AX_3 layers and their cation-deficient structures
5	Layered crystals with perovskite-like layers, belonging to D^1_{4h} group: ABX_4 and other types
6	$A_{n+1}B_nX_{3n+1}$, Ruddlesden – Popper's phases and related structures
7	$A_2X'_2(A_{n+1}B_nX_{3n+1})$, Aurivillius's phases and related structures
8	Other homologues of anion-deficient layered crystals
9	Compounds of $A_nB_nX_{3n+2}$ series with perovskite-like octahedral blocks cut from perovskite frame by $(110)_0$ planes

The second group contains the crystals with cation vacancies, in particular-ordered point vacancies as in $\square ReO_3$, $\square_2NaSbF_6$, $A_2B\square X_6$. The first two families have vacancies instead of A-ions on Figures 1a, b; the last one-ordered vacancies instead of one half B-ions on Figure 1a. Other combinations of the ordered B vacancies exist in $K_4Mn_3\square F_{12}$ ($x = 0$, $y = 1/4$) or $Nd_{2/3}Nb_2O_6$ ($x = 4/3$, $y = 0$) *etc.*

PL-crystals with three-dimensional frame of structure containing rows of anionic vacancies along $[100]_0$ or $[110]_0$ directions of the initial cubic perovskite structure belong to the third group. Many examples of such structures have been found.[4, 5] $Ca_2Fe_2O_5$, $LaSrCuAlO_5$ and $La_2Ni_2O_5$ can be mentioned as examples. Depending on directions and mutual positions of the vacant rows the frames can be formed by octahedra and pyramids, octahedra and tetrahedra, octahedra and rows of squares, or tetrahedra alone, as in the case of $Ca_2Mn_2O_5$. Into the same group we include the few crystals with anionic vacancies located at $(001)_0$ planes. Their general formula can be written as $A_nB_nX_{3n-\delta}$. When the planes of vacancies are located in each second plane connecting the octahedra in the initial structure (as in the case of $YBaFeCuO_{5+\delta}$) the unit cell is doubled ($n = 2$) along $(001)_0$ and becomes a tetragonal one. There exist other crystals of the same type with $n = 3, 4, 5$, see for example.[6] A well known $YBa_2Cu_3O_{7-\delta}$ type belongs to the group also ($n = 3$). Anionic vacancies are located here both in $(001)_0$ planes and $[100]_0$ and/or $[010]_0$ rows. As it will be shown below it's better to consider these crystals as intercalations of single layers of pyramids

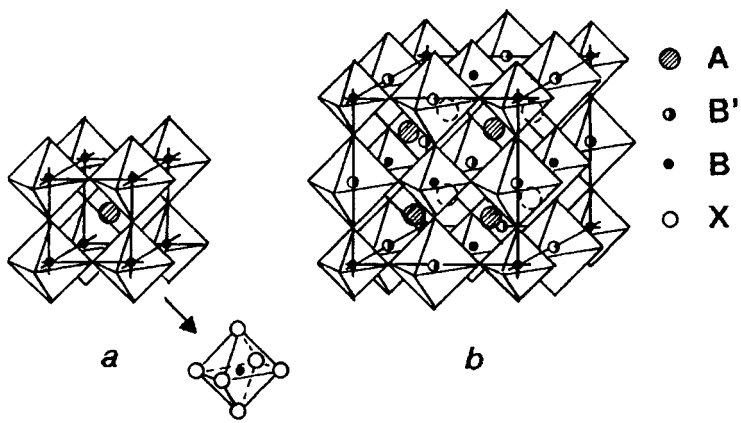

FIGURE 1 Structures of perovskite (a) and elpasolite, (b) concerning the cation deficient versions of these structures-see text.

connected by intermediate blocks containing the rows of BX_4 squares or BX_2 dumbbells. The reason for such a conclusion is found in many examples of crystals where these blocks contain triangle or tetrahedral groups such as CO_3, NO_3, AlO_4 *etc.* [1]

Relatively far from perovskites are located ABX_3 polytypes and their cation-deficient structures such as *h*-$BaTiO_3$, $KNiCl_3$, $Ba_3Re_2\square O_9$, $Cs_3Cr_2\square Br_9$, *etc.* These structures of group 4 are composed of h-, hhc-, hcc-sequences of AX_3 layers, where *B*-ions form rows or three-dimensional frames of octahedra, linked both by vertices and planes. In some deficient crystals octahedra form PL-blocks, cut from perovskite frame by $(111)_0$ planes.

Rather rich families of PL-crystals with the ideal tetragonal P4/mmm structures form group 5 of Table I. Crystals ABX_4 of $TlAlF_4$-type is one of its subgroups. Single layers of octahedra are linked in their structure by blocks containing individual *A*-ions. Multilayered crystals of the family with general formula $AA'_{n-1}B_nX_{3n+1}$, $n = 2, 3\ldots$ are unknown yet. But some anion-deficient structures such as *t*-$(Sr_{1-x}A_x)CuO_2$ and $YBaFe_2O_5$ could be considered as members of the subgroup. Much broader subgroup includes the oxides (AO_δ) $A'_2A''_{n-1}B_nO_{2n+2}$. They are designated usually as $A12(n-1)$ *n*-type crystals and many anion-deficient multilayered structures with $n = 1, 2, \ldots, 8$ are known now among Tl-, Hg- (Tl, Pb)- Cu- (Ag, Cu), *etc.*, superconductors. PL-slabs of *B*-type, see Figure 2, are linked here by AO_δ-layers, forming (together with apical oxygens of neighboring slabs) one of the possible types of intermediate blocks, see F_1 $(+\alpha)$ on Figure 3. The same subgroup can include related crystals with similar B-type slabs and other α-blocks. According to Tokura and Arima [7] sign α means that the block does not shift the neighboring slabs in *ab*-plane of the layered structure. These α-blocks contain CO_3, BO_3 groups and combinations of CO_3 or SO_4 groups with CuO_4 squares, Figure 3.

Group 6 in Table I contains the family of Ruddlesden–Popper phases: $AX(A'BX_3)_n$ and related structures included. Up to now many crystals with $n = 1, 2, 3$ are known in the R–P family. They may have both ideal tetragonal structures (I4/mmm, $Z = 2$) or distorted ones due to octahedral tilts or the Jahn–Teller effect. La_2CuO_4 and its solid solutions were the most intensively studied during the last decades as the first HTSC. The crystal has so the called T-type structure, and two structural phase transitions to the orthorhombic and new tetragonal phases are known in these crystals. This group includes many anion-deficient cuprates, such as tetragonal $Sr_2CuO_{3+\delta}$, $Sr_3Cu_2O_{5+\delta}$, *etc.* and T′-T*-types of A_2BX_4, Nd_2CuO_4 for example.

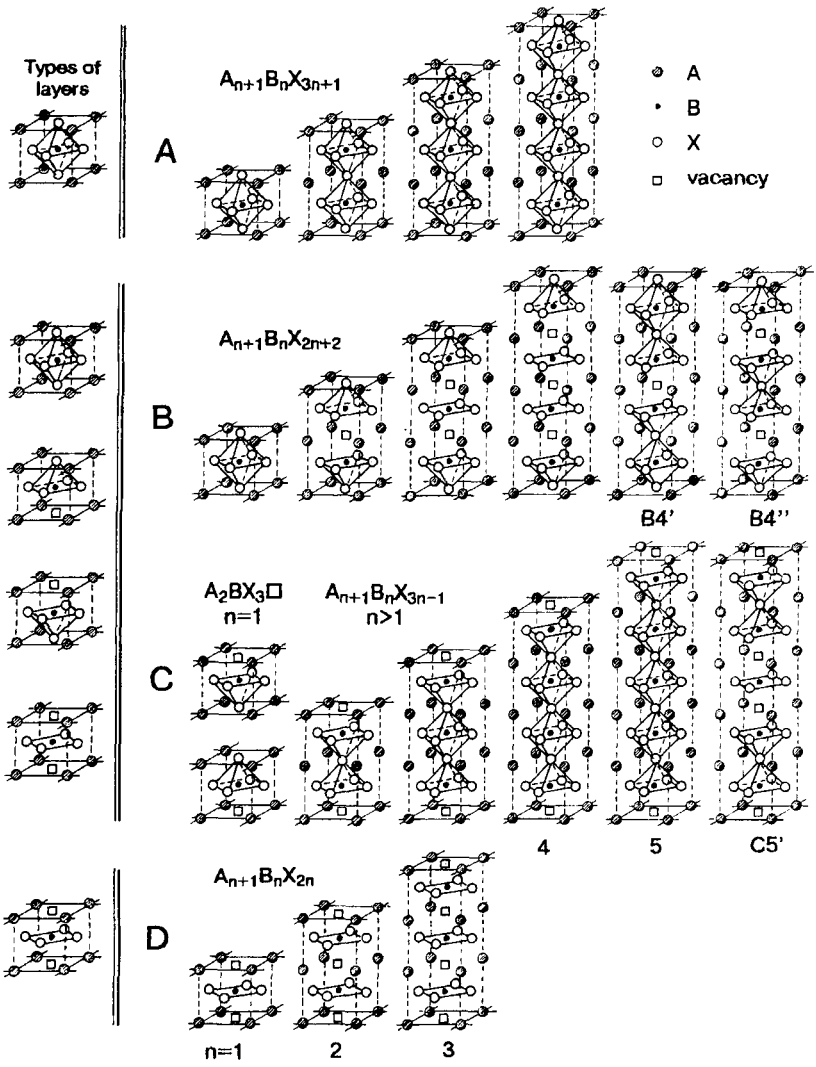

FIGURE 2 Types of perovskite-like slabs with n-layers ($n = 1, 2, 3, \ldots, \infty$).

Aurivillus phases: $(A_2X_2)\ A'_{n-1}B_nX_{3n+1}$ and related homologues, belong to group 7 of Table I. Many ferroelectrics are known here,[8] where B = Ti, Zr, Nb, Ta, W and X = O. Crystals with $n = 8$ have been obtained. The most known are $Bi_4Ti_3O_{12}$ ($n = 3$) and $Bi_2SrTa_2O_9$. The last one is intesively studied as a medium for memory elements. Similar structures appear in the aniondeficient superconducting cuprates of Tl_2- and Bi_2-series: $A22\ (n-1)n$.

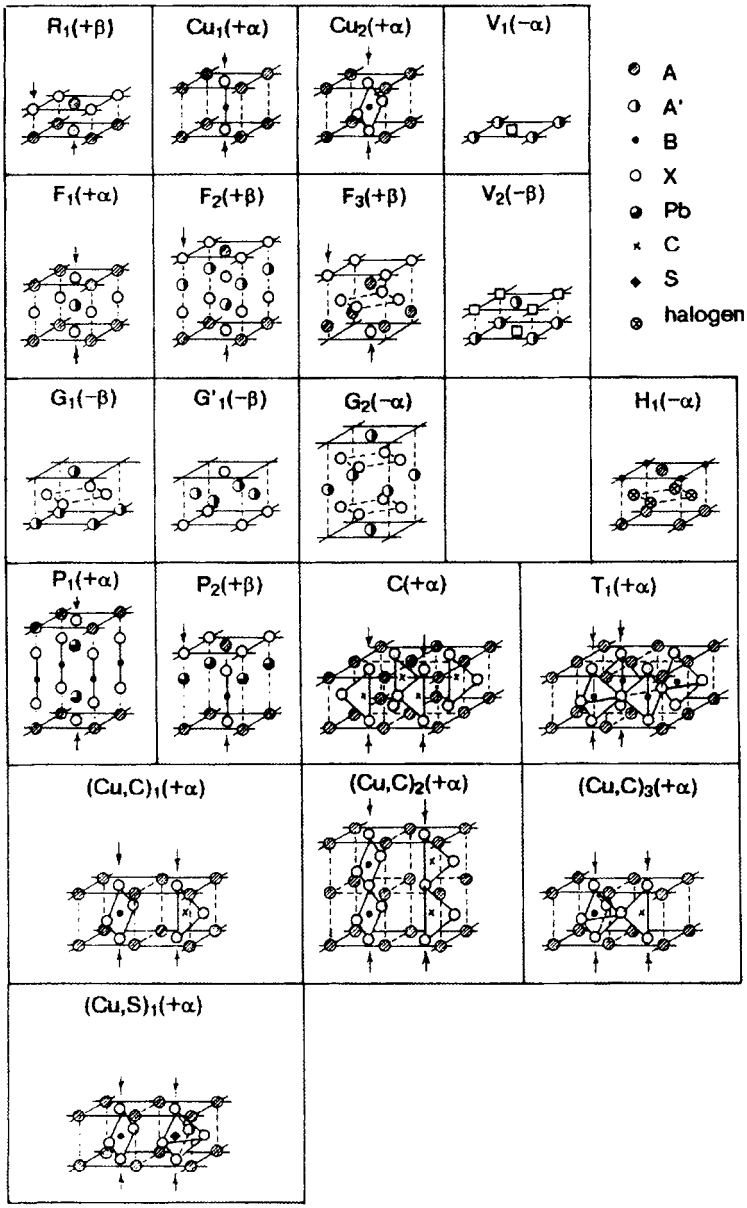

FIGURE 3 Types of blocks known in the layered perovskite-like structures.

The block $F_3(+\beta)$ in Figure 3 is formed by nearly planar layers in the first series but it is incommensurately modulated in another one. Other related structures are built of the same slabs and other β-blocks.[1]

The eighth group in Table I contains many other structural types, mainly cuprates composed of slabs and blocks, shown in Figures 2, 3. Some of them contain the same slabs as groups 5, 6, 7, but other blocks also, for example $(Pb_2CuO_2)Sr_2CuO_4$ or (Bi, CuO)$Sr_2NdCu_2O_6$, *etc.* More complex structures with the slabs of one type intergrown with different blocks, or the same block intergrown with different slabs, are known. As an example consider the structure of $(Bi_2O_2)Sr_2Ln_2Cu_2O_8$ which belongs to so called A2222-type; here single layers of pyramids ($C1$ on Fig. 2) intergrow with $F_2(+\beta)$ and $F_3(+\beta)$ blocks, Figure 3.

The last line in Table I is devoted to crystals of type $A_nB_nX_{3n+2}$. Their structures are composed by octahedral slabs which are cut from the perovskite frame by $(110)_0$ planes. As examples $BaMnO_4$ ($n = 2$) and $Sr_2Ta_2O_7$ ($n = 4$) can be mentioned. These series of structures and polytypes of group 4 have not been included in Figures 2, 3.

All other types of the known perovskite-like crystals are built from slabs and blocks shown in Figures 2 and 3. Interrelations between the families briefly discussed above were considered by the authors and a hierarchy of perovskite-like crystals was built.[2, 3] As the result it was concluded that a number of new structural types could be found using the known slabs and blocks. Moreover new representatives of the listed families can exist.[1-3] One of these families, the Ruddlesden–Popper's one, is considered in the next section.

3. POSSIBLE NEW RUDDLESDEN–POPPER CRYSTALS

As shown above there exist close relations between RP-stoichiometric phases and anion-deficient cuprates. Some new representatives of these structures have been proposed earlier.[1, 2] More detailed crystal–chemical analysis has been done later. It was based on a consideration of the early proposed conception [9] of tensions in interatomic distances in real structures with respect to the corresponding values calculated as sums of ionic radii. The known fluorides and oxides A_2BX_4 and multilayered RP-crystals are shown on Figure 4 (filled squares) on $R_A - R_B$ diagrams. All known substances are located inside the regions restricted by straight lines. The empty squares correspond to the most probable new representatives of RP-stoichiometric phases. As examples some oxides with B^{4+} ions and fluorides with B^{2+} ones are presented in Table II. It seems that the number of possible structures unknown to the authors is rather large. It would be interesting to prepare some of them. We hope that they may present properties useful for practical applications.

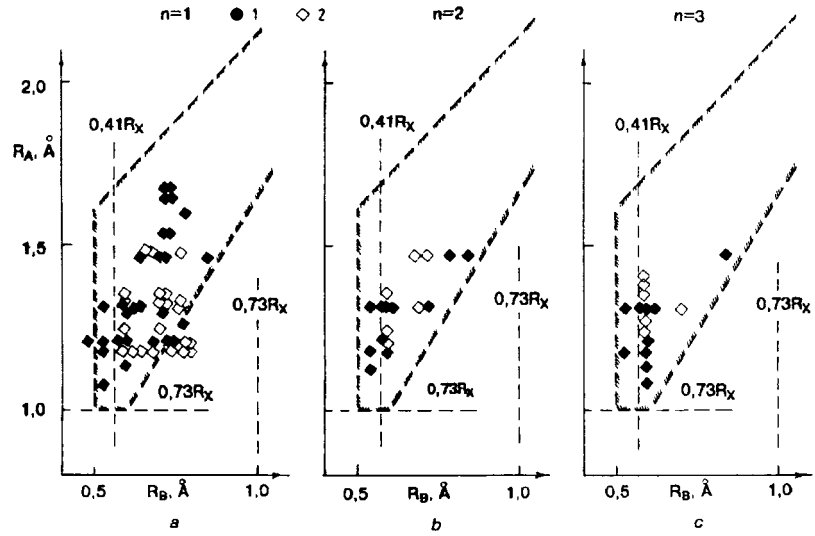

FIGURE 4 Regions of existence for Ruddlesden–Popper's phases with $n = 1, 2, 3$. Filled squares -the known substances, bright ones-possible new crystals.

TABLE II Prognosis of possible new representatives having the Ruddlesden–Popper's structures: $AX(A'BX_3)_n$, $n = 1, 2, 3$ (I_4/mmm)

Symbols

Substances	*Known*	*Unknown*	*Formula*
$n = 1$	1	**1**	A_2BX_4
$n = 2$	2	**2**	$A_3B_2X_7$
$n = 3$	3	**3**	$A_4B_3X_{10}$
$n = 1$		**1′**	distorted
$n = 2$	2′		distorted
$n = 3$	3′		distorted
	RP-phases are less probable		

B^{4+}-oxides

$A^{2+}\downarrow$	*Ti*	*Zr*	*Cr*	*Mn*	*V*	*Fe*	*Sn*	*Pb*	*Hf*	*Tb*	*Rh*	*Ru*
Ba		**12**					**12**	123	1	**1**		1
Sr	123	1	123	123	123	123	**12**		1	**1**	1	123
Ca	1′2′3′			123	**123**							
Nd	**123**	**1**			**1**	**1**			**1**	**1**		
Sm	**123**	**1**			**1**	**1**			**1**			
Eu	123	1			**1**	**1**			**1**			
Dy	**123**				**1**	**1**			**1**			

B^{2+}-fluorides

$A^{+}\downarrow$	*NI*	*Co*	*Fe*	*V*	*Mn*	*Ti*	*Cu*	*Cr*	*Zn*	*Cd*	*Hg*	*Mg*	*Ag*
Cs	**1**	**1**	**123**	**1**	1	**1**	1			**1**	1	**123**	1
Rb	1	1	1	**1**	123	**1**	1	**1**	1	123	1	1	
Tl	1	1	1	**1**	**1**	**1**	1	**1**	1	**1**		1	
NH_4	1	**1**	**1**	**1**	**1**	**1**	**1**	**1**	1	**1**		1	
K	123	123	123	**1**	123		123	**1**	123	**1**		1	
Ag		**1**	**1**		**1**				**1**			**1**	

Acknowledgement

The work was supported by grants 96-02-16542 and 96-15-96700 of the Russian Foundation for Basic Research.

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