A general description and review is given of a new type of anion-deficient perovskite-based structure where the perovskite parent structure is fragmented by periodically spaced translational interfaces. These interfaces demonstrate properties similar to those of the crystallographic shear (CS) planes in the ReO$_3$-type oxides and can be considered to be CS planes in the perovskite framework that contains cations at the A positions. The building principles and chemical compositions of such CS structures will be discussed.

I. Introduction

The perovskite structure is apparently one of the most popular and widely studied oxide structures. Because of its inherent flexibility, the perovskite parent structure easily acquires different types of distortions and/or compositional changes, adapting to the various sizes and characteristic coordination numbers (CNs) of the constituting cations. Although the perovskite-related structures have already been investigated extensively for many years, some blank spots in this field have still not been unraveled. In this short review, we present a new family of anion-deficient perovskite-based compounds, where the parent structure is periodically modulated by translational interfaces with properties similar to those of crystallographic shear (CS) planes in ReO$_3$-type binary oxides.$^1$ The conception of the CS planes in perovskites containing cations at the A positions was inspired by structural investigations on the oxides with rather ‘‘simple’’ compositions Pb$_2$Fe$_2$O$_5$ and PbMnO$_2$.)$^2$ The former compound is already known for 50 years,$^4$ but its structure remained unsolved till recently because of a high concentration of intergrowths and planar defects. The structure was semiquantitatively solved only when the advanced techniques of transmission electron microscopy, such as high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM), became available. The details on the structure solution and diffraction features have already been reported in the relevant publications,$^2,5$ and the building principles and chemical aspects of these structures will be discussed here more extensively.

$^{\text{ABO$_3$-type perovskites containing an easily polarizable A cation with a sterically active lone electron pair (Bi$^{3+}$, Pb$^{2+}$) and mostly covalent bonding to oxygen and a magnetically active transition metal B cation are attracting considerable attention nowadays due to expectations of finding new multiferroic materials. Multiferroics are materials that are (anti) ferromagnetically ordered, being at the same time in a ferroelectric state. The coupling between the electric and magnetic polarization, i.e., the magnetoelectric effect, imparts great value to such materials for practical applications due to the possibility of controlling the magnetic polarization by an electric field and vice versa. Off-center displacements of the A cations with a stereochemically active $\delta^0$ lone electron pair are considered to be a possible source of the magnetoelectric effect in BiMnO$_3$ and BiFeO$_3$. It will be shown in the present article that the important feature of the perovskites with CS planes is the presence of A cations with a stereochemically active lone electron pair, which provides a new field of research for complex oxides with multiferroic properties.

(1) Anion Deficiency in the Perovskite Framework: Point Defects and CS Planes

The perovskite structure ABO$_3$ is based on a framework of corner-sharing oxygen octahedra with a small metal cation at the center, which is most often the transition metal cation. Decreasing the sum of the formal charges of the A and B cations in the oxide perovskites below $+6$ requires anion vacancies to appear in order to compensate for the charge misbalance. The ability of many transition metals to reduce the amount of surrounding oxygen atoms from six down to five, four, and two defines the disposition of the perovskite structure toward anion deficiency. The anion deficiency can range from negligibly small $\delta$ values in ABO$_3$-$\delta$ to a remarkably high concentration of the anion vacancies, as occurs in the so-called ‘‘infinite layer’’ compound ABO$_2$, where all AO layers completely lose the oxygen atoms.$^2,8$ (Fig. 1). At a high concentration limit, the interaction between point defects promotes their ordering. The anion vacancies in perovskites are usually grouped along certain crystallographic directions, for instance, along the [100]$_p$ (subscript index $p$ stands for the perovskite subcell) rows, which transform the BO$_6$ octahedron into a BO$_5$ tetragonal pyramid or a BO$_4$ square.$^9$ Arranging the anion vacancies along the [110]$_p$ rows transforms the BO$_6$ octahedra into BO$_4$ tetrahedra. All oxygen atoms can be removed from the complete BO$_3$ perovskite layer, reducing the coordination environment of the B cations in this layer down to a dumbbell as well. The exact ordering pattern of the oxygen vacancies depends strongly on the properties of the A and B cations.$^{10,11}$ For the Jahn–Teller-active cations, such as Mn$^{3+}$ or Cu$^{2+}$, removal of one or two apical oxygen atoms from the octahedral environment is promoted, resulting in a tetragonal pyramidal or a square planar coordination. The typical structure arising from the ordered arrangement of the tetragonal pyramids occurs in A$_2$Mn$_2$O$_5$ (A = Ca, Sr) (Fig. 2(a)).$^{12,13}$ In anion-deficient copper-based perovskites, numerous frameworks comprising corner-sharing CuO$_6$ octahedra, CuO$_5$ tetragonal pyramids, CuO$_4$ squares, and CuO$_2$ dumbbells (if Cu$^+$ is present) can be realized. A systematic overview of these various ordering patterns is given by Hadermann et al.$^{14}$ For the Fe$^{3+}$ cations with a $t_2g^0$ electronic configuration (high spin state), according to the simple ligand field theory, no energetic preference is expected between the octahedral and tetrahedral coordination. The A$_2$Fe$_2$O$_5$ (A = Cu, Sr) compounds adopt a brownmillerite-type structure.
with alternating layers of FeO$_4$ tetrahedra and FeO$_6$ octahedra (Fig. 2(b)). The preference of Ni$^{2+}$ with a $t_{2g}^6 e_g^2$ electronic configuration to have a square planar coordination rather than a tetrahedral one is reflected in the La$_2$Ni$_2$O$_5$ structure, where half of the nickel atoms are located in octahedra and the other half reside in a square planar coordination (Fig. 2(c)). The anion vacancy ordering can also be coupled with the A-site ordering if there are two A cations with a clearly distinct ionic size and CN. The Gd and Ba atoms in GdBaFe$_2$O$_5$ structure are ordered in separate layers (Fig. 2(d)). Oxygen vacancies reside in the Gd layer and reduce the CN of the Gd cations down to eight, whereas the Ba atoms maintain the CN at 12.

Numerous other ordering patterns of oxygen atoms and anion vacancies are possible in the ABO$_3$ perovskite structure. The common feature of all these structures is that the anion deficiency is realized due to point defects reducing the CN of at least part of the B cations. Another possibility has been observed in binary oxides with the ReO$_3$-and/or TiO$_2$-type structure. A decrease in the anion content in these compounds occurs through translational interfaces called CS planes. The ReO$_3$-type structure is based on a perovskite octahedral framework but with all cuboctahedral sites vacant. A formation of CS planes in this structure changes the connectivity scheme of the octahedral units, but does not alter the CN of the B cations. Along the CS planes, the octahedra share edges instead of sharing corners in the initial framework, so that the number of oxygen atoms is reduced. Formally, the CS plane can be generated starting from a cut of the basic structure along a certain crystallographic plane. A cut along the (102)$_p$ plane is shown in Fig. 3. The white squares on Fig. 3(a) indicate the oxygen atoms, which appear to be artificially duplicated due to this cut, and the black squares indicate the oxygen atoms that must be eliminated in order to accommodate the anion deficiency. This elimination occurs by a displacement of one part of the structure with respect to the other over a vector, which is a fraction of the lattice translation of the basic structure (Fig. 3(b)). In this particular case, the displacement vector is $R = 1/2[101]_p$. As a result of this displacement, the groups of four octahedra along the cut plane do not share corners, but become shearing edges, eliminating part of the oxygen atoms and reducing the overall oxygen content. Such an operation is called a shear operation and the resulting translational interface is a CS plane. The shear operation leads to a composition change if the displacement vector $R$ has a component perpendicular to the shear plane. If the displacement vector lies in the cut plane, the resulting interface is conservative and does not reduce the oxygen content. In fact, such an interface is an antiphase boundary (APB). The complex shear planes with high $(h0l)$ indices can be equidistantly spaced, forming long-range superstructures and homologous series. The composition can be calculated as a function of the separation between two adjacent shear planes that leads to the $M_nO_{3n−p}$ formula for the homologous series. It is possible to define a formal generalized derivation of such translational interfaces. The parent structure is separated into parallel blocks by $(hkl)$ lattice planes equally spaced over $nd_{hkl}$, where $n$ is an integer and $d_{hkl}$ is the interplanar
spacings of the (hkl) lattice planes. Then, a thin layer of material is subtracted along the planes with a thickness that is a fraction of \( \delta_{hkl} \gamma_{hkl} \) with \( 0 < \gamma < 1 \). By this subtraction, a gap is formed, which is closed by the displacement of the blocks with respect to each other over a shear vector \( \mathbf{R} \) with a component \( R_0 = -\gamma \delta_{hkl} \) perpendicular to the (hkl) planes. One should note that such a procedure defines the shear plane irrespective of the parent structure and the disturbance introduced into the parent structure by the shear operation. Particularly, it does not impose any restriction to retain the CN and coordination polyhedra along the shear planes.

However, an application of the shear operation to the perovskite framework with filled A positions results in difficulties because the translation over 1/2 of the face diagonal of the perovskite subcell brings the A and B cations at the \( p(001) \) parts to be positioned at very short distances equal to 1/2\( a_p \) (\( \sim 1.9 \) Å). The A cations at the \( q(101) \) part form double chains, where the A–A distance becomes as short as 1/2 of the face diagonal of the perovskite subcell (\( \sim 2.8 \) Å), which is also unacceptable. This is the reason why the CS plane structures never appear to be a possible mechanism for anion deficiency in perovskites. This commonly accepted opinion is perfectly reflected by Mitchell in his famous book *Perovskites: Modern and Ancient*. The A\(_2\)BO\(_5\) framework perovskite bronzes ... do not form crystallographic shear structures as the presence of even a limited number of such \( \gamma \) the A cations prevents the shear operation. Consequently, any anion defects which might exist in A\(_2\)BO\(_5\) compounds will occur as random or ordered point defects." There is a challenging question: would translational interfaces with properties similar to those of the CS planes exist in the anion-deficient perovskites? Is it possible to create such interfaces? It is commonly accepted that the anion vacancies in perovskites are created by the departure of A atoms from the octahedral sites. However, a recent study by Jirouchová et al. (2018) has shown that anion vacancies can also be created by the departure of O atoms from the octahedral sites. The authors propose a model in which the departure of O atoms from the octahedral sites creates a vacant site in the anion sublattice, which can then be filled by an A atom. This model has been supported by recent experimental studies on anion-deficient perovskites.
tunnels is also reflected in the structure of the Pb2
between the A cations in the perovskite block and in the six-sided
coordination. The strong difference in the chemical nature be-

strates lobes near the Pb atoms corresponding to the domains of
using the electron localization function (ELF), which demon-
the Pb atoms in the six-sided tunnels can be directly visualized
randomly occupied by Sr and the rest of the Pb cations. It seems
Pb atoms, whereas the A positions in the perovskite blocks are

chemical compositions. The 1/2[110](100)p part was found in the
“PbMnO2.75” structure,3 which was prepared by a solid-state reaction under high-pressure high-temperature conditions
(P = 7.8 GPa, T = 880°C). 1/2[110](704)p CS planes are realized in this structure (Fig. 8). These planes can be resolved into sim-
ple parts as (704)p = (3100)p + 4(101)p. The 1/2[110](100), interface is presented in Fig. 6(b). There is a significant difference
between how the composition is affected by the 1/2[110] shear vector being applied either to the {101}p, or to the {100}p planes. In
the {101}p plane, the loss of oxygen atoms occurs, but the ratio between the A and B cations is not changed. As can be seen
from Fig. 6(b), the displacement over the vector 1/2[110] along the (100)p plane omits a complete AO layer from the FeO2–AO–
FeO2–AO perovskite sequence so that two FeO2 layers become positioned next to each other and the polyhedra become edge
sharing. The composition of this interface can be derived as AB2O5 and, in combination with nABO3 perovskite blocks, this
yields the composition A

= Pb1.33Sr0.67Fe2O5 structure. The lobes of the 6s² lone electron pairs are indicated in yellow.

The “PbFe2O4” sample demonstrates a large variety of CS structures.2,5 1/2[110](104)p, 1/2[110](102)p, and
1/2[110](305)p (Fig. 10) interfaces were observed using transmission electron microscopy. The construction of these interfaces includes the 1/2[110](001)p part (Fig. 6(c)). Because the displacement vector has no component normal to the (001)p-interface plane, this interface should be conservative and can be consid-
ered to be an APB. Indeed, the 1/2[110](001)p interface does not change the oxygen content. However, the 1/2[110]-displacement vector applied along the FeO2 perovskite layer transforms the corner-sharing FeO6 octahedra into twice the number of edge-
sharing tetragonal pyramids, thus creating twice the number of cation positions available for the Fe atoms (Fig. 11). In the CS
structures in “Pb2FeO4,” all these positions were assumed to be fully occupied, which results in a decrease in the Pb:Fe ratio
below 1. Then, the composition of the interface is described as AFe2O3, and, by adding nFeO3 perovskite blocks, one can obtain the A1+nFe2+nO3n+3 formula for the possible homolo-
gous series.

It is easy to imagine that by combining the different simple parts of the CS interfaces and by varying the thickness of the perovskite blocks between them, numerous perovskite-derived structures can be constructed. However, a limitation in the num-
ber of possible structures is imposed by the oxidation state of the transition metal cations.

(3) Compositional Variability of the Shear Structures in Perovskites
The 1/2[110](101)p shear plane is a purely nonconservative in-
terface. One can expect that the other nonconservative or con-
servative low-index interface parts can be added to this basic plane, thus resulting in the ability of such interfaces to adopt
different crystallographic orientations corresponding to various

Fig. 6. Schematic representation of the structures of the low-index interfaces: (a) 1/2[110](101)p, (b) 1/2[110](100)p, (c) 1/2[110](001)p. The edge-sharing polyhedra are painted in blue.
(4) Oxidation State of the B Cations

Up to now, compounds where the parent perovskite structure is fragmented by translational interfaces are known only for divalent A cations (A = Pb, Sr, Ba). Only such structures of the translational interfaces are possible that match with the average oxidation state of the B cations determined by the synthesis conditions. For example, it was demonstrated by Mössbauer spectroscopy that the Fe atoms in “Pb$_2$Fe$_2$O$_5$” are in the...
Structures in Perovskites and ReO₃-Type Oxides

(5) Formation Mechanism: A Comparison between the Shear Structures in Perovskites and ReO₃-Type Oxides

Several mechanisms for nucleation and growth were proposed for the CS planes in MO₃₋ₓ (M = Mo, W) oxides. The experimental observations, such as the occurrence of single CS planes in the ReO₃-type matrix, the mobility, and the longitudinal growth of the CS planes, are to some degree accounted for in these mechanisms. The nucleation of a single CS plane in the ReO₃-type matrix by forming an anion-vacancy loop limited by two partial dislocations explains the appearance of single CS planes and their longitudinal growth, but does not take into account the Sideways displacement of the CS planes resulting in their ordered arrangements. Such a lateral displacement is explained by a cation cooperative migration model, which involves jumps of whole cation planes from octahedral sites to the adjacent empty interstices. The “hairpin’ mechanism is based on cooperative migration of a narrow strip of cations from the surface inside the crystal leaving a trace of two parallel CS planes. It explains both lateral displacement and longitudinal growth, although assuming that the CS planes are always arranged in pairs. All these mechanisms are based on a preformed ReO₃-type matrix. However, the nucleation and growth of the CS planes in perovskites cannot be explained by the models involving the preformed perovskite matrix. Indeed, in case of “Pb₂Fe₂O₅,” the parent “PbFeO₃” perovskite matrix cannot be obtained in an extended form under the synthesis conditions chosen (800°C, air), which are not favorable for stabilizing Fe⁴⁺.

The difference in the possible generation mechanism is reflected in the significantly different defect structure in “Pb₂Fe₂O₅” compared with that typical for the shear structures in ReO₃-type oxides. In “Pb₂Fe₂O₅,” single CS planes in a perovskite matrix have never been observed and the CS planes with the same crystallographic orientation are always equidistant, maintaining a constant thickness of the perovskite block between two adjacent CS planes. The CS planes in “Pb₂Fe₂O₅” are most probably nucleated at the surface of the crystal along with the growth of the perovskite block, which causes numerous microtwins, also experimentally observed in the “Pb₂Fe₂O₅” sample. Coexisting domains with CS planes with different (hvO₢) in “Pb₂Fe₂O₅” can most probably be attributed to local cation inhomogeneity, which is difficult to avoid at the rather low synthesis temperature limiting the cation diffusion. In WO₃, reducing the oxygen content decreases the interplanar spacing of the (101) set of CS planes until the increasing free energy associated with the interaction between neighboring shear planes causes I to increase and changes the orientation of the CS planes. This is not possible in “Pb₂Fe₂O₅” because the CS planes are always equidistant and this free energy term is not supposed to vary.

II. Conclusions

The derived basic principles of structural organization of the anion-deficient perovskites with CS planes allow the prediction of various compositions corresponding to numerous new structures. However, the preparation of such compounds in certain cases in a single-phase form appears to be a difficult problem. This can be exemplified by the chemical compositions of the CS structures found in the “Pb₂Fe₂O₅” sample, which correspond to the formulae Pb₉₀Fe₂O₂₄ (104)ₚ, Pb₀Fe₂O₃ₕ (30ₕₚ)ₚ, and Pb₀Fe₂O₃ₕ (102)ₚ. All these compositions correspond to the general formula Pb₂FeO₂₋ₓₓPbₓO, where x = 0.0625, 0.1, and 0.125. Because of the equal oxidation state of the Fe cations, all these structures can be formed in the same range of temperatures and partial oxygen pressures. The preferential formation of a single CS structure and the suppression of other possible variants in this case require precise control of the cation composition and especially the degree of cation inhomogeneity in the samples, which should be as small as possible. One can expect that advanced techniques of chemical homogenization would result in a breakthrough in the preparation of such perovskite-like compounds. Another approach can be based on using two B cations with stable CNs six and five in the ratio required by a crystallographic orientation of a certain family of CS planes. The high-pressure high-temperature technique might be of great help in this case, extending the range of B cations for these types of structures.

Although all potential properties of perovskites with CS planes have not yet been unraveled, one can expect their possi-
ble ferroelectric behavior from comparison with other Pb-based perovskites. It can be expected that the Pb atoms in the perovskite blocks of the "Pb_xFe_2O_3" and PbMnO_2.75 structures are not located exactly at the centers of the cuboctahedral cavities, but can demonstrate off-center displacements due to the influence of the long electron pair, as was observed in PbTiO_3 and PbVO_3. It could lead to a ferroelectric polarization, which, coupled with the ordering of the magnetic moments on the transition metal cations, could make these materials potential multiferroics.

References

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