Perovskites and thin films—crystallography and chemistry

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Abstract
We discuss the crystallographic and chemical basis of the perovskite family (ABX_3) of oxides
that are used in different thin film applications. Starting with the original structure we extend
our scope to several modifications. Basic parameters like the ionic radii, the tolerance factor, the
occupation of the oxygen sublattice and their effect on the structural parameters will be
mentioned together with examples of relationships between structural and physical properties in
the bulk and at interfaces.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The intense and wide interest in the perovskite family (ABX_3) of oxides is based on the large variety of physical properties and ground states that are realized. Furthermore, the related electrical/ionic transport or dielectric and magnetic polarizations show a large and in many cases non-linear response to external magnetic or electric fields and temperature. This lies behind the use of perovskites as key materials in numerous applications based on their sensor and switching functionalities.

With respect to chemistry this versatility has to be searched for in the large number of combinations that the two cation sites, A and B, give in ABX_3, leading to a considerable freedom of ionic radii and ionic charges that can be incorporated into the cation lattice. Indeed, the resulting electronic configurations allow bonds with different ionicity/covalency to be the basis for enhanced dielectric or magnetic moments of the polarized electron densities. The oxide anion lattice, on the other hand, promotes large displacements and dipole moments leading in the extreme to complex oxygen defect structures. With respect to crystallography, an enormous variation of the original perovskite cell as discussed below is given by a large number of known crystallographic structures that are still assigned to perovskite and its relatives [1].

A search in the Inorganic Crystal Structure Database (ICSD)[4] yields 2454 hits for the term 'perovskite'. Most of those (2272) are oxides and most of the remaining compounds are either sulfides or halides. The oxides are very numerous because the sum of the charges on the A and B sites ($+6$) may be made of $1 + 5$, $2 + 4$, $3 + 3$ and also in more complex ways as in $Pb(B_{1/2}B'_{1/2})O_3$ where $B = Sc$ or Fe and $B' = Nb$ or Ta.

Although the perovskite family crystallographic structures have been studied for a long time their basic physical properties are still leading to surprising discoveries. Some examples of bulk as well as phenomena observed at interfaces are given in figure 1. Exceptional and intensively studied properties associated with compounds of perovskite structure are superconductivity with very high transition temperatures, as in $YBa_2Cu_3O_7$ [2], and colossal magnetoresistance in manganites, as $(La, Sr)MnO_3$ [3]. In high temperature superconductors the role of the crystal lattice is limited to being the geometrical basis for the two-dimensional hybridized Cu–O states. In contrast, in manganites the interplay of local lattice distortions with the orbital occupation of the d shell of Mn^{3+}/Mn^{4+} is an important constituent for understanding their complex phase diagram and transport properties. It leads to the formation of so-called orbital polarons.

Further important properties are related to long range ordered states of a magnetic or polar nature. Bulk

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[4] For structural details of the discussed perovskites we refer to the ICSD, Version 2007-02, FIZ Karlsruhe, Germany.
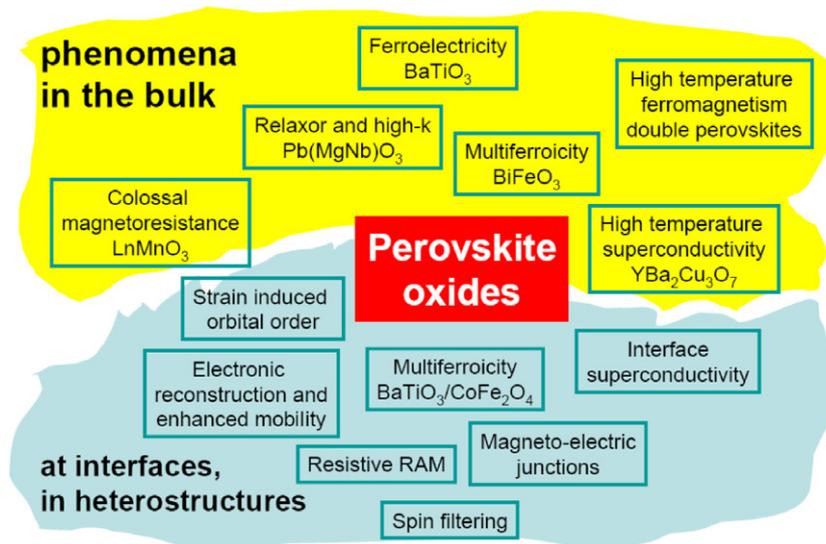
Figure 1. Functionalities of perovskite oxides as bulk and interface phenomena. Examples for compounds or stoichiometries are given.

ferromagnetism observed in many perovskites may show extraordinarily high transition temperatures up to 750 K [4], as in the double perovskites [5], or a very large spin polarization at interfaces. Both properties are relevant for spintronics [6] where charge degrees of freedom in conventional semiconductor electronics are anticipated to be partially replaced by spins and orbitals. Possible applications as spin filters and injectors for electrons or an improvement of existing schemes for magnetic random access memory (MRAM) have been discussed.

Oxide interfaces and heterostructures from, e.g. $SrTiO_3$/$LaTiO_3$, $LaAlO_3$/$SrTiO_3$ or the strongly polar interface ZnO/$Mg_xZn_{1-x}O$, have recently been a focus of interest due to the exceptional electronic properties that are not present in the bulk of the materials [7]. The observed enhanced mobility [8], quantum Hall effect [9], and even superconductivity [10] are related to a proposed electronic reconstruction (e.g. charge transfer, change of orbital occupation) [11] at the interface that sensitively depends on its termination and polarity. On the other hand it has also been shown that deviations from stoichiometry, e.g. due to oxygen defects within the interface and the substrate, play a decisive role [12]. Finally we mention multiferroic behaviour, the mutual coupling of dielectric and magnetic polarization, as another interesting phenomenon where structural properties and interfaces of perovskites are decisive. Multiferroic behaviour is a rare bulk phenomenon as non-filled d-shells contributing to the magnetic moment and completed shells for large spontaneous dielectric polarization are exclusive. Interfaces between two different compounds release these restrictions and further symmetry constraints and allow an application-relevant coupling with switching functionality.

The above mentioned aspects can be summarized in the sense that perovskites and related oxides with electronic correlations are expected to contribute to advanced oxide-based electronic materials and spintronics. Review articles by Bibes and Barthémély [6], Fiebig [13], Ramesh and
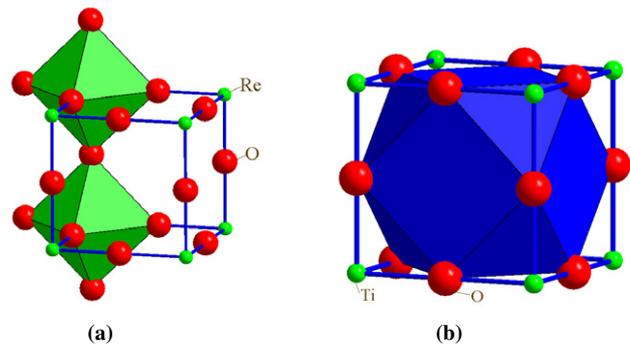

Figure 2. (a) The cubic ReO_3 structure consists of corner sharing octahedra. (b) The ideal cubic perovskite structure ABX_3 is derived from the ReO_3 structure by adding a 12-coordinated ion at the cuboctahedral hole in the centre of the unit cell. $SrTiO_3$ has this structure.

Spaldin [14] describe these respective developments. The interplay of electronic correlations and orbital degrees of freedom with crystals structure and chemistry has been reviewed in [15].

2. The perovskite crystal structure

Perovskites are a large family of compounds; however, the ideal cubic structure (space group $Fm3m$) is rare and the mineral perovskite itself, $CaTiO_3$, is actually slightly distorted. The ideal cubic perovskite structure can be derived from the ReO_3 structure that is formed from corner sharing octahedra (see figure 2(a)). The perovskite structure is subsequently formed by adding a 12-coordinated ion at the body centre of the unit cell in the middle of the cube of eight such octahedra (see figure 2(b)). The A and X atoms in the idealized cubic ABX_3 structure, that is realized for example in $CaRbF_3$ and $SrTiO_3$, form cubic close packed layers of A + 3X corresponding to the atomic packing in the ordered alloy $AuCu_3$ (see figure 3).
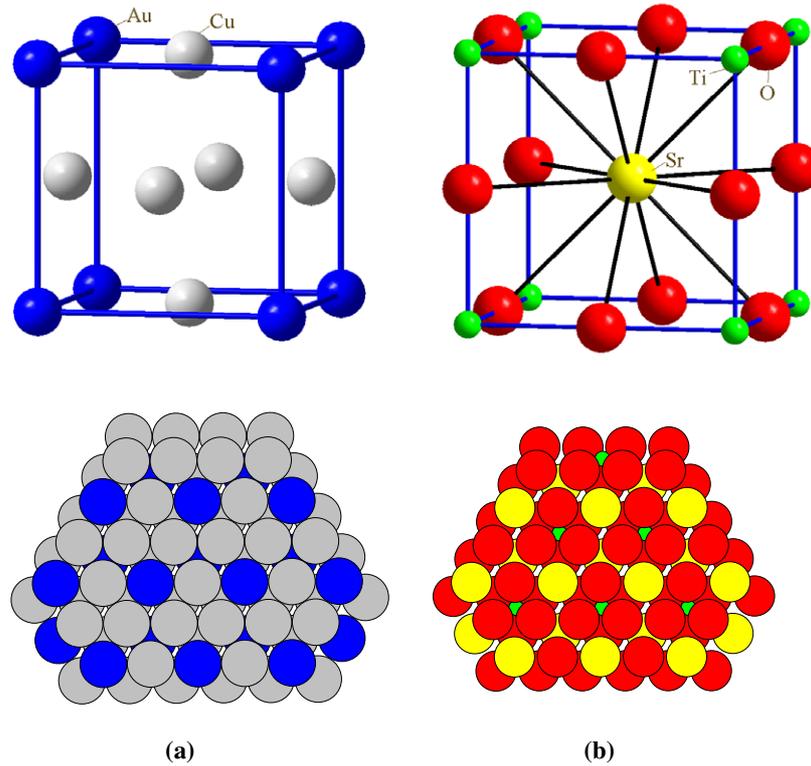
Figure 3. (a) Cubic close packed ($1\bar{1}1$) layers in the ordered alloy $AuCu_3$. (b) The Sr and O atoms in the perovskite $SrTiO_3$ jointly form cubic closest packing. The Ti atoms occupy one-quarter of the octahedral voids, i.e. those that are surrounded by only O atoms.
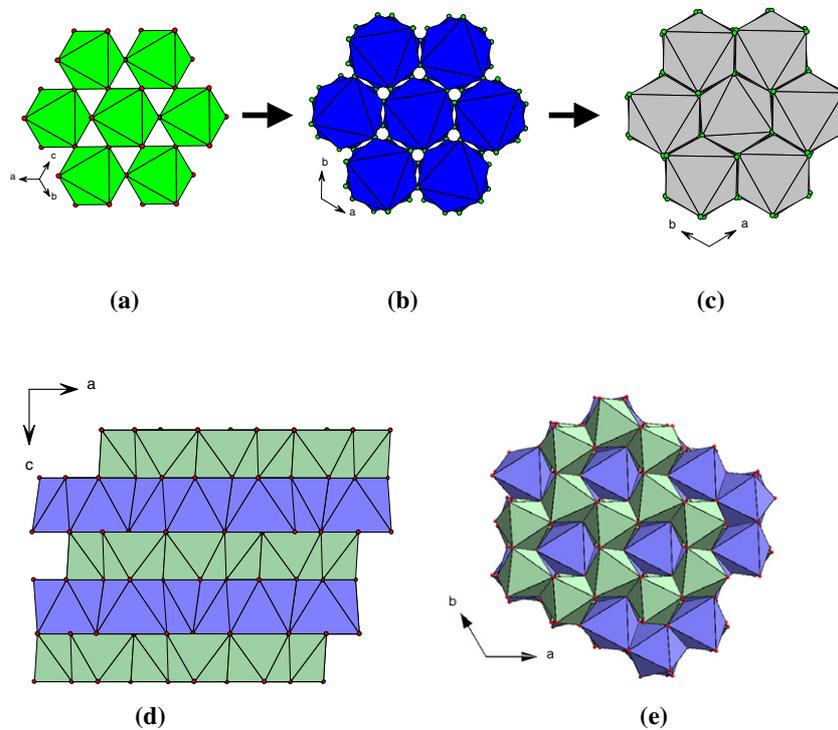
Figure 4. The degree of space filling of the ReO_3 type structure can be increased by rotating the corner sharing octahedra: (a) ReO_3, cubic $Pm\bar{3}m$ along [111]; (b) VF_3 trigonal $R\bar{3}c$; (c) RhF_3 trigonal $R\bar{3}c$. Filling the octahedral voids in the RhF_3 type structure yields the ilmenite, $FeTiO_3$, structure type (trigonal $R\bar{3}$) consisting of two types of octahedra: (d) view along [010]; (e) view along [001]. The octahedra within a layer are connected by edge sharing and the octahedra in between different layers are connected by face sharing.
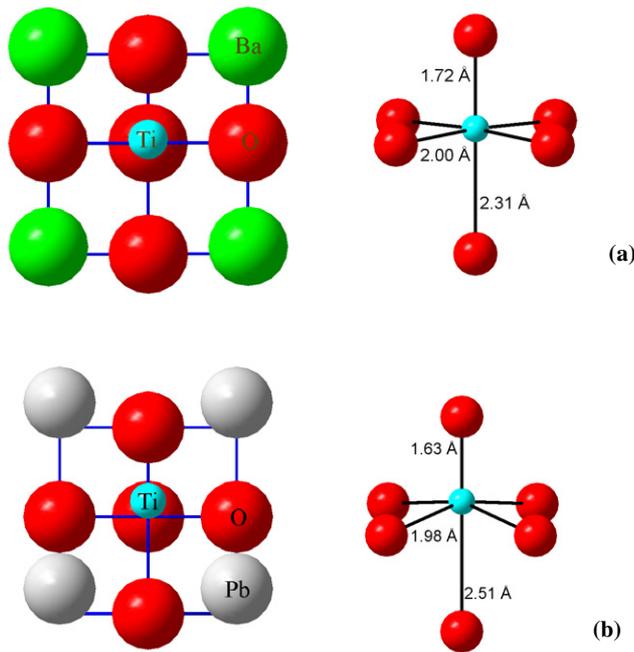
Figure 5. (a) Tetragonal $BaTiO_3$. The shifts of Ti and Ba relative to the O_6 octahedra around the original Ti position: Ti and Ba both shift by 0.30 Å in the same direction. (b) In tetragonal $PbTiO_3$ Ti and Pb are shifted by 0.44 Å.

The A and B ions in the perovskite structure can be varied, leading to a large number of compounds with related structures. Most compounds in the perovskite family have the [BX_6] octahedra tilted in various ways to give other types of coordination of the A atoms than the cuboctahedral in the ideal cubic structure. For example in $GdFeO_3$ the coordination of Gd is reduced to 8. The reduced symmetry in distorted perovskites is important for their magnetic and electric properties. There are three main factors responsible for the distortions: (i) size effects, (ii) deviations from the ideal composition, and (iii) the Jahn–Teller effect.

The oxygen atoms in ReO_3 occupy three-quarters of the positions for cubic close packing and the structure type can be transformed to a denser packing by rotating the corner sharing octahedra until a hexagonal close packing of the RhF_3 type is obtained. The void in the centre then has an octahedral surrounding. If this octahedral hole is occupied we have the ilmenite structure type, $FeTiO_3$ (see figure 4).

### 2.1. Distorted perovskites—size effects

The cell axis, a, in the ideal cubic unit cell depends on the ionic radii (r_A, r_B, and r_X) as described by equation (1):

$$a = \sqrt{2}(r_A + r_X) = 2(r_B + r_X). \quad (1)$$

The ratio of the two expressions for the cell length is called the Goldschmidt *tolerance factor* t and allows us to estimate the degree of distortion as described in equation (2):

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}. \quad (2)$$

The cubic perovskite $SrTiO_3$ has $t = 1.00$. If the size of the A cation decrease then t becomes smaller than 1. As a result
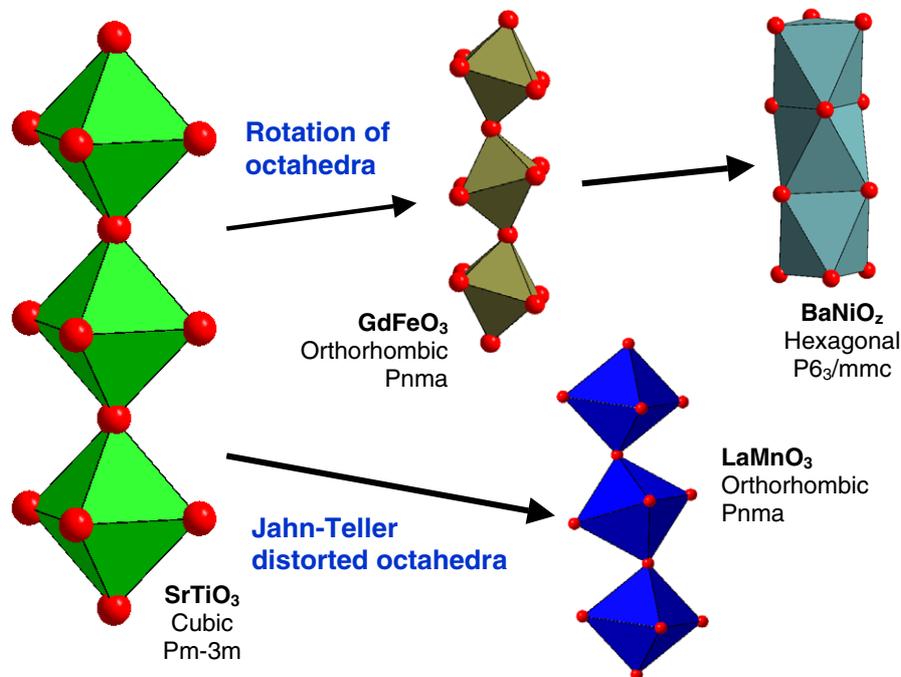
Figure 6. Low values of the tolerance factor t will lower the symmetry of the crystal structure. $GdFeO_3$ have tilted [FeO_6] octahedra and crystallize in the orthorhombic system. If the tolerance factor $t > 1$ as for $BaNiO_3$ due to a large A or a small B ion then hexagonal variants of the perovskite structure form. In $LnMnO_3$ the octahedra around Mn are Jahn–Teller distorted.
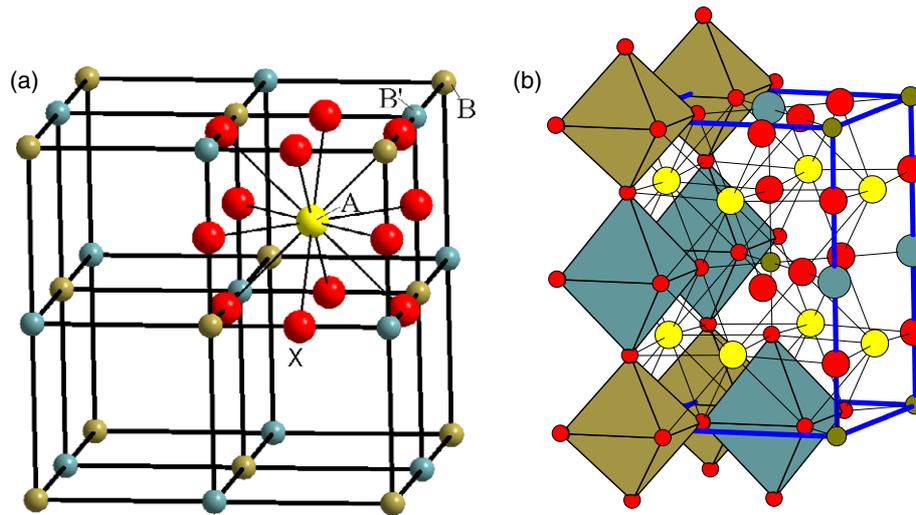
Example	A	B	B′	X
SrTiO₃	Sr^{2+}	Ti^{4+}	Ti^{4+}	O^{2-}
Sr₂FeMoO₆	Sr^{2+}	Fe^{3+}	Mo^{5+}	O^{2-}
Ca₂FeReO₆	Ca^{2+}	Fe^{3+}	Re^{5+}	O^{2-}

Figure 7. (a) The double perovskites $A_2BB'X_6$ can be described by doubling the perovskite unit cell. When the unit cell edges are doubled it is possible to occupy equivalent positions with atoms of different elements. The one-to-one relation can be recognized by comparing with the doubled formula of perovskite. In reality there exist many distorted forms of the idealized cubic cell (space group $Fm3m$) with lower symmetry, e.g. tetragonal or monoclinic. (b) Tetragonal ($I4/mmm$) form of Sr_2FeMoO_6. The unit cell is smaller than for the cubic form having the a-axis and b-axis along the pseudocubic [110] and [$\bar{1}$10] directions.

the [BO₆] octahedra will tilt in order to fill space. However, the cubic structure occurs if $0.89 < t < 1$ [16, 17]. Lower values of t will lower the symmetry of the crystal structure (see figure 5).

GdFeO₃ (see footnote 4) with $t = 0.81$ is orthorhombic (see figure 6). The mineral perovskite itself, CaTiO₃, also has this structure. With values less than 0.8 finally the ilmenite structure (cf figure 5) is more stable. On the other hand if t is larger than 1 due to a large A or a small B ion then hexagonal variants of the perovskite structure are stable, e.g. BaNiO₃ type structures. In this case the close packed layers are stacked in a hexagonal manner in contrast to the cubic one found for SrTiO₃, leading to face sharing of the [NiO₆] octahedra (see figure 6). The t value for BaNiO₃ is 1.13. The tolerance factor is only a rough estimate and also the nature of the A and B ions influences the structure. For example LnFeO₃ (Ln = lanthanide ion) have all-perovskite-type structures, this is true for $LnMn^{3+}O_3$ only if Ln is La or Ce–Dy. The compounds in which Ln = Y or Ho–Lu adopt a different hexagonal structure, with 5- and 7-coordination of Mn and A, respectively [16].

2.2. Distorted perovskites—oxygen vacancies

The family of compounds $SrFeO_x$ ($2.5 \leqslant x \leqslant 3$) is an example of how oxygen vacancies influence the crystal structure. The valency of the Fe ions can be changed by heating a sample in either an oxidizing or a reducing environment, and as a result the oxygen content can vary between 2.5 and 3. In $SrFeO_{2.875}$,

for example, some Fe ions can be assigned to the oxidation state +3 and others to +4. The oxygen vacancies order so that FeO₅ square pyramids are formed. The $SrFeO_x$ compounds are examples of defect perovskites. Their chemistry can be described according to the homologous series $A_nB_nO_{3n-1}$, $n = 2-\infty$.

2.3. Distorted perovskites—Jahn–Teller effects

In some perovskites the distortion of the structure can be assigned to Jahn–Teller active ions at the B position. For example in LnMnO₃ (Ln = La, Pr or Nd) with Mn^{3+} ions the $3d^4$ electrons divide up into 3 t_g electrons and 1 e_g electron. The odd number of electrons in the e_g orbital causes an elongation of the [MnO₆] octahedron (see figure 6).

2.4. Superstructures

Doubling the unit cell edges of the ideal cubic perovskite structure makes it possible to occupy equivalent positions with atoms of different elements (see figure 7(a)). If the B position is partly replaced by a second metal a double perovskite of the general formula $A_2BB'X_6$ may form where the BO₆ and the B′O₆ octahedra are alternatively arranged (see figure 7(b)). A number of double perovskites exist where the A site is occupied with an alkaline or rare earth atom and the B and B′ sites are occupied by transition metals (B = Cr, Mn, Fe, Co; B′ = Mo, Re, W, several of those compounds express ferromagnetism above room

temperature and are extensively studied, e.g. Sr_2FeMoO_6 and Ca_2FeReO_6). The double perovskites frequently exhibit distortions, e.g. when small cations occupy the A site and the octahedra are then tilted resulting in a lowering of the symmetry. A tolerance factor can be defined in the same way as for perovskites [5].

Acknowledgments

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