

**[o.m2.o1] The crystallography of perovskites: past, present and future.** P.G. Radaelli, ISIS facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, United Kingdom.

Keywords: perovskites.

Research on perovskites and perovskite-related compounds has enjoyed a continuing fortune for a very significant portion of the twentieth century, in many fields of physics, chemistry and earth sciences. This interest is amply justified, not least for the very fact that a  $\text{MgSiO}_3$ -rich perovskite, as a main constituent of the mantle, is probably the most abundant mineral on Earth.

The basic perovskite structure,  $\text{ABX}_3$ , is extremely simple, yet very flexible, in that it can tolerate large size variations of the A cation through "tilt" distortions of the  $\text{BX}_3$  corner-sharing octahedral framework. This structural flexibility enables solid solutions to be stabilised over wide composition ranges, making the perovskite the prime structure type for the study of mixed valence. Another interesting aspect of perovskites is their ability to accommodate a huge number of structural defect types, such as X- and A-site vacancies, crystallographic shear (Magneli phases) and channels occupied by larger cations (tungsten bronzes). Finally, perovskites give rise to a number of superstructures, due to ordering of cations, vacancies or, more subtly, electronic charges and/or orbitals. Perovskite blocks can also be found in a number of derived structure types, such as the well-known Ruddlesden-Popper series, where they are interleaved with rock-salt-type blocks.

Much of the condensed-matter physics of the twentieth century is inextricably related with these structure types, which support such phenomena as ferro- and antiferromagnetic ordering, ferroelectricity, high-temperature ionic transport, superconductivity, and, more recently, Colossal Magnetoresistance and 'unusual' magnetic ground states. All these effects, to a greater or lesser degree, also elicit structural responses. Unsurprisingly, therefore, neutron and x-ray crystallography have enormously contributed to shape our understanding of perovskite structural chemistry and physics.

We will overview some of the most significant contributions of perovskite crystallography of the past few decades, with particular emphasis on the open questions in each field. We will also show that our hope of answering these questions rests on a continuing development of the crystallographic instrumentation and analysis techniques, both in the laboratory and at the new planned large-scale facilities.

**[o.m2.o2] Perovskites as ionic conductors.** S. García-Martín, A. Morata, E. Morán and M.A. Alario-Franco. Departamento de Química Inorgánica, Facultad de C.C. Químicas, Universidad Complutense de Madrid, Madrid-28040, Spain.

Keywords: perovskites.

Materials with perovskite-related structure are attractive candidates for a great variety of applications. The perovskite structure  $\text{ABO}_3$  tolerates total or partial substitution of the A and B cations by ions with different valence states, affecting the structure and physical properties of the oxides. Deviations from oxygen or/and cation stoichiometry are also allowed by chemical substitution, playing an important role in their electrical properties. Perovskites with oxygen-vacancies have shown to be proton conducting (e.g. doped  $\text{BaCeO}_{3-x}$ ) or oxygen conducting (e.g. doped  $\text{LaGaO}_{3-x}$ ) ceramics and compounds with A-cation deficiency can present A ionic conductivity.

Very high values of lithium-ion conductivity have been demonstrated in  $\text{Li}_{0.5-3x}\text{La}_{0.5+x}\text{TiO}_3$ . Transmission electron microscopy has proved to be a powerful, almost inevitable tool to study the crystal structure of this kind of A-deficient perovskites due to the complexity of the A-cation sublattice, which can adopt different ordering states and produce different structural distortions. The structure determined by powder X-ray or neutron diffraction is usually an average structure while electron diffraction and microscopy can provide complementary information on local arrangements, distortions and defects of the materials.

We have studied the microstructure of  $\text{Li}_{0.5-3x}\text{RE}_{0.5+x}\text{TiO}_3$  (RE=La, Nd) and related perovskite-type oxides by selected area electron diffraction and high resolution transmission electron microscopy in combination with powder X-ray diffraction techniques. Dependence of the crystal structure of the materials with the composition and annealing temperature is observed. A basic common lattice related to the perovskite subcell ( $a \sim \sqrt{2}a_p$ ,  $b \sim \sqrt{2}a_p$ ,  $c \sim 2a_p$ ) is proposed. The distortion of the perovskite structure in these materials is most likely due to the tilting of the octahedra framework to accommodate the different sizes of the A-cations. The crystals present a domain microstructure with different orientations of the c-axis in each domain. A more complex twinning of the octahedra framework is observed in the Nd-system.

We have prepared new oxides with perovskite-related-structure to improve the ionic conducting properties of the titanates. We have successfully carried out substitutions on both A or/and B cation sublattices. Short-range ordering phenomena are observed when there is a great amount of vacancies in the A-sublattice. The  $\text{La}_{1/3-x}\text{Li}_{3x}\text{NbO}_3$  materials show a modulated structure, giving place to a lattice of dimensions  $a \sim 3.5\sqrt{2}a_p$ ,  $b \sim \sqrt{2}a_p$ ,  $c \sim 4a_p$  most probably due to the La-Li-vacancies ordering within the A-positions.