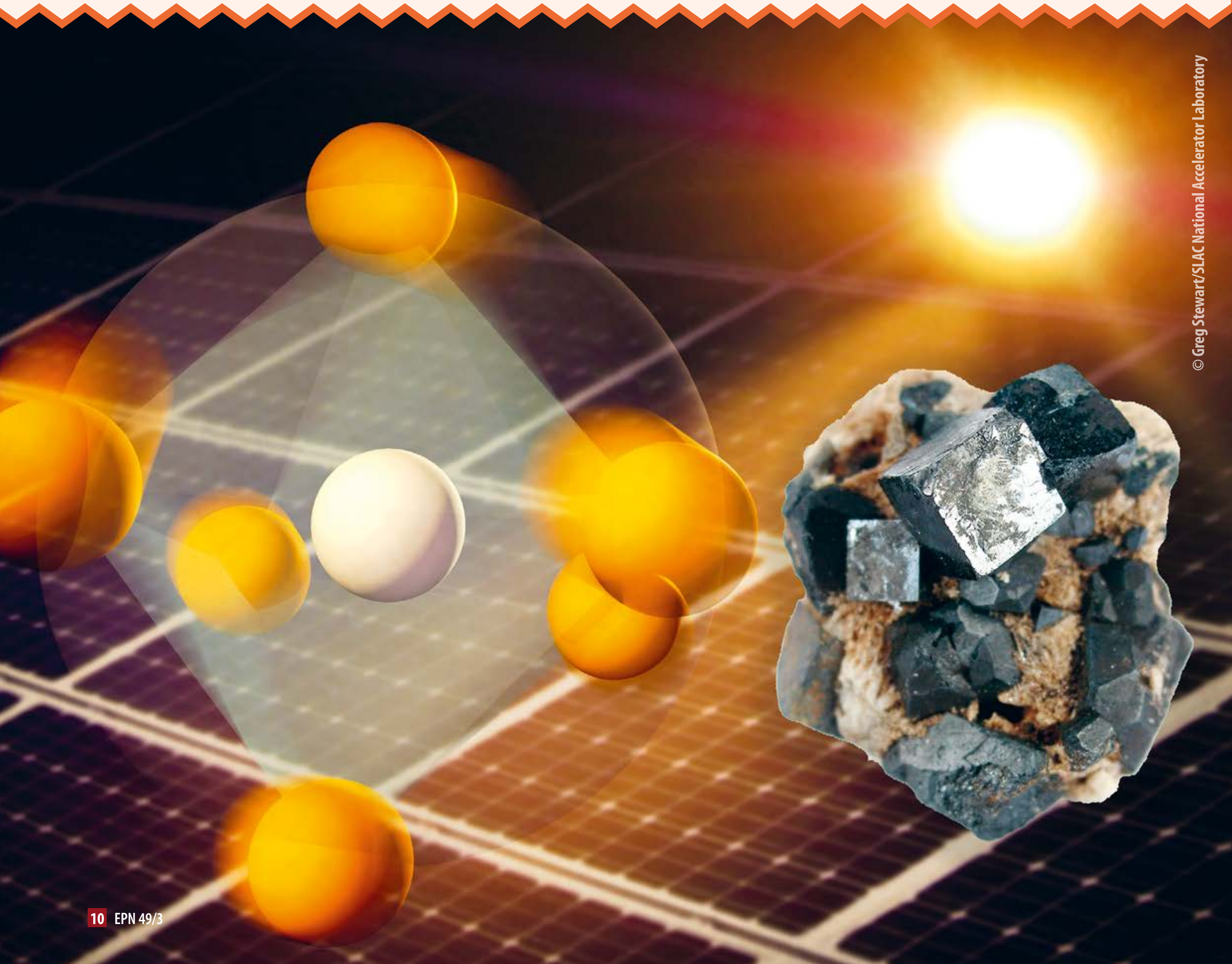
PEROVSKITES:

A CLASS OF MATERIALS WITH MULTIPLE FUNCTIONALITIES AND APPLICATIONS

Christophe Rossel – DOI: https://doi.org/10.1051/epn/2018301
IBM Research – Zurich, Säumerstrasse 4 – CH 8803 Rüschlikon – Switzerland – rsl@zurich.ibm.com

First discovered in 1839 by Gustav Rose and named after the Russian mineralogist L. A. Perovksi, the perovskites have been extensively studied. These materials have a wide range of properties and many potential applications. The discovery of high temperature superconductivity in layered copper oxides in the mid-eighties and of efficient photovoltaic properties in hybrid organic-inorganic perovskite solar cells less than 10 years ago, have boosted the research efforts on these materials as well as the number of yearly publications.

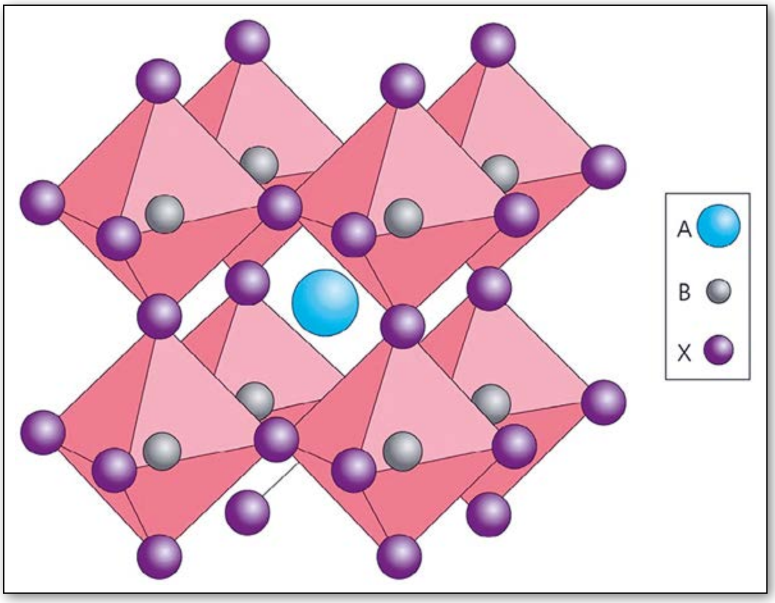


© Greg Stewart/SLAC National Accelerator Laboratory

Structure

Perovskites have a cubic structure with the general formula ABX_3 (Fig. 1). In this ideal structure, the A-site ion is usually an alkaline earth or rare earth element. The B site ions can be 3d, 4d, and 5d transition metal elements and form an octahedral BX_6 with the X ion. Even if the best known perovskites contain oxygen ($X = O$) such as in the high temperature superconductors, a few others form with $X = B, C, F$, or Ni. The recent demonstration of high power conversion up to 22% in photovoltaic films of the hybrid halide perovskites $CH_3NH_3PbX_3$ with $X = I$, Br, or Cl made these materials more extraordinary.

The requirements on the relative ion size is rather stringent for the stability of the cubic structure because slight buckling and distortion can produce several lower-symmetry distorted versions [1]. The symmetry breaking under the effect of pressure, temperature change, or doping can lead to tetragonal, orthorhombic or rhombohedral structures. When thin sheets of intrusive materials are inserted in this network, various layered structures can be obtained, as exemplified with the discovery of the high temperature superconductors by J.G. Bednorz and K. A. Müller in 1986 [2].

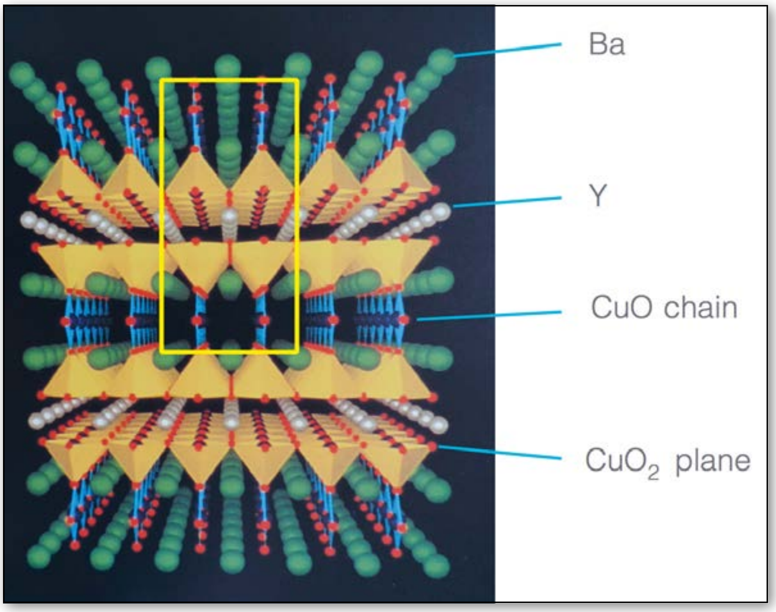


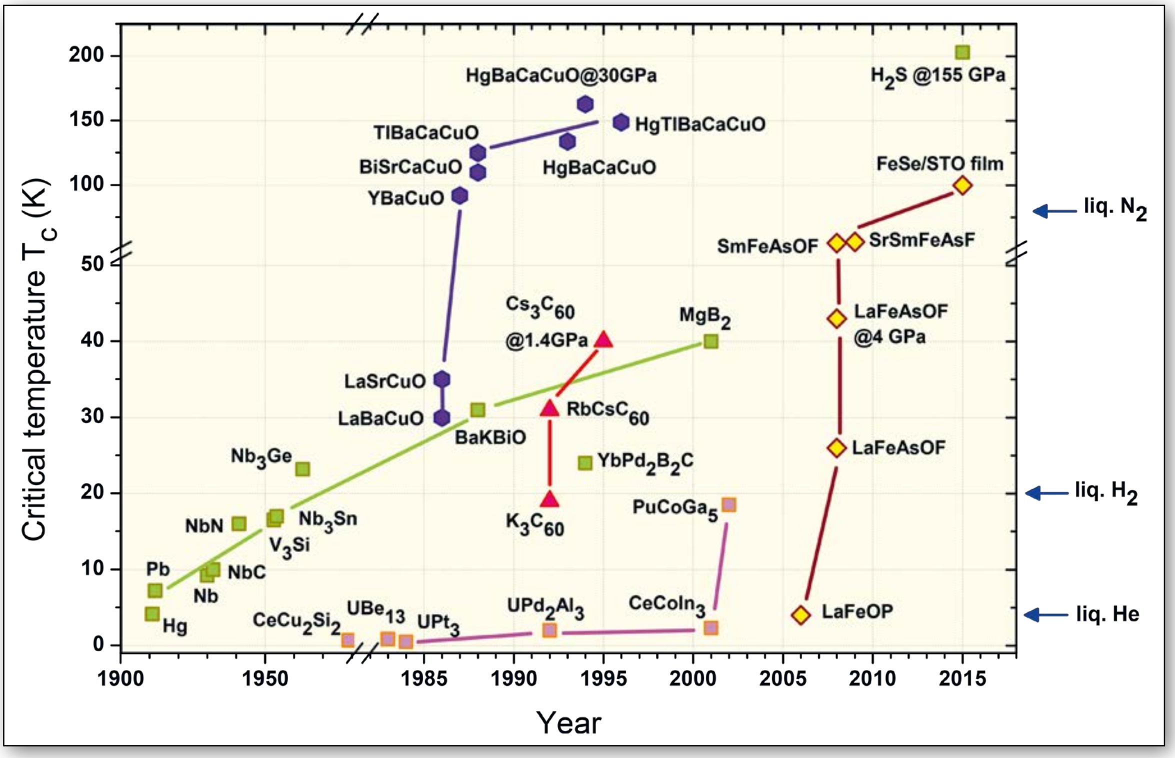
▲ **FIG. 1:** Cubic perovskite structure of ABX_3 type

Scientific Developments and Ongoing Research

Earlier studies of the perovskites, in particular of its most famous representative member $SrTiO_3$ were performed by K.A. Müller (KAM) [3] using electron paramagnetic resonance (EPR), applied in particular to investigate the binding and local structure of defects and the different valence states of transition metals such as V, Cr, Mn, Fe, Co, *etc.* A fruitful application of EPR was also the study of the Jahn-Teller (J-T) distortion of ions in a lattice and more generally structural phase transformations, cubic to tetragonal/orthorhombic symmetry or order-disorder transitions. The experimental evidence of Fermi glasses and itinerant polarons in ionic solids with variable range hopping mechanisms [3] and the enhanced superconducting transition temperature Tc in granular Al immersed in amorphous Al_2O_3 [4] convinced KAM that superconductivity at higher T can be found in oxides. The knowledge of vibronic interactions via the J-T effect lead in 1986 to the discovery of superconductivity at 35 K in the layered perovskite Ba-La-Cu-O with mixed copper valence (Cu^{3+} and Cu^{2+}). The discovery by Bednorz and Müller [2] was soon confirmed by many groups, notably P. Chu in Houston and S. Tanaka in Tokyo [5], leading to a huge tsunami of activity in this field. New layered copper oxide superconductors such as $YBa_2Cu_3O_{7-x}$ (Fig. 2) and the Bi-, Tl- and Hg-based cuprates were rapidly identified and Tc raised up to ~134 K (Hg-1223) [6] (Fig. 2). Very quickly theoretical models suggested that high-temperature superconductivity (HTS) might involve d-wave pairing, an idea confirmed by a variety of experiments such as the direct observation of an anisotropic superconducting gap (with four lobes of alternating signs and nodes in between where the gap is zero) by Angle Resolved Photoemission Spectroscopy (ARPES) or from tunneling experiments. Indirect demonstration came from the temperature dependence of the penetration depth, specific heat and thermal conductivity. But other experiments showing a possible mixing of s- and d-wave pairing and more exotic pairing symmetries were also presented. After thirty years of intensive research, the exact origin of HTS is still not clear and the possible mechanisms are subject of considerable debates. Similarities and differences in the properties of hole- and electron-doped cuprates are visualized in the generic phase diagram [6] showing the evolution from an antiferromagnetic phase at zero doping to the superconducting phase at optimal doping, with the presence of a pseudogap phase. Other families of materials referred as high-Tc materials were later discovered, in particular the iron-based superconductors or ferropnictides (Tc_{max} ~ 56 K) [7], the magnesium

▼ **FIG. 2:** Structure of the layered $YBa_2Cu_3O_{6+d}$ superconductor ($T_c = 92$ K) with the outline of the unit cell.





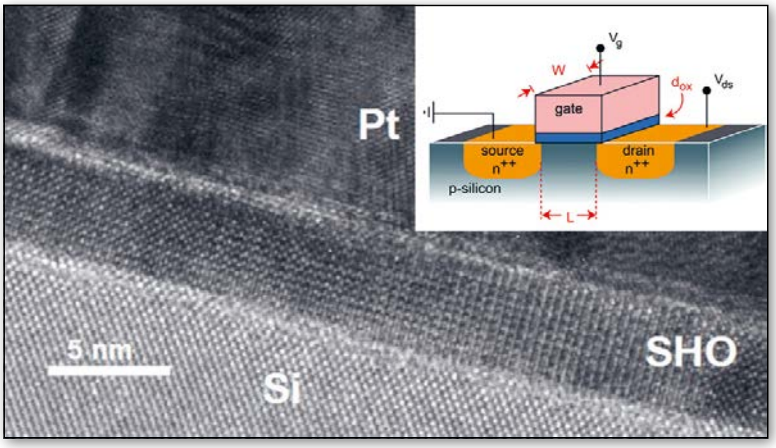
▸ FIG. 3: Evolution of T_c with time for different superconductors since the discovery of superconductivity in 1911.

diboride MgB_2 (Tc ~ 39 K) [8] and the fullerides such as Cs_3C_{60} (Tc ~ 40 K, under pressure) [9]. The latest sensation was the report of superconductivity at 203 K in H_2S under very high pressure [10], the highest reported Tc today (Fig. 3). The commercial applications of HTS cuprates have not reached the initial expectations so far, partly because of the brittle nature of these ceramics but also due the unusual properties of the magnetic vortex lattice (depinning, melting) [11]. Some of the potential applications include anyway induction heaters, transformers, fault current limiters, power lines and storage, motors and generators, magnets for fusion reactors and magnetic levitation devices.

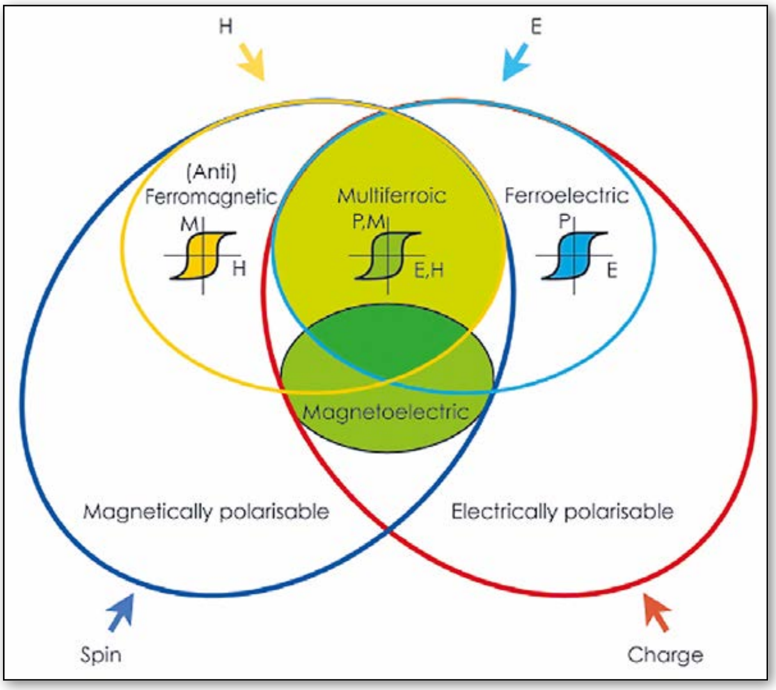
The perovskites gained a lot of attention with other discoveries such as the colossal magnetoresistance (CMR) in the rare earth manganates $Ln_{1-x}A_xMnO_3$ (Ln = rare earth, A = divalent cation) because of its technological implications [12]. CMR occurs when the manganates become ferromagnetic and transform from an insulating state to a metallic state close to the Curie temperature. It must be distinguished from the giant magnetoresistance discovered by A. Fert and P. Grünenberg (Nobel Prize laureates 2007) in ferromagnetic heterostructures such as Co/Cu/Co, called spin valves and commonly used as magnetic read heads in hard disk drives.

The phenomenal improvements of deposition techniques have allowed to produce very high quality thin films, superlattices and nanodevices based on the perovskites. Following the pioneering work of McKee *et al.* [13] it has been possible to grow by molecular beam epitaxy (MBE) epitaxial $SrTiO_3$, or similar perovskite structures, on silicon wafers. One possible application was to use these materials as high-permittivity (high-k) gate oxides in the new generations of high performance Metal Oxide Semiconductor Field Effect Transistors (MOSFET) [14] (Fig. 4). The large linear electro-optical coefficient of the ferroelectric $BaTiO_3$ has been used to modulate light [15], paving the way in Si photonics towards efficient integrated devices, such as modulators, tuning elements, and bistable switches. Among the piezoelectric materials known today, PZT *i.e.*, $Pb(Zr_xTi_{1-x})O_3$ is certainly the most prominent one, used as ultrasound transducer, ceramic capacitor or STM/AFM actuators [16]. A more general type of materials that attracted a great attention are the multiferroics [17], which exhibit the primary ferromagnetic, ferroelectric and ferroelastic order parameters coexisting in the same phase. The field of multiferroics has become important not only to understand the basic interaction between magnetic and electric coupling, but also for their potential application in devices such as actuators, switches, magnetic field sensors or new types of electronic memories. In spite of the large

▾ FIG. 4: High resolution TEM view of a thin $SrHfO_3$ layer grown on Si by Molecular Beam Epitaxy (MBE) and used as high-k gate oxide insulator in a MOSFET structure (inset) [14]



number of magnetic and ferroelectric materials, there are relatively few multiferroic materials, because of the stringent conditions for co-existence of the different types of order, as shown in Fig. 5.



▲ **FIG. 5:** Schematic phase diagram representing the different spin and charge ordering phases and their coexistence in a multiferroic state.

Typical materials showing such properties are perovskite transition metal compounds including, for example, $TbMnO_3$, $HoMn_2O_5$, $LuFe_2O_4$, or $BiFeO_3$, *etc.* There is an active ongoing research to understand the main classes of multiferroics.

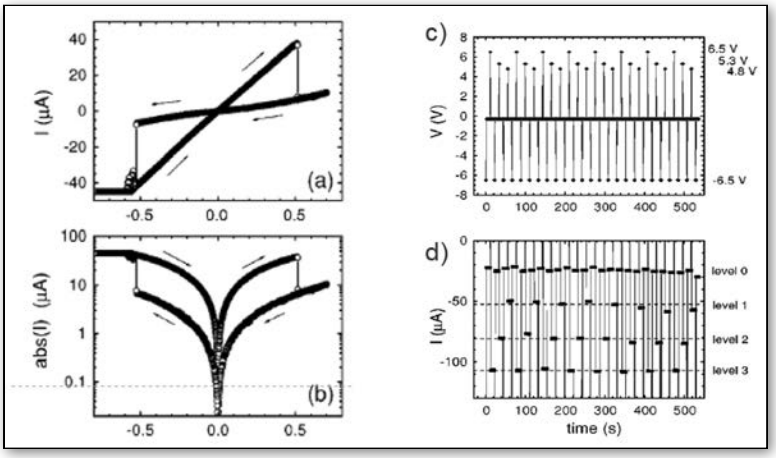
Finally among other properties found in perovskites, it is worth to mention the early demonstration of reproducible resistance switching and non-volatile memory in epitaxial Cr-doped $(Ba,Sr)TiO_3$ or $SrZrO_3$ metal-insulator-metal (MIM) devices [18]. In addition to long retention times it was also shown that multilevel switching could be achieved, allowing the storage of more than one bit per memory cell (Fig. 6). Alternative types of memristors have been very broadly investigated [19] and are today aimed in applications like neuromorphic computing where attempt is made to replicate the functions of neurons and synapses [20], a concept developed in the late 1980's by Carver Mead [21]

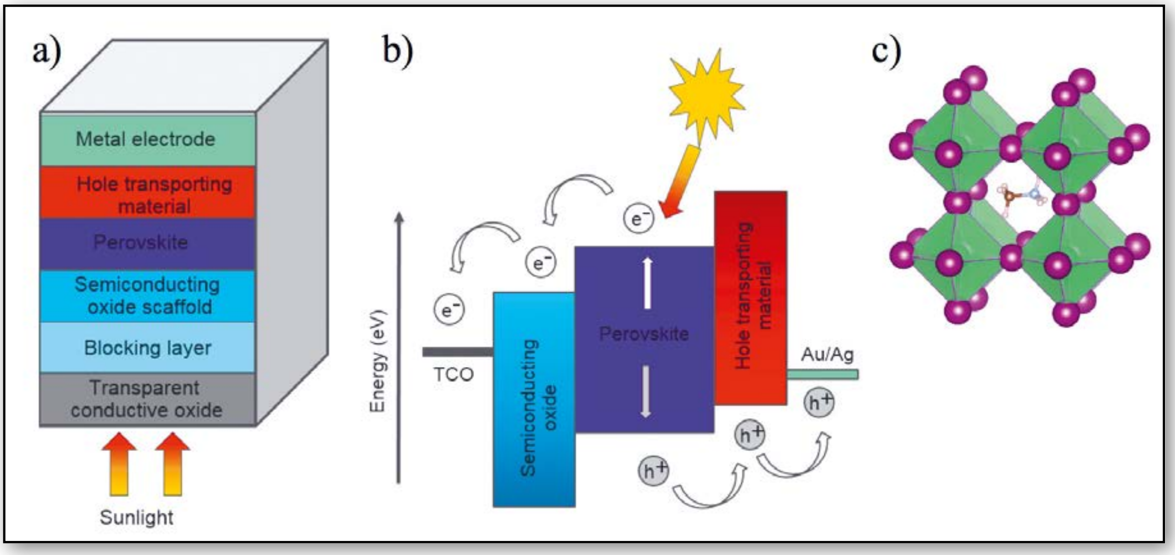
An incredible revival of interest for the perovskites happened a few years ago in the field of solar cells thanks to advances in power-conversion efficiency up to 22% in the organic-inorganic hybrid perovskite methylammonium halide $CH_3NH_3PbI_3$ ($MAPbI_3$) as the primary semiconductor of interest [22]. Such a value rivals the performance of industry standard silicon photovoltaic cells (PC).

In fact since the first announcement, the number of yearly publications that include the word perovskite in their title or abstract exponentially increased from typically 2600 articles/year in 2012 up to ~6500 in 2017, according to Web of Science. An example of such a cell based on $MAPbI_3$ is shown in Fig. 7. The three major components for such a high efficient PC are a good light absorber (perovskite), a semiconductor to accept electrons from photo excited perovskite and a hole transporter p-type semiconductor. Recently thiocyanate (CuSCN) has been found to be an attractive and cheaper hole transporter as compared to the usual materials. The global efficiency is tuned essentially by an optimization of the morphology (grain size, porosity) and thickness of the device layers. Two issues have still to be solved for commercial applications: first, fabricate large areas of high quality and stable perovskites while retaining the high power-conversion efficiency above 20% and secondly, find efficient nontoxic lead-free alternatives. Another recent advance that could foster applications in medical imaging is the use of such organic-inorganic perovskites layers for X-rays detectors, as they can be 10 times more sensitive that the usual amorphous selenium photoconductors [23].

This exceptional class of materials exhibits also promising potential for light emitting diodes (LED) and lasers [24]. The direct bandgap and nearly defect free crystalline films favors efficient charge collection and long range charge transport. In spite of their moisture sensitivity these structures achieved in two years the brightness and efficiency that organic LED reached in two decades. Typically materials with photoluminescence quantum yields close to 100% have been achieved whereas LEDs with external quantum efficiency of 8 % and current efficiency up to 43 cd/A have been demonstrated. The effective light-emission of the hybride perovskites is due to the low defect densities, low non-radiative electron-hole recombination and their high photoluminescence. By tuning the halide composition, thin film devices with bright green and red light emission can be obtained. High quantum yields, narrow emission, high exciton binding energy and color tunability, can be achieved also in nanostructured

▼ **FIG. 6:** Switching current-voltage (I-V) curves in a $Pt/SrZrO_3/SrRuO_3/SrTiO_3$ MIM heterostructure demonstrating the non-volatile memory effect in perovskites **a)** linear scale, **b)** log scale and the potential of multilevel storage **c)** applied voltage pulses, **d)** corresponding current levels [18]





▸ FIG. 7: a) & b) Schematic view of a perovskite-based photovoltaic cell heterostructure based on $CH_3NH_3PbI_3$ (Methylammonium lead iodide) with the different layers for collecting the photo excited electrons and holes **c)** Corresponding ABX_3 perovskite structure with $A = CH_3NH_3$, $B = Pb$ or Sn, $X = I$, Br or Cl.

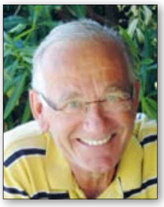
organic-inorganic or all-inorganic perovskites such as nanoparticles, nanoplates and nanowires. The nanostructuring of such materials by a judicious control of their synthesis conditions enables to generate nanoscale properties such as quantum confinement effects. At lower dimension higher intrinsic structural stability is also achieved as compared to 3D perovskites.

In addition to the mentioned LED developments, amplified spontaneous emission and lasing properties are also in the focus of researchers. Thus the success in photovoltaics has triggered a strong interest in developing perovskite optoelectronics for future commercial applications lasers and light-emitting devices.

Conclusions

Many research and review articles have been written on the role of the composition, crystalline structure, symmetry, and dimensionality of the perovskites on their physical and chemical properties. More will follow. In this short overview some important developments and applications of these materials have been outlined. The list is far from being exhaustive, but I hope that the reader will appreciate the extraordinary structural flexibility of this family of materials and the impressive progress that have been made in particular in the last 30 years, since the discovery of high-T superconductivity. ■

About the Author



Dr. Christophe Rossel is a Condensed Matter physicist with education and academic professional experience in Switzerland and in USA. In 1987 he joined the IBM Research-Zurich Laboratory pursuing a scientific career focused on the physics of superconductors and later on nanoscience and the integration of advanced functional materials for semiconductor technology. As member of various panels and president of the Swiss (2008-2012) and European Physical Societies (2015-2017) he has engaged in science policy issues, representing the community of physicists and advocating the contribution of physics and open science to the economic, social and cultural advancement in Europe.

References

[1] https://en.wikipedia.org/wiki/Perovskite_ (structure).

[2] J. G. Bednorz and K. A. Müller, *Z. Phys. B - Condensed Matter* **64**, 189 (1986)

[3] K.A. Müller and T. W. Kool, *Properties of Perovskites and Other Oxides*, World Scientific Publishing, Singapore 2010.

[4] K.A. Müller *et al.*, *Phys. Rev. Lett.* **45**, 832 (1980)

[8] S. Tanaka, *JSAP International* **4**, 17 (2001)

[6] https:/wikipedia.org/wiki/high-temperature_superconductivity

[7] H. Takahashi *et al.*, *Nature* **453(7193)**, 376 (2008)

[8] J. Nagamatsu *et al.*, *Nature* **410(6824)**, 63 (2001)

[9] A. Ganin *et al.*, *Nature Materials* **7(5)**, 367 (2008)

[10] A. Drozdov *et al.*, *Nature* **525**, 73 (2015)

[11] M. Willemin *et al.*, *Phys. Rev. Lett.* **81(19)**, 4236 (1998)

[12] C. N. R. Rao, *Chem. Eu. J.* **2**, 1499 (1996)

[13] R. McKee, F. Walker and M. Chisholm, *Science* **293**, 468 (2001)

[14] C. Rossel *et al.*, *Appl. Phys. Lett.* **89**, 053506 (2006)

[15] S. Abel *et al.*, *Nature Communications* **4**, 1671 (2013)

[16] M. J. Haun, *et al. Ferroelectrics* **99**, *63 (1989) & C. Rossel et al. J. Appl. Phys.* **115**, 034105 (2014)

[17] https://en.wikipedia.org/wiki/Multiferroics

[18] A. Beck *et al.*, *Appl. Phys. Lett.* **77**, 139 (2000) & C. Rossel *et al.*, *J. Appl. Phys.* **90**, 2892 (2001)

[19] R. Waser, *Nanoelectronics and Information Technology : Advanced Electronic Materials & Novel Devices*, Wiley-VCH Verlag GmbH, Weinheim (D), May 2003.

[20] Doo Seok Jeong *et al.*, *Adv. Electron. Mater.* **2(9)**, 1600090 (2016).

[21] C. Mead, *"Neuromorphic electronic systems". Proceedings of the IEEE.* **78**, 1629 (1990)

[22] See review in *MRS Bulletin* **40**, 641 (2015)

[23] Y.C. Kim *et al.*, *Nature* **550**, 87 (2017)

[24] S. A. Veldhuis *et al.* Adv. Mater. **28**, 76804 (2016)