Transition metal oxides: Promising functional materials

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Available online 16 April 2005

Abstract

Transition metal oxides represent a considerable potential for the generation of new frameworks with new magnetic and transport properties with a view of applications in the field of electronics. Three examples of ceramics are reviewed herein, which are all characterized by a mixed valence of the transition element, allowing electronic delocalization to be produced: high T_c superconducting cuprates (Cu^{2+}/Cu^{3+}), thermoelectric cobaltites (Co^{3+}/Co^{4+}) and colossal magnetoresistance manganites (Mn^{3+}/Mn^{4+}).
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Keywords: Functional applications; Electrical properties; Magnetic properties; Superconductivity

For a long time considered as compounds of academic interest, transition metal oxides have been studied these last 15 years for their extraordinary magnetic and transport properties susceptible of various applications. In this respect, oxides involving copper, manganese and cobalt have a great potential. Their remarkable magnetic and transport properties originate from the ability of these elements to adopt various oxidation states and electronic configurations. For these oxides, the mixed valence Cu^{2+}/Cu^{3+}, Mn^{3+}/Mn^{4+} or Co^{3+}/Co^{4+} reflects the possibility of electronic delocalization over the metal–oxygen framework, whereas the Jahn Teller effect of several of their cations, such as Cu^{2+}, Co^{2+} or Mn^{3+}, favors the formation of anisotropic structures and consequently of anisotropic transport and magnetic properties. The spin configurations of several of these cations are also very complex especially for cobalt, so that complex magnetic transitions are often generated.

The cuprate family[1–4] exemplifies the great impact of the transition metal oxides in the discovery of new concepts in solid state physics, and in the realization of new functional materials. Beside the famous cuprate $La_{2-x}Ba_xCuO_4$ synthesized for the fist time in the 80s[5] and which was found to be superconductor below $T_c = 40$ K,[6] the cuprates $YBa_2Cu_3O_7$ (often called "123"), $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+\delta}$ (called "2212" and "2223", re-

spectively) are now considered as materials for the future. Their critical temperature, ranging from 92 K for $YBa_2Cu_3O_7$ to 110 K for Bi-2223 allows to use liquid nitrogen, a cheap cooler, for working. Moreover they are almost ecological, since they contain few or even no heavy toxic elements such as thallium, mercury or lead. The high Curie temperature of these oxides originates from the bidimensionnal character of their structure (Fig. 1). The latter forms indeed layers built up of CuO_5 pyramids and CuO_4 square planar groups, sharing corners. High temperature superconductivity results form the delocalization of hole carriers in the CuO_2 planes, whereas in classical superconductors the delocalization is tridimensionnal. In contrast to the latter, the high T_c superconductors exhibit a low coherence length. The latter characteristic is a handicap for the propagation of holes and requires an almost perfect alignment of the CuO_2 planes in order to reach high current densities for applications. For this reason, numerous studies of the sintering of these ceramics were carried out these last years, bearing in mind the complex chemistry of these compounds. For instance in the case of $YBa_2Cu_3O_7$, the most successful methods are based on the texturation, using either the melt textured growth (MTG) or the top seeding melt growth (TPMG). These methods allow to elaborate discs of reasonable size (5–10 cm diameter) without any microcracks, which can then be assembled by soldering for various applications. In this way, current density values of 70,000 A/cm^2 can be reached in "YBCO". Thus, this material is close to the application for the realization of

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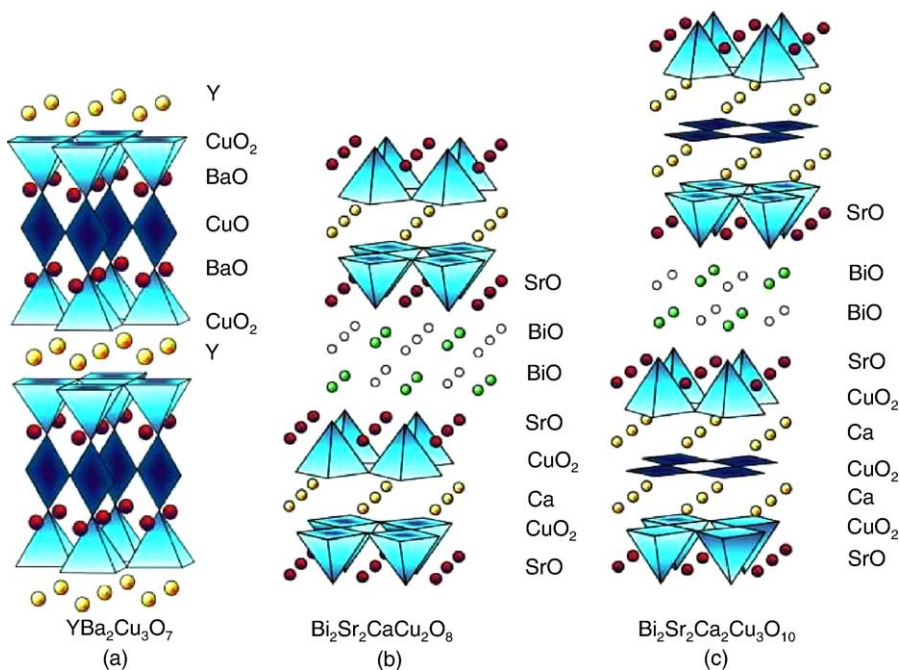
Fig. 1. Structures of the high T_c superconductors (a) $YBa_2Cu_3O_7$ $T_c = 92$ K (b) $Bi_2Sr_2Ca_2Cu_2O_{8+\delta}$, $T_c \approx 90$ K and (c) $Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_{10+\delta}$, $T_c = 110$ K.

generators and magnets. Propulsion motor developing a power of 100 kW, were realized by several staffs in Moscow and Iena. In the same way, magnetic levitation of this material is actually being used for the realization of magnetic bearings. The magnetic levitation train "MAGLEV", realized by Japanese researchers, which runs over 45 kms, is another example of the potential of "YBCO". For bismuth cuprates, the shaping methods are different, using either forging or hot rolling for the realization of wires. For these materials the application is close at hand for the realization of connecting cables, transformers and generators and MHD ship propulsion systems. Several prototypes have been realized by different companies. This is exemplified by the realization of fault current limiters of 1.2 MVA, made of Bi cuprate "2212", realized by ABB and current leads of 13 kA realized by Alcatel, whereas with the Bi "2223" cuprate current transformers were realized by ABB and EDF and connecting cables at Detroit Edison. The latter show the great potential of this cuprate since current transportation can be performed in cables of 120 m length, and 110 kg of Bi-2223 replace efficiently 8 tons of copper. Superconductivity coils based on Bi-2223 cuprate, were also fabricated recently to be used in nuclear magnetic resonance for medical imaging. The applications in the field of electronics are more distant, especially for fast electronics which requires to adapt these materials to the silicon technology, main unsolved problem to date. Nevertheless, important progresses have been achieved in the field of interconnectors and hyperfrequency transmission. The realization of superconducting quantum interference devices (SQUIDs) for various detection (submarine, brain etc...) is also close to the outcome. Less than twenty years after their discovery, cuprates appear as functional materials with great

potential. The recent discovery of superconductivity in the layered cobalt oxide $NaCoO_2$, yH_2O,[7] shows that the exploration of oxides in view of discovering new superconductors is so far not finished, and that efforts have to be done to understand this phenomenon in oxides whose chemistry is complex.

Lamellar cobaltites are the second example of oxides whose transport properties are much studied due to their potential application in the field of energy conversion especially at high temperature. The cobaltite $NaCo_2O_4$ whose structure (Fig. 2) consists of layers of edge-sharing CoO_6 octahedra, interleaved with Na^+ cations[8] shows very attractive transport properties.[9] This oxide exhibits at room temperature a high thermoelectric power $S = +100\,\mu V/K$, a low resistivity close to that of a metal, $\rho = 0.2\,m\Omega\,cm$, and a rather low thermal conductivity $K = 2\,W\,m^{-1}\,K^{-1}$. This leads for this material to a figure of merit, $Z = S^2/\rho K$, very acceptable at high temperature which should allow the realization of thermoelectric generators. The recent discovery of cobalt oxides with a "misfit" structure[10–16] speeds up the research activity on the thermoelectrics technology[17,18] especially in Japan. The misfit cobaltites are in fact composite structures built up of two distinct layers with different crystal lattices. This family is exemplified by $Ca_3Co_4O_9$ whose structure (Fig. 3) consists of the stacking of "CoO_2" layers with a monoclinic symmetry ($a \sim 4.8$ Å, $b_1 \sim 4.6$ Å, $c \sim 10.9$ Å, $\beta \approx 98°$) and of "$CaCoO_3$" layers with the same symmetry, a, c and β parameters being identical but b parameter being different, $b_2 \approx 2.8$ Å. These two sorts of layers have thus a very different structure, namely CdI_2 type for "CoO_2" and rock salt type for "Ca_2CoO_3". The structural misfit between these two types of layers is better evidenced by the chemical

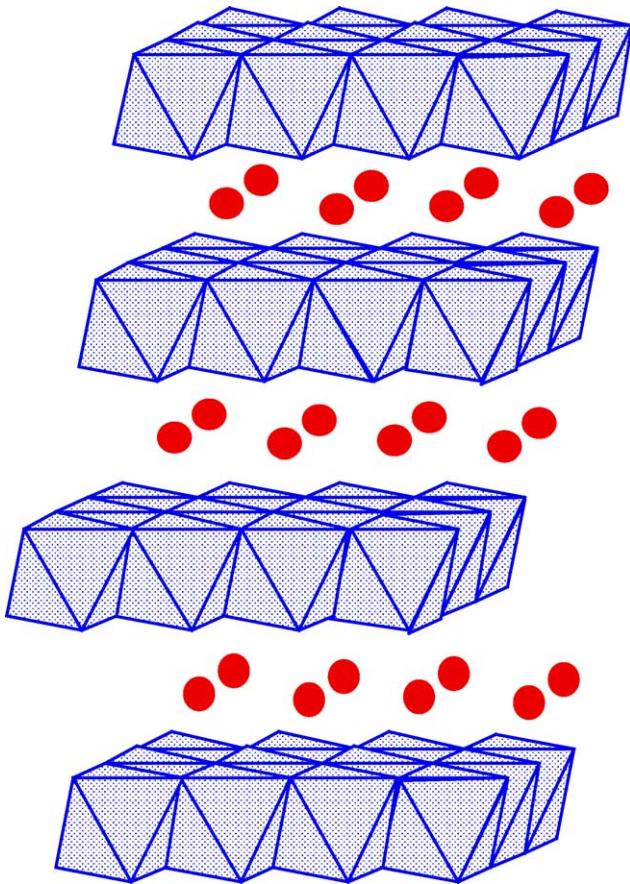Fig. 2. Structure of the cobaltite $NaCo_2O_4$.

formula $[Ca_2CoO_3][CoO_2]_{b1/b2}$, with $b_1/b_2 = 1.625$. Thanks to its high thermoelectric power $S = +120\ \mu V/K$, independent on the temperature for $T > 200\ K$, and to its low resistivity (Fig. 4), $Ca_3Co_4O_9$ has a great potential for thermoelectric application, similar to $NaCo_2O_4$. Advantageously, this oxide has a better stability than $NaCo_2O_4$ and has a greater po-
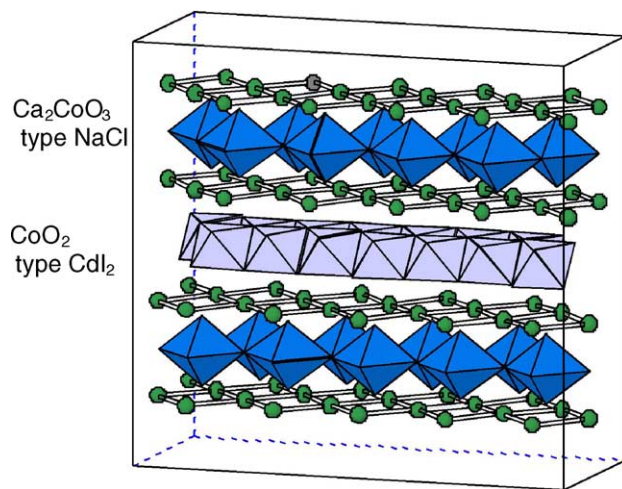

Fig. 3. Misfit structure of the cobaltite $Ca_3Co_4O_9$, $(Ca_2CoO_3)(CoO_2)_{1.62}$, built up of CdI_2 type "CoO_2" layers and rock salt type "Ca_2CoO_3" layers.
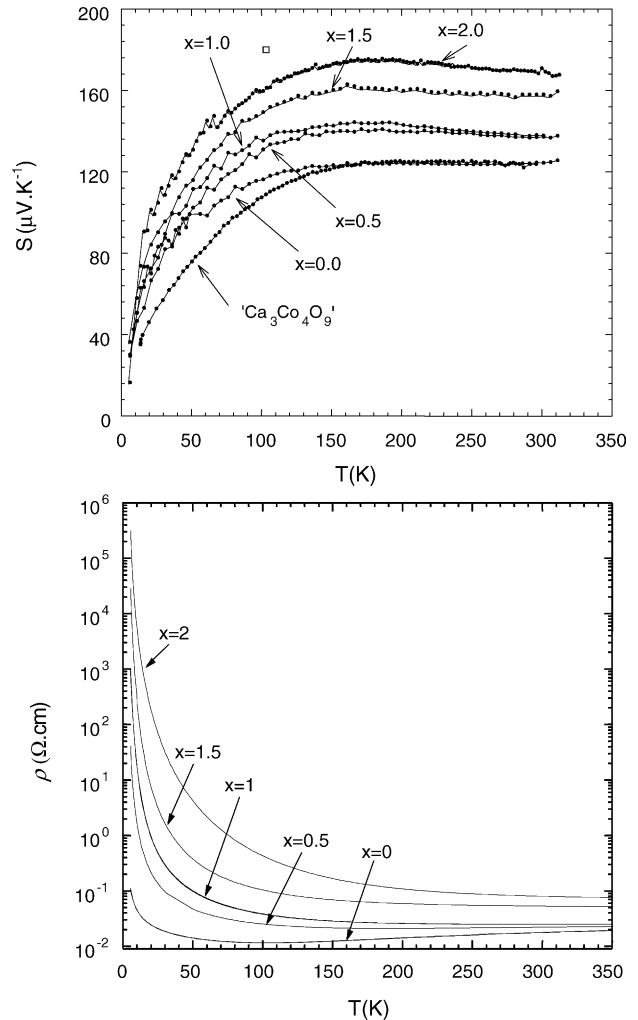

Fig. 4. Evolution of the thermoelectric power S and of the resistivity ρ of the cobaltite vs. temperature.

tential for high temperature utilization. The great flexibility of the "misfit" structure has allowed a large family of compounds to be generated, where the rock salt layer can host various cations such as strontium, barium, thallium, bismuth, mercury and lead. As a result, the structural misfit characterized by the b_1/b_2 ratio can vary significantly. The thickness of the rock salt layers, or more exactly their multiplicity can also vary. This is illustrated by the recent discovery of the bismuth cobaltites $[Bi_{1.7}Sr_2O_4][CoO_2]_{1.82}$ whose structure (Fig. 5) is also built up of single "CoO_2" layers but in which double "bismuth–oxygen" are sandwiched between single strontium–oxygen layers, replacing the "$Ca_2Co_2O_3$" layers. This great variety in the composition, but also in the stoichiometry, influences significantly the carrier density and consequently the thermoelectric properties of these oxides. In this way, a thermoelectric power of $160\ \mu V/K$ can be reached in lead misfits $[PbSr_{2-x}Ca_xO_3][CoO_2]_{b1/b2}$. The physics of these materials is so far not perfectly elucidated. The origin of metallic conductivity stems to the mixed valence, engendered by the Co^{3+} and Co^{4+} species, which exhibit a low spin

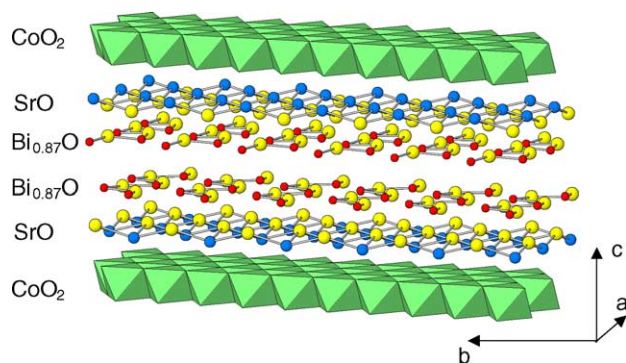Fig. 5. Structure of the misfit cobaltite $[Bi_{1.7}Sr_2O_4][CoO_2]_{1.82}$ built up of "CoO_2", layers and rock salt type "$Bi_{1.74}Sr_2O_4$" layers.

Fig. 6. Evolution of the resistivity versus magnetic field for the perovskite $Pr_{0.7}Ca_{0.26}Sr_{0.04}MnO_3$, (a) in zero magnetic field (b) under $H = 5$ T.

configuration. It results in a splitting of the t_{2g} states into e'_g and a_{1g}, leading to a broad e'_g band, which is necessary for the appearance of metallicity. On the other hand the magnetic interactions are attenuated by the magnetic frustration which results from the triangular geometry of the "CoO_2" layers. Finally, the weaker thermal conductivity could be due to the disordering of cations and anions in the rock salt layers, which would then behave as phonon glass. Thus it appears that the bidimensionnal character of theses oxides and their mixed valence, play a very crucial role in their remarkable thermo-electric properties. In this respect these oxides show a great similarity with high T_c superconducting cuprates which also require a bidimensionality of the structure and the mixed valence Cu^{2+}/Cu^{3+}. The route is thus opened to the optimization of these materials by modifying the chemical composition of their rock salt layers, but also by texturing the corresponding ceramics in order to use advantageously their anisotropy. Demonstrators based on Peltier effect, using these materials in modules where p and n conductors are assembled, are actually working in different laboratories.

The third family deals with the manganites of generic formulation $Ln_{1-x}A_xMnO_3$ [19–21] where Ln^{3+} is a lanthanide cation and A^{2+} is an alkaline earth. These oxides are the object of a considerable number of studies, due to the spectacular variation of their resistance, when submitted to a magnetic field. For instance, by tuning carefully the composition, i.e. the average size of the A-site cations, the resistance can be decreased by several orders of magnitude by applying a magnetic field as illustrated for the oxide $Pr_{0.7}Ca_{0.26}Sr_{0.04}MnO_3$ (Fig. 6). For this reason, these oxides are known as CMR effect (colossal magnetoresistance). The great sensitivity of the resistance of these materials to the magnetic field, offers a great potential for magnetic recording and as magnetic sensors and actuators. Differently from the two above families, these manganites have a tridimensionnal structure. They exhibit the classical perovskite structure, built up of corner-sharing MnO_6 octahedra, but whose distortions play a major role in the magnetic and transport properties, especially via Jahn Teller distortion of the Mn^{3+} species. In fact, like cuprates and cobaltites, the CMR manganites exhibit a mixed valence Mn^{3+}/Mn^{4+}. The latter is at the origin of the dou-
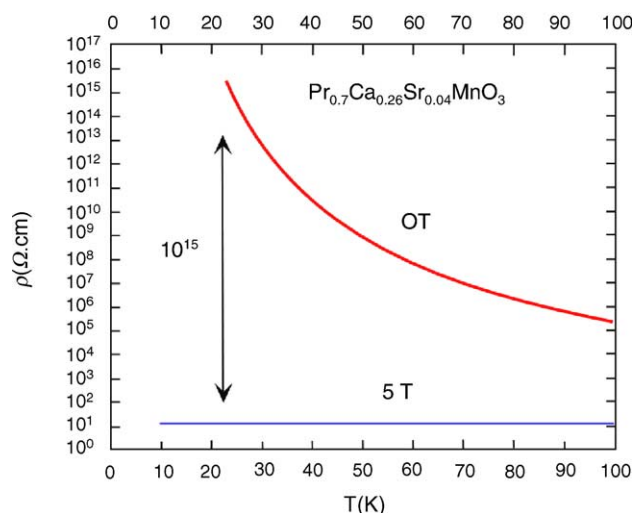
ble exchange (DE) mechanism between the Mn^{3+} and Mn^{4+} species [22] and is consequently responsible for the appearance of ferromagnetism and metallic conductivity often observed simultaneously at low temperature. The transition from an insulating state (paramagnetic or antiferromagnetic) to a ferromagnetic metallic state, by application of a magnetic field is thus the key of the CMR effect in these oxides. In fact, this phenomenon is often related to the existence of charge and orbital ordering between the Mn^{3+} and Mn^{4+} species. Such a behavior is exemplified by the perovskite $Pr_{0.5}Ca_{0.5}MnO_3$ which exhibits at low temperature an ordering of the Mn^{3+} and Mn^{4+} species and of the e_g orbitals in the form of stripes as schematized on Fig. 7. In this antiferromagnetic CE-type insulator the "Mn^{3+}" octahedra are strongly elongated, whereas the Mn^{4+} octahedra are much more symmetric. By applying a magnetic field larger than 25 T to this structure, a more symmetric structure is obtained, which is characterized by a charge delocalization, over the Mn–O–Mn lattice. In other words the application of a magnetic field induces a structural transition and simultaneously a magnetic transition to a magnetic metallic state. Starting from this observation, one can predict the important role of doping in the appearance of the CMR in these oxides. The substitution of a small amount of foreign elements for manganese (a few atoms per cent), such as Cr^{3+}, Co^{2+}, Ni^{2+}, Ru^{4+} destabilizes the orbital and charge ordering, making locally the structure more symmetric, even in the absence of magnetic field. In zero field, ferromagnetic islands with a symmetry higher than that of the antiferromagnetic matrix are generated coherently with the matrix around the impurities. By applying a magnetic field, these small domains tend to extend and the material becomes metallic when the domains percolate. This doping allows by structural effect, coupled with the magnetic effect of doping cations to lower considerably the critical magnetic field so that only a few teslas are necessary to obtain a magnetoresistance effect, against 25 T for the pristine phase $Pr_{0.5}Ca_{0.5}MnO_3$. Similar

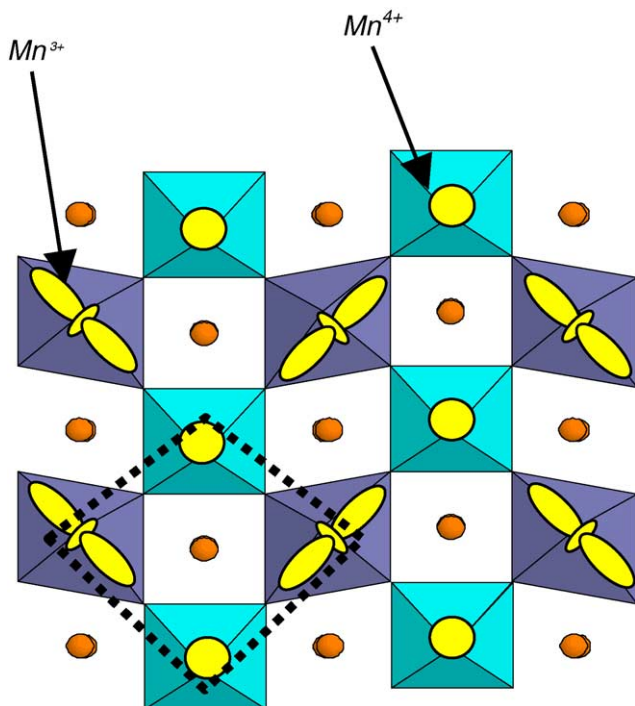Fig. 7. Schematized structure of the antiferromagnetic insulating perovskite $Pr_{0.5}Ca_{0.5}MnO_3$, built up of octahedral "Mn^{3+}" stripes alternating with "Mn^{4+}" stripes.

effects can be obtained by doping the A sites with cations such as Ba^{2+} or Sr^{2+} which have larger size than Ca^{2+}. The latter have clearly a structural role: they generate more symmetric regions within the matrix, which become ferromagnetic. Consequently, the CMR manganites evidence a new phenomenon, called electronic phase separation which is itself generated by coherent structural phase separation. The nucleation of a more symmetric ferromagnetic phase within a less symmetric antiferromagnetic phase, and its coherent growth, is the key of the mechanism of the CMR effect. It is thus easy to understand that the possibilities of optimization of the CMR properties of these materials are still numerous and are so far not completely explored. However, all the applications in the field of magnetic recording require to work at room temperature, with magnetic fields as low as possible, i.e. smaller than 1/10 T. In these conditions, the performances that have been reached recently, corresponding to magnetoresistance values close to 10% at 300 K under 0.5 T, appear promising. The interface effects and of grain boundaries, obtained in ceramics and especially in thin films of these materials, called tunneling magnetoresistance (TMR) should allow to reach the required characteristics for applications.

In conclusion, these few examples show that the transition metal oxides are, due to the physical properties they can generate, functional materials for the future. Numerous physical properties remain to be discovered and to be explained in such strongly correlated electron systems, which have not been studied to date, because of their structural and chemical complexity. The route is opened to their exploration, which should open on applications.

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