

Magneto-resistive ceramics. Recent progress: from basic understanding to applications

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Magneto-resistive ceramics, based on half-metallic ferromagnetic oxides have received renewed attention in the last few years because of their possible applications. Here, we review some recent progress on the development of magneto-resistive ceramic materials such as $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ and $\text{Sr}_2\text{FeMoO}_6$ ceramic materials. We shall revisit their basic properties, the strategies that have been employed to understand and to improve their intrinsic properties, pushing the limits of their operation at temperatures well above room-temperature, and the development of some applications. This effort has required the contribution of a number of actors. Starting from research laboratories, it has progressively involved industries that nowadays are able to supply high quality raw-materials or to manufacture magneto-resistive components at large scale.

Keywords: magneto-resistive ceramics, manganese oxides, magnetic sensors

Cerámicas magneto-resistivas. Progresos recientes: desde el entendimiento básico a las aplicaciones.

Las cerámicas magneto-resistivas, basadas en óxidos semi-metálicos ferromagnéticos han recibido una renovada atención en los últimos años debido a sus posibles aplicaciones. Se revisan aquí algunos de los recientes progresos en el desarrollo de materiales cerámicos magneto-resistivos como $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ y $\text{Sr}_2\text{FeMoO}_6$. Se revisitan sus propiedades básicas, las estrategias empleadas para entender y mejorar sus propiedades intrínsecas, llevando sus límites de operación a temperaturas muy por encima de temperatura ambiente, y el desarrollo de algunas aplicaciones. Este esfuerzo ha requerido al contribución de un gran número de actores. Comenzando por laboratorios de investigación, se ha implicado progresivamente a industrias que hoy en día están capacitadas para suministrar materias primas de alta calidad o para fabricar componentes magneto-resistivos a gran escala.

Palabras clave: cerámicas magneto-resistivas, óxidos de manganeso, sensores magnéticos

1. INTRODUCTION

Magneto-resistive sensors (MR-S) rely on the change of electrical resistance of a material under a magnetic field. Thus, very generally, a MR sensor is a magnetic field probe. A MR-S gives a direct measure of a magnetic field, rather than its time-variations as other magnetic sensors do, thus meaning that a MR-S are DC field-sensors. MR-S are sensitive to small fields (or its changes): they can be typically operated to detect magnetic fields as low as $1\mu\text{G}$ (one million times smaller than the earth magnetic field), up to some few 1kG (permanent magnets and common electromagnets). MR-S can be used as sensitive probes of position or displacements in linear or rotational systems. The extremely small size of some of the sensing element may even allow an enhanced position sensitivity using gradiometric configurations.

A magneto-resistive material is a material where the electrical transport properties are intimately linked to the spin orientation of the charge carriers. The spin orientation can be determined and modified by using an external magnetic field. Thus, in general, in a spin device not only the charge of the carriers is exploited but also their spin orientation.

On very general grounds, it could be anticipated that the magneto-resistive response of a material, i.e its sensitivity on an applied magnetic field, would be larger if the spins of *all* itinerant carriers are pointing to the same direction. In a ferromagnetic metal, this is not the most common situation as the itinerant carriers have spins pointing into two different directions (i.e the Fermi level crosses the spin-up and the spin-down sub-bands); any spin unbalance results in the appearance

of a net-ferromagnetic behaviour. It follows that ideal materials for spin manipulation (and thus materials for spin devices) will be those where all itinerant carriers have the corresponding spins pointing into the same direction. In other words, the Fermi level shall cross only one spin sub-band. This is the case of the so-called half-metals.

The difference in populations of spin-up and spin-down sub-bands can be simply monitored by the net spin polarization P defined as $P=[N(+)-N(-)]/[N(++)+N(-)]$ where $N(+)$ and $N(-)$ are the density of electrons at the Fermi level having its spin up or down respectively. Thus in normal ferromagnetic metals, such Co or Ni, $P<50\%$, whereas in the half-metallic ferromagnets $P=100\%$.

Which materials are half-metallic ferromagnets?. Unfortunately the list of these materials is rather short. Among typical metals, only the so-called Heusler alloys display this property. However, little progress has been made of using this family of compounds. The difficulty essentially relies on the complex metallurgy of these alloys and on the fact that single-phased materials can be hardly produced in the due shape (thin films,...). Among metallic oxides, four different families of materials have been proposed to be half-metallic ferromagnets: (i) the $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ -type manganites, (ii) the long-ago known magnetite Fe_3O_4 , (iii) the chromium dioxide CrO_2 and (iv) the so-called double perovskites of the $\text{Sr}_2\text{FeMoO}_6$ family.

Half-metallic ferromagnets shall be operated below its ferromagnetic Curie temperature, as they must be used in its ordered magnetic state. Thus the Curie temperature (T_c) is a critical parameter

of the material. Whereas Fe_3O_4 and CrO_2 have their T_c well above room temperature, the celebrated manganites have T_c upper-bounded by some 360K and thus are of limited interest. Despite of being long-time known, moderate progress has been achieved using Fe_3O_4 and CrO_2 oxides as magnetoresistors. In the case of Fe_3O_4 , the difficulties arise due to the delicate synthesis conditions required to avoid the appearance of other ferric/ous oxides and the presence, almost ubiquitous, of the so-called antiphase boundaries. Chromium dioxide on the other hand is a well known material in other field of applications, such as magnetic recording, although the critical role of surface and interfaces in magnetoresistive materials has limited the progress for applications involving carrier transport across grain boundaries. Indeed, CrO_2 shall be prepared under strongly oxidizing atmosphere (in bulk material preparation, a very high oxygen pressure is required) otherwise an antiferromagnetic Cr_2O_3 phase is formed at grain's surface. Therefore synthesis conditions are extremely critical and difficult to obtain in thin film deposition systems.

$\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ perovskites are nowadays very much known, and enormous progress has been made in the last few years towards understanding this material and its synthesis is rather well controlled [1]. However, $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ has two severe drawbacks. First, its Curie temperature is about 360K, which is critically close to room-temperature and certainly its application above 80°C is not possible. Second, it is experimentally observed that the performance of a $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ magnetic sensor is ideal, as expected, due to its $P=100\%$ characteristic. However, this ability is rapidly suppressed when heating up the material and the response at temperatures well below T_c becomes disappointingly reduced. Although the intimately reasons for this behaviour are still a subject of debate and research, it is obvious that materials with still higher Curie temperature will be welcomed. This is the case of the double perovskites $\text{Sr}_2\text{FeMoO}_6$, which has been reported to have T_c above 400K, thus opening renewed promises for technological applications.

The conceptually simplest way of imaging a MR sensor, is through the image of the so called *magnetic tunnel junction* (MTJ). In this structure two ferromagnetic and metallic electrodes (FM1 and FM2) are sandwiching a thin layer of an insulator material. In this device, charge carriers in one of the electrodes can cross the insulating barrier from FM1 to FM2 only if its spin orientation is preserved. This means that if the magnetization of both electrodes are parallel, the electrical current flow is possible whereas if the magnetization of both electrodes are reversed the current can not flow. The orientation of the magnetization of the electrodes can be switched by an external (small) magnetic field. The magnetoresistance, defined as $\text{MR} = [\text{R}(\text{H}=0) - \text{R}(\text{H})] / [\text{R}(\text{H}=0)]$ -where $\text{R}(\text{H})$ is the resistivity of the junction under a magnetic field-, will have its maximum value ($\text{MR}=100\%$) if the spin polarization of the electrodes is complete ($P=100\%$) and the relative orientation of magnetization is switched from antiparallel to parallel under the external field. This is the interest of using the half-metallic ferromagnets as FM electrodes.

MTJ have been made using all type of the half-metallic ferromagnetic oxides just described above, thus confirming essentially the full spin polarization of the itinerant carriers and the viability of the concept of the MTJ as a very sensitive magnetic probe. These structures have been made using epitaxial growth, on suitable single crystalline substrates, of the corresponding electrodes and barrier [2]. This is an appropriate technological approach for some applications although the cost of manufacturing precludes its use in other cost-effective developments. At this point it is useful to note that one can substitute in the MTJ the concept of the FM electrodes by a FM grains in a ceramic matrix. If the magnetization of the different grains can be rotated independently, a ferromagnetic ceramic can be viewed as

a random array of MTJ, where the intergranular and/or grain surface playing the role of the insulating tunnel barrier. Indeed, it has been shown that in Fe_3O_4 , CrO_2 , $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ and $\text{Sr}_2\text{FeMoO}_6$ ceramics a substantial magnetoresistance is observed under application of relatively small magnetic fields [3]. These observations opened the possibility of using granular ceramic samples of these oxides in low-cost magnetoresistive applications.

In this paper we shall review, some progresses we have made on the development of magnetoresistive materials and sensors based on $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ and $\text{Sr}_2\text{FeMoO}_6$ ceramics. Efforts have been directed towards targets relevant for automotive applications.

2. MAGNETORESISTIVE $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ AND $\text{Sr}_2\text{FeMoO}_6$ CERAMICS.

2.1. Preparation of raw materials

Both $\text{La}_{1/3}\text{Sr}_{2/3}\text{MnO}_3$ (LSMO) and $\text{Sr}_2\text{FeMoO}_6$ (SFMO) can be prepared by solid state reaction routine, by appropriate thermal treatment at high temperature of precursor oxides and carbonates. See references 4 and 5 for details. Here, we only mention that the manganites such as LSMO, are prepared under air conditions at temperatures around 1100°C whereas the double perovskites require higher temperature of synthesis (>1250°C) and a strongly reducing atmosphere. Typically, a mixture of Ar/H₂ (5%) is used. Under appropriate synthesis conditions single phase materials of LSMO and SFMO can be obtained.

In the case of SFMO, it is of crucial importance for optimizing the magnetic properties, to reach a complete ordering of the Fe and Mo ions in the double perovskites structure. In fact, in the ideal material Fe-Mo should be ordered in a chess-board three-dimensional network. Misplaced Fe(Mo) ions in the Mo(Fe) sites are called *antisites* (AS) and are the most common defect in the structure and have dramatic impact on the saturation magnetization of the oxide. Whereas in the ideal material the saturation magnetization (M_s) should be of about $4\mu_B/\text{f.u.}$, the presence of AS progressively reduces the M_s . Therefore it is of prime importance to control the AS concentration. This can be achieved as reported in Ref. 4, and materials having M_s of about $3.8\mu_B/\text{f.u.}$ (Fig. 1) and Curie temperatures close to 410K [6] can be nowadays routinely obtained at laboratory scale (Fig. 2).

Whereas LSMO powders under normal conditions are stable,

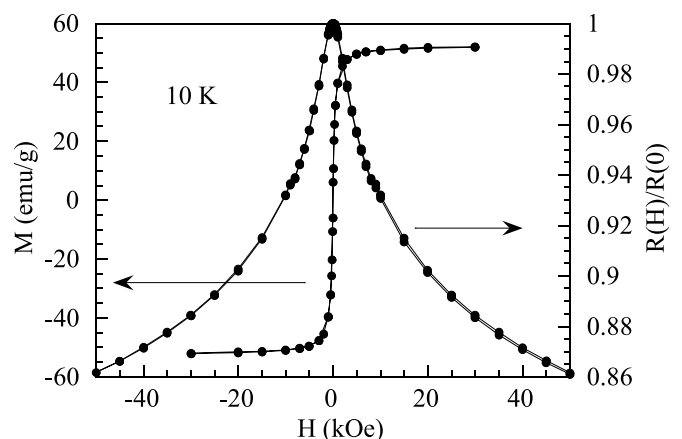


Figure 1. Field dependence of the resistivity (right) and magnetization (left) of a $\text{Sr}_2\text{FeMoO}_6$ ceramics at 10K.

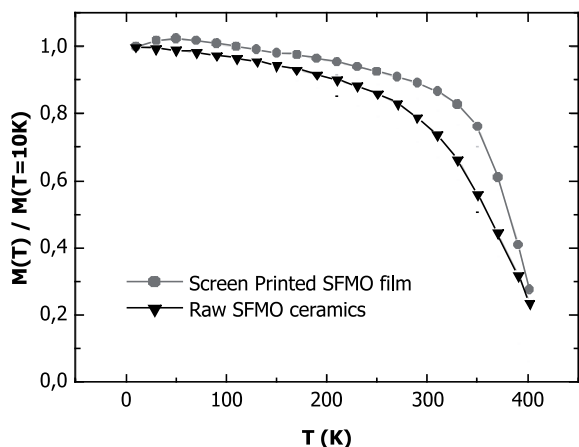


Figure 2. Temperature dependence of the magnetization of a SFMO ceramics (squares) and a screen-printed thick film (triangles).

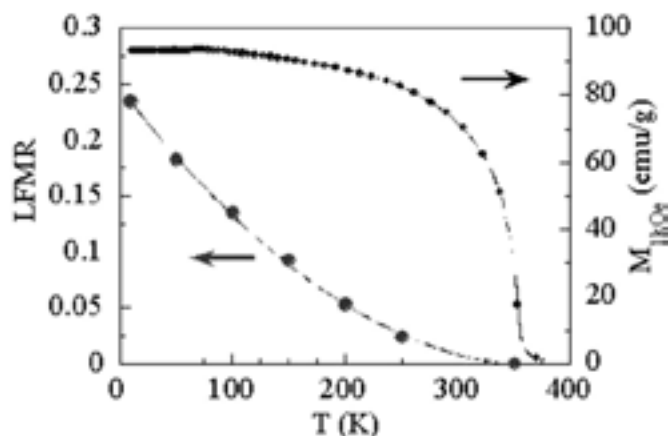


Figure 4. Temperature dependence of the magnetization (right axis) and low-field magnetoresistance (left axis) of a LSMO ceramics.

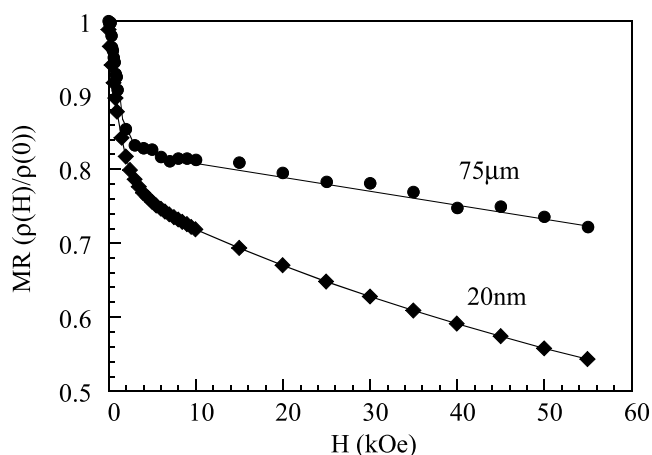


Figure 3. Field dependent resistivity, at 10K, of LSMO ceramics of different grain sizes: 20 and 75 nm.

that is without appreciable modification of their properties, this is not the case of SFMO, where we have clearly found that it decomposes and traces of SrMoO₄ become readily visible in their X-ray diffraction pattern [7]. This process become even more relevant if the H₂O content of the atmosphere or the storing temperature are increased. It follows that any further processing or development of this material shall take into account these observations.

2.2. Magnetoresistive properties

It has been shown that in polycrystalline La_{1-x}A_xMnO₃ (A=Ca, Sr, Ba,...) samples, application of relatively low magnetic fields promotes a substantial reduction of the resistivity (low-field magnetoresistance, LFMR) [8]. The LFMR can be enhanced by using submicrometric particles and LFMR values of about 30% can be routinely obtained at low temperatures and under fields in the range of 1kOe as shown in Fig. 3 [9].

We mentioned in the Introduction that applications at temperatures close to or above room temperature are dampened by the fact that the LFMR decays rather fast with temperature and becomes almost negligible already below T_c (<360K in La_{1-x}A_xMnO₃) (Fig. 4) [2,8,9]. This crucial observation raises questions about the role of interfaces in these oxides and eventually in other ferromagnetic systems mediated by double exchange interactions.

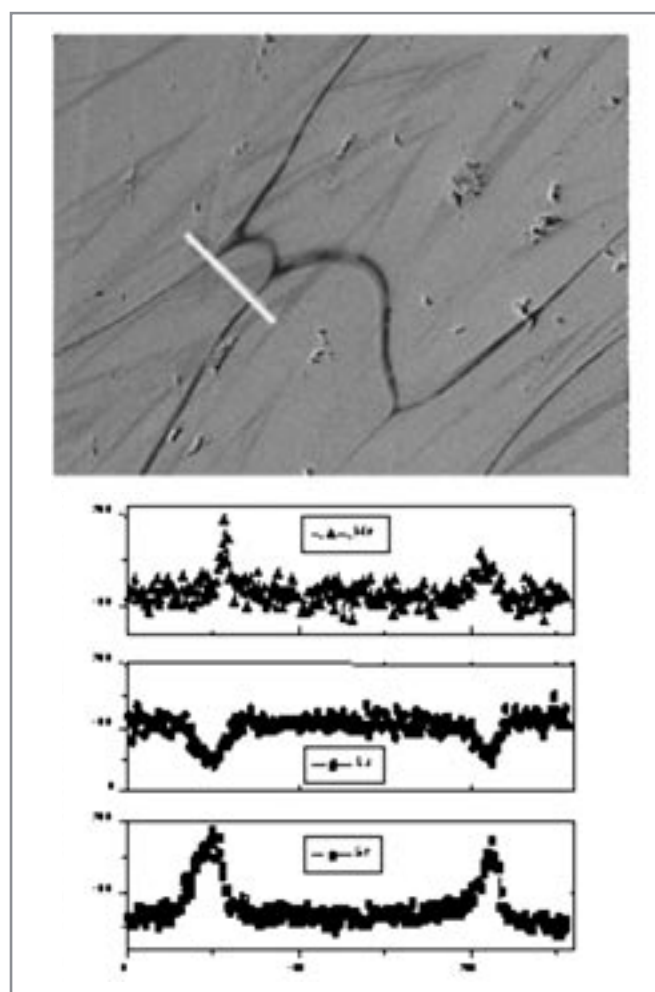


Figure 5. Scanning Electron Microscopy image of a LSMO ceramics. The composition line scans are shown on the right.

We have addressed this issue as follows. We have found evidences of chemical and electronic phase segregation at (or close) to interfaces in LSMO. Chemical segregation becomes apparent when scanning atomic composition across grain boundaries in samples processed at very high temperature. For instance, in LSMO samples sintered at 1400°C there is an enrichment of Sr and a depletion of La at the grain surface (Fig. 5) [10]. This problem becomes less relevant when reducing the synthesis temperature, thus limiting the temperature range of processing at temperature below 1250°C. On the other hand,

we have disclosed the existence of an electronic phase separation at the surface of grains of the very similar compound $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO). This has been observed by using a microscopic analysis tool as $\text{Mn}^{55}\text{-NMR}$ which has allowed identifying that beside the majority intrinsic $\text{Mn}^{3+/4+}$ resonances in the spectra, corresponding to the ferromagnetic and metallic Mn ions, there is also a weaker signal arising from ferromagnetic Mn^{4+} ions that do not contribute to the transport (Fig. 6). In addition, the presence of non-ferromagnetic and localized Mn^{3+} ions can also be inferred from the analysis of the spectra. These spurious signals become more relevant as the grain size of the ceramic is reduced, thus illustrating that are likely related to surface effects [11,12]. As tunnelling carriers shall cross the surface, detrimental contribution of these non-ferromagnetic and metallic regions could be expected. Therefore, it follows that grain size of LSMO-type ceramics can not be reduced much below 100nm. Under these conditions LFMF values of 3% at 1kOe can be routinely obtained at RT and some 30% at low temperature (10K). Very recently, we have also found that magnetoresistance of LSMO ceramic pellets can be further enhanced by using appropriate composites [13].

Synthesis and crystallochemistry of $\text{Sr}_2\text{FeMoO}_6$ oxides is more delicate. Not only stoichiometry and sample purity are issues of major concern, but also the Fe/Mo ordering have been found to play a fundamental role on the sample magnetization and magnetoresistance [5,14]. In spite of these difficulties, the control of the synthesis protocol has rapidly progressed [5,14] and nowadays the magnetic properties of ceramic samples are well controlled and rather well understood. To illustrate the extreme sensitivity of transport properties to detailed oxygen treatment, we include in Fig. 7 a plot where we compare the resistivity of SFMO samples treated as-prepared and after annealing in a flow of commercial Ar (99.99%). It is clear that the resistivity of the samples changes dramatically although the bulk magnetic properties do not change [15]. This illustrates the role of intergrains on the transport properties and its instability. Detailed X-ray characterization (Fig. 8) revealed the appearance of traces of SrMoO_4 , probably linked to surface oxidation [7].

The results overviewed above show that the material's processing in bulk form is mature enough and thus the steps towards the fabrication of thick films have been undertaken. Activities in that direction will be reported in the following sections.

3. SCREEN-PRINTED MAGNETORESISTIVE FILMS AND MAGNETIC SENSORS.

3.1. $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ based films and devices.

Thick films prepared by screen printing constitute an appropriate low-cost approximation to the fabrication of functional materials and devices. Polycrystalline thick films can be tailored in the appropriate shape for particular sensing purposes. Printable magnetoresistive ink is made by mixing appropriate amounts of finely grain sized preformed magnetoresistive powders (LSMO, SFMO, ..) and an appropriate organic vehicle. By printing through a mask, films of several tenths of microns thick can be prepared. The process ends by sintering the films under the appropriate conditions to obtain the necessary intrinsic properties (a high T_c and saturation magnetization) and the mechanical properties suitable for further handling and manipulation of the device. Using this approach, position sensors and contactless magnetic sensor have been developed [16].

Early on 1998 we reported the preparation of screen-printed $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) thick films on Al_2O_3 (AO) substrates [16, 17]. In Figure 9(a) we show an image of the sensitive part (the

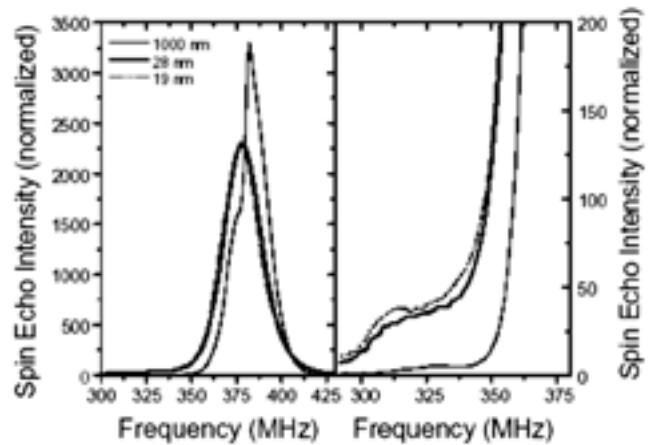


Figure 6. Left: ^{55}Mn NMR spectra, recorded at 4.2K, of LSMO ceramics with different grain sizes. Right: Blow-up of the spectra in the low frequency region.

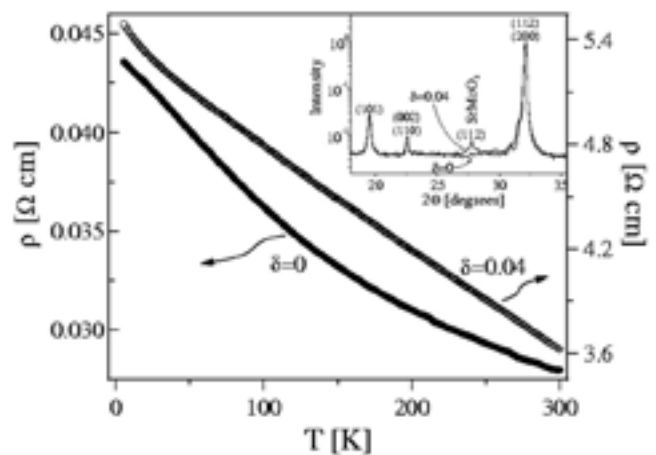


Figure 7. Temperature dependence of the resistivity of SFMO ceramics (as-grown ($\delta=0$) and oxidized ($\delta=0.04$)). The inset shows the progressive formation of SrMoO_4 after oxidation.

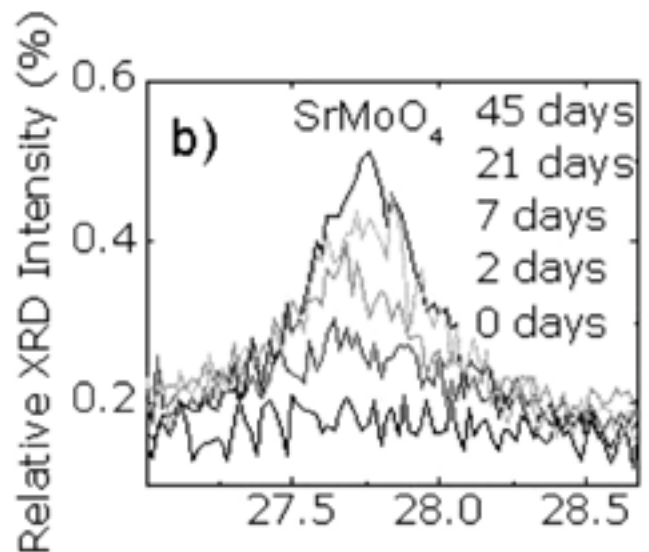


Figure 8. Detail of X-ray diffraction patterns of SFMO ceramics showing the progressive formation of SrMoO_4 by room temperature aging.

magnetoresistive element) of one of these devices -made using LSMO powders-. In the Scanning Electron Microscopy (SEM) image of Fig. 9(b) it can be appreciated that the films consist of a well-sintered disordered array of LSMO grains. The output signal at room-temperature of a device operated by rotating a permanent magnet on top of the magnetoresistive track is shown in Fig. 10. As expected when increasing the temperature, the MR decays and practical operation is limited to about 90°C.

Nowadays, fabrication of LSMO raw-materials and magnetoresistive elements and assembling in functional devices is well tailored. We have also verified that some improvement of magnetoresistance of screen-printed films can be gained by using composites [18].

3.2. Sr₂FeMoO₆ based films and devices.

SFMO films have also been grown by using the screen-printing technology. It turns out that under the necessary conditions of synthesis of SFMO the adherence of SFMO films on polycrystalline Al₂O₃ substrates is very low and films suffer from severe mechanical instability and film /substrate interdiffusion. To overcome this problem a suitable buffer layer -of about 5 microns- has been screen printed

and appropriately sintered on the bare substrate. The adherence of the buffer layer to the Al₂O₃ becomes good enough. Subsequent printing of the SFMO layer and high temperature sintering has allowed obtaining films with thicknesses in the range 40-80 microns, with stability strong enough to be manipulated and measured.

As shown in Fig. 11, SFMO films have been grown on suitable polycrystalline Al₂O₃ substrates. After the sintering process, the films display magnetic properties (M_s, T_c) and structural properties identical to those of the raw (bulk) material Fig. 2. The measured room-temperature magnetoresistance of a piece of screen printed film is shown in Fig. 12.

We note that at room-temperature the MR values are in the range

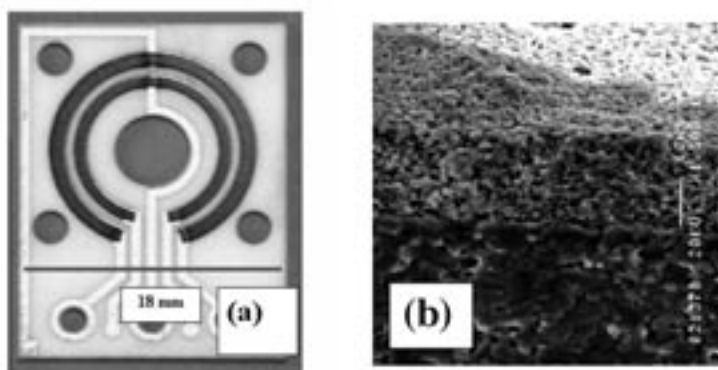


Figure 9. a) The sensitive part (in black) of a contact-less potentiometer; b) Transverse SEM view of a screen-printed LSMO film on Al₂O₃ substrate.

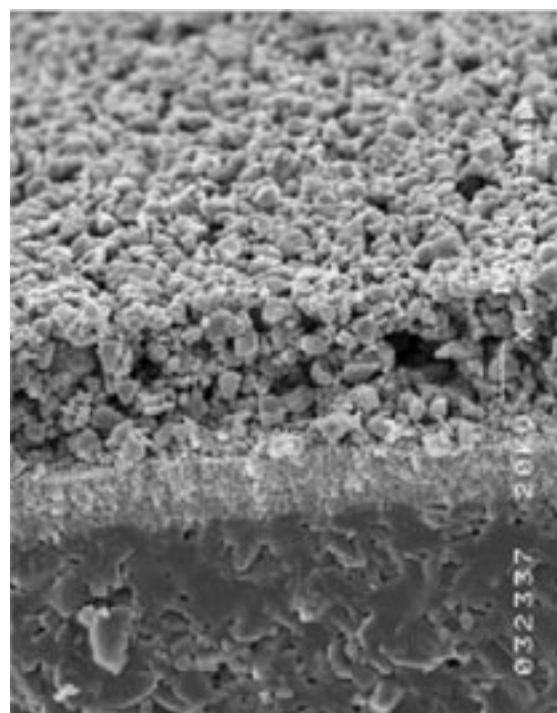


Figure 11. Transverse SEM view of a SFMO thick film screen-printed on top of a buffered Al₂O₃ polycrystalline substrate.

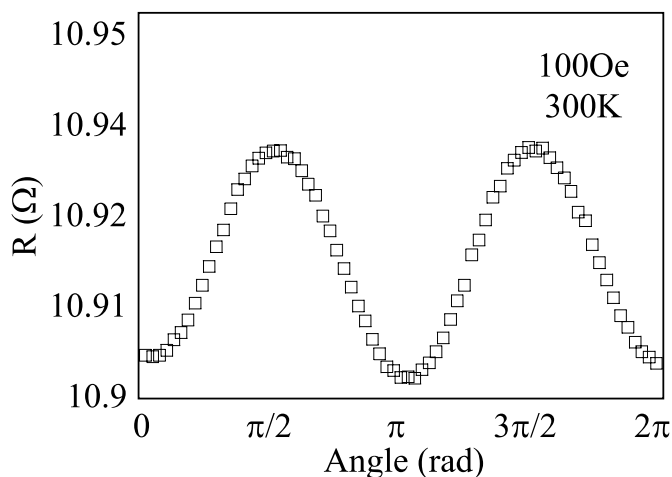


Figure 10. Room-temperature output signal of the device of Fig. 9.

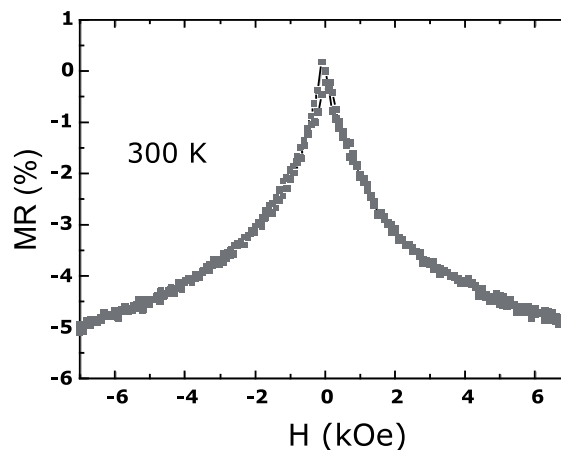


Figure 12. Room-temperature magnetoresistance of a SFMO screen-printed film

of 1.5-3% at 1kOe. This value is in the range of that obtained from bulk ceramic samples and suggests that the material is now ready to be included in a functional device. However, it shall be mentioned that, so-far, although laboratory tests have been successful, attempts to transfer technology to a industry-scaled process has given a much more modest values of magnetoresistance and thus more work is still to be done. Indeed, much work is needed to understand the microstructure of intergranular junctions in these materials.

4. IS THERE A CHANCE FOR FURTHER RISING OF THE CURIE TEMPERATURE?

The discovery of new metallic ferromagnets having Curie temperatures above that of the pristine $\text{Sr}_2\text{FeMoO}_6$ could have impact on the science of materials for magnetoelectronics. Although it has been reported that $\text{Sr}_2\text{FeReO}_6$ may have a T_c of about 500K, Re-based materials face significant cost problems. So it would be highly desirable to obtain ferromagnetic metals based on SFMO oxides.

In order to progress in this direction a necessary step is to understand the origin of the ferromagnetic coupling in these oxides. In the families of compounds here discussed (manganites and Fe-Mo double perovskites) we have shown [19] that a double exchange mechanism operates. That means that the ferromagnetic coupling between the orientations of localized atomic moments ($S=3/2$ in $3d^3$ in manganites or $S=5/2$ in $3d^5$ in SFMO) is mediated by the itinerant carriers of the conduction band. The strength of the ferromagnetic coupling is thus controlled by the carrier mobility in the conduction band and the density of charge carriers. Therefore a possible strategy to enhance T_c could be to dope SFMO oxides with electrons. Indeed, this has been successfully achieved by partial substitution of the divalent Sr^{2+} ions by trivalent Ln^{3+} ($\text{Ln} = \text{La}$ and Nd) ions in $\text{Sr}_{2-x}\text{Ln}_x\text{FeMoO}_6$ [20,21,22]. As illustrated in Fig. 13, the Curie temperature of the $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ doped oxide rises substantially -more than 70K- above that of the undoped material, reaching about 480K for $x=0.5$. Therefore it appears that there are alternatives for rising T_c by electron doping. Extensive neutron diffraction experiments have allowed to determine that the mean $\langle\text{Fe}(\text{Mo})\text{-O}\rangle$ distance expands upon La^{3+} substitution. This is just what one should expect from carrier injection into the antibonding Fe-O-Mo orbitals [23, 24]. Recent photoemission experiments have also confirmed that the density of states at the Fermi level increases with the La content [25].

Naturally, for the operation of these materials as ferromagnetic electrodes, the magnetization should also be large. Unfortunately in the $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ oxides synthesized so far, the Fe/Mo antisite disorder is large. It increases gradually with La doping and thus the magnetization of the sample is reduced. This effect, in part is due to the fact that electrons are injected mainly into Mo^{6+} states. It follows that the driving force for the ordering of Fe/Mo species in the SFMO structure -which is mainly controlled by the charge difference between these ions- shall be reduced [21]. It is nowadays unknown if improved synthesis conditions may allow to overcome this severe drawback and to take advantage of the enhancement of T_c in these electron doped oxides.

5. TRANSFER OF TECHNOLOGY

The results reported in the previous sections have been obtained using raw materials synthesized by solid-state reaction of the corresponding precursors. This approach may not be the most appropriate for an eventual large scale production of the

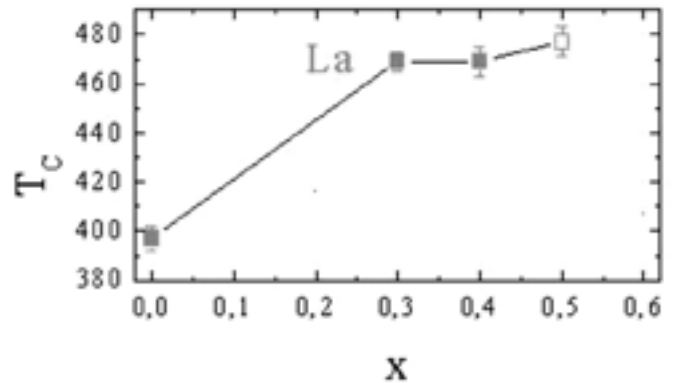


Figure 13. Variation of the Curie temperature of $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ upon La substitution (x) as deduced from neutron diffraction experiments.

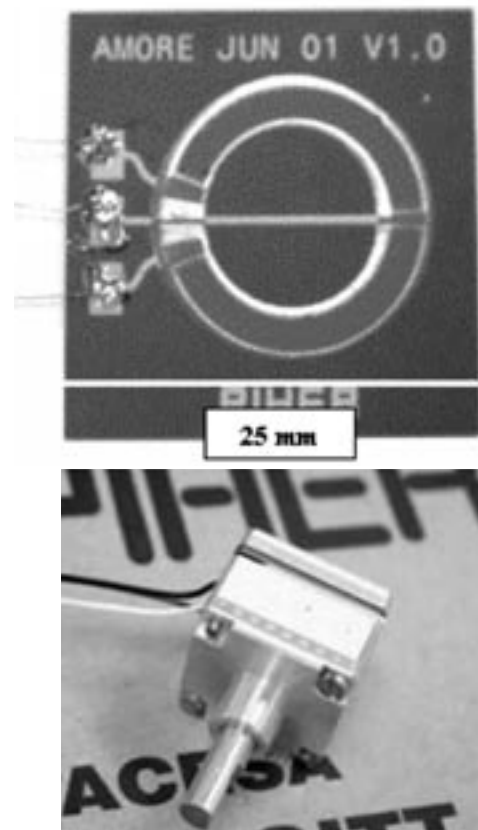


Figure 14. Layout (top) of the active part of an assembled contact-less magnetoresistive potentiometer (bottom).

magnetoresistive powders. Therefore, one of the industrial teams involved in this Project has undertaken the development of a different route of synthesis involving low-temperature processes. Nowadays, the synthesis protocols of LSMO and SFMO have been completed and optimized and materials with similar characteristics as those obtained from solid state reaction can be produce at larger batches.

Regarding the thick films of these oxides, the achievements can be summarized as follows. Films of LSMO can now be produced at industrial premises and the magnetoresistive properties of the films have been optimized and the films implemented in functional prototypes. A fully assembled and packaged LSMO-based contact-less potentiometer is shown in Fig. 14.

6. CONCLUSIONS.

Magnetoresistive manganese perovskites have proved to be useful for the development of field sensitive magnetic sensors operative at room temperature. In fact, some devices based on screen-printed polycrystalline materials oxides have been built showing that there is some possible niches for applications. We have shown here that performance of these devices can be further improved by taking advantage of the anisotropic magnetoresistance that can be added to the LFMR naturally occurring across grain boundaries. However, the fast decay of the LFMR with temperature and the fact that the Curie temperature remains critically low represent serious drawbacks for applications requiring operation temperatures up to 150-180°C. We have shown that interfaces in manganese perovskites are prone to phase separation and tend to be electronically inhomogeneous. Although if this key observation could be at the origin of the reduction of LFMR with temperature remains to be elucidated, it strongly signals an important role of interfaces and the concomitant stress/strain, reconstruction, etc phenomena occurring there.

In any event, half-metallic ferromagnets of higher Curie temperature are needed. Progress on crystallochemistry of double perovskites such as $\text{Sr}_2\text{FeMoO}_6$, has been impressive and nowadays oxides of almost ideal bulk properties can be prepared. However, detailed understanding of the LFMR in these oxides and the nature of grain boundaries remain elusive. Shaping of materials suitable for some applications is also starting and in addition to tremendous progress in thin film preparation, thick films are already available. However much efforts on microstructural and structural analysis are required in order to understand and progress controlling the LFMR. Recent results on possible ways to further rise the Curie temperature in double perovskites are encouraging and there is room for new ideas and progress. However other magnetic oxides shall not be neglected and particularly magnetite may offer some advantages if reproducible synthesis of optimal materials is achieved.

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BIBLIOGRAFÍA

1. J. Fontcuberta, "Colossal magnetoresistance", *Physics World*, pp.33, February 1999; J. Fontcuberta, L. Balcells, M. Bibes, J. Navarro, C. Frontera, J. Santiso, J. Fraxedas, B. Martínez, S. Nadolski, M. Wojcik, E. Jedryka and M.J. Casanove, "Magnetoresistive oxides: new developments and applications", *J. Magnetism and Magnetic Materials*, **242-245** 98-104 (2002)
2. M. Viret, M. Drouet, J. Nassar, J. P. Contour, C. Fermon and A. Fert, "Low-field colossal magnetoresistance in manganite tunnel spin valves", *Europhys. Lett.* **39** 545-549 (1997)
3. J. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, "Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films", *Science* **264** 413-415 (1994); K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, "Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure", *Nature (London)* **395** 677-680 (1998).
4. J. Fontcuberta, B. Martínez, A. Seffar, J.L. García-Muñoz, S. Piñol, X. Obradors, "Colossal Magnetoresistance of Ferromagnetic Manganites: Structural Tuning and Mechanisms", *Phys. Rev. Lett.* **76** 1122-1125 (1996).
5. Ll. Balcells, J. Navarro, M. Bibes, A. Roig, B. Martínez and J. Fontcuberta, "Cationic ordering control of magnetization in $\text{Sr}_2\text{FeMoO}_6$ double perovskite", *Appl. Phys. Lett.* **78** 781-783 (2001).
6. J. Navarro, J. Nogués, J.S. Muñoz and J. Fontcuberta, "Antisites and electron-doping effects on the magnetic transition of $\text{Sr}_2\text{FeMoO}_6$ double perovskite", *Phys. Rev. B* **67** 1744161-1744166 (2003).
7. J. Navarro, C. Frontera, D. Rubi, N. Mestres and J. Fontcuberta, "Aging of $\text{Sr}_2\text{FeMoO}_6$ and related oxides", *Mat. Res. Bull.* **38** 1477-1486 (2003)
8. H.Y. Hwang, S.W. Cheong, P.G. Radaelli, M. Marezzio and B. Batlogg, "Lattice Effects on the Magnetoresistance in Doped LaMnO_3 ", *Phys. Rev. Lett.* **75** 914-917 (1995)
9. Ll. Balcells, J. Fontcuberta, B. Martínez, and X. Obradors, "High-field magnetoresistance at interfaces in manganese perovskites", *Phys. Rev. B* **58** R14697-R14700 (1999).
10. J. Fontcuberta, L. Balcells, M. Bibes, J. Navarro, C. Frontera, J. Santiso, J. Fraxedas, B. Martínez, S. Nadolski, M. Wojcik, E. Jedryka and M.J. Casanove, "Magnetoresistive oxides: new developments and applications", *J. Magnetism and Magnetic Materials*, **242-245** 98-104 (2002)
11. M. Bibes, Ll. Balcells, S. València, J. Fontcuberta, M. Wojcik, E. Jedryka and S. Nadolski, "Nanoscale Multiphase Separation at $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3/\text{SrTiO}_3$ Interfaces", *Phys. Rev. Lett.* **87** 672101-672104 (2001)
12. M. Bibes, Ll. Balcells and J. Fontcuberta; M. Wojcik, S. Nadolski, E. Jedryka, "Surface-induced phase separation in manganites: A microscopic origin for powder magnetoresistance", *Appl. Phys. Lett.* **82** 928-930 (2003)
13. Ll. Balcells, A.E. Carrillo, B. Martínez and J. Fontcuberta, "Enhanced field sensitivity close to percolation in magnetoresistive $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{CeO}_2$ composites", *Appl. Phys. Lett.* **74** 4014-4016 (1999)
14. J. Navarro, Ll. Balcells, F. Sandiumenge, M. Bibes, A. Roig, B. Martínez and J. Fontcuberta, "Antisite defects and magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$ double perovskite", *J. Phys.: Condens. Matter* **13** 8481-8488 (2001); J. Navarro, Ll. Balcells, B. Martínez, and J. Fontcuberta, "Paramagnetic susceptibility and ferromagnetism in $\text{Sr}_2\text{FeMoO}_6$ perovskites", *J. Appl. Phys.* **89** 7684-7686 (2001)
15. D. Niebikikwiat, A. Caneiro, R.D. Sánchez, J. Fontcuberta, "Oxygen-induced grain boundary effects on magnetotransport properties of $\text{Sr}_2\text{FeMoO}_{6-\delta}$ ", *Phys. Rev. B* **64** R1804061-R1804064 (2001)
16. Ll. Balcells, R. Enrich, A. Calleja, J. Fontcuberta and X. Obradors, "Manganese perovskites: Thick-film based position sensors fabrication", *Appl. Phys. Lett.* **69** 1486-1488 (1996)
17. Ll. Balcells, R. Enrich, A. Calleja, J. Fontcuberta and X. Obradors, "Designing and testing of a sensor based on a magnetoresistive manganese perovskite thick film", *J. Applied Phys.* **81** 4298-4300 (1997). Ll. Balcells, J. Cifre, A. Calleja, J. Fontcuberta, M. Varela and F. Benítez, "Room-temperature magnetoresistive sensor based on thick films manganese perovskite", *Sensors and Actuators* **81** 64-66 (2000). Ll. Balcells, E. Calvo and J. Fontcuberta, *J. Magnetism and Magnetic Materials*, "Room-temperature anisotropic magnetoresistive sensor based on manganese perovskite thick films", **242-245** 1166-1168 (2002).
18. L. Durand, Ll. Balcells, A. Calleja, J. Fontcuberta and X. Obradors, "Screen printed $\text{La}_2/3\text{Sr}_{1/3}\text{MnO}_3$ thick films on alumina substrates", *J. Mater. Res.* **13** 2623-2631 (1998)
19. S. Valencia, O. Castañó, J. Fontcuberta, B. Martínez and Ll. Balcells, "Enhanced low field magnetoresistive response in $(\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3)/(\text{CeO}_2)_{1-x}$ composite thick films prepared by screen printing", *J. Appl. Phys.* **94** 2524-2528 (2003)
20. M. Tovar, M. Causa, A. Butera, J. Navarro, B. Martínez, J. Fontcuberta and M. Passegi, "Evidence of strong antiferromagnetic coupling between localized and itinerant electrons in ferromagnetic $\text{Sr}_2\text{FeMoO}_6$ ", *Phys. Rev. B* **66** 0244091-0244095 (2002)
21. J. Navarro, C. Frontera, L. Balcells, B. Martínez and J. Fontcuberta, "Raising the Curie temperature in $\text{Sr}_2\text{FeMoO}_6$ double perovskites by electron doping", *Phys. Rev. B* **64** 0924111-0924114 (2001)
22. D. Sánchez, J.A. Alonso, M. García-Hernandez, M.J. Martínez-Lope, M.T. Casais and J.L. Martínez, "Microscopic nature of the electron doping effects in the double perovskite $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ ($0 \leq x \leq 1$) series", *J. Mater. Chem.* **13** 1771-1777 (2003)
23. D. Rubi, C. Frontera, J. Nogués, and J. Fontcuberta, "Enhanced ferromagnetic interactions in electron-doped $\text{Nd}_{1-x}\text{Sr}_x\text{FeMoO}_6$ double perovskites", *J. Phys.: Condens. Matter*, **17**, 3173-3182 (2004).
24. C. Frontera, D. Rubi, J. Navarro, J.L. García-Muñoz, J. Fontcuberta and C. Ritter, "Effect of band filling and structural distortions on the Curie temperature of Fe-Mo double perovskites", *Phys. Rev. B* **68** 0124121-0124124 (2003)
25. J. Navarro, J. Fontcuberta, M. Izquierdo, J. Avila, and M. Asensio, "Curie temperature enhancement of electron doped $\text{Sr}_2\text{FeMoO}_6$ perovskites studied by photoemission spectroscopy", *cond-mat/0303464*, *Phys. Rev. B* in press (2003).