

Magnetic Properties of Mixed Valence La(AgSr)MnO₃ Manganites Obtained by Solid-State Reaction Method

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In this work, we present a systematic study on the effect of monovalent and divalent cation inclusion on the magnetic properties of the manganites series La_{0.80}(Ag_{1-x}Sr_x)_{0.20}MnO₃ ($x = 0.0$ – 1.0) synthesized by the solid-state reaction method. The decreasing Sr:Ag proportion across the compositional series was verified by X-ray photoelectron spectroscopy. Concerning magnetic properties, the hysteresis curves manifested an initial paramagnetic response at $x = 0.0$, followed by a progressive ferromagnetic behavior with an optimum Ag:Sr ratio at $x = 0.75$, for which an enhanced saturation magnetization of 51 Am²/kg and a Curie temperature of 336 K were recorded. Results are explained on the basis of the effect of the increasing unit cell volume on the double exchange interaction between magnetic Mn³⁺–Mn⁴⁺ atoms.

I. Introduction

LANTHANUM–manganese-based perovskites, also known as “manganites”, with mixed valence substitutions described by the formula La_{1-x}A_xMnO₃ (where A can be a divalent metal like Ca, Ba, or Sr or a monovalent cation like Ag, Na, or K) have been a subject of intense research due to their interesting electronic properties, which include a variety of phenomena like colossal magnetoresistance, charge ordering, isotopic effect, phase separation, and magnetocaloric effect, together with multiple possible magnetic states, such as canted antiferromagnetic, paramagnetic isolator, ferromagnetic isolator, ferromagnetic metallic, and antiferromagnetic.^{1–3} In particular, divalent substitution represented by partial La³⁺ replacement by Sr²⁺ have shown to be effective for tailoring magnetic properties such as the saturation magnetization M_s and Curie temperature T_c .^{4–6} Large variations as large as $\Delta T_c = 200$ K have been reported for Sr contents x between 0.1 and 0.50 for La_{1-x}Sr_xMnO₃ series⁷ together with intermediate M_s values (around 35 Am²/kg, compared with La_{1-x}Ca_x systems with high M_s around 50 Am²/kg⁶) for Sr concentration lower than $x = 0.30$ at room temperature.^{4,6,8} This marked dependence of the magnetic response with the Sr concentration has been explained in terms of the influence of the divalent atoms affecting the superexchange mechanism in favor of the double exchange interaction, which leads to higher T_c and M_s . In addition, the crystal structural deformation caused by the incorporation of large Sr atoms (with respect to O and Mn ions) significantly influences the charge-carrier band structure and hence, the electronic properties of these materials.^{4–6} For instance, a change in order–disorder magnetic transition type (from first to second order) has been described as a result of the increasing Sr

concentration in La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO₃ polycrystalline manganites.⁶ Monovalent partial substitution of La³⁺ by Ag⁺ has been also reported as having a noticeable influence on the magnetic response of La_{1-x}Ag_xMnO₃ manganites through the increasing number of Mn³⁺–Mn⁴⁺ ion pairs (according to the formula La³⁺_{1-x}Ag_xMn³⁺_{1-2x}Mn⁴⁺_{2x}O²⁻₃) which in turn, enhances the double exchange interaction and hence, leading to significant improvements for both M_s and T_c .⁹ In addition, when the amount of Mn⁴⁺ is fixed, the progressive inclusion of large monovalent ions induces marked variations on the ionic radius of the La site within the perovskite structure, affecting the Mn–O bonding distance as well as the Mn–O–Mn angle, and thus, the magnetic properties.¹⁰ Similar effects have been reported for Na and K partial substitutions by La.^{11,12} Unfortunately, these La_{1-x}Ag_xMnO₃ manganites are characterized by rather low saturation magnetization values, well below 20 Am²/kg for Ag contents x lower than 0.20 at room temperature,^{9,10,13} which represent an important disadvantage for potential technological applications, such as the magnetocaloric effect.^{2,3} In this work, we explore the enhancement of the double exchange interaction for saturation magnetization improvement in La-based manganites by means of a systematic unit cell expansion induced by variable monovalent:divalent proportion via partial substitution of the La³⁺ cation by Ag⁺ and Sr²⁺.

II. Experimental Procedures

The polycrystalline manganites series La_{0.80}(Ag_{1-x}Sr_x)_{0.20}MnO₃ ($x = 0.00, 0.25, 0.50, 0.75, 1.0$) was prepared by the solid-state reaction method with the following precursors: La₂O₃ (99.99%), MnO₂ (99.99%), AgO (II) (99.99%), and Sr(NO₃)₂ (II) (99.99%), which were weighted according to stoichiometric calculations and mixed for each case for a calcination process at 900°C for 12 h. A subsequent sintering at 1100°C for 48 h was carried out on pellets obtained from re-pulverized samples. The phase distribution was characterized by means of XRD analysis in a Bruker D8 Adv AXS diffractometer (Bruker, Karlsruhe, Germany) with CuK α radiation. In addition, the Ag content across the compositional series was verified by means of X-ray photoelectron spectroscopy (XPS) in a VG Microtech Multilab ESCA2000 coupled with a CLAM4 MCD detector (VG Microtech, Sussex, UK) with AlK α radiation. The elemental analysis was carried out using the sensitivity relative factor reported by Scofield¹⁴ and by correcting the transmission function of the electron analyzer with the reference materials La₂O₃, SrCO₃, MnO, and AgO. The XPS spectra were fitted with the program SDP v4.1.¹⁵ The magnetic properties were determined by means of a LDJ 9600 Vibrating Sample Magnetometer (VSM; LDJ Electronics, Troy, MI) at a maximum applied field of 1200 kA/m.

III. Results

XRD diffractograms for the compositional series La_{0.80}(Ag_{1-x}Sr_x)_{0.20}MnO₃ is shown in Fig. 1, for which the

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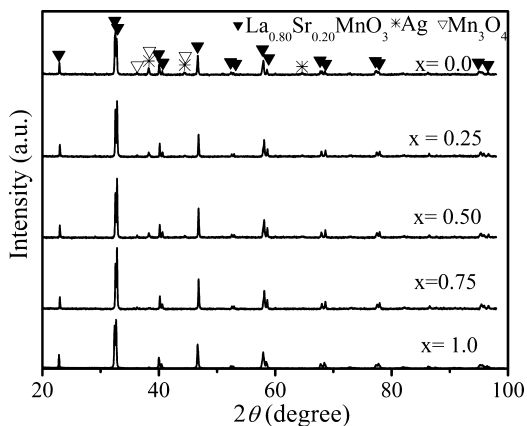


Fig. 1. XRD diffractograms for the compositional series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$.

main phase was identified as perovskite with rhombohedral symmetry ($R\bar{3}c$ space group, ICDD-PDF 00-053-0058). Minor peaks corresponding to secondary phases, namely metallic Ag (PDF 03-065-2871) and Mn_3O_4 (PDF 01-080-0382), were also observed. The intensity of the secondary peaks decreases with increasing Sr concentration and, for the LaSr-containing sample, no secondary phases were recorded. This phase distribution is consistent with previous reports concerning $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ manganites.^{9,10,15} The role of the secondary phases on the magnetic behavior of present manganites is negligible as metallic silver is nonmagnetic, while Mn_3O_4 is paramagnetic over a very wide temperature range, including room temperature. In fact, its ordering temperature (Neel temperature) is as low as 43 K.¹⁶

To determine the variation in the unit cell parameters a and c (hexagonal coordinates) caused by the progressive incorporation of Sr^{2+} ions, the metallic Ag was considered as internal standard, for which the reflection (220) at $2\theta = 44.30^\circ$ was taken as a reference to quantify the variation in the interplanar distances caused by the unit cell changes. Such dependence with the Sr content is displayed in Fig. 2, for which an increasing tendency is observed for both parameters [Fig. 2(a)–(b)] as the divalent ion concentration x increases up to $x = 0.75$. For $x = 1.0$, a reduction in the unit cell parameters is manifested. The unit cell volume V follows the same trend. This unit cell volume variation is consistent with other reports concerning $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ ^{10,13} and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ^{7,8} manganites, for which an increasing tendency of V was described for low Ag content, while, on the other hand, a systematic decrease in the unit cell volume was

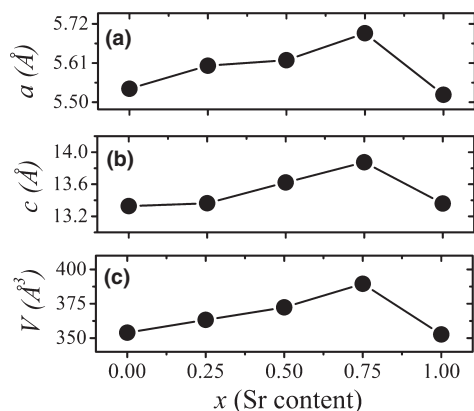


Fig. 2. Unit cell parameters a , c (hexagonal coordinates), and the associated volume V as a function of Sr content x for the compositional series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$. The connecting line does not represent a mathematical fitting.

observed for increasing Sr concentration. Hence, for present $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ perovskites, we found that the increasing V effect—afforded by the reducing Ag content—is predominant over the decreasing effect of Sr incorporation up to $x = 0.75$, whereas at $x = 1.0$, the total Ag replacement by Sr yields the smaller unit cell parameters reported. These contradictory effects can be attributed to the influence of Ag^+ and Sr^{2+} atoms on the formation of Mn^{4+} and Mn^{3+} cations, as explained in the “Introduction” section, since the ratio $\text{Mn}^{4+}/\text{Mn}^{3+}$ also affects the unit cell volume due to the difference between the ionic radii of such atoms, $\langle r_{\text{Mn}^{3+}} \rangle = 0.6245 \text{ \AA}$ and $\langle r_{\text{Mn}^{4+}} \rangle = 0.530 \text{ \AA}$.¹⁷

An important aspect in this work is to determine whether the Ag^+ ions are entering into the unit cell structure of the rhombohedral main phase. To verify this, Fig. 3 displays the XPS results for the compositional series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$. The 3d orbital signals of Ag (3/2 and 5/2 transitions) exhibits a decreasing intensity, i.e., a diminishing Ag content for increasing Sr concentration x . In agreement with this, the deconvolution of such signals (Fig. 4) reveals that the majority of the Ag atoms present a bonding energy considerably shifted from the metallic state (Ag^0) and from the precursor AgO (Ag^{2+}), which implies a monovalent state Ag^+ , and thus, silver atoms being part of the rhombohedral unit cell. The elemental analysis confirmed decreasing Ag concentrations of 2.4, 1.9, 1.7, 0.5, 0.0 (at.%) for increasing Sr content $x = 0.0, 0.25, 0.50, 0.75, 1.0$, respectively, with marginal decreasing metallic Ag (from 0.5 at.% to 0.2 at.%) up to $x = 0.75$. No silver atoms were detected for $x = 1.0$.

Concerning magnetic properties, the hysteresis loops of magnetization M versus applied field H for the whole manganites series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ at room temperature are shown in Fig. 5. An initial paramagnetic response at $x = 0.0$ (manifested as a linear M – H plot), evolves progressively toward an enhanced ferromagnetic behavior, for which increasing saturation magnetization M_s values are observed up to $x = 0.75$, followed by a shallow decrease at $x = 1.00$ (inset, Fig. 5). The paramagnetic response for $x = 0.0$ is in agreement with previous reports on solid-state reaction prepared $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ manganites with $x \leq 0.20$.^{9,18–20} The Curie temperature T_c across the compositional series (determined from thermomagnetization curves obtained by means of a fixed applied field of 50 Oe and variable temperature) is shown in Fig. 6. An equivalent increasing tendency of T_c is manifested for increasing Sr content up to $x = 0.75$, for

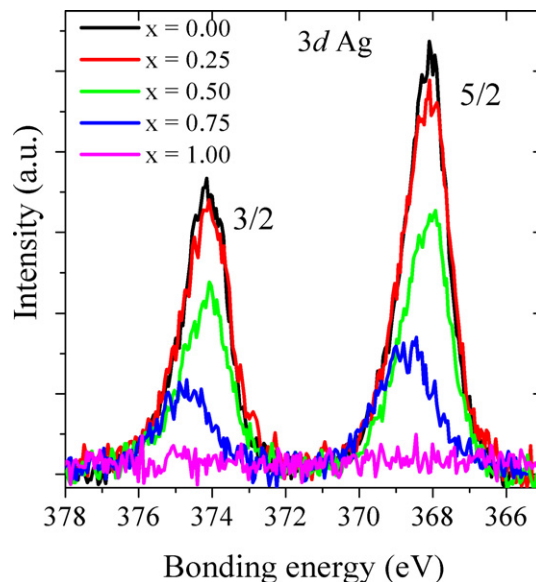


Fig. 3. XPS results for the compositional series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$. The signals corresponding to the 3/2 and 5/2 transitions for the 3d orbital of Ag exhibits a decreasing intensity for increasing Sr concentration x , which reflects the decreasing Ag concentration.

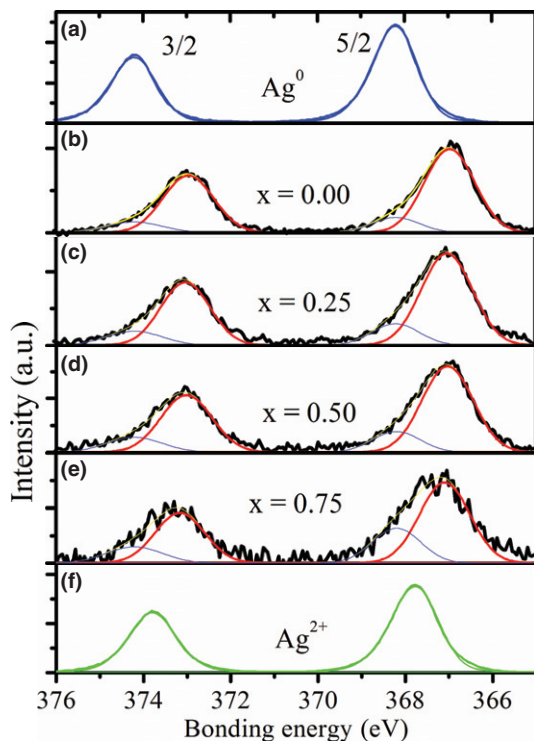


Fig. 4. XPS results for the compositional series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$. Deconvolution of signals displayed in Fig. 3. The majority of the Ag atoms present a bonding energy considerably shifted from the metallic state (Ag^0) and from the precursor AgO (Ag^{2+}), which implies a monovalent state Ag^+ (The contribution of metallic Ag -blue line- is subtracted from the experimental signal -irregular, black line-. The resulting line is shown in red).

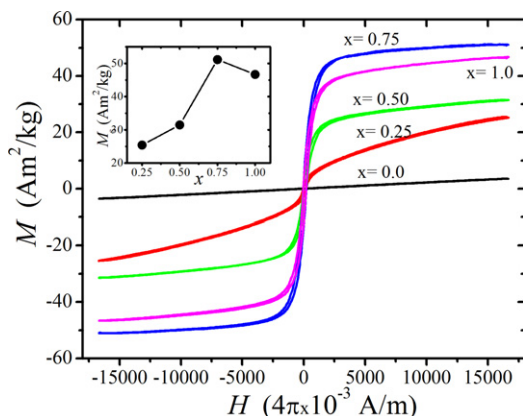


Fig. 5. Hysteresis curves (M - H) for the manganites series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$. Inset: Saturation magnetization as a function of the Sr content x .

which a maximum of 336 K is attained, followed by a slight reduction at $x = 1.0$. The observed increasing ferromagnetic ordering with augmenting Sr content is also congruent with increasing M_s and T_c values described for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxides.^{4,5,8,21,22} In fact, present M_s values for $x \geq 0.50$ (between 31 and 51 emu/g, inset Fig. 5) represent a considerable enhancement with respect to the low-magnetization $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ manganites (with M_s well below 20 Am^2/kg for $x \leq 0.20$ ^{9,10,13}) and the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxides with intermediate saturations (around 35 Am^2/kg for $x \leq 0.30$ ^{4,6,8}). Therefore, an optimum Ag:Sr ratio can be established for our $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ series at $x = 0.75$ with maximum $M_s = 51$ emu/g. and $T_c = 336$ K.

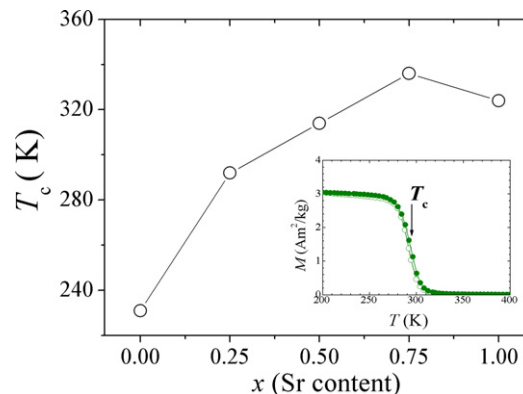


Fig. 6. Curie temperature T_c for the manganites series $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ as a function of Sr content x . Connecting lines do not represent a mathematical fitting. Inset: Thermomagnetic curve corresponding to the $\text{La}_{0.80}(\text{Ag}_{0.75}\text{Sr}_{0.25})_{0.20}\text{MnO}_3$ manganite as an example for T_c determination. Open/closed symbols indicate cooling and heating measurements, respectively

IV. Discussion

The enhancement of the ferromagnetic response observed on the mixed valence $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ manganites with increasing Sr content can be explained in terms of the influence of the crystal structure on the double exchange mechanism, which is fundamental for the magnetization and Curie transition in these kinds of materials. According to Zener,²³ the intra-atomic Hund's rule exchange is strong in atoms with 3d electrons, so the charge carrier can only hop from one ion to the next if the spins of the two ions are parallel (i.e., ferromagnetically ordered). The exchange interaction between Mn^{3+} and Mn^{4+} cations via an oxygen ion, for which a simultaneous transfer of an electron from the Mn^{3+} (with configuration $t_{2g}^3e_g^1$) to the oxygen and from this to the neighboring Mn^{4+} (with configuration $t_{2g}^3e_g^0$), was termed as "double exchange" (DE) by Zener.²³ This ferromagnetic Mn^{3+} - Mn^{4+} interaction is favored when the atoms of the transition metal are fairly separated and conduction electrons are present. For instance, starting from an initial insulating antiferromagnetic LaMnO_3 phase (with valence states $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3^{-2}$) where electrons are localized on the atomic orbitals, Zener showed how the system should gradually become more ferromagnetic after creation of holes via the electron deficit provoked by the introduction of Mn^{4+} cations (to maintain charge neutrality), which in turn results from the partial replacement of La^{3+} for Ca^{2+} through the substitutional formula $(\text{La}_{1-x}\text{Ca}_x^{2+})(\text{Mn}_{1-x}\text{Mn}_x^{4+})\text{O}_3$.²⁴ Apart from the hole formation provoked by the incorporation of Ca^{2+} cations, a significant concomitant effect on the DE is the crystal structure variation induced by atoms with different ionic radii compared with La^{3+} , since the overlap between manganese d -orbitals and oxygen p -orbitals that forms the electronically active band (or W charge-carrier band) can be strongly influenced by the internal stress generated by La partial substitution with cations of distinct radii.^{25,26} This internal stress caused by the mismatching atoms is accompanied by variations in the Mn-O-Mn angles. For the present $\text{La}(\text{AgSr})\text{MnO}_3$ manganites, the observed increasing unit cell volume for Sr contents up to $x = 0.75$ (Fig. 2), suggest an increasing Mn-O-Mn bond angle, i.e., being closer to 180° . In fact, such angle has been estimated as 163.5° for $\text{La}_{0.80}\text{Ag}_{0.20}\text{MnO}_3$ ¹⁰ and 167.7° for $\text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3$,⁸ and thus, an increasing tendency is feasible up to $x = 0.75$. The augmenting Mn-O-Mn angle favors a wider W charge-carrier bandwidth that facilitates electron transfer between Mn^{3+} and Mn^{4+} atoms, which implies an enhanced double exchange interaction and thus, improved ferromagnetic coupling between such cations yielding superior magnetic properties with increasing Sr content up to $x = 0.75$. Such

crystal structure-magnetic response correlations have been established for similar $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ manganite series.^{4,5,8,21,22,26} For the final composition ($x = 1.0$), the observed decrease in the unit cell volume of the $\text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3$ phase implies a reduction in the Mn–O–Mn angle and consequently, a weakening of the double exchange via a narrower W bandwidth, which leads to the observed reduction in the M_s and T_c properties.

V. Conclusions

The inclusion of monovalent and divalent cations for the $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ manganites series causes a noticeable variation in their unit cell volume as a function of the Sr content, which improves the double exchange interaction between Mn^{3+} and Mn^{4+} ions up to $x = 0.75$ through wider W charge-carrier bandwidth that facilitates electron transfer between Mn^{3+} and Mn^{4+} atoms, and consequently, the magnetic response rises rapidly from an initial paramagnetic state for $x = 0.0$, to the optimum composition $\text{La}_{0.80}(\text{Ag}_{0.25}\text{Sr}_{0.75})_{0.20}\text{MnO}_3$, for which a maximum saturation magnetization value of $51 \text{ Am}^2/\text{kg}$ was recorded together with a maximum Curie temperature of 336 K .

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