Structural properties, electric response and magnetic behaviour of La$_2$SrFe$_2$CoO$_9$ triple complex perovskite

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Abstract. The triple perovskite La$_2$SrFe$_2$CoO$_9$ was prepared by the solid state reaction method from the high purity precursor powders La$_2$O$_3$, SrCO$_3$, Fe$_2$O$_3$, Co$_2$O$_3$ (99.9%). The crystalline structure was studied by X-ray diffraction experiments and Rietveld refinement analysis. Results reveal that this material crystallizes in an orthorhombic triple perovskite belonging to the space group Pnma (#62) with lattice constants $a=5.491978(2)$ Å, $b=7.719842(2)$ Å and $c=5.436260(3)$ Å. The granular surface morphology was studied from images of Scanning Electron Microscopy. The electric response was studied by the Impedance Spectroscopy technique from 10.0 mHz up to 0.1MHz, at different temperatures (77–300K). Measurements of magnetization as a function of temperature permitted to determine the occurrence of a paramagnetic – ferromagnetic transition for a Curie temperature of 280K, which suggests its application in nanoelectronic devices. From the fit of the magnetic response with the Curie-Weiss equation it was concluded that the effective magnetic moment is particularly large due to the contribution of La, Fe and Co cations.

1. Introduction

Ceramic materials represent a great percentage of systems which are actually investigated by the physics and chemistry of solids because their interesting properties. Particularly, the perovskite family has concentrated important attention in last decades. From the point of view of chemical composition, perovskites have been characterized by the ideal formula ABX$_3$, where A generally is an alkaline earth element, B represents a transition metal or rare earth element and X, more of times, is the oxygen [1]. Modifications of atomic radii of A and B, introduces structural distortions and new crystalline phases. Inclusions of rare earth elements instead the alkaline earth in the A site, and magnetic elements in the B site, give the possibility to produce materials with exotic electric and magnetic properties [2,3]. Partial substitutions of the A and B cations give rise to complex materials as the triple perovskites A$_2$A’B$_2$B’O$_9$ [4]. It chemical configuration supplies multiple chances to combine different elements, generating the possibility to synthesize new materials, which involve a more large gamma of physical properties. Depending on magnetic and electric characteristics of A, A’, B and B’, it is relatively simple to create new perovskite systems with half-metallic properties [5], magnetoelectric response [6] or magnetic ordering [7], which offer promissory perspectives in the new spintronics technology [8]. In order to analyse the possibility to create new magnetic perovskite materials, in this work we report the synthesis, the structural characterization and the electronic properties of the new triple perovskite La$_2$SrFe$_2$CoO$_9$, which was idealized as the introduction of the lanthanide La in the A site, the alkaline earth Sr in A’, and the magnetic transition metals Fe and Co in the B and B’ locations of the A$_2$A’B$_2$B’O$_9$ formula, in order to construct a triple complex perovskite.
2. Experimental
The samples were synthesized by the solid state reaction recipe. The precursor powders \( \text{La}_2\text{O}_3, \text{SrCO}_3, \text{Fe}_3\text{O}_3 \) and \( \text{Co}_3\text{O}_4 \) (Aldrich 99.9%) were mixed in stoichiometric proportions. Mixture was ground to form a pellet and annealed at 1100°C for 48h. The sample was then reground, repelletized and sintered at 1200°C for 48h. X-Ray diffraction (XRD) experiment was performed by means a PW1710 diffractometer with \( \lambda_{\text{CuK}\alpha}=1.5406\text{Å} \). Rietveld refinement of diffraction pattern was carried out by the GSAS code [9]. Scanning Electron Microscopy (SEM) images and Electron Dispersive X-ray spectra were obtained by the utilization of a VEGA 3 electronic microscope. Electrical impedance spectroscopy measurements were performed by the application of frequencies from 10.0mHz up to 0.10MHz and AC voltage of 10mV rms in the range of temperatures between 77K up to 300K. Measurements of magnetic susceptibility in the Zero Field Cooling (ZFC) and Field Cooling (FC) recipes and curves of magnetization as a function of applied fields were carried out by means a VersaLab Quantum Design equipment.

3. Results and discussion
The analysis of XRD pattern showed in Figure 1 reveals the presence of characteristic peaks of complex perovskite systems.

In Figure 1, crosses represent the experimental data and line corresponds to simulated pattern by means of GSAS code. Base line is the difference between theoretical and experimental results. Rietveld refinement permitted to establish that this material crystallizes in an orthorhombic triple perovskite, space group Pnma(#62), lattice constants \( a=5.491978(2)\text{Å} \), \( b=7.719842(2)\text{Å} \) and \( c=5.436260(3)\text{Å} \). These results show deviation of no more than 3% when compared with the theoretical values obtained from the Structure Prediction Diagnostic Software SPuDS [10], which predicts that lattice constants \( a=5.5286 \text{Å} \), \( b=7.7805\text{Å} \) and \( c=5.4756\text{Å} \) for the \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \) material. Parameters of refinement are: \( R_F^2=9.82\% \) and \( x^2=2.196 \). The numeric results of the Rietveld analysis are shown in the Table 1.

A qualitative approximation to the surface structure of the \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \) triple perovskite is obtained from the SEM technique as exemplified in Figure 2. The surface of material is constituted by sub-micrometric grains which form groups with appearance of clusters. These have a mean size of 5μm and appear strongly sintered with a texturized morphology in the external surface and granular, as gravel, with weak inter-granular coupling in the deepest regions.
Table 1. Atomic positions of cations and anions on the unit cell for \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \).

| Atom | Wyckoff Site | x     | y     | z     |
|------|--------------|-------|-------|-------|
| La   | 4c           | 0.5000| 0.2500| 0.4978|
| Sr   | 4c           | 0.5000| 0.2500| 0.5035|
| Fe   | 4b           | 0.0000| 0.0000| 0.5000|
| Co   | 4b           | 0.0000| 0.0000| 0.5000|
| O    | 4c           | 1.0120| 0.2500| 0.4745|
| O    | 8d           | 0.2739| 0.0382| 0.7401|

Measurements of Impedance Spectroscopy permit to establish the electric feature of the \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \) material. The impedance plots \( Z(\omega) \) or Nyquist plot are shown in Figure 3(a). This picture not only derives the information about the electrical properties of our compound but also gives an idea of the relaxation mechanism and the conductance in the material. The impedance spectrum is characterized by the appearance of semicircle arc whose patterns changes, but not its shape, when the temperature is decreased [11].

Figure 2. SEM image of \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \) material.

Figure 3. (a) Curve of Nyquist and (b) Bode diagram for the \( \text{La}_2\text{SrFe}_2\text{CoO}_9 \) material.

The Nyquist plot is related to the electrical processes occurring within the sample and their correlation with the microstructure of material. Figure 3(b) shows the variation of \( Z' \) as a function of the frequency for several temperatures. The impedance value is typically higher at lower temperatures in the low-frequency region and decreases gradually with increasing frequency. Also, \( Z' \) decreases
with increasing temperature, indicating an increase of the ac conductivity. The value of $Z'$ appears to merge in the high-frequency region irrespective of temperature. This result may possibly be related to the release of space charge as a result of the reduction in the barrier properties of material with rise in temperature, and may be a responsible factor for the enhancement of conductance of the material with temperature at high frequencies. The merge of the value of $Z'$ for all temperatures at higher frequencies can be interpreted by the presence of space charge polarization [12]. The magnetic response was studied in curves of susceptibility as a function of temperature on the application of constant fields $H=50$, 600, 1200, and 5000 Oe, as shown in figure 4(a). As observed in the picture, the temperature of ferromagnetic ordering is $T_C=280$K. Close to this temperature value an irreversibility occurs between the ZFC and FC susceptibility curves. This behaviour, which is characterized of disordered magnetic systems as spin glasses [13], is attributed to the cationic disorder of the La and Sr ions in the A and A' sites of the triple perovskite, and Fe and Co in the B and B' sites, because their values of ionic radii are very similar and its individual magnetic spins can have essentially different orientations, in groups or clusters of spins that respond in different ways under the application of an external magnetic field. In the ZFC procedure, when the temperature is decreased in absence of external field, these clusters of spins are frozen, so that the magnetic field and low temperature are not sufficient to break the correlation of exchange between them to orientate them in the direction of the external field. In the FC procedure, the temperature is decreased in the presence of magnetic field and all spin clusters are effectively oriented in the direction of the applied field. Therefore, in the ZFC-FC curve a bifurcation of the magnetic response has place, which results in a lower susceptibility to ZFC and higher for the other. Furthermore, magnetic irreversibility temperature $T_i$ is sensitive to the intensity of the applied magnetic field. As it is increased, the value of $T_i$ increases from $T_i=320$K for $H=500$Oe to $T_i=370$K for $H=1200$Oe. Subsequently, the value of $T_i$ begins to decrease until $T_i=275$K for $H=5000$Oe. This behavior may be due to the occurrence of a value limit of applied field, below which the sizes and the grain boundaries can contribute to increasing the value of $T_i$.

![Figure 4](image.png)

**Figure 4.** (a) Magnetic susceptibility as a function of temperature in the ZFC – FC procedures and (b) magnetization as a function of applied fields $H=50$, 600, 1200 and 5000 Oe for the La$_2$SrFe$_2$CoO$_9$ perovskite.

On the other hand, Figure 4(b) shows the hysteretic ferromagnetic behaviour of this material at low temperature values, below $T_C$. Magnetic parameters as coercive field $H_C=1.1$Koer and remnant magnetization $M_r=0.37$emu/g were obtained from the picture. We notice that no magnetization saturation is observed in this experimental result. However, a quasi-linear behaviour is observed in the moderately high field regime, which is typical of granular systems with sub-micrometric crystallite sizes, in accordance with the SEM images showed in Figure 2.
4. Conclusions
We have synthesized the La2SrFe2CoO9 complex perovskite by the standard solid reaction method. Structural characterization from XRD experiments and Rietveld refinement reveals that this material crystallizes in an orthorhombic triple perovskite belonging to the Pnma (#62) space group. SEM images showed the strongly sub-micrometric granular morphology of the material with crystallite clusters in the surface and weak coupled grains in the deepest regions. Impedance spectroscopy measurements reveal a systematic increase of the conductivity in this material as a function of the temperature. Results of the magnetic response in curves of susceptibility as a function of temperature permitted to determine the ferromagnetic character of this material with ordering temperature about 280K. Irreversibility between the ZFC and FC susceptibilities were observed and attributed to the cationic disorder of the Fe and Co magnetic cations. Eventually, the cationic disorder of La and Sr cations can be relevant due the strongly paramagnetic character of the La3+ ion. At last, from the hysteretic behaviour of magnetization as a function of applied fields the coercive field and remnant magnetization was characterized for this interesting material.

Acknowledgments
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References
[1] Hazen R 1988 Perovskites Scientific American 258-6 74
[2] Sharma P, Ahn J, Hur N, Park S, Kim S, Lee S, Park J, Guha S, Cheong S 2004 Physical Review Letters Lett 93 177202
[3] Moreno L, Valencia J, Landinez D, Arbey J, Rodriguez M, Martinez M, Roa-Rojas J, FajardoF 2008 Journal of Magnetism and Magnetic Materials 320 19
[4] Albornoz J, Téllez D, Roa-Rojas J, Munévar J, Baggio-Saitovich E 2013 Journal of Superconductivity and Novel Magnetism 26 pp 2313-2317
[5] Bonilla M, Téllez D, Rodríguez J, Aguiar J, Roa-Rojas J 2008 Journal of Magnetism and Magnetic Materials 320 397
[6] Roa-Rojas J, León-Vanegas A, Téllez D, Pureur P, Dias F, Vieira V 2008 Journal of Magnetism and Magnetic Materials 320 104
[7] Viola M, Martinez-Lope M, Alonso J, Velasco P, Martinez J, Pedregosa J, Fernandez-Diaz M 2002 6 Chemistry of Materials 14 812
[8] Majewski P, Geprägs S, Sanganas O, Opel M, Gross R, Wilhelm F, Alff, L. 2006 arXiv preprint cond-mat/0602071
[9] Larson A, Von Dreele R 1994 Los Alamos National Laboratory Report (USA: LANSCE MS-H805)
[10] Lufaso M, Woodward P 2001 Structural Science 57 725
[11] Prasad K, Chandra K, Kulkarni A 2011 Journal of materials science 46 2077
[12] Rahmouni H, Nouiri M, Jemai R, Kallel N, Rzigua F, Selmi A, Alaya S 2007 Journal of Magnetism and Magnetic Materials 316 23
[13] Mantilla J, Ter Haar E, Coaquira J, Bindilatti V 2007 Journal of Physics Condensed Matter 19 386225