

Magnetic feature, compositional and structural analysis of the $\text{La}_2\text{SrFe}_2\text{CoO}_9$ complex perovskite

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Abstract. In this work, we report the synthesis and characterization of the new $\text{La}_2\text{SrFe}_2\text{CoO}_9$ triple perovskite material. Samples were produced by the solid state reaction method from high purity precursor powders of La_2O_3 , SrCO_3 , Co_2O_3 and Fe_3O_4 . XRD pattern was analyzed by Rietveld refinement through the GSAS code, revealing that observed diffraction peaks are indexed, to the complex perovskite system, and showed that $\text{La}_2\text{SrFe}_2\text{CoO}_9$ crystallizes in an orthorhombic structure, space group *Immm* (#71). The lattice parameters were $a=5.4314(3)$ Å, $b=5.4583(3)$ Å and $c=7.7018(2)$ Å. SEM micrographs evidence a strongly diffused granular morphology with mean grain size of $1\text{ }\mu\text{m}$ and EDX spectra show that the chemical composition of samples are in good agreement with the nominal values of the stoichiometric formula. Measurements of magnetization as a function of temperature permitted to determine the ferromagnetic characteristic of material with an effective magnetic moment of $6.18\text{ }\mu_B$, which is in agreement with the value calculated from the Hund's rules.

1. Introduction

Ceramic perovskite-like materials have been extensively investigated in last decades, because small structural distortions, vacancies and compositional modifications can induce a wide variety of physical and chemical properties [1]. When ideal perovskite formula ABO_3 is modified to introduce different kind of cations on into the octahedral site of the primitive perovskite unit cell, the cationic ordering leads to a complex triple perovskite, which is identified by the $\text{A}_2\text{A}'\text{B}_2\text{B}'\text{O}_9$ formula [2]. This circumstance permits to infer the possibility to produce new materials by the introduction of an alkaline or rare earth ion in the A, A' sites and transition metal ions in the B, B'. Depending on magnetic or electric characteristic of B and B', it is relatively easy to create new perovskite systems with half-metallic properties [3-4], magnetoelectric response [5] or magnetic ordering [6], which offer promissory perspectives in the recent spintronics technology [7].

However, our focus is on the production of new ferromagnetic materials whose response takes place at high temperatures, i.e., near room temperature, in order to enable their application in devices for storing information such as hard drives, portable memories, spin valves, magnetic readers and writers,

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for example. In this work, we report the synthesis, structural characterization and magnetic studies of novel ferromagnetic triple perovskite $\text{La}_2\text{SrFe}_2\text{CoO}_9$, which was idealized as the introduction of a lanthanide ion in the A site, an alkaline earth in the A' and a mixture of two magnetic transition metals in the B and B' sites of the $\text{A}_2\text{A}'\text{B}_2\text{B}'\text{O}_9$ formula, to construct a triple complex perovskite.

2. Experimental

Samples were synthesized by the solid state reaction recipe. Precursor powders of La_2O_3 , SrCO_3 , Co_2O_3 and Fe_3O_4 (Aldrich 99.9% purity) were mixed in stoichiometric proportions according to the chemical formula $\text{La}_2\text{SrFe}_2\text{CoO}_9$. Mixture was ground to form a pellet and annealed at 1250°C for 12 hours. Then, samples were regrinded, repelletized and annealed at 1250°C for 24 hours and 1350°C for 24 hours. X-ray powder diffraction (XRD) pattern was collected using a PW1710 diffractometer with $\lambda_{\text{CuK}\alpha}=1.5406 \text{ \AA}$. Rietveld refinement of diffraction pattern was made by the GSAS code [8]. Scanning electron microscopy (SEM) images were obtained by using a FEI QUANTA 200 microscope, which possess a system for Energy Dispersive X-ray (EDX) analysis. Zero Field Cooling (ZFC) and Field Cooling (FC) measurements of magnetization as a function of temperature were carried out by using a MPMS Quantum Design SQUID.

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.

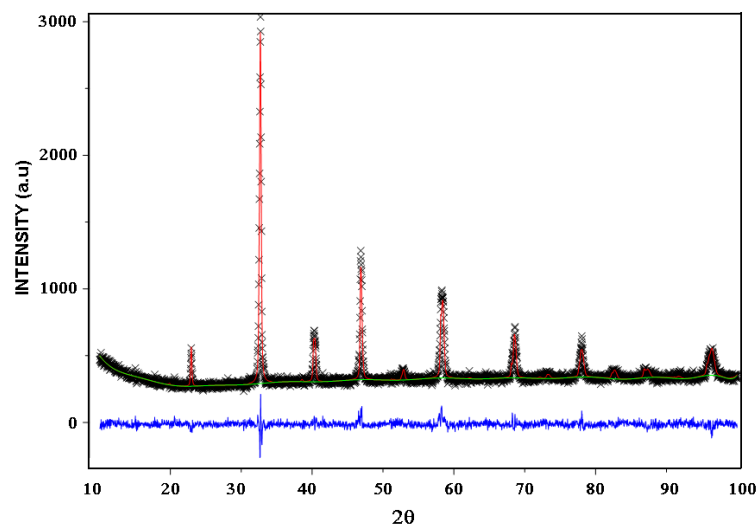


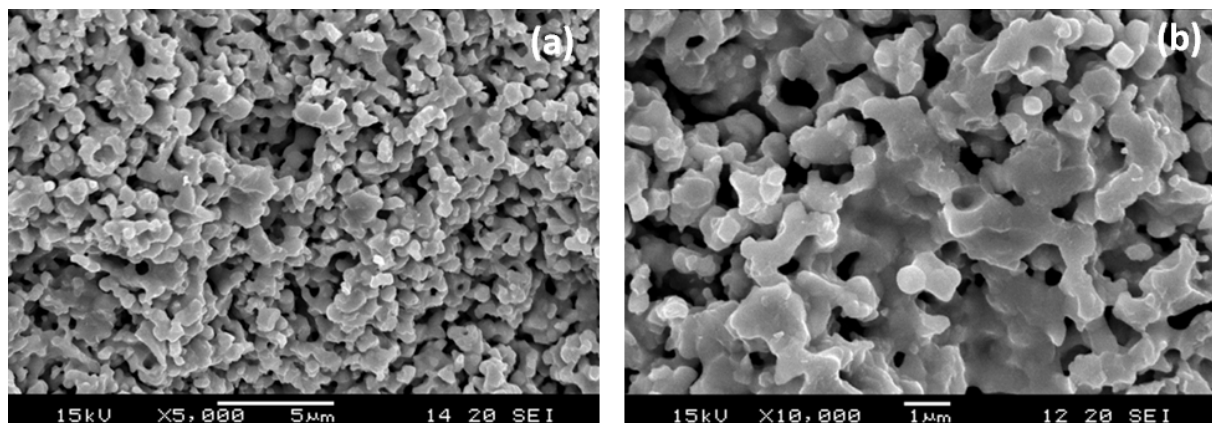
Figure 1. XRD pattern for $\text{La}_2\text{SrFe}_2\text{CoO}_9$ triple perovskite. Symbols represent the experimental diffraction data and base line corresponds to the difference between experimental and simulated patterns (continuous line).

Rietveld refinement permitted to establish that this material crystallizes in an orthorhombic triple perovskite with space group *Immm* (#71) with lattice constants: $a=5.4314(3) \text{ \AA}$, $b=5.4583(3) \text{ \AA}$ and $c=7.7018(2) \text{ \AA}$. These results are 99.8% in agreement with the theoretical values obtained from the Structure Prediction Diagnostic Software *SPuDS* [9], which predicts that lattice constants $a=5.458(8) \text{ \AA}$, $b=5.427(1) \text{ \AA}$ and $c=7.688(9) \text{ \AA}$ for the $\text{La}_2\text{SrFe}_2\text{CoO}_9$ material. Parameters of refinement are: $R_F^2=2.67 \%$; $\chi^2=1.313$; $R_{WP}=3.82 \%$ and $R_P=3.20 \%$. Numeric results of the Rietveld analysis are listed in table 1.

Table 1. Atomic positions and site occupancy calculated for the $\text{La}_2\text{SrFe}_2\text{CoO}_9$ complex perovskite.

<i>Ion</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>Occupancy</i>
Sr	0.5000	0.0000	0,2476	0.3379
La	0.5000	0.0000	0.2476	0.6804
Co(1)	0.0000	0.0000	0.0000	0.6025
Fe(1)	0.0000	0.0000	0.0000	0.4371
Co(2)	0.5000	0.5000	0.0000	0.7491
Fe(2)	0.5000	0.5000	0.0000	0.2015
O(1)	0.2295	0.2809	0.0000	1.7620
O(2)	0.0000	0.0000	0.2509	1.3551

Surface morphology of $\text{La}_2\text{SrFe}_2\text{CoO}_9$ sample was studied by SEM images as shown in figure 2. Performed analysis reveals the occurrence of granular topology with sub-micrometric grain sizes. As observed in the micrograph, there are large topographic regions where the grains are strongly diffused between them and others nanosized regimes formed by few grains, which are surrounded by much porosity in the surface of the sample. However, it is important to notice that the sample evidences a single type of grain which is related with the obtaining of a single crystallographic phase.

**Figure 2.** SEM micrograph of $\text{La}_2\text{SrFe}_2\text{CoO}_9$ obtained from the SEI detector (secondary electrons). Picture (a) shows a surface region with X5000 magnification and (b) X10000.

The EDX spectrum is shown in figure 3. No other chemical elements than expected were observed. Experimental composition of material was obtained from EDX semi-quantitative analysis, considering the spectrum areas for each element, and compared with the theoretical composition, calculated from the $\text{La}_2\text{SrFe}_2\text{CoO}_9$ stoichiometric formula.

The experimental composition values corroborate with 97% regard theoretical values, a crystalline single phase which corresponds to the stoichiometry of $\text{La}_2\text{SrFe}_2\text{CoO}_9$. The presence of two small Au peaks is observed in the spectrum. This is due to coating done on the samples as part of the preparation for SEM imaging experiment. From structural, morphologic and compositional characterizations, no other crystallographic phases or impurities were identified in the samples.

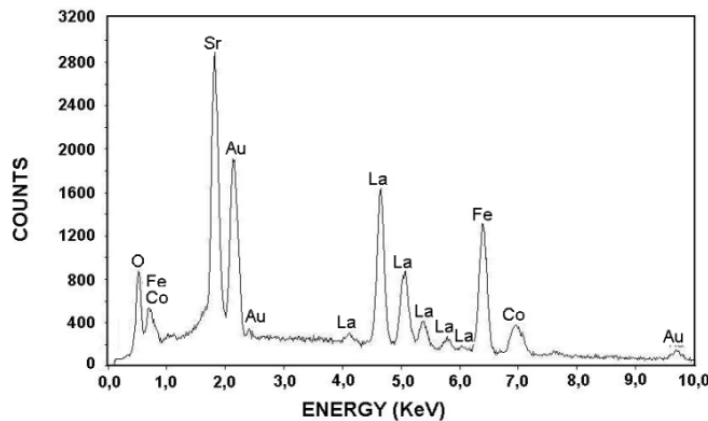


Figure 3. EDX spectrum obtained from the grains of $\text{La}_2\text{SrFe}_2\text{CoO}_9$.

Magnetic properties of $\text{La}_2\text{SrFe}_2\text{CoO}_9$ have been investigated by measuring the DC susceptibility in the temperature range from 2 to 300 K under an applied magnetic field of 50 Oe. Figure 4 shows the dependence of susceptibility as a function of temperature for $\text{La}_2\text{SrFe}_2\text{CoO}_9$ when it is measured by the ZFC and FC recipes.

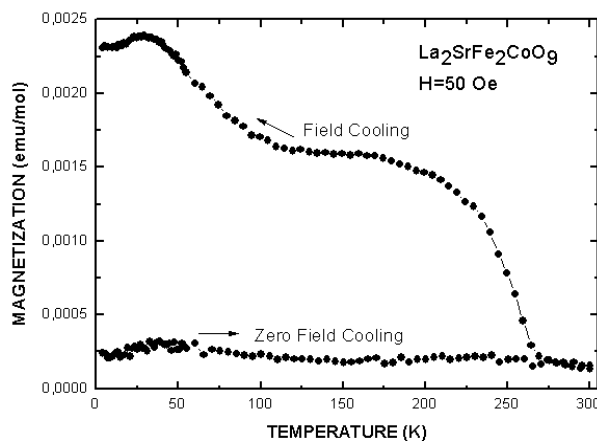


Figure 4. Magnetic behavior of $\text{La}_2\text{SrFe}_2\text{CoO}_9$ obtained from measurements of magnetization as a function of temperature by the ZFC and FC recipes.

It is observed in picture that the ZFC and FC curves present an irreversibility point for a temperature close to 270 K. However, this behavior occurs in a temperature regime above the critical temperature of the paramagnetic-ferromagnetic transition, which is known as Curie temperature. This effect may be due to a cluster-glass percolative scenario [10]. When temperature is decreased from 300 K, the ferromagnetic character is obtained in two steps: first a strong transition is observed close to 260 K; then, at low temperatures (50 K) another ordering effect of the spin moments is detected. In order to verify the ferromagnetic behavior of the $\text{La}_2\text{SrFe}_2\text{CoO}_9$ triple perovskite, figure 5 shows the magnetization dependence with the applied magnetic field at $T=150$ K. In the picture it is observed that the magnetization shows a hysteretic behavior with a saturation magnetization value of 250 emu/cm^3 . From this result and the volume of the crystallographic cell calculated from the Rietveld refinement, we obtain an effective magnetic moment of $6.18 \mu_B$. Theoretical calculations by the Hund's rule, with $p_{\text{eff}} = g\sqrt{J(J+1)}$, predict that magnetic moments of the isolated ions Co^{2+} and Fe^{4+} must be $\mu_{\text{Co}^{2+}} = 3.0\mu_B$ and $\mu_{\text{Fe}^{4+}} = 4.5\mu_B$, respectively [11-12]. The effective magnetic moment of $\text{La}_2\text{SrFe}_2\text{CoO}_9$ is obtained to be $\mu_{\text{eff}} = 7.04\mu_B$, where we have used $\mu_{\text{eff}} = \sqrt{\mu_{\text{Co}^{2+}}^2 + \mu_{\text{Fe}^{4+}}^2}$, by considering two Fe^{4+} cations in the crystallographic unit cell. Our experimental result corresponds to 88% of the theoretical value. This is because at 150 K not all the magnetic moments are oriented in the direction

of the applied magnetic field. Based on the results of the figure 5, we predict that at $T < 50$ K the difference between theoretical and experimental values is less than 2%.

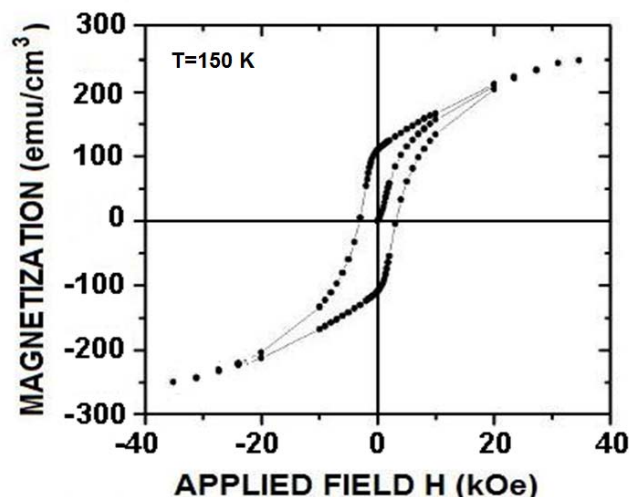


Figure 5. Hysteretic behavior of magnetization as a function of applied field for La₂SrFe₂CoO₉.

4. Conclusions

The synthesis and structural characterization of the new La₂SrFe₂CoO₉ perovskite-like material was performed. The Rietveld analyses reveal that this material crystallizes in an orthorhombic complex perovskite which corresponds to the *Immm* (#71) space group. Morphologic surface study by SEM images shows a single type of grains which is interpreted as an evidence of the formation of a single crystallographic phase. EDX analysis permitted to determine that the composition of material corresponds 97% with the expected from the stoichiometric formula. Measurements of magnetization as a function of temperature show the occurrence of a ferromagnetic ordering transition for a Curie temperature close to 260 K. From the saturation magnetization in the hysteretic curve of magnetization as a function of applied field we obtain the magnetic moment of the unit cell to be $6.18 \mu_B$.

5. References

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