Crystallographic and Electronic Structure of the Sr₃Sb₂CoO₉ Triple Perovskite

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Abstract. Compounds perovskites are materials with physical and chemical characteristics that make them optimal for application in the technological and scientist. When the ideal formula of perovskite ABO₃ is modified by introducing a special structural arrangement can get to get triple perovskites, which correspond to the formula A₃B₂B'O₉. In this work we report the synthesis process and the study of electronic structure and crystal Sr₃Sb₂CoO₉ new triple perovskite. From the experiments of X-ray Diffraction and the application of the Rietveld refinement method was revealed that the system crystallizes in a perovskite structure with a characteristic triple given by the space group Immm (#71) and lattice parameters a=9.791(9) Å, b=5.656(7) Å and c=16.957(8) Å. Ab initio calculations of density of states (DOS) and electronic structure were carried out for this perovskite-like system by using the Quantum EXPRESSO code. The exchange-correlation potential was treated using the Generalized Gradient Approximation (GGA). All calculations were carried-out using spin polarization.

Keywords: Ceramic materials; crystal structure; electronic properties.

1. Introduction
Ceramic materials represent a great percentage of systems which are actually investigated by the physics and chemistry of solids. Particularly, the perovskite family has concentrated important attention in last decades. From the point of view of chemical composition, perovskites have characterized by the ideal formula ABX₃, 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 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,B₂B'O₉ [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 B and B’ it is relatively easy 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 analyze 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 Sr$_3$Sb$_2$CoO$_9$, which was idealized as the introduction of the alkaline earth Sr in the A’ site, the transition metalloid Sb in the B location and the magnetic element Co in the B’ site of the A$_3$B$_2$B’O$_9$ formula, to construct a triple complex perovskite.

2. Experimental
The samples were synthesized by the solid state reaction recipe. The precursor powders SrCO$_3$, Co$_3$O$_4$ and Sb$_2$O$_3$ (Aldrich 99.9%) were mixed in stoichiometric proportions according to the chemical formula Sr$_3$Sb$_2$CoO$_9$. Mixture was ground to form a pellet and annealed at 900 °C for 24 hours. The samples were then reground, repelletized and reannealed at 1000 °C for 24 hours. At last, the sample was sintered at 1100 °C for 24. X-Ray diffraction (XRD) experiment was performed by means a PW1710 diffractometer with $\lambda_{CuK\alpha}=1.5406$ Å. Rietveld refinement of diffraction pattern was carried out by the GSAS code [9].

3. Theoretical calculations
The calculations have been performed using the Quantum ESPRESSO code [10], which is based on the density functional theory (DFT) [11]. The electronic exchange-correlation potential was calculated using the generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof expression [12]. The electron-ion interaction was treated by using Vanderbilt ultrasoft ab-initio pseudopotentials [13], with the following valence electron configuration, Sr(5s$^2$), Sb(5s$^2$ 5p$^3$), Co(3d$^7$ 4s$^2$) and O(2s$^2$ 2p$^4$). The irreducible Brillouin zone was sampled using the Monkhorst–Pack scheme [14]. The atomic-projected DOS were calculated by the Lowdin populations [15].

4. 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 a monoclinic triple perovskite with space group P2$_1$/c (#14) and lattice constants are $a=9.791(9)$ Å, $b=5.656(7)$ Å, $c=16.957(8)$ Å and tilt angle $\beta=125.339^\circ$. These results show deviation of no more than 3% when compared with the theoretical values obtained from the Structure Prediction Diagnostic Software SPuDS [16], which predicts that lattice constants $a=9.608(3)$ Å, $b=5.478(4)$ Å, $c=16.808(0)$ Å and tilt angle $\beta=125.645^\circ$ for the Sr$_3$Sb$_2$CoO$_9$ material. Parameters of refinement are: $R_F^2=0.1407$; $x^2=1.145$ and $R_{WP}=0$.

![Figure 1. XRD pattern for the Sr$_3$Sb$_2$CoO$_9$ triple perovskite. Symbols represent the experimental diffraction data and base line corresponds to the difference between experimental and simulated patterns (continuous line).](image-url)
The numeric results of the Rietveld analysis are shown in the table 1. Figure 2 shows the schematically representation of the structure of Sr₃Sb₂CoO₉ which was drawn from the lattice parameters, tilt angle, atomic positions and bond distances obtained from the Rietveld refinement of the experimental XRD data.

**TABLE 1. Atomic positions for the Sr₃Sb₂CoO₉ complex perovskite.**

| Ion | Site | x   | y   | z   |
|-----|------|-----|-----|-----|
| Sr  | 4e   | 0.2500 | 0.5014 | 0.0777 |
| Sr  | 4e   | 0.7500 | 0.0014 | 0.0777 |
| Sr  | 4e   | 0.2500 | 0.0014 | 0.2444 |
| Co  | 2a   | 0.0000 | 0.0000 | 0.0000 |
| Co  | 2d   | 0.5000 | 0.0000 | 0.5000 |
| Sb  | 4e   | 0.5047 | 0.5000 | 0.0000 |
| Sb  | 4e   | 0.0048 | 0.0000 | 0.3381 |
| O   | 4e   | 0.9400 | 0.6900 | 0.2500 |
| O   | 4e   | 0.5600 | 0.8100 | 0.2900 |
| O   | 4e   | 0.2500 | 0.6200 | 0.2500 |
| O   | 4e   | 0.9400 | 0.6774 | 0.9125 |
| O   | 4e   | 0.4400 | 0.2974 | 0.8725 |
| O   | 4e   | 0.5600 | 0.8226 | 0.9525 |
| O   | 4e   | 0.0600 | 0.2026 | 0.9125 |
| O   | 4e   | 0.7374 | 0.1200 | 0.9125 |
| O   | 4e   | 0.2374 | 0.6200 | 0.9125 |

Figure 3 shows the total DOS calculated from the charge density for the Sr₃Sb₂CoO₉ material close to the Fermi level which is the reference for energies. It is observed on the picture that the Sr₃Sb₂CoO₉ perovskite behaves as a conductor material for both up and down spin orientations. Due to the difference between the up and down spin contributions in the vicinity of the Fermi level it can be suggested that this material is magnetic. In order to examine in detail the contributions of each of the constituent atoms of the Sr₃Sb₂CoO₉ material has been developed a picture of partial DOS which is presented in Figure 4.

**Figure 3.** Total DOS with spin polarization for the Sr₃Sb₂CoO₉ tri-perovskite.

**Figure 4.** Partial DOS due to contributions of Sr, Co, Sb and O orbitals including spin polarization for the Sr₃Sb₂CoO₉ material.
From the analysis of our results we can affirm that the main contributions to the DOS, in the valence and conduction regimes, close to the Fermi level are due to 3d-Co and 2p-O orbitals. This may be because in this type of structures the distortions that occur in the Co-O octahedra have significant effects on all physical properties of the material. Important contributions due to 5s-Sr and 5p-Sb orbitals throughout the region near the Fermi level were not observed.

5. Conclusions
The synthesis and structural characterization of the new Sr$_3$Sb$_2$CoO$_9$ perovskite-like material was performed. The Rietveld analyses reveal that this material crystallizes in an orthorhombic complex perovskite which corresponds to the $P2_1/c$ (#14) space group. Calculations of density of states by the Quantum EXPRESSO code reveal the conductor character of this material, mainly due to 3d-Co and 2p-O orbitals. Differences between the DOS of spin-up and spin-down orientations close to the Fermi level suggest the magnetic character of the Sr$_3$Sb$_2$CoO$_9$ tri-perovskite.

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