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Synthesis, structure and magnetic properties of $La_3Co_2SbO_9$: A double perovskite with competing antiferromagnetic and ferromagnetic interactions

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ABSTRACT

The synthesis, structural characterization, and magnetic properties of $La_3Co_2SbO_9$ double perovskite are reported. The crystal structure has been refined by X-ray and neutron powder diffraction data in the monoclinic space group $P2_1/n$. Co^{2+} and Sb^{5+} have the maximum order allowed for the $La_3Co_2SbO_9$ stoichiometry. Rietveld refinements of powder neutron diffraction data show that at room temperature the cell parameters are $a=5.6274(2)$ Å, $b=5.6842(2)$ Å, $c=7.9748(2)$ Å and $\beta=89.999(3)^\circ$. Magnetization measurements indicate the presence of ferromagnetic correlations with $T_C=55$ K attributed to the exchange interactions for non-linear Co^{2+}–O–Sb^{5+}–O–Co^{2+} paths. The effective magnetic moment obtained experimentally is $\mu_{exp}=4.38\ \mu_B$ (per mol Co^{2+}), between the theoretical one for spin only (3.87 μ_B) and spin-orbit value (6.63 μ_B), indicating partially unquenched contribution. The low magnetization value at high magnetic field and low temperature (1 μ_B/f.u., 5 T and 5 K) and the difference between ZFC and FC magnetization curves (at 5 kOe) indicate that the ferromagnetism do not reach a long range order and that the material has an important magnetic frustration.

1. Introduction

Perovskites and double perovskites in particular are very attractive because of the interest in applications and fundamental areas of advanced materials, catalysis and the many interesting physical properties they have [1].

The general formula of a simple perovskite is ABO_3 and is a highly flexible structure. It can accommodate almost all elements of the periodic table on its cuboctahedral (A) and octahedral (B) sites. The structure of a cubic ideal perovskite can be seen as a three-dimensional array of BO_6 octahedra linked by the vertex, with the A ion in the cuboctahedral cavity surrounded by 8 BO_6 octahedra. Usually an alkali-earth ion occupies the A site [2,3], but a smaller ion, like a lanthanide, can also be accommodated in this site. However, several distortions can arise if the A ion is too small [4]. There are three common distortions: cation displacement within the BO_6 octahedra and distortions and tilting of these octahedra.

When two ions, B and B′, are located on two different crystallographic sites, a double perovskite, $A_2BB'O_6$, is formed. B and B′ ions can be completely or partially ordered among the two different sites. The degree of order depends on the size and charge differences between the B ions. In general, a big difference in size and charge facilitates ordering at the B-site. Nevertheless, other factors, such as specific bonding interactions and synthesis condition may affect the degree of order [5,6]. The magnetic properties are largely affected by the nature of the B cations, for example, B could be a transition metal with unpaired electrons, and if B′ ion has a close shell configuration, then the interactions between B ions and their neighbors will determine the magnetic behavior. Consequently the B order-disorder relationship strongly affects the magnetic properties of these materials [7–9].

In the last years, the synthesis of new double perovskite has resulted in a very attractive topic of research, after it has been informed that Sr_2FeMoO_6 has room temperature colossal magnetoresistance (CMR) [10]. Besides, its half-metallicity, high magnetic transition temperature along with its spin polarized charge transport has a very large importance in the field of spintronics [11] and in applications in read heads, magnetic memories, recording media or field sensors [12].

If the ratio B/B′ in double perovskites is one, the general formula will be $A_2BB'O_6$. For this stoichiometry, in the most ordered case, one of the sites will be fully occupied by B ions, while the other fully occupied by B′. Usually, the formula in this case is written as $A_2(B)(B')O_6$. But if the stoichiometry is $A_3B_2B'O_9$, the maximum order that can be present within B and B′ cations can be written as: $A_2(B)(B_{1/3}B'_{2/3})O_6$ [7], a situation which has an intrinsic disorder, i.e., one of the sites is fully occupied by B but

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the other one has a disordered situation, additional disorder could be obtained by moving some B′ to the site fully occupied by B, strongly affecting the magnetic properties [7]. For example, anti-site disorder has been shown to be responsible for spin-glass behavior for different double perovskites, i.e., Sr_2FeTeO_6 [13], $Sr_2Mn_{0.7}Fe_{0.3}O_6$ [14], Sr_2FeMoO_6 [15] among others. The double perovskites $La_3Co_2NbO_9$ and $La_3Co_2TaO_9$ were prepared by our group [16,17] by sol–gel and solid state methods and the correlation between the B order-disorder and magnetic behavior was reported. Samples prepared by solid state showed spontaneous magnetization bellow 72 K for $La_3Co_2TaO_9$ and 62 K for $La_3Co_2NbO_9$ and positive θ values, showing prevalence of ferromagnetic interactions, while those prepared by sol–gel present low spontaneous magnetization (below 40 and 20 K, respectively) and negative θ values, showing prevalence of antiferromagnetic interactions. This behavior was explained by a simple model which shows that the most B-site ordered compounds favors the ferromagnetic Co^{2+}–O–M^{5+}–O–Co^{2+} interactions while the most disordered ones favor the antiferromagnetic Co^{2+}–O–Co^{2+} interactions [16]. These Co^{2+}–O–M^{5+}–O–Co^{2+} ferromagnetic interactions, according to this model, are present in nanoclusters, whose amount and size are highly dependent on the degree of disorder on the B sites.

Here, we describe the synthesis, structure and magnetic characterization of the double perovskite $La_3Co_2SbO_9$, completing in this way the synthesis and characterization of the double perovskites family $La_3B_2B'O_9$ (with B'^{5+} ions) containing Co^{2+} as magnetic ion. $La_3Co_2SbO_9$ was actually informed by the first time by G. Blasse [18] as an orthorhombic perovskite; however no detailed structural or magnetic studies were informed.

2. Experimental

$La_3Co_2SbO_9$ was obtained as reddish-black polycrystalline powder by solid state method. The starting materials, weighed in stoichiometric amounts, were La_2O_3, Co_3O_4 and Sb_2O_3 in analytical grade. The sample was first heat-treated at 950 °C for 12 h, with a second heat treatment, after regrinding, at 1400 °C for 12 h, both in air atmosphere.

Powder X-ray diffraction (PXRD) patterns were measured on a PANalytical X'Pert PRO diffractometer (40 kV, 40 mA) in Bragg–Brentano geometry with Cu K_α radiation (λ=1.5418 Å) at room temperature, between 5° and 120° 2θ in steps of 0.02°. Neutron powder diffraction (NPD) patterns were collected in the D2B powder diffractometer at Institute Laüe-Langevin, Grenoble, France, at room temperature (RT), 150 and 2 K. The measurements were performed between 0° and 160° in 2θ with steps of 0.05°, and the wavelength used was 1.594 Å. Structure refinement of the diffraction patterns were performed by the Rietveld method [19] using the Fullprof program [20]. A pseudo-Voigt shape function was always adequate to obtain good fits for experimental data.

The magnetic characterization was performed in a commercial SQUID magnetometer on powdered samples, between 5 and 300 K, and magnetic fields up to 5 T. The magnetization (M) vs. temperature (T) curves were measured under Zero Field Cooling (ZFC) and Field Cooling (FC) conditions.

3. Results and discussion

3.1. Structural characterization

The PXRD pattern at RT shows a perovskite-like phase with no impurities at all. According to Rietveld refinement result, Fig. 1, $La_3Co_2SbO_9$ crystallizes in a monoclinic structure, space group $P2_1/n$.

Using the following effective ionic radii [21]: rO^{2-}=1.26 Å, $^{XII}(rLa^{3+})$=1.50 Å, $^{VI}(rCo^{2+})$ (HS)=0.885 Å and $^{VI}(rSb^{5+})$=0.74 Å the Goldschmidt tolerance factor (t) calculated for $La_3Co_2SbO_9$ taking into account the partial occupation of the B site by two different cations (Sb^{5+} and Co^{2+} (HS)) is t=0.931, low enough bellow unity to give rise to large deviations from the cubic symmetry. Small shifts in the oxygen positions necessary to accommodate the small La^{3+} ion in the cuboctahedral cavity produce the tilting of the BO_6 octahedra, these tilting generates the reduction in symmetry. These shifts can only be accurately detected by neutrons powder diffraction (NPD) due to the large scattering length of the O nucleus.

The Rietveld fits for the NPD data at RT, 150 and 2 K are displayed in Fig. 2 and also show a good agreement between the calculated and the measured patterns with the space group $P2_1/n$. This space group has two different crystallographic sites for the octahedral ions, Co^{2+} and Sb^{5+}. Anti-site disorder was then refined by assuming Co^{2+} and Sb^{5+} ions can be randomly distributed over these two sites: 2d (½, 0, 0) and 2c (0, ½, 0) Wyckoff positions. The obtained distribution of Co^{2+} and Sb^{5+} was the most possible ordered one for the stoichiometry of the compound, that is the 2d site fully occupied with Co^{2+}, and the 2c site occupied with the remaining Co^{2+} ions and all of the Sb^{5+} ions. Then, the formula of the double perovskite can be written as $La_2(Co)_{2d}(Co_{1/3}Sb_{2/3})_{2c}O_6$. The oxygen occupancies were also refined but they remained close to one within the standard deviations so they were fixed to unity.

Table 1 includes lattice parameters and cell volume, obtained from NPD data refinement at the three temperatures. There is a very small decrease of the cell volume as T decreases. The monoclinic structure obtained shows a β angle very close to 90° for all temperatures, which could show the presence of a tetragonal or orthorhombic symmetry. Because of this situation the tetragonal $I4/m$ and orthorhombic $Immm$ models were also tested. These space groups also allow the order of B and B′ ions as the $P2_1/n$ space group, but show the absence of important Bragg reflections observed in the experimental data, see inset in Fig. 1.

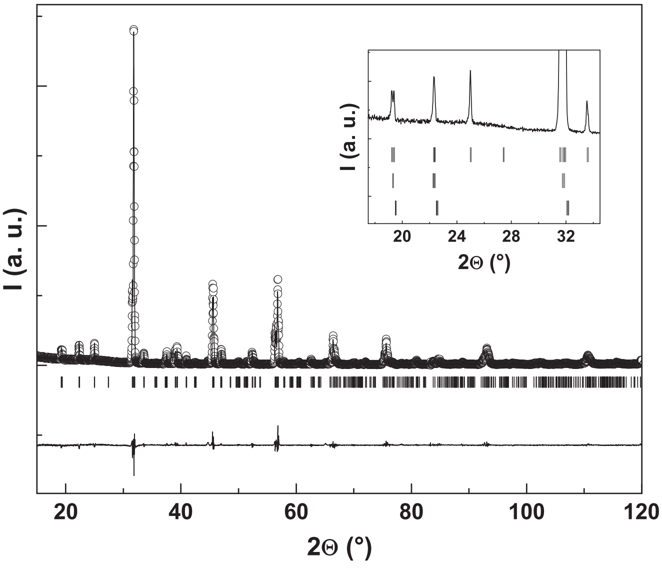

Fig. 1. Rietveld refinement of PXRD data at RT for $La_3Co_2SbO_9$. Observed (circles), calculated (line), and difference (bottom line). Vertical bars represent positions of Bragg reflections for monoclinic double perovskite, space group $P2_1/n$. Reliability factors: χ^2=3.25, R_{wp}=20.1, R_p=17.1, Bragg R-factor=7.70. The inset shows only the experimental data and the Bragg reflections calculated for the space groups $P2_1/n$ (top), $I4/m$ (middle) and $Immm$ (bottom).