Structural properties, magnetic and oxygen-vacancies order in \( Y(Ba_{1-x}Sr_x)Co_2O_{5.5} \) layered cobaltites

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Abstract. We present a study of the family \( Y(Ba_{1-x}Sr_x)Co_2O_{5.5} \) \((x = 0, 1/8, 1/4, 1/3, 3/8, 1/2) \). The complex magnetic behavior characterizing the parent \((x = 0)\) compound and other \( R BaCo_2O_{5.5} \) compounds can still be guessed in \( M(T) \) curves of \( x = 1/8 \) compound, but it disappears under substitution of Ba by Sr for all the studies cases \((x \geq 1/8)\). This is linked to the fact that the order of oxygen vacancies is lost, as found by neutron and synchrotron X-ray powder diffraction.

Research on Co oxides, that has been much less intense than in manganites or cuprates, is at present one of the most scientifically appealing areas in the scope of highly correlated electron systems. Cobaltites constitute a group of materials with wide possibilities that is being actively investigated. The recent discovery of superconductivity in laminar cobalt oxide \( NaCoO_2 \cdot yH_2O \) [1], is a first example that confirms the need of exploring new Co oxides. One of the reasons for the richness of these oxides is that, in addition to charge, lattice and spin degrees of freedom (that are present in other transition metal oxides), Co ions show an unusual (almost unique) ability to present different spin states.

The motivation of the present work is to gain insight into the understanding of the mechanisms involved during spin state transitions in octahedral \( Co^{3+} \) by studying the family \( YBa_{1-x}Sr_xCo_2O_{5+\delta} \) \((\delta \simeq 0.5, \text{ and } x = 0, 1/8, 1/4, 1/3, 3/8, 1/2) \). The parent compound \( YBaCo_2O_{5.5} \) and other \( R BaCo_2O_{5.5} \) have been intensively studied during the last years and present a highly ordered structure with \( R \) and Ba ions in alternating \((001)\) planes and oxygen vacancies located at \( R \) layers forming ordered patterns. This drives to the formation of octahedral \((CoO_6)\) and pyramidal \((CoO_5)\) environments [2]. Although results are not free from controversy[3], it is widely accepted that these compounds present a spin state transition that mainly involves octahedral positions [4]. This transition changes with the rare earth size. This is partially attributed to the fact that crystal symmetry confines oxygen ions in highly symmetric sites hampering the rotation of octahedra. This makes Co-O distances sensitive to lattice parameters and, therefore, to the size of the ions at the A position of the perovskite [5]. It is worth mentioning that Co-O distances govern the crystal field and, therefore, the spin state of Co ions.

Polycrystalline \( YBa_{1-x}Sr_xCo_2O_{5+\delta} \) specimens (with \( x = 0, 1/8, 1/4, 1/3, 3/8 \) and 1/2) have been prepared by sol-gel method. Yttrium acetate hydrate, barium acetate, strontium acetate
and cobalt acetate tetrahydrate (Alfa Aesar) were dissolved in the suitable stoichiometric ratio in distilled water at 60°C for few minutes. Then, an excess of citric acid monohydrate (Sigma-Aldrich) was added to the solution until saturation (∼70 g of citric acid for 15 g of sample). The mix was held at 110°C under vigorous stirring in order to evaporate the water solvent and the resultant acetic acid. The final product was a dark violet gel which was thermally fired at 550°C in a muffle furnace for 5 hours in order to eliminate the organic material. The black powder obtained was pressed into pellets at 10 Tons and calcined in a tubular furnace under air at 1050°C for 24 hours. The bars were then cooled slowly (−6°C/h) to RT. After regrinding and pressing again, the heat treatment was repeated under pure O₂ atmosphere. X-ray powder diffraction (XRD) data show that initial compounds were well crystallized. An small amount (1-3 wt.-%) of Y₂O₃ was detected for Sr containing samples.

Magnetic measurements have been done using a superconducting quantum interferometer device (SQUID, Quantum Design) with an applied field of 1000 Oe on heating after zero field cooling (ZFC) and field cooling (FC). Neutron powder diffraction (NPD) data have been collected at Institut Laue Langevin (Grenoble) at RT using high resolution D2B (λ = 1.594 Å) and during a heating ramp from 5 K to RT using high-flux D1B (λ = 2.52 Å). Synchrotron X-ray powder diffraction (SXRPD) has been collected at ID31 beamline of ESRF (Grenoble, France) at RT. A short wavelength λ = 0.39978(25) Å, to reduce the absorption, was selected with a double-crystal Ge (111) monochromator and calibrated with Si NIST (a = 5.43094 Å). Optimum transmission was achieved by enclosing the finely grounded sample in a 0.5 mm diameter borosilicate glass capillary, and appropriate spinning of the capillary in the beam ensured for a good powder averaging. Diffraction data has been analyzed by using FullProf suite of programs.[6]

The joint Rietveld refinement of NPD and SXRPD collected at RT reveals that the orthorhombic structure (with a ≃ ap and b ≃ c ≃ 2ap and P mmm space group) characterizing RBaCo₂O₅.₅ family disappears under the substitution of Ba by Sr. In contrast, for x ≥ 1/8 the cell becomes tetragonal with a ≃ b ≃ ap and c ≃ 2ap. NPD and SXRPD data collected at RT can be very well refined using space group P 4/mmm. The refinement allows us to confirm that the order between the trivalent (Y) and the divalent ions (Ba, Sr) in alternating (0 0 1) planes is kept by this substitution but the order of oxygen vacancies within YO₃-planes disappears. From this refinement, we have also estimated the oxygen content for the five samples and, in all the cases the deviation from δ = 0.5 is no larger than 6%. Figure 1 shows the changes in the unit cell parameters (at RT). After the orthorhombic to tetragonal transition, a cell parameter slowly decreases with x while c parameters is almost constant along the series.

A very intriguing aspect of RBaCo₂O₅.₅ family is their magnetic behaviour. It is characterized by a series of magnetic transitions that have been widely studied during last years [7, 8, 9, 10]. In order to investigate the changes in the magnetic behavior under the introduction of Sr, we have first performed magnetization measurements along the series. Figure 2 shows the magnetization (and its inverse) measured for different samples. Our YBaCo₂O₅.₅ sample presents a small FM
signal (near 0.3 \(\mu_B/f.u.\)) for a short temperature interval. This corresponds to the appearance of a canted antiferromagnetic (CAF) state that disappears due to the formation of a purely antiferromagnetic (AFM) structure on further cooling. For \(x = 1/8\) there is still a maximum in \(M(T)\) curve but the value reached is about one order of magnitude smaller than for \(x = 0\). This behaviour completely disappears for \(x > 1/8\), where the values reached by the magnetization are always below \(5 \cdot 10^{-3} \mu_B/f.u.\), signaling the complete absence of any kind of FM order.

We have further investigated the dependence on \(x\) of the magnetic behaviour by means of neutron powder thermodiffraction on high-flux D1B diffractometer. Figures 3(a), (b) and (c) show the variations of the measured intensity when changing the temperature from 5 K to near RT for compounds with \(x = 0\), 1/8 and 1/2 respectively. From these plots, it is evident that different magnetic peaks appear. The integrated intensity of these peaks is plotted in Figs. 3(d), (e) and (f). The magnetic complexity of YBaCo\(_2\)O\(_{5+\delta}\) can be clearly appreciated in these figures. Different peaks evidencing different magnetic lattices appear (and disappear) with temperature. The complexity of \(x = 0\) compound strongly contrast with the simplicity of \(x = 1/8\) where only one magnetic transition characterized by a magnetic cell doubling \(a\) and \(b\) lattice parameters (of the tetragonal lattice) is detected. It is worth mentioning that \(x = 1/4, 1/3,\) and \(3/8\) behave in the same way that \(x = 1/8\), with the appearance of \((\frac{1}{2} \frac{1}{2} 0)\) magnetic reflection (indexed according to lattice parameters in Fig. 1) at a temperature around \(T_N = 250\) K. This situation changes when the substitution of Ba by Sr reaches 50%. At this point, two different transitions can be well appreciated in these figures. One takes place at about \(T_{N_1} \approx 300\) K and is characterized by the appearance of \((0 0 \frac{1}{2})\) reflection. Thus, magnetic lattice doubles \(c\) lattice parameter but keeps \(a\) and \(b\). Under further cooling, at \(T_{N_2} \approx 150\) K, \((\frac{1}{2} \frac{1}{2} 0)\) magnetic reflection comes out, while \((00 \frac{3}{2})\) reflection remains unaltered. Further analyses to interpret these results are under way.

In summary, we have prepared good quality samples of YBa\(_{1-x}\)Sr\(_x\)Co\(_2\)O\(_{5+\delta}\) family with \(x = 0, 1/8, 1/4, 1/3, 3/8\) and 1/2. By means of high-resolution NPD and SXRPD we have been able to determine that the oxygen content is \(\delta = 0.50 \pm 0.03\). In addition, there is a change in crystal system from orthorhombic (\(x = 0\)) to tetragonal (\(x \geq 1/8\)) that signals the loss of the order of vacancies within YO\(_{0.5}\) plane. Associated to this disorder the complex magnetic behaviour of the
Figure 3. (Color online) (a), (b) and (c) panels show, as color-maps, the intensity measured by NPD (D1B) for different \(2\theta\) and temperature. Plots are centred in the low-\(Q\) region where magnetic pics appear. Panels (d), (e) and (f) show the integrated intensity of the most intense magnetic peaks: (d) (0 0 \(\frac{1}{2}\)) at \(2\theta \simeq 9.6^\circ\), (0 1 \(\frac{1}{2}\)) at \(2\theta \simeq 20.9^\circ\), (\(\frac{1}{2} 1 \frac{1}{2}\)) at \(2\theta \simeq 28.2^\circ\), and (\(\frac{1}{2} 1 1\)) at \(2\theta \simeq 32.9^\circ\); (e)-(f) (0 0, 0 \(\frac{3}{2}\)) at \(2\theta \simeq 29.7^\circ\), and (\(\frac{1}{2} \frac{1}{2} 1\)) at \(2\theta \simeq 33.2^\circ\). These are indexed according to cell parameters reported in Fig. 1.

parent compound, disappears and a only one magnetic structure stabilizes for \(1/8 \leq x \leq 3/8\). More complex is the case of \(x = 1/2\) where two different magnetic arrangements, with different propagation vectors, are evidenced by NPD data.

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