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Structural study of Ni-substituted $YBaCo_{4-x}Ni_xO_7$ frustrated cobaltites

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ABSTRACT

In this work we report a study of the thermal stability and the evolution of the crystal structure of Ni-substituted $YBaCo_{4-x}Ni_xO_7$ cobaltites, for $x=0$, 0.10 and 0.20. Synchrotron X-ray powder diffraction and thermodiffraction experiments show that the structural transition $P31c \rightarrow Pbn2_1$, which occurs around room temperature for the parent compound, is shifted up to 40° by the partial substitution Ni-for-Co. Moreover, the transition is shown to be of first order with a volume collapse of $\approx 0.05\%$ and an abrupt contraction of the cell along the c-direction. The monoclinic distortion below 100 K reported for the parent compound is also observed in the Ni-substituted samples, suggesting that they also get to order antiferromagnetically below that temperature. Magnetization measurements allowed us to detect a small amount of a ferromagnetic impurity in the sample with $x=0.20$, indicating that the solubility limit of Ni lies below that value. The magnetic susceptibility in the paramagnetic region, as well as the cell parameters in each crystallographic phase, is not significantly modified by these amounts of Ni substitution, in contrast to the marked enhancement of the $P31c$ phase stability upon substitution.

1. Introduction

Cobalt oxides have always constituted a focus of interest, due to the wide spectrum of physical properties they exhibit. These properties originate from the very strong interplay among crystal structure, magnetism and electronic transport, giving rise to rich phase diagrams tuned by temperature, pressure, magnetic fields, oxygen content and cationic size. A quite novel member of the cobalt-rich oxides family is the so-called "114-cobaltite" $RBaCo_4O_7$, discovered in 2002 for $R=Y$ [1] and later synthesized with $R=$lanthanides and calcium. This compound soon gained attention because it displays two very attractive features. First, it offers the possibility to study frustrated magnetism in the unique topology of a three-dimensional framework of Co tetrahedra in interconnected triangular and Kagomé lattices. Geometric frustration is related to intensively studied phenomena in spin ices and multiferroic materials [2,3], and this compound opens a new possible scenario for its study. A second remarkable property is its capacity of absorption and desorption of gases, which turns these cobaltites outstanding candidates for oxygen-storage and gas-sensors applications [4,5]. They show an extreme affinity for oxygen, being able to uptake up to 1.5 extra atoms per formula unit at 350 °C, and release them again, very abruptly, at 400–450 °C [6–8].

The stoichiometric compound $YBaCo_4O_7$ has a nominal valence for Co of 2.25, so it is assumed that Co is present as Co^{2+} and Co^{3+} in a 3:1 proportion. The structure of this compound is shown in Fig. 1. In its high–temperature form, in the trigonal space group $P31c$, the symmetry imposes a high magnetic frustration. However, it has been shown that for the strictly stoichiometric compound with $\delta=0$, a first–order phase transition to an orthorhombic $Pbn2_1$ space group at a temperature T_S (close to room temperature for $YBaCo_4O_7$ [9,10]) lifts this frustration and allows for the development of a long-range antiferromagnetic (AFM) structure below $T_N \sim 110$ K [9]. The origin and driving force for the structural transition at T_S remain under debate. It was originally suggested that a charge ordering mechanism would occur at T_S [11]; it was also proposed that the transition is driven by the condensation of a phonon mode associated to the rigid-body rotation of the tetrahedra in the Kagomé layers [12]. Finally, Huq et al. [13] proposed that it is driven by a severe under-bonding of Ba^{2+} ions. In Fig. 2 we show the schematic geometrical relation between the unit cells of the $P31c$ and $Pbn2_1$ phases in the a–b plane. The lattice parameters are related as $a_O \approx a_T$, $b_O \approx \sqrt{3}a_T$ and $c_O \approx c_T$.

It is interesting to note that the oxygen stoichiometry plays an important role in the trigonal to orthorhombic transition, which is suppressed already for very small values of δ (as low as 0.02 [14]). A second variable which modifies the transition temperature T_S is the R-cation size, as has been shown and discussed by various

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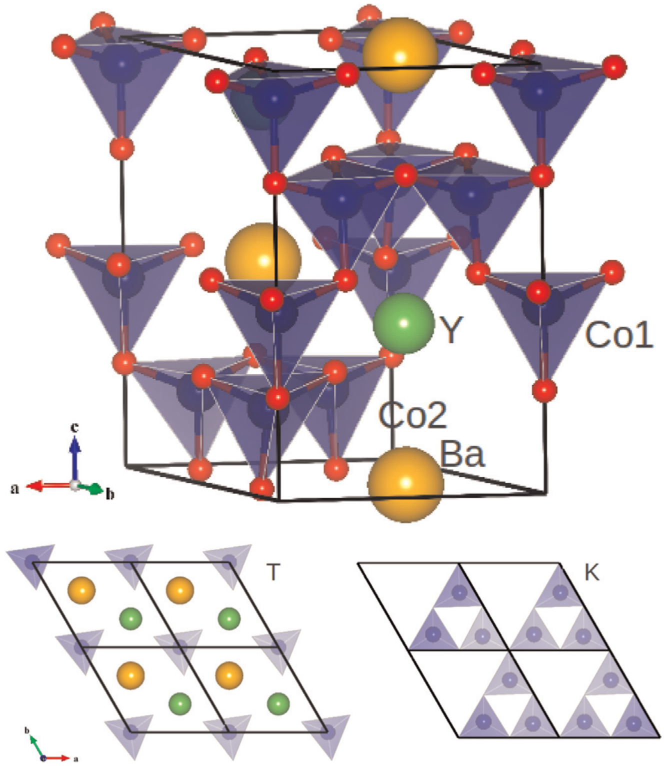

Fig. 1. Crystal structure of $YBaCo_4O_7$ above 310 K in the *P*31*c* space group, showing the Co tetrahedra geometry. Labels indicate the different sites. Co1 are located at the triangular layers (T) and Co2 are in the Kagomé layers (K). Bottom: view along the *c*-axis of the T and K layers.

authors [11,15]. Less studied has been the effect on the structural transition of replacing Co with other magnetic ions [16,17]. In this paper, we report a structural study of Ni-doped $YBaCo_4O_7$ cobaltites based on synchrotron X-ray powder diffraction (SXPD).

2. Experimental methods

2.1. Synthesis

Polycrystalline samples of nominal $YBaCo_4O_7$ (hereafter called Ni-0) and $YBaCo_{4-x}Ni_xO_7$ with $x=0.10$ and 0.20 (alias Ni-10 and Ni-20) were prepared by conventional solid–state reaction. High-purity powders of Y_2O_3, $BaCO_3$, Co_3O_4 and metallic Ni were thoroughly mixed in an agate mortar at stoichiometric weights. After a de-carbonation process at 1173 K for 12 h, the mixtures were pressed into pellets, annealed during 24 h at 1473 K and slowly cooled at 1 K/min in the furnace. The compression and annealing at 1473 K in air were repeated after re-grinding. Sample Ni-0 was quenched from 1473 K to L-N_2 to obtain the stoichiometric compound. The samples containing Ni were cooled inside the furnace at 1 K/min and their precise oxygen stoichiometry was later adjusted by a treatment at 823 K followed by a slow cooling under He flow inside a thermobalance. Samples were checked for impurities using laboratory XRD. Sample Ni-0 was found to contain very small amounts of Y_2O_3 and CoO, whereas samples Ni-10 and Ni-20 showed no impurity phases within the detection limit of such technique. In particular, none of the Ni-substituted samples showed any evidence of Ni-based compounds' segregation.

2.2. Thermogravimetry

The oxygen uptake and release of $YBaCo_4O_7$ and related compounds have been widely investigated in the literature [6,7,18,14]. It is well established that even small deviations from the precise stoichiometry ($\delta \geq 0.018$) have profound effects on the crystal structure and magnetism of the system [14]. For such reasons, the final oxygen content in our samples was fine-tuned and controlled using TGA (thermogravimetric analysis). The as-synthesized pellets were crushed into smaller pieces of less than 250 mg. Measurements were carried under He flow (50 ml/min at 1000 Torr). Samples were heated from room temperature to 823 K at 5 K/min, then cooled back to room temperature (1st cycle) and the process was repeated (2nd cycle). For data treatment, the initial mass was selected just above 400 K (after any possible loss of water) and the mass loss was computed with respect to this value, after a baseline subtraction.

2.3. Synchrotron X-ray powder diffraction

In situ SXPD measurements were performed on the D10B-XPD beamline of the Brazilian Synchrotron Light Laboratory, LNLS, Campinas. An X-ray beam with a wavelength of ~1.0335 Å in a high-resolution configuration using a crystal analyzer was chosen to detect subtle differences between different space groups. The SXPD measurements were performed using copper sample holders with flat-plate shape in reflection geometry, placed inside a cryostat. X-ray diffractograms were recorded in situ between 300 K and 10 K at selected temperatures with a 2θ angular step of 0.005° and 10,000 monitor counts per step. Samples for the SXPD experiment were sieved using a 10 μm mesh in order to reduce crystallite size, increasing the number of crystallites in Bragg condition and their randomness. Nevertheless, the 10 μm mesh

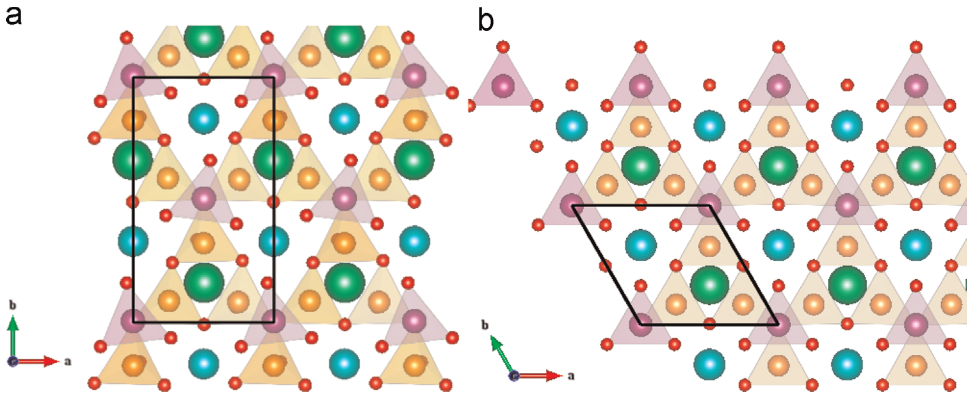

Fig. 2. View along *c* of the *P*31*c* (a) and *Pbn*2_1 (b) phases of $YBaCo_4O_7$ showing the geometrical relation between them. Only one half of the planes along *c* are projected for simplicity. Co atoms in the triangular and Kagomé layers are represented using different colors only as a guide. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)