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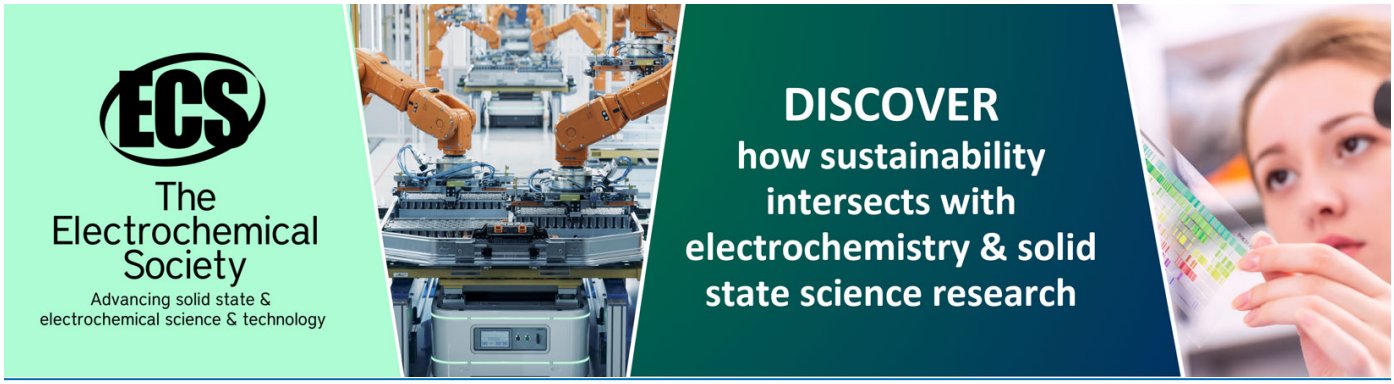

Structural and magnetic properties of $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ cobaltites

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Abstract. The magnetic and structural properties of non-stoichiometric $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ cobaltites have been studied by neutron and synchrotron powder diffraction. The oxygen content decrease leads to transformation of the magnetic structure from ferromagnetic to G-type antiferromagnetic through the two-phase state. Both coexisting phases have a cubic crystal structure with different volume of the unit cell.

1. Introduction

Rare earth cobaltites with an $LnCoO_3$ perovskite structure and hole-doped $Ln_{1-x}A_xCoO_3$ (Ln = lanthanide, A = alkaline earth metal: Ca, Sr or Ba) attract much interest as they exhibit a variety of unusual magnetic and transport properties. However the nature of the ferromagnetic state in cobaltites has been a subject of debates for a long time [1]. Three main mechanisms were suggested for magnetic properties of mixed-valence cobaltites: the superexchange model based on the localized electron interaction via oxygen ion, the Zener double exchange via charge transfer and the itinerant electron ferromagnetism [1].

The structural studies performed on the cubic oxygen-stoichiometric perovskite $La_{0.5}Ba_{0.5}CoO_3$ have revealed the onset of a long-range tetragonal phase accompanying a para-ferromagnetic transition occurring at T_C = 180 K [4]. The tetragonal distortion has been discussed in terms of cooperative and static Jahn-Teller distortions of the CoO_6 octahedra. It was assumed that the Jahn-Teller effect is favored by the intermediate spin-state configuration, of the $Co^{3+}(d^6)$ and $Co^{4+}(d^5)$ ions derived from the measured ferromagnetic moment 1.9 μ_B per cobalt ion. However, the Sr-doped ferromagnetic cobaltites have approximately the same magnetic moment value and do not exhibit a structural transition at the Curie point. Moreover EXAFS and neutron diffraction studies do not reveal an appreciable local Jahn-Teller distortion in $La_{1-x}Sr_xCoO_3$ [6,7].

It was shown that the oxygen content in the Ln and Ba ordered perovskite systems $LnBaCo_2O_y$ can be varied in a wide range from y = 4.5 to y = 6 that leads to a change of the average oxidation state of the cobalt ions from 2+ to 3.5+. The reduction of the oxygen content from y = 3 down to y = 2.25 has been reported for $La_{0.5}Sr_{0.5}CoO_y$ perovskite [6]. This oxygen content corresponds to nominal Co^{2+} oxidative state. Considering these reports we have decided to investigate the effect of oxygen deficiency on structural and magnetic properties of $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ cobaltites.

2. Experimental

Ceramic samples of $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ compositions were prepared by a solid-state phase reaction method using high-purity $BaCO_3$, La_2O_3 and CoO taken in stoichiometric ratio and thoroughly mixed with a planetary ball mill (RETSCH PM-100). The synthesis was performed at 1200 °C for 10 hours in air, followed by cooling at rate of 50-300 °C/h down to 300 °C or quenching. Synchrotron powder diffraction (SPD) experiments ware carried out at the Swiss Light Source synchrotron of the Paul Scherrer Institute using MS beamline (wavelength 0.49 Å) The neutron powder diffraction (NPD) experiments were performed using a high-resolution diffractometer E9 in Helmholtz-Zentrum Berlin (HZB) and HRPT spectrometer in Paul Scherrer Institute. The neutron and X-ray powder diffraction data were analyzed using the Rietveld method incorporated into the FullProf software package [8].

3. Results and discussion

Figure 1 presents the temperature dependence of the magnetization of the $La_{0.5}Ba_{0.5}CoO_{2.87}$ sample. In the temperature range of 160 –170 K the M(T) dependencies exhibit a sharp drop in both the FC and ZFC magnetization confirming a transition into paramagnetic state. The temperature onset of the magnetic ordering ($T_C \sim 170$ K) is slightly lower than in stoichiometric $La_{0.5}Ba_{0.5}CoO_3$ in which the ferromagnetic-paramagnetic transition occurs near $T_C \sim 180$ K [2]. The estimated magnetic moment per Co ion is close to 1.1 μ_B at liquid helium temperature. This value is much lower compared with 1.9 μ_B/Co reported for stoichiometric $La_{0.5}Ba_{0.5}CoO_3$ [2].

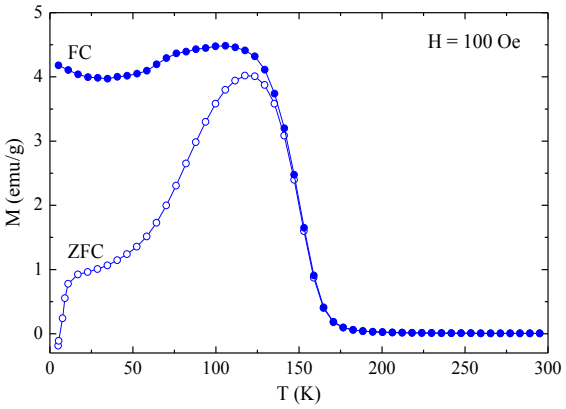

Figure 1. Temperature dependences of the dc magnetization in a field of 100 Oe for $La_{0.5}Ba_{0.5}CoO_{2.87}$.

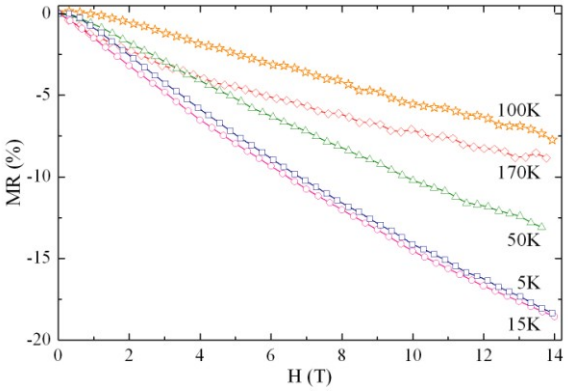

Figure 2. Field dependence of the magnetoresistance ratio MR=[ρ(H)–ρ(H=0)]/ ρ(H=0)*100% for the ferromagnetic $La_{0.5}Ba_{0.5}CoO_{2.95}$

Figure 2 shows magnetoresistance ratio for the ferromagnetic sample $La_{0.5}Ba_{0.5}CoO_{2.95}$ as a function of magnetic field at various temperatures. The magnetoresistance exhibits a local maximum near Tc, and increases gradually with further cooling. At 5K we obtained the MR value of about 20% in the field of 14 T. The MR varies gradually with the field and does not show any tendency to saturation with the temperature decrease.

NPD patterns of $La_{0.5}Ba_{0.5}CoO_{2.87}$ were recorded at room temperature, 150, 120, 80 and 2 K, and for clarity only one of them are displayed in figure 3. The first pattern recorded at 293 K is characteristic of the high-temperature structural state which extends down to ~ 200 K as follows from the SPD study. At room temperature the Rietveld refinements lead to a simple cubic cell $a_p \times a_p \times a_p$ with the space group $Pm\bar{3}m$ (global $\chi^2 = 1.76$). The observed, calculated and difference patterns of this sample recorded at 2K are displayed in figure 3. At 150 K we have noticed an asymmetric broadening of all the peaks which develops strongly upon cooling to 120 K. For the patterns recorded at 80 and 2 K we

clearly observed a splitting of all the peaks at $2\theta > 60°$ and an appearance of new small peaks strongly separated from the basic peaks described with $Pm\bar{3}m$ space group.

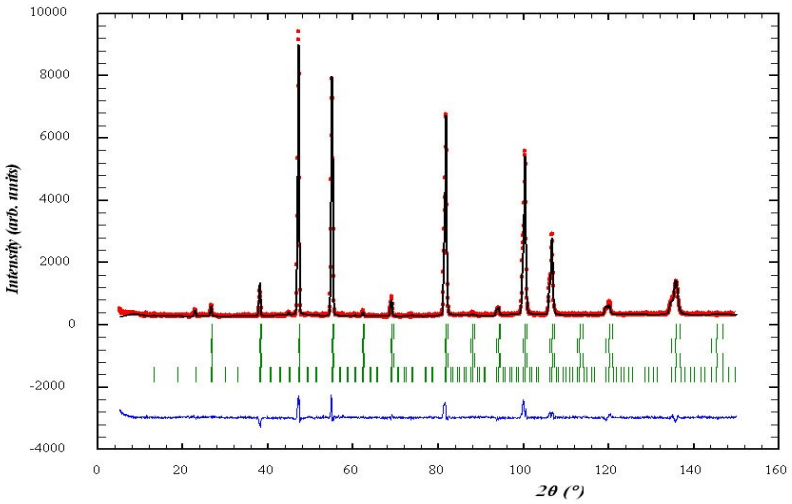

Figure 3 Neutron powder diffraction data collected from $La_{0.5}Ba_{0.5}CoO_{2.87}$ at 2K. Experimental curve and Rietveld refinement of crystal and magnetic structures are shown.

SPD experiments were performed in order to clarify a reason for NPD peaks splitting and appearance of the new peaks. The SPD spectra were recorded at every 5 K from 4 K up to room temperature using the same sample as for the NPD study. The volume ratio between the two phases at 2 K is approximately 1:2 where the major phase is closer to the high-temperature structural state. The amount of the minor phase, which has a larger unit cell decreases gradually upon warming up, and disappear completely above 200 K where the sample consists of one cubic phase. In contrast with NPD study we did not observe additional diffraction peaks associated with deviation from cubic symmetry of both low temperature phases, suggesting that additional peaks observed at low temperature in NPD patterns result from magnetic ordering. We suggest that both phases have a cubic unit cell at low temperature which can be described with $Pm\bar{3}m$ space group. The Rietveld refinement in this model gave a satisfactory fit for the SPD pattern recorded at 4 K. In the temperature range where two phases coexist the unit cell parameters of both phases slightly increase with temperature. There is no evidence for intermediate state between phases with close unit cell parameters.

The Rietveld refinement of the NPD spectra acquired at 2 K in the two cubic phase model leads to satisfactory description of basic structural peaks for both the structural phases. The fit was further improved by taking into account magnetic neutron scattering. The additional peaks appearing at low temperature can be well indexed in $2a_p \times 2a_p \times 2a_p$ supercell where a_p is unit cell parameter for the minor phase with larger unit cell parameter. This means that the magnetic structure associated with the minor phase is G-type antiferromagnetic. The estimated magnetic moment for this phase is around $\pm 2\ \mu_B$/Co. The major phase is ferromagnetic with magnetic moment close to 1.6 μ_B/Co. The oxygen content of the minor phase was roughly estimated as smaller in compered with the major ones. Apparently phase separation is associated with different spin state of the cobalt ions in the ferromagnetic and ferromagnetic phases.

The neutron powder diffraction of strongly oxygen-deficient $La_{0.5}Ba_{0.5}CoO_{2.6}$ has been recorded at T = 2, 50, 100, 150 and 250K. Figure 4 presents the pattern at the T = 2 K, together with Rietveld

refinement of crystal and magnetic structures. All data can be refined only with one phase in the frame of cubic $Pm\bar{3}m$ space group, the magnetic structure is G-type antiferromagnetic.

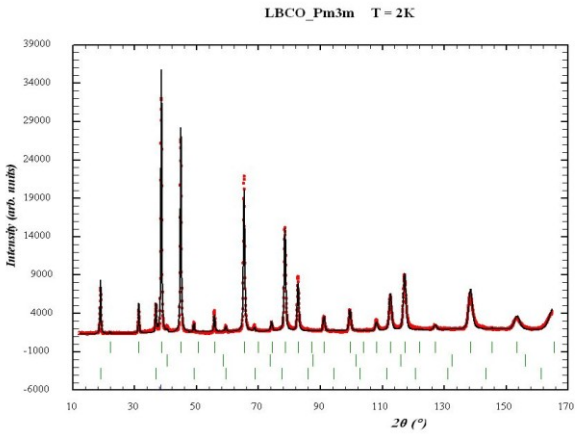

Figure 4. Neutron powder diffraction data for $La_{0.5}Ba_{0.5}CoO_{2.6}$ at 2 K. Experimental data and Rietveld refinement are shown.

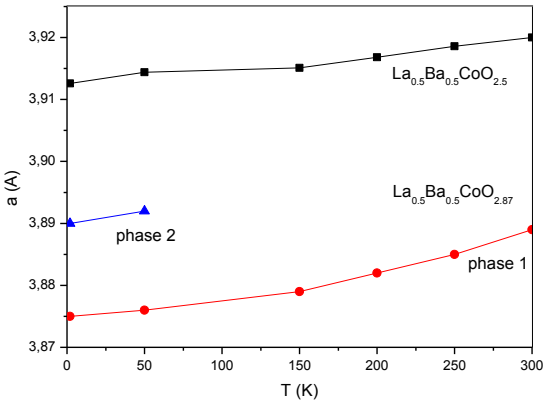

Figure 5. Temperature dependence of the unit cell parameters for $La_{0.5}Ba_{0.5}CoO_{2.6}$ and two phases of $La_{0.5}Ba_{0.5}CoO_{2.87}$

The temperature dependence of the cubic unit cell parameters for $La_{0.5}Ba_{0.5}CoO_{2.5}$ (upper curve) and $La_{0.5}Ba_{0.5}CoO_{2.87}$ (two lower curves) respectively is presented on the Figure 5. There is no evidence for the existence of intermediate state between phases with close unit cell parameters for $La_{0.5}Ba_{0.5}CoO_{2.87.}$

In conclusion, high-resolution neutron and synchrotron powder diffraction studies of the non-stoichiometric compounds $La_{0.5}Ba_{0.5}CoO_{3-\delta}$ show that the decrease of the oxygen content leads to a transformation of the ferromagnetic structure into G-type antiferromagnetic one via intermediate region of the compositions demonstrating a macroscopic phase separation into different structural and magnetic phases. Both antiferromagnetic and ferromagnetic phases have a cubic crystal structure with different volume of the unit cell. The amount of antiferromagnetic phase increases gradually with cooling, and the calculated ratio between antiferromagnetic and ferromagnetic phases at 2 K is about 1:2 for the $La_{0.5}Ba_{0.5}CoO_{2.87.}$ The estimated magnetic moment is around $\pm 2\ \mu_B$/Co for the antiferromagnetic and 1.6 μ_B/Co for the ferromagnetic phase. The strongly reduced $La_{0.5}Ba_{0.5}CoO_{2.6}$ is pure antiferromagnetic.

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