ESRF	**Experiment title:** **Pressure dependence of crystal structure of $La_{0.5}Ba_{0.5}CoO_{2.75}$**	**Experiment number:** **HC-4661**
Beamline: **ID-15B**	**Date of experiment:** from: **10.11.2021** to: **13.11.2021**	**Date of report:** 15.03.2022
Shifts: 9	**Local contact(s):** **Michael Hanfland**	*Received at ESRF:*

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The main goal of this proposal is to obtain reliable experimental data on the crystal structure, isotropic ADP for Co and O, as well as lattice parameters of La0.5Ba0.5CoO2.75 under applied pressure. The combination of X-ray with neutron (D20, ILL) diffraction and XMCD data (ID-12, ESRF, accepted proposalHC-4142) taken at high pressure will give us the opportunity to analyze the crystal with magnetic and electronic structure distortions in order to establish the correlations between crystal and magnetic structure changes and clarify the origin of magneto-structural phase transition in La0.5Ba0.5CoO2.75 at ambient pressure near the AFM-FM, PM-FM, the ST as well as to provide an input for detailed state-of-the-art DFT calculations to verify the mechanism of selective pressure effect on the magnetic ground state and small structural distortions, including the analysis of isotropic ADP for Co and O have been collected at the 50 and 300 K.

The cobaltites with perovskite structure are systems with fascinating transport and magnetic properties [1-7]. In comparison to manganites, they have additional degree of freedom: the spin state of Co ion. The parent compound $LaCoO_3$ (LCO) is a paramagnetic (PM) insulator at low temperature (LT). As temperature increases a gradual spin transition (ST) from a low spin (LS, $t_{2g}^6e_g^0$) to intermediate (IS, $t_{2g}^5e_g^1$) or high (HS, $t_{2g}^4e_g^2$) spin-state occurs, accompanied with insulator to metal transition at ~550 K[1-5]. Previous studies showed that chemical substitutions in LCO can induce a long-range magnetic antiferromagnetic (AFM) or ferromagnetic (FM) order [1-6]. For example, low doped $La_{1-x}Ba_xCoO_{3-\delta}$ become AFM insulators [3]. One possible explanation for these phenomena is stabilization of the HS state. Surprisingly, the T_c at these compositions increases under applied pressure [7], however the origin of the magnetostructural phase transition is still unclear. In a medium-doped oxygen deficit compound $La_{0.5}Ba_{0.5}CoO_{2.75}$ all cobalt atoms are in the oxidative state of 3+ and FM ordering is gradually suppressed upon temperature decrease. It leads to a large magnetic anisotropy and giant magnetoresistance. At LT the stabilization of AFM phase was found by the neutron diffraction measurements.

Rietveld refinement carried out on the XPD patterns (Fig. 1) assumes cubic symmetry of the lattice (space group *Pm*3*m*) for $La_{0.5}Ba_{0.5}CoO_{2.75}$ at 50 K and 300 K.

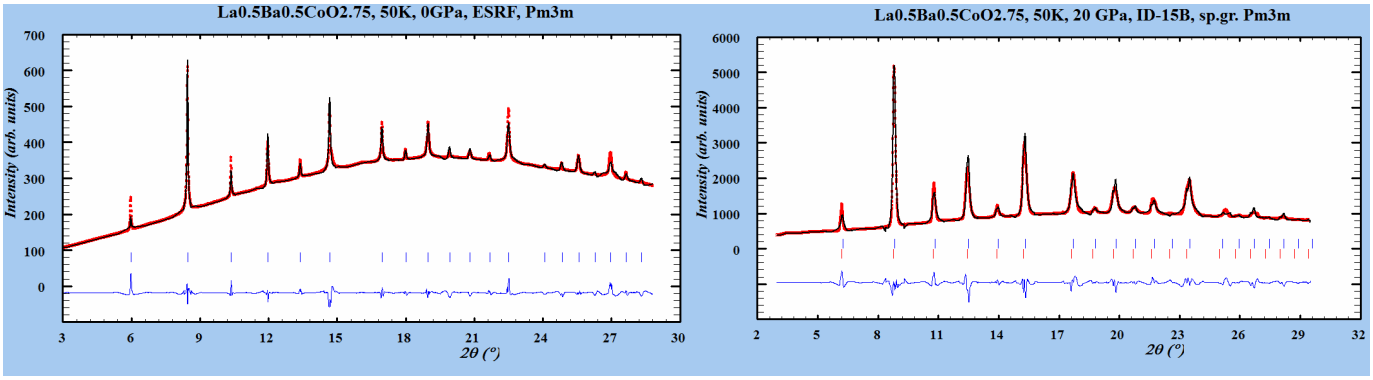

Fig. 1. The Rietveld refinement of the synchrotron X-ray diffraction data for $La_{0.5}Ba_{0.5}CoO_{2.75}$ measured at 50 K at 0 GPa and 20 GPa, with experimental data in open circles, the calculated pattern in blue, and the difference curve in blue. The tick marks indicate Bragg peak positions for one *Pm*3*m* (blue) at ambient pressure and two *Pm*3*m* (blue + red) at 20 GPa.

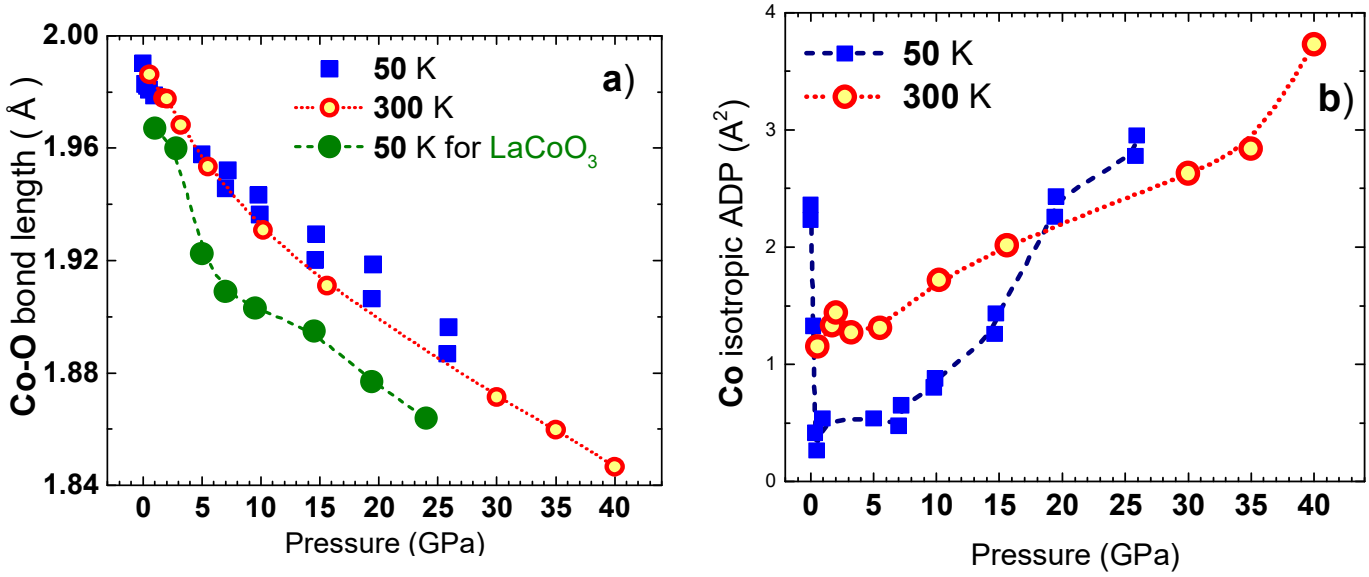

Fig. 2. The pressure dependence of the $La_{0.5}Ba_{0.5}CoO_{2.75}$ and reference $LaCoO_3$ (sp.gr. R-3c) (**a**) Co-O bond length for $La_{0.5}Ba_{0.5}CoO_{2.75}$ at 50 K and 300 K and for $LaCoO_3$ only at 50 K; (**b**) Isotropic ADP of Co for the $La_{0.5}Ba_{0.5}CoO_{2.75}$ at 50 K and 300 K.

When pressure is applied, the Co-O bond length of the $La_{0.5}Ba_{0.5}CoO_{2.75}$ and reference $LaCoO_3$ is gradually decreasing at 50 K and 300 K (Fig.2a). However, above pressure 7 GPa at 50 K for $La_{0.5}Ba_{0.5}CoO_{2.75}$ the Rietveld refinement confirmed the transformation of one cubic phase into the two ones.

The Isotropic ADP of Co for the $La_{0.5}Ba_{0.5}CoO_{2.75}$ shows a sharply growth below 2 GPa at 50 K and the linear behavior at room temperature (Fig.2b). Such behavior is an indication of the HS→LS transition of Co^{3+} ions, which are absent at room temperature. We suppose that this spin-sate transition is best described by a mixture of LS and HS or IS. It is well documented that the ionic radius of the HS state (0.61 Å) is significantly larger than that of the LS (0.54 Å) and IS (0.56 Å) states.

References

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