Experiment Report Form

	Experiment title: Phase diversity and patterns of phase transformations in $RBaCo_4O_{7+x}$	**Experiment number**: CH-4999
Beamline: ID22	**Date of experiment**: from:05.05.2017 to:09.05.2017	**Date of report**: 09.06.2017
Shifts: 12	**Local contact(s)**: Andy Fitch	*Received at ESRF:*

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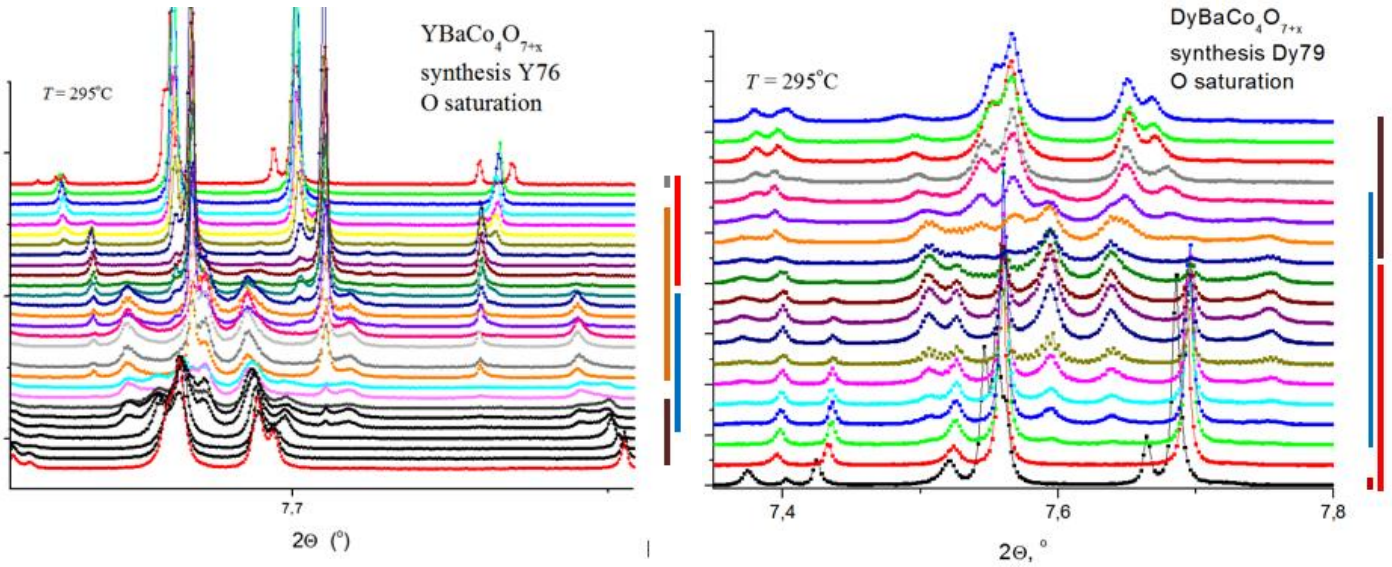
The aim of this project is to investigate in details the phase diversity in layered cobaltates *R*$BaCo_4O_{7+x}$ (further *R*114) for *R* = Y, Dy, Lu and to elucidate the phase transformations that occur upon the variation of oxygen concentration and temperature. We investigated 94, 29 and 14 samples of Y, Dy and Lu *R*114 ceramics with different oxygen content, which were *ex situ* prepared and preliminary characterized using *in house* laboratory and synchrotron powder diffractometers at ambient conditions. For Y114 and Dy114 samples, obtained by both oxygen saturation of $x = 0$ samples (“direct synthesis”) and desaturation of some different saturated samples (“reverse synthesis”), were investigated. Lu114 samples were obtained only by direct synthesis.

For each of the samples “low-exposition” powder diffraction patterns were obtained using high-resolution detector (T=295.0 K, λ=0.354216 Å, 0.5–27.9° 2θ range, 5°/min). “High-exposition” (T=295.0 K, 0.5–27.9° 2θ range, 1°/min) and “temperature movie” (T = 295.0 K → 80 K→ 500 K → 295 K, 360 Kph, 6.1–10.5° 2θ range, 10°/min) were performed for 37 and 8 preselected samples.

Existence of diversity of oxygen-saturated phases were shown for each of the system. There are **five** (**0**, **α**, **β**, **γ**, **δ**), **four** (**α**, **β**, **γ**, **δ**) and **two** (**α**, **β**) distinctly different *R*114-based phases were found in Y (fig. 1a), Dy (fig. 1b) and Lu (fig. 2a) systems at room temperature. Phases **α**, **β** are hexagonal with different unit cell volumes, which are close to one of parent structure. Phase **0** (low-temperature modification of unsaturated *R*114) and **δ** (maximally

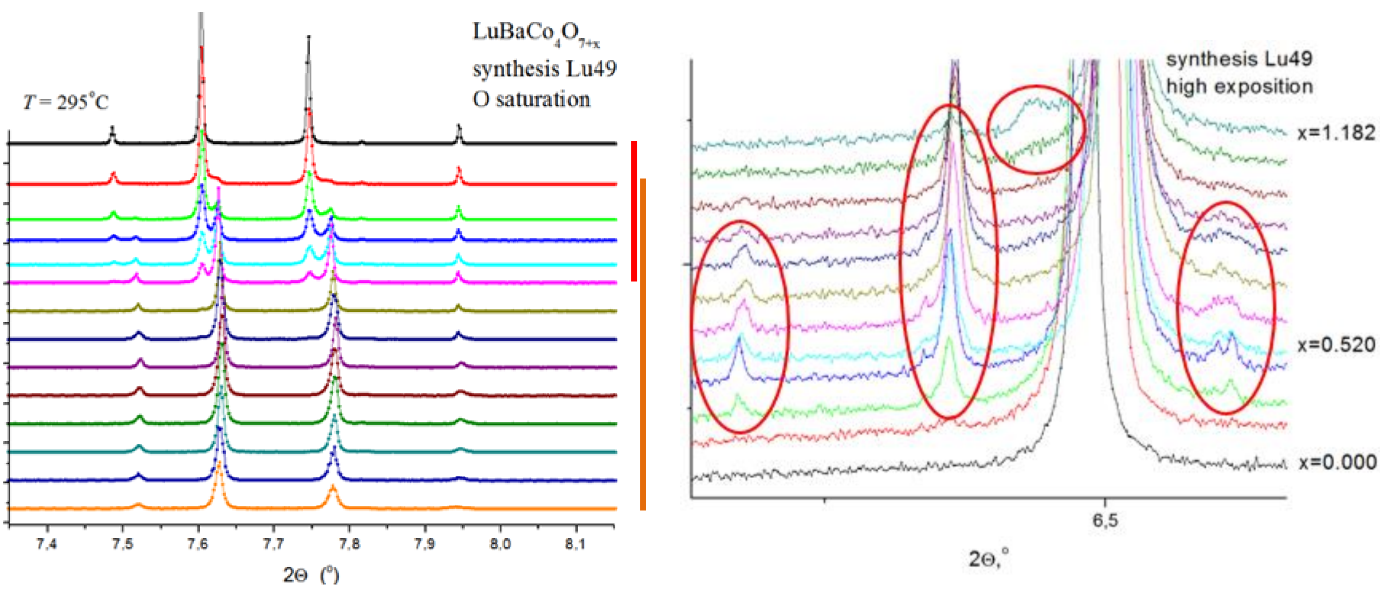


a b

Figure 1. Evolution of powder diffraction patterns of Y114 (a) and Dy114 (b) at oxygen saturation. Regions of different phases existence are shown by vertical color bars (**0** – gray, **α** – red, **β** – orange , **γ** – blue, **δ** – brown).

saturated *R*114 with x → 1.5) are of orthorhombic system with doubled unit cell volumes. Phase **γ** is a complex modulation of orthorhombic distortion of parent phase.

Existence of additional phases in each of the investigated systems is expected after more accurate data processing. For Y114 splitting of both **α** and **δ** phases onto two different "subphases" is expected based on anomalous behavior of unit cell parameters dependence on *x* (fig. 3). For Lu114 determination of regions of special modulations of **β** phase is possible based on comparison of high-exposition powder diffraction (fig. 2b) and available single crystal diffraction data.



a b

Figure 2. Evolution of powder diffraction patterns of Lu114. Regions of different phases existence are shown by vertical color bars (a) (**α** – red, **β** – orange). Changing of satellite reflections during oxygen uptake of **β** phase (b).

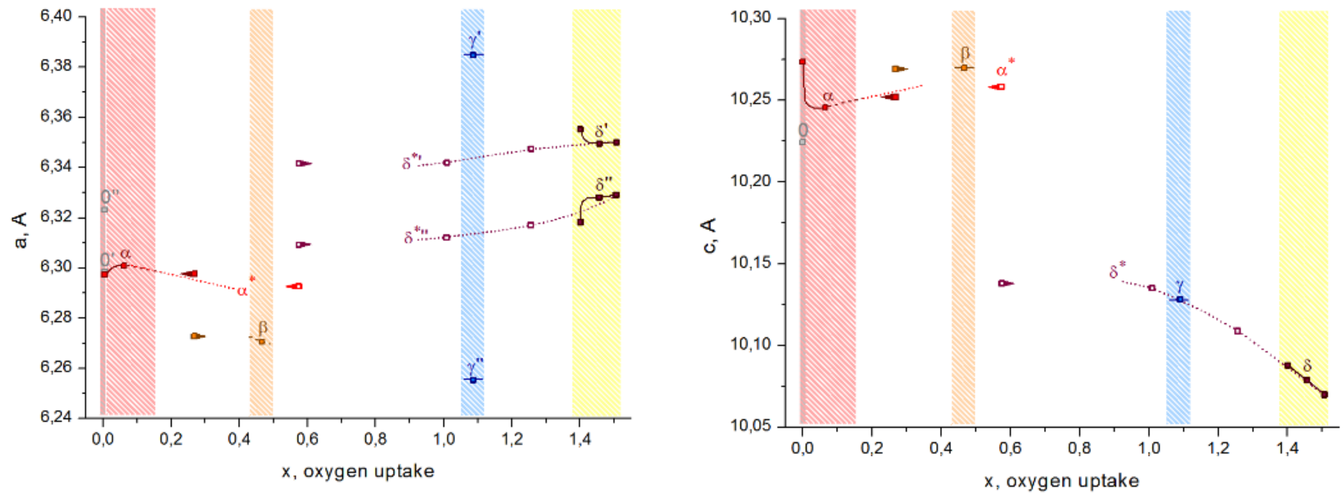


Figure 3. Changing of unit cell parameters for Y114 phases depending on oxygen composition *x*. Vertical color bars show regions of stability of corresponding phases. Unit cell parameters for phases obtained by direct synthesis shown with filled squares, for ones, obtained by reverse synthesis (**α*, δ***) – with empty squares. For orthorhombic phases two *a* parameters are given ($a' = a/k$, $a'' = b/\sqrt{3}$, where *k* is order of modulation in *a* direction).

Possibility of obtaining of metastable phases of the same composition depending on synthesis conditions (initial state, direction of oxygen composition changing) was demonstrated (fig. 3).

Obtained results will be presented in three articles in peer-reviewed scientific journals. Obtained data and characterized samples will be used for further structure and thermodynamic investigation of *R*114 phases.