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Experiment Report Form

	Experiment title: **Superstructures and short-range ordering in $YBaCo_4O_{7+x}$ microcrystals**	**Experiment number**: CH-5321
Beamline: ID11	**Date of experiment**: from:23.07.2018 to:27.07.2018	**Date of report**: 2.03.2020
Shifts: 9	**Local contact(s)**: Marta Majkut	*Received at ESRF:*

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The aim of this project was to investigate structural reasons of the phase diversity in "layered" cobaltates $YBaCo_4O_{7+x}$ (*Y114*) as a function of oxygen content. The existence of at least six distinct phases in this system possessing essentially the same structural motif at different oxygen contents was previously confirmed using high-resolution powder X-ray diffraction on ceramic samples. This work was dedicated to eliminate a number of uncertainties in the powder diffraction data interpretation as well as to obtain high-quality diffraction data in 3D reciprocal space for more reliable understanding of the regularities of oxygen sites in $RBaCo_4O_{7+x}$ crystals.

The data were collected as sets of 2D frames (FReLoN 4M detector, λ = 0.30996 Å, 20×20 μm^2 beam size) at (1) x-y grid scan of ceramics grains sown on amorphous SiN membranes, assisted by XRF spectroscopy, (2) integrating φ-scans (Δφ 0.25°), centered on selected grains, and (3) diffraction tomography x-y-φ-scan performed on one grain agglomerate.

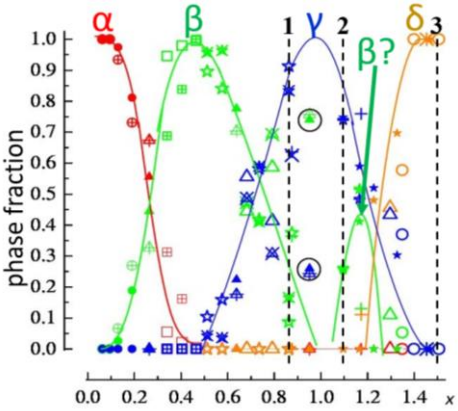

Figure 1. Dependence of Y114 phase content on oxygen saturation (x) based on ID22 XPD data.

The first stage was used for preliminary selection of appropriate size grains with the simplest (ideally, one-domain) diffraction. Three SiN membranes with the samples of $RBaCo_4O_{7+x}$, x = 0.866 (**1**), 1.065 (**2**) and 1.497 (**3**) were scanned. As a result, five grains (**1a**, **1b**, **2a**, **3a**, **3b**) were selected for detailed φ-scaning. 3D reciprocal space analysis based on obtained data was done using CrysAlis/Ewald program, the results are listed in Table 1.

The obtained results confirm existence of three distinct Y114 phases with high oxygen content (β, γ and δ with x>0.4). Similarity of diffraction modulation of β phase in **1a** and **2a** grains gives strong evidence of their similarity and proves non-equilibrium character of γ to δ transformation. Difference in diffuse scattering of the

Table 1. Crystallographic data on domains, found in φ-scanned grains. Major domains IDs are in bold.

grain ID	domain ID	Bravais lattice	phase	unit cell parameters, Å	reduced hex. cell parameters, Å	diffraction peculiarities
1a	**1**	hP	β	21.74; 10.28	6.28; 10.28	no diffuse scattering
	2	oP	γ	10.16; 10.85; 12.77	6.26/6.38; 10.16	almost without diffuse scattering
1b	**1**	oP	γ	10.14; 10.87; 12.75	6.28/6.37; 10.14	almost without diffuse scattering
	2,3	—≠—	—≠—	—≠—	—≠—	domains are rotated at ±120° around $\boldsymbol{c}_{hex}$ related to the 1st domain
2a	**1**	hP	β	21.74;10.28	6.27; 10.28	no diffuse scattering
	2	oP	γ	10.14; 10.84; 12.75	6.26/6.38; 10.14	strong diffuse scattering in hkl_{hex}, l=n layers
	3	oP	—≠—	10.14; 10.86; 12.79	6.26/6.40; 10.14	—≠—
	4	oP	—≠—	10.15;10.83;12.80	6.25/6.40; 10.15	—≠—
	5-9	hP	β(?)		6.27; 10.31	very small domains
3a	**1**	oC	δ	10.09; 21.97; 38.13	6.36/6.34;10.09	strong diffuse scattering in hkl_{hex}, l=n layers
	2	oC?	δ		6.38/6.35; 10.10	very small domain
3b	**1**	oC	δ	10.07; 21.91; 38.04	6.34/6.32;10.07	strong diffuse scattering in hkl_{hex}, l=n layers
	2	oC?	δ		6.33/6.32; 10.08	very small domain

domains of γ in **1a**,**b** (almost absent) and **2a** demonstrate changes in the short-range order during its oxygen saturation and well agrees with interpretation of this phase as a solid solution. Chmaissem's orthorhombic phase structure model is an approximant of the γ phase. There are no any structure models both for β (seemingly ordered ×12 hexagonal superstructure), and for δ (×24 – concerning most localized diffuse peaks, or ×2 – concerning Bragg peaks only – orthorhombic superstructure with long-range order violations). Determination of the crystal structures based of hklFs generated via CrysAlis using direct methods was failed due to high R_{int} of the data. Nonetheless, the data may be used for the structure solution via direct-space or hybrid methods and apply strong limitations at high oxygen saturated Y114 phases structure modelling.

One of the most intriguing result is an absence of highly modulated orthorhombic phase (×10 orthorhombic superstructure with long-range order violations) solved via XRD analysis for large scale (linear size >100 μm) saturated single crystal. It may point on significant mechanochemical influence on the oxygen saturation-desaturation processes for the *R*114 cobaltates (*R* is for rare earth elements).

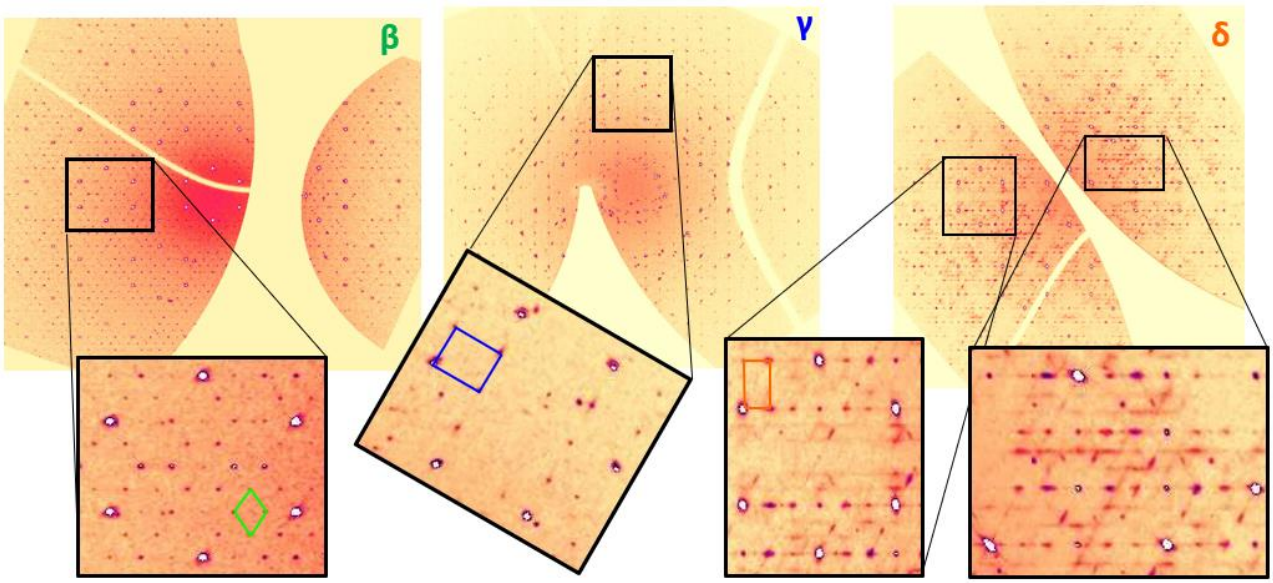

Figure 2. Reconstructions of diffraction intensity distribution over hk3 plains in high-saturated Y114 phases.