ESRF	**Experiment title:** Crystallographic structure of the new perovskite based Compounds $HoBaCo_2O_{5.5}$ and $TbBaCo_2O_{5.8}$	**Experiment number**: HE-803
Beamline: BM16	**Date of experiment**: from: 04 February 2000 to: 06 February 2000	**Date of report**: 28/02/2001
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Report:

The aim of the experiment was to determine the crystallographic structure of both compounds $HoBaCo_2O_{5.5}$ and $TbBaCo_2O_{5.8}$ which from previous neutron powder diffraction (NPD) measurements appear much more complex than the parent compounds $LnBaCo_2O_5$ (Ln=Y [1], Nd [2], Tb, Dy, Ho [3]) and $LaBaCo_2O_6$ [4], but exhibit spectacular magnetic properties. The complexity in the crystal structure arises from the multiple possibilities to distribute the oxygen ions in the Ln layer where half of the sites have to be occupied. Up to now, several studies using either laboratory X-ray and/or electron diffraction techniques, have been performed on $LnBaCo_2O_{5+\delta}$ (δ~0.5)-type compounds, have generally concluded to a crystal structure involving the doubling of the unit cell compared to the (δ~0) case [5,6] (Fig.1). However, a more complex structure involving a larger cell (tripling of the unit cell along the *a*- and *b*- crystallographic directions) have been reported in some cases based on electron diffraction observations [6,7]. Nevertheless, none of these two models could reproduce our NPD patterns.

Synchrotron powder diffraction, measurements on BM16 were performed, according to the proposed experiment, on $HoBaCo_2O_{5.5}$ and $TbBaCo_2O_{5.8}$ compounds using a λ=0.49116 Å wavelength. Samples were enclosed in 0.5mm diameter capillaries. For a better matching of NPD and SPD measurements, we have used in this experiment the same samples as for the previous NPD data collection. Unfortunately, due to the long delay between the NPD experiments and the synchrotron measurements, it appeared that our samples have lost their

original structure. This was particularly the case for $HoBaCo_2O_{5.5}$ for which we noticed on the first pattern collected at room temperature that the original structure almost completely transformed into the oxygen deficient phase $HoBaCo_2O_5$ (Fig.2). In the case of $TbBaCo_2O_{5.8}$, the "decomposition" of the sample was less advanced but could be detected from singular peak broadenings. Since then, similar sample instability has also been reported [1].

The remaining time was thus devoted to the study of a $LaBaCo_2O_6$ compound for which a phase transition from the pure cubic perovskite structure (S.G. *Pm-3m*, a_p~3.9 Å) was suspected to occur below the onset of Co ferromagnetism (T_C~210K). Careful comparisons of patterns collected at 150K and RT confirmed a reduction of symmetry. Here, we note that the sample environment (nitrogen cryoblower) installed on BM16 during experiment did not allow to cool down below 100K. This observed distortion is however much more pronounced at 2 K as it has been recently demonstrated by both NPD experiments performed on D2B/ILL using the highest possible resolution of the instrument (see ILL experimental report 5-23-513) and by SPD measurements performed on BM01b/ESRF.

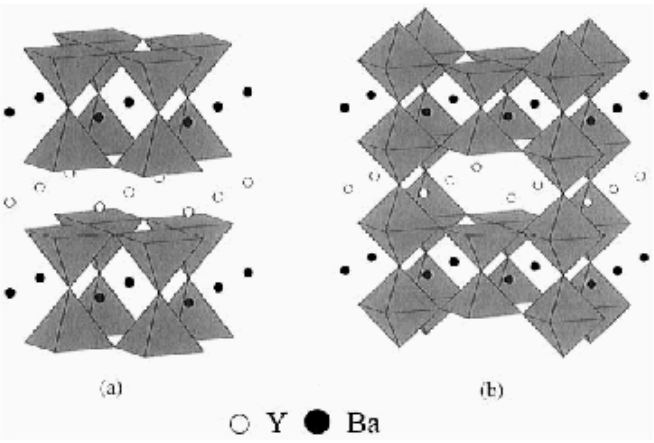

Fig 1 : Crystallographic structure of (a) $LnBaCo_2O_5$ [1-3] and (b) proposed structure for $LnBaCo_2O_{5.5}$ [5,6]

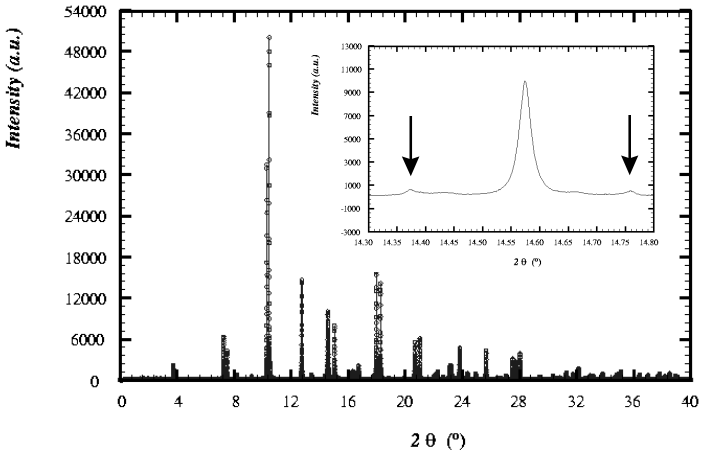

Fig 2 :SPD pattern of our assumed $HoBaCo_2O_{5.5}$ compound. The main phase is $HoBaCo_2O_5$, arrows indicate the remaining original phase.

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