ESRF	**Experiment title:** Observation of a ferroelastic phase transition in the $YBaCo_{4-x}Zn_xO_{7+\delta}$ system	**Experiment number**: HS-3394
Beamline: ID09A	**Date of experiment**: from: 04 Dec 2007 to: 7 Dec 2007	**Date of report**: 23.12.2008
Shifts: 9	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

E.A. Juarez-Arellano*, M. Avdeev, L. López-de-la-Torre*, S. Yakovlev*, L. Bayarjargal*, B. Winkler, A. Friedrich.

Goethe-Universität, Institut für Geowissenschaften, Frankfurt am Main, Altenhöferallee 1, D-60438, Germany.

Bragg Institute, ANSTO, PMB 1, Menai, NSW 2234, Australia.

Report:

Recently, a new family of isostructural cobaltates (MBaCo$_{4-x}R_x$O$_7$, M = In, Y, Ln; R = Co, Fe, Zn) has been synthesized [1]. These cobaltates belong to a new class of geometrically frustrated magnets which exhibit interesting physical properties. These compounds have a remarkable low-temperature oxygen absorption/desorption capability. It has been shown that up to ~20% of the total oxygen content is readily loaded or removed by just a minor change in temperature or atmosphere (O_2, N_2, air), and that the oxygen- absorption process is closely related to the mixed-valency of cobalt atoms [2-3]. A reversible transformation from a hexagonal structure (oxygen stoichiometric phase) to an orthorhombic structure (oxygen hyper-stoichiometric phase) has been reported [4]. At low temperature, diverse structural and magnetic phase transitions had been reported in several MBaCo$_{4-x}R_x$O$_7$ members. At high pressures, the study of single crystals of $HoBaCo_4O_7$ showed that the structure is stable up to 9 GPa [5].

We investigated the high-pressure behaviour of the isotypic compounds $YBaCo_4O_7$, $YBaCoZn_3O_7$ and $YBaCo_4O_{7+\delta}$ by in situ high-pressure powder diffraction experiments up to pressures of 30 GPa. We used synchrotron X-ray radiation at a wavelength of 0.4131 Å and a MAR345 image plate system. The samples were loaded into DACs using stainless steel gaskets and helium as a pressure-transmitting medium (PTM). Pressure was determined by means of the laser-induced ruby-fluorescence technique. The images were processed and integrated with FIT2D. LeBail refinements were carried out with Fullprof.

Main Results

Indications for pressure induced phase transitions were observed in all the samples followed by a continuous degree of amorphization upon increasing pressure. The ambient-pressure structure was recovered upon pressure release (Figure 1). It is known that amorphization can

be induced by the presence of large non-hydrostatic stresses. However, due to the use of helium as a PTM the pressure-induced broadening should be small in the present experiments. Therefore, we currently interpret that the amorphization is due to a pressure-induced ferroelastic phase transition, which can, according to Tolédano & Machon [6], lead to an amorphous phase due to the formation of a frustrated multidomain state.

The occurrence of a ferroelastic phase transition in the $YBaCo_{4-x}Zn_xO_{7+\delta}$ system is derived from several observations. First, the maximal amorphization was observed at different pressures: ~12 GPa ($YBaCo_4O_7$), ~14 GPa ($YBaCo_4O_{7+\delta}$) and ~ 18 GPa ($YBaCoZn_3O_7$), Fig. 1. Therefore, an amorphization only due to non-hydrostatic conditions is unlikely. Second, several new peaks appear in the pattern before the amorphization disguises them. Third, the reversibility of the amorphization process shows that it is not related to the decomposition of the materials under pressure. Unfortunately, with the data currently available it is not possible to identify the high pressure phase(s). Clearly what is needed now are high pressures experiments in which the residual strain is reduced by laser annealing in order to fully identify the high pressure phase(s).

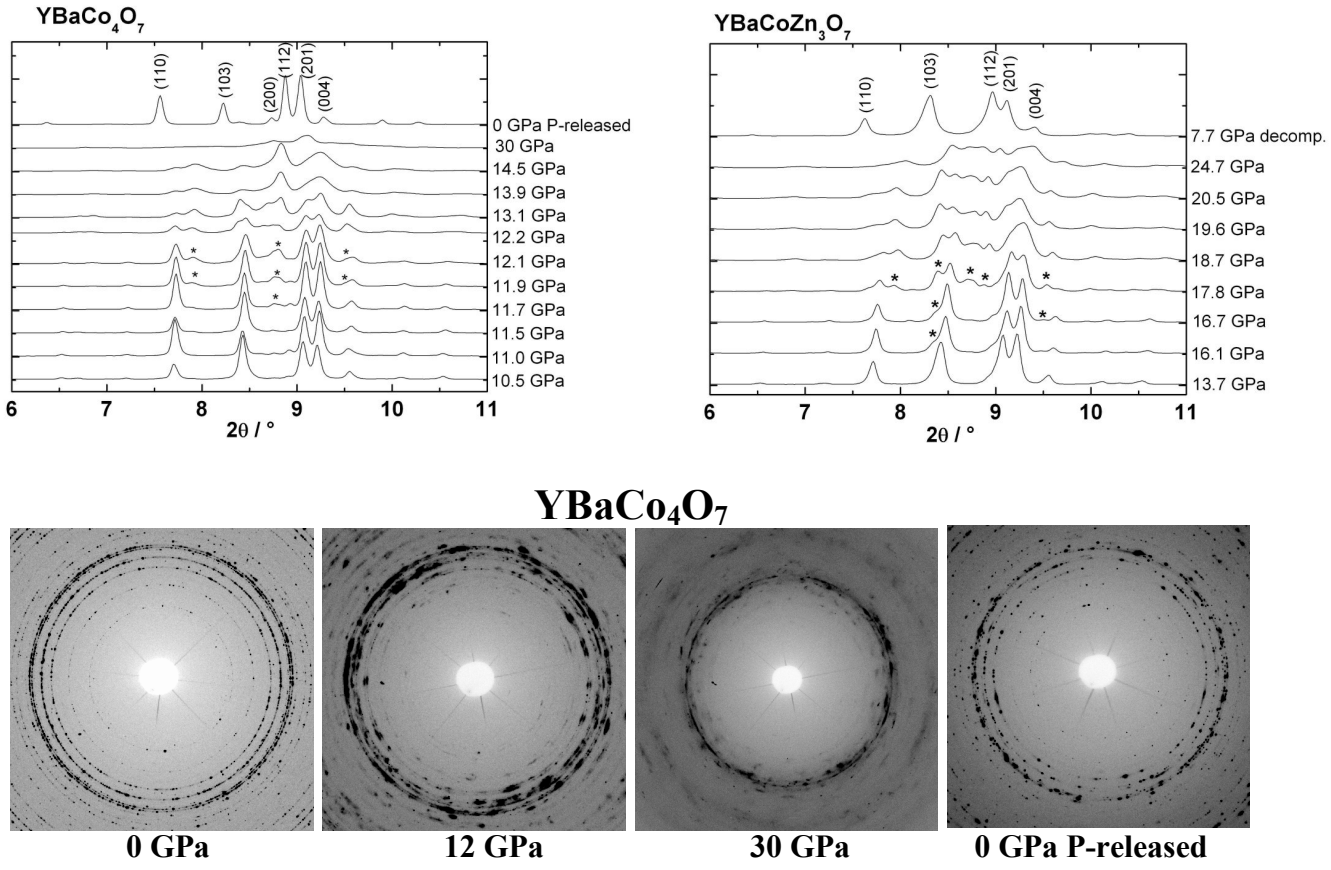

Figure 1. **Top**: Selected X-ray diffraction patterns of $YBaCo_4O_7$ and $YBaCoZn_3O_7$ at various pressures. Asterisks show new reflections. **Bottom**: X-ray diffraction images of $YBaCo_4O_7$ at different pressure.

References

[1] Valldor, M. (2004). Solid State Sciences **6**, 251-266. [2] Tsipis, E.V., Kharton, V.V., Frade, J.R. (2006). Solid State Ionics **177**, 1823-1826. [3] Karppinen, M., Yamauchi, H., Otani, S., Fujita, T., Motohashi, T., Huang, Y.H., Valkeapää, M., Fjellvag, H. (2006). Chemistry of Materials **18**, 490-494. [4] O. Chmaissem, H. Zheng, A. Huq, P. W. Stephens, and J. F. Mitchell, J. Solid State Chem. 181, 664 (2008). [5] E.A. Juarez-Arellano, A. Friedrich, D.J. Wilson, L. Wiehl, W. Morgenroth, B. Winkler, M. Avdeev, R. B. Macquart, C.D. Ling. Phys. Rev. B. submitted (2008). [6] P. Tolédano & D. Machon. (2005). Phys. Rev. B. **71**, 024210.