| ESRF | **Experiment title:** High-temperature structural anomalies in the mixed neodymium cobaltites-ferrites | **Experiment number:** MA2320 |
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| **Beamline:** ID22 | **Date of experiment:** from: 04. February to: 08. February 2015 | **Date of report:** 24. 02. 2016 |
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## Report:

Series of X-ray synchrotron powder diffarction experiment has ben performed at the high-resolutuion powder diffractometer at ID22 beamline in order to study of phase and structural behaviour of the mixed cobaltites-ferrites $NdCo_{1-x}Fe_xO_3$ in the temperature range of 298–1100 K.

The interest in the rare earth (*R*) cobaltites and ferrites is stimulated by their unique fundamental physical properties. In particular, $RCoO_3$ compounds exhibit temperature induced metal-insulator (*M–I*) transitions and different types of magnetic ordering, which are strongly dependent on the spin state of $Co^{3+}$ cations, whereas $RFeO_3$ ferrites exhibit spin-reorientation transitions at 80–200 K and the para- to antiferomagnetic transitions at 620–750 K. Probing of the thermal expansion is very sensitive tool to study the spin-state transitions and crystal-field excitations as well as their coupling to the lattice. Especially this is important for the Pr- and Nd-based compositions, where the spin-state transition is much better detectable in the thermal expansion data than in the magnetic susceptibility due to the large contribution of the 4*f* moments of Pr and Nd ions on the magnetic properties.

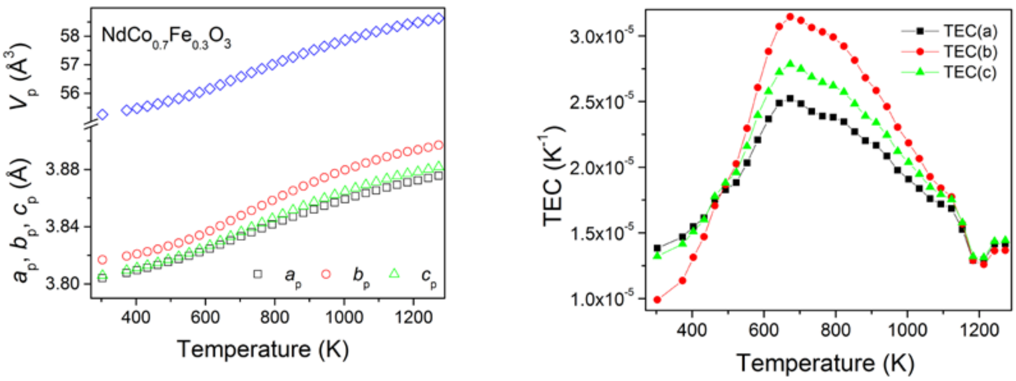


**Fig. 1.** Temperature dependence of the unit cell dimensions (left) and thermal expansion coefficients (right) of $NdCo_{0.7}Fe_{0.3}O_3$.

*In situ* powder diffraction investigations of the Nd cobaltites-ferrites at beamline ID22 of ESRF revealed anomalous lattice expansion, which is reflected in a sigmoidal dependence of the unit cell dimensions and in anomalous anisotropic increase of the thermal expansion coefficients (TEC) with (several) broad maxima in the temperature range of 500–1000 K, depending on the composition. Corresponding examples for $NdCo_{0.7}Fe_{0.3}O_3$ are shown on Fig. 1.

Pronounced anomalies were also detected in the selected bond lengths and octahedra tilt angles, as well as in the atomic displacement parameters (Fig. 2).

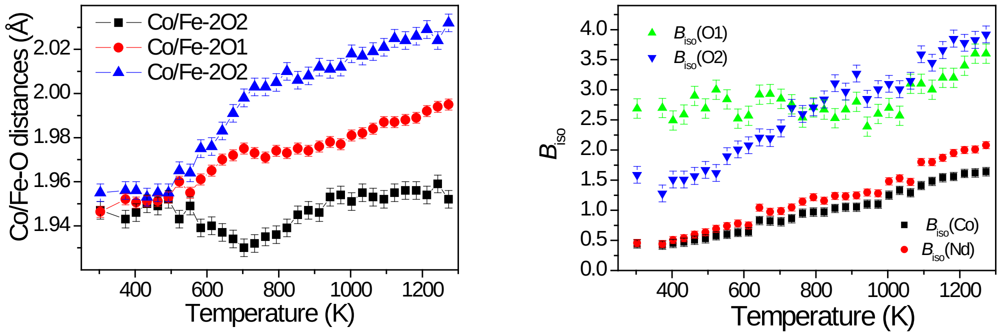


**Fig. 2.** Temperature dependence of intraoctahedral distances (left) and atomic displacement parameters (right) in $NdCo_{0.7}Fe_{0.3}O_3$.

The observed anomalies in the mixed cobaltites-ferrites are less pronounced comparing with the "pure" $NdCoO_3$ phase and decrease progressively with decreasing cobalt content in the $NdCo_{1-x}Fe_xO_3$ series (Fig. 3).

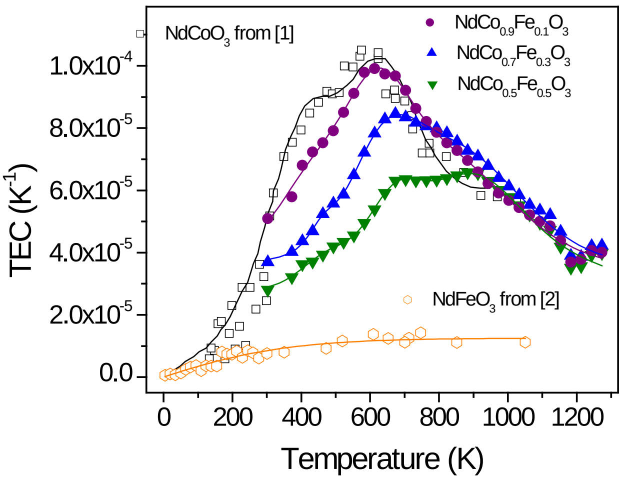


**Fig. 3.** Temperature dependence of average linear thermal expansion coefficients of $NdCo_{1-x}Fe_xO_3$ series ($x$ = 0.3, 0.5 and 0.1) in comparison with the literature data for the "pure" $NdCoO_3$ and $NdFeO_3$.

Obviously, the detected structural anomalies in $NdCo_{1-x}Fe_xO_3$ series are associated with the magnetic and electronic phase transitions occurred in the end members of the system. In particular, $NdCoO_3$ undergoes magnetic, spin-spin and metal-insulator transitions at 337 K, 466 K and 635 K [1], whereas corresponding ferrite $NdFeO_3$ shows the spin-reorientation transitions at 160 K and para- to antiferomagnetic transitions at 760 K [2,3]. It is evident that the coupling of the electronic and magnetic transitions with the lattice will result in extremely complicated magnetic and electronic phase diagram of the mixed cobaltite-ferrite systems.

## References

[1] K. Knížek, J Zirák, J. Hejtmánek, M. Veverka, M. Maryško, G. Maris, T.T.M. Palstra, *Eur. Phys. J. B47*, 213 (2005).

[2] W. Sławiński, R. Przeniosło, I. Sosnowska, E Suard, *J. Phys.: Condens. Matter* 17, 4605 (2005)

[3] J.-H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son, J. F. Scott, *Phys. Rev. Lett.* 107, 117201 (2011)