ESRF	**Experiment title:** High-temperature structural anomalies in the mixed samarium cobaltites-ferrites	**Experiment number**: 01-02-1065
Beamline: BM01A	**Date of experiment**: from: 14. Dezember to: 17. Dezember 2014	**Date of report**: 24. 02. 2016
Shifts: 9	**Local contact(s)**: CHERNYSHOV Dmitry	*Received at ESRF:*

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Report:

Series of X-ray synchrotron powder diffarction experiment has ben performed at the mulipurpose PILATUS@SNBL diffractometer at BM1A beamline in order to study of phase and structural behaviour of the mixed cobaltites-ferrites $SmCo_{1-x}Fe_xO_3$ in the temperature range of 298–1100 K.

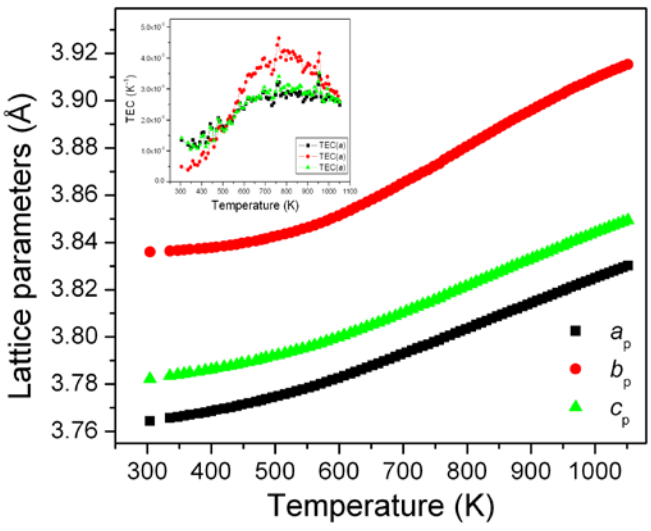

Fig. 1. Temperature dependence of the normalized cell parameters and thermal expansion coefficients (TEC) (insert) of $SmCo_{0.7}Fe_{0.3}O_3$.

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 for study of the spin-state transitions and crystal-field excitations as well as their coupling to the lattice.

Our *in situ* powder diffraction examinations of the mixed cobaltites-ferrites $SmCo_{1-x}Fe_xO_3$ at BM1A beamline of ESRF revealed anomalous lattice expansion, which is reflected in a sigmoidal dependence of the cell dimensions and broad maxima at the thermal expansion coefficients (TEC) curves (Fig. 1).

Anomalous anisotropic increase of the TEC's of $SmCo_{0.7}Fe_{0.3}O_3$, which passes through broad maximum at ~800 K (Fig. 1, insert) is apparently related to the changes in the spin state of Co^{3+} ions, which occurs in $SmCoO_3$ at 605 K [1]. Thorough analysis of the selected bond lengths and octahedra tilt angles, as well as atomic displacement parameters (adp's) reveals several structural anomalies in $SmCo_{0.7}Fe_{0.3}O_3$, among which the ~450 K and 720-730 K ones are especially pronounced (Fig. 2). Significant bond-length stretching inside Co/FeO_6 octahedra both at ~450 K and at 720-730 K and corresponding extrema at adp's curves (Fig. 2a, b) indicate the Jahn-Teller distortion (which may be dynamic) associated with IS/HS Co^{3+} species.

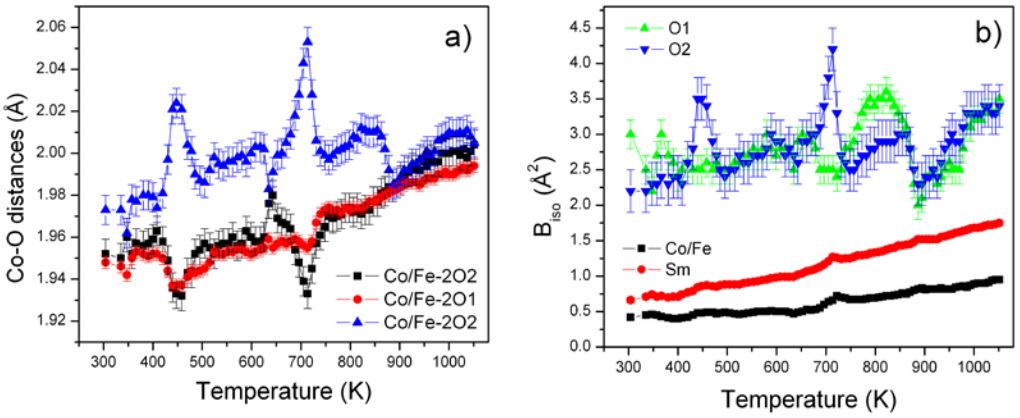

Fig. 2. Temperature dependencies of the Co/Fe-O bond lengths (a) and displacement parameters of atoms (b) in $SmCo_{0.7}Fe_{0.3}O_3$ structure.

According to Ref. [1] the transition from LS to IS/HS states of Co^{3+} in $RCoO_3$ cobaltites (R=La, Pr and Nd) introduces bond-length fluctuation that suppress the phonon contribution to thermal conductivity. It is possible that ~450 K and 720-730 K anomalies in $SmCo_{0.7}Fe_{0.3}O_3$ are associated with the magnetic and electronic phase transitions occurred in the end members of the system. In particular, "pure" $SmCoO_3$ undergoes magnetic and metal-insulator transitions at 493 K and 693 K [1], whereas $SmFeO_3$ shows the spin-reorientation transition at 480 K and para- to antiferomagnetic transition at 670 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.

The observed anomalies in the mixed cobaltites-ferrites are less pronounced comparing with the "pure" $SmCoO_3$ compound and decrease progressively with decreasing cobalt content in the $SmCo_{1-x}Fe_xO_3$ series (Fig. 3).

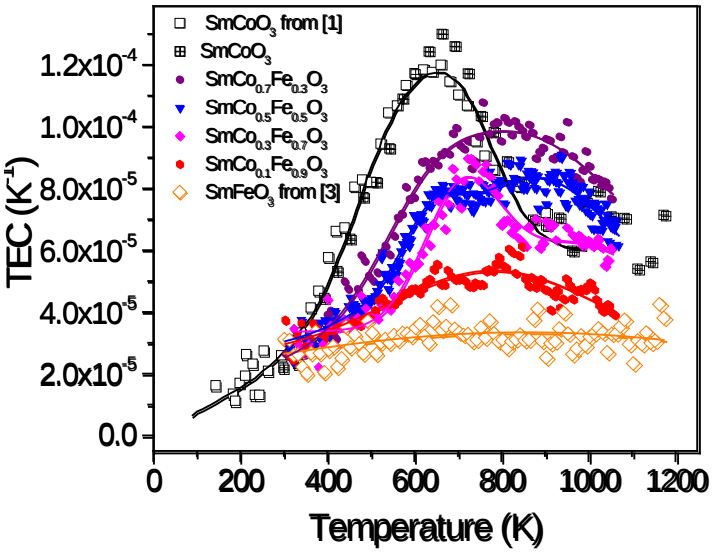

Fig. 3. Temperature dependence of average linear thermal expansion coefficients of $SmCo_{1-x}Fe_xO_3$ series (x = 0, 0.3, 0.5, 0.7 and 0.9) in comparison with the literature data for the "pure" $SmCoO_3$ and $SmFeO_3$.

Obviously, the detected structural anomalies in $SmCo_{1-x}Fe_xO_3$ series are associated with the magnetic and electronic phase transitions occurred in the end members of the system. 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

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