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Structural, electronic and magnetic phase transitions in complex oxide perovskites probed by X-ray synchrotron powder diffraction

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In situ temperature-dependence powder diffraction examinations and analysis of thermal expansion is very useful tool not only for the study of structural phase transitions, but also for the investigation of diverse electronic and magnetic phase transformations occurred in complex oxide and intermetallic systems. Especially this is important for the Pr- and Nd-based compositions, where the spin-state transition is seen much better 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.

Our recent *in situ* X-ray synchrotron powder diffraction investigations of the mixed cobaltites-ferrites RCo$_{1-x}$Fe$_x$O$_3$ (R = Pr, Nd, Sm, Eu, Gd, Tb) performed at ESRF beamlines BM1A and ID22 revealed anomalous lattice expansion, which is reflected in a sigmoidal dependence of the unit cell dimensions and in abnormal anisotropic increase of the thermal expansion coefficients (TEC) with (several) broad maxima in the temperature range of 500–1000 K, depending on the composition. Thorough analysis of the selected bond lengths and octahedra tilt angles, as well as the atomic displacement parameters (adp's) allows to detect extra structural anomalies, which are evidently associated with the electronic and magnetic phase transitions occurred in the RCoO$_3$–RFeO$_3$ systems at the elevated temperatures. As an example, significant bond-length stretching inside Co/FeO$_6$ octahedra in SmCo$_{0.7}$Fe$_{0.3}$O$_3$ structure at ~450 K and at 720–730 K (Fig. 1a) and corresponding extrema at the adp's curves (Fig. 1b) indicate the Jahn-Teller distortion (which may be dynamic) associated with excited spin states of Co^{3+} species. According to Ref. [1] the transition from low-spin to intermediate/high-spin state of Co^{3+} ions in RCoO$_3$ series introduces bond length fluctuation that suppresses the phonon contribution. It is evident that observed structural anomalies in SmCo$_{0.7}$Fe$_{0.3}$O$_3$, like as in other RCo$_{1-x}$Fe$_x$O$_3$ perovskites are associated with the magnetic and electronic phase transitions occurred in the end members of the systems. In particular, SmCoO$_3$ cobaltite undergoes magnetic, spin-spin and metal-insulator transitions at 493 K, 605 K and 693 K, respectively [2], whereas the SmFeO$_3$ ferrite shows spin-reorientation at 480 K and para- to antiferromagnetic transition at 670 K [3]. Clear sign for a magnetoelastic coupling has been detected in SmFeO$_3$ at the Néel-temperature of 675 K [4].

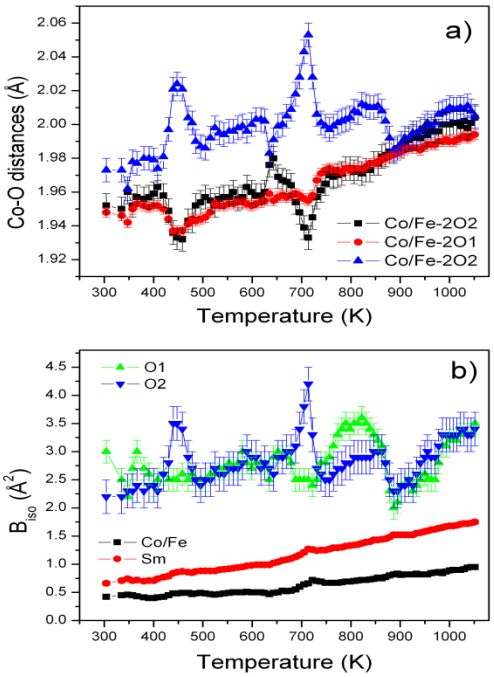

Figure 1. Temperature dependence of Co/Fe-O bond lengths (a) and atomic displacement parameters (b) in SmCo$_{0.7}$Fe$_{0.3}$O$_3$ structure reflecting a coupling of electronic and magnetic phase transitions to the lattice

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