The role of oxygen stoichiometry on phase stability and crystal structure of Sr$_2$CoIrO$_{6-\delta}$

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Recently we have synthesized a series of double perovskites La$_{2-x}$Sr$_x$CoIrO$_{6.00}$ for the first time and investigated temperature and composition (x) dependence of their crystal and magnetic structures [1]. In this work [2] we have prepared the end member Sr$_2$CoIrO$_{6-\delta}$ (x=2) with different oxygen stoichiometries and have analysed the structural behaviour and the magnetic properties in dependence on temperature and oxygen content.

The crystal structure of Sr$_2$CoIrO$_{6-\delta}$ in dependence on temperature was analysed by synchrotron powder diffraction at the beamline B2 at HASYLAB/DESY (Hamburg, Germany) and in dependence on both, temperature and gas atmosphere (air or Ar), by neutron powder diffraction on SPODI at the FRM II in Garching by Munich (Germany).

The investigations with synchrotron radiation in the temperature range of 10-1173 K were performed for $\delta = 0$ in a quartz capillary in air in Debye-Scherrer mode using the on-site readable image-plate detector OBI and a He closed-cycle cryostat or a STOE furnace equipped with a EUROTERM temperature controller. Measurements were performed with a temperature step of 25 K.

All diffraction patterns have been analysed by full-profile Rietveld refinements, using the software package WinPLOTR. In order to reduce the degree of correlation between B-site disorder and thermal displacement parameters, the structure model was refined with an isotropic approximation for the thermal parameters of all atoms, which were constrained into three groups: one value for all oxygen atoms, one for Sr and one common for Co- and Ir-atoms.

The structural symmetry of the solid solution Sr$_2$CoIrO$_{6-\delta}$ is strongly dependent on temperature and oxygen stoichiometry. Temperature and stoichiometry induced symmetry changes with preserved stoichiometry are caused by tiltings of CoO$_6$- and IrO$_6$-octahedra. The crystal structure of Sr$_2$CoIrO$_{6-\delta}$ without oxygen deficiency ($\delta = 0$) is monoclinic (I2/m) at room temperature, while Sr$_2$CoIrO$_{5.80}$ is tetragonal (I4/m). Synchrotron measurements of Sr$_2$CoIrO$_{6.00}$ in air showed a sequence of phase transitions at elevated temperatures: with increasing temperature it becomes tetragonal (I4/m) and cubic (Fm-3m): I2/m $\xrightarrow[620 K]{\text{620K}}$ I4/m $\xrightarrow[700 K]{\text{700K}}$ Fm-3m. There is no significant change of oxygen content in air at these temperatures according to thermogravimetric measurements. The measurements have shown that Sr$_2$CoIrO$_{6-\delta}$ is stable in Ar-atmosphere (p(O$_2$) $\leq 10^5$ bar) up to 1323 K, which corresponds to a $\delta$ of about 0.35, and decomposes with elimination of metallic Ir at higher
temperatures. The decomposition process is reversible and depends strongly on the oxygen partial pressure: after annealing of the decomposition products at 1423 K in air \( (p(O_2) = 0.21 \text{ bar}) \) only \( \text{Sr}_2\text{CoIrO}_{6.00} \) was formed again.

The low-temperature structural behaviour of \( \text{Sr}_2\text{CoIrO}_{6.00} \) and \( \text{Sr}_2\text{CoIrO}_{5.80} \) is different: synchrotron and neutron experiments revealed a structural phase transition \( I2/m \rightarrow P2_1/n \) of stoichiometric \( \text{Sr}_2\text{CoIrO}_{6.00} \) with a coexistence of both modifications below 220 K (Fig. 1), whereas oxygen deficient \( \text{Sr}_2\text{CoIrO}_{5.80} \) does not demonstrate any change in lattice symmetry, but only a decrease of the average interatomic Co-O and Ir-O distances at lower temperature. The relative amount of the \( I2/m \) modification in \( \text{Sr}_2\text{CoIrO}_{6.00} \) decreases with decreasing temperature as expected for a metastable phase, which is still coexisting after a first order phase transition.

Figure 1. A section of synchrotron powder diffraction patterns \( (\lambda = 0.50206 \text{ Å}) \) of \( \text{Sr}_2\text{CoIrO}_{6.00} \), recorded for increasing temperatures between 100 and 300 K in steps of 20 K (from top to bottom), revealing the existence of a two-phase region with \( I2/m \) and \( P2_1/n \) structures below 220 K.

References
