

Chemical Composition of the $\text{Sr}_x\text{CoO}_z \cdot r\text{H}_2\text{O}$ Misfit-Layered Cobalt Oxide Determined using TGA-MS

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Layered cobalt oxides - described with the general formula, $[\text{M}_m\text{A}_r\text{O}_{m+r-\delta}]_q\text{CoO}_2$ ($M = \text{Co}, \text{Bi}, \text{Pb}, \text{Tl}, \text{etc.}; A = \text{Ca}, \text{Sr}, \text{Ba}, \text{etc.}; m = 0, 1, 2; q \geq 0.5; r \geq 0; \delta \geq 0$) - possess a layered crystal structure consisting of two types of layer blocks: hexagonal $[\text{CoO}_2]$ block and rock-salt-structured $[\text{M}_m\text{A}_r\text{O}_{m+r-\delta}]$ block stacked incoherently to each other forming a composite crystal. The high structural anisotropy and weak inter-block interaction results into an easy modifiability of the physical and chemical properties of these compounds making them interesting objects for the research exploring oxide materials.

In this work we have focused on ($r = 2, m = 0$)-type phases of the layered cobalt-oxide family. First reported in year 2006, only two compounds have been discovered so far with $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$ and $[\text{Ca}_2\text{O}_2]_q\text{CoO}_2$ fundamental stoichiometries. Synthesis of the ($r = 2, m = 0$)-type phases is a sintering procedure taking place under elevated pressures of O_2 (g) and is known to be facilitated by the presence of H_2O (g). [1]

To understand the stabilizing role of H_2O for the ($r = 2, m = 0$)-type phases, Sr_xCoO_2 and $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$ containing sample-mixtures with a general sample stoichiometry of $\text{Sr}_x\text{CoO}_z \cdot r\text{H}_2\text{O}$ were synthesized and analyzed for their elemental compositions using TGA-MS. The TGA measurements were performed for each sample in both inert and reductive atmospheres. While the sample decomposition under the inert atmosphere leads into a formation of mixture of $\text{SrCoO}_{2.5+\delta}$ (s) (orthorhombic perovskite compound) with CoO (s), the decomposition under the reductive atmosphere results into a residual mixture of SrO (s) and Co (s). Under the inert atmosphere, the H_2O extraction steps were also possible to resolve from the O_2 -generating thermal reduction steps with the help of the MS observation of the TGA exhaust gas flow. Additionally, X-ray diffraction (XRD) was used for a qualitative confirmation of the sample compositions and the TGA residuals. Combining the data of the two different TGA runs under different atmospheres enabled an explicit determination the sample composition.

TGA-MS measurements revealed for the first time, that the phase commonly known as $[\text{Sr}_2\text{O}_2]_q\text{CoO}_2$ is flexible with its Sr^{2+} -cation stoichiometry and most interestingly contains large amounts of H^+ bound into the structure either as H_2O or OH^- species. The almost 1:1 relation of the Sr and H^+ in the $[\text{Sr}_2\text{O}_2]$ block implies that the given block might be rather of hydroxide than oxide character.

[1] H. Yamauchi, L. Karvonen, T. Egashira, Y. Tanaka, M. Karppinen, *J. Solid State Chem.* **184** (2011) 64.