Oxygen-deficient complex cobalt oxides attract special attention in the last years as potential materials for construction of dense membranes for the separation of oxygen from gas mixtures. We have prepared several new complex cobalt oxides with perovskite-like structure and different types of oxygen ordering.

New compounds with brownmillerite structure \( \text{Sr}_2\text{Co}_{1+x}\text{Ga}_{1-x}\text{O}_5 \) \( 0.3 \leq x \leq 0.8 \) have been synthesized. Crystal and magnetic structures were calculated using X-ray and neutron diffraction data. Compounds were found to have high Neel temperatures. In contrast to \( \text{Sr}_2\text{Co}_{1+x}\text{Ga}_{1-x}\text{O}_5 \) no compounds with a brownmillerite structure was found in the Ca-Ga-Co-O system. A new complex oxide \( \text{Ca}_2\text{Co}_{0.8}\text{Ga}_{1.2}\text{O}_{4.8} \) has been synthesized. It crystallizes in F-centered cubic structure with \( a = 15.0558 \) Å. High-temperature conductivity measurements revealed higher activation energy in comparison with \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-y} \) which can be explained by spatial separation of cobalt polyhedra in the structure.

We have synthesized new compounds in the system \( \text{Sr}_{1-x}\text{Ln}_x\text{CoO}_{3-\delta} \), where \( \text{Ln} = \text{Y}, \text{Sm}-\text{Tm} \) with \( x \leq 0.5 \). Refinement of the crystal structure of \( \text{Sr}_{0.7}\text{Y}_{0.3}\text{CoO}_{2.62} \) revealed new type of ordering of the oxygen vacancies where octahedral layers are separated by layers containing disordered oxygen vacancies.

Barium-contained oxides \( \text{Ba}_2\text{Co}_{2-x}\text{MxO}_{5+\delta} \), \( \text{M} = \text{In} \) and Sb depending on the nature of the second B-cation were found to have a cubic (\( \text{M} = \text{In} \)) structure or 6-H perovskite-like one (\( \text{M} = \text{Sb} \)).

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