Designing Composite Spin Chain Structures Built up of Dimeric and Trimeric Polyhedral Units: The oxides $A_{1+y}[(\text{Mn}_{1-x}\text{Co}x)_{1-z}\text{Co}z\text{O}_6]_3$ ($A = \text{Ca}, \text{Sr}; x = 3/8$)

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Spin chain oxides containing cobalt and manganese whose structure is closely related to the 2H hexagonal perovskite [1-5] offer a very attractive field for the investigation of magnetic and multiferroic properties. The structure of the prototypic one-dimensional manganate and cobaltate $\text{Sr}_2\text{Mn}_2\text{CoO}_6$ consists of chains of face-sharing $\text{Mn}_6$ octahedra and trigonal $\text{CoO}_6$ prisms. According to the very important study performed by Perez-Mato et al [2], these spin chain oxides can be described as a composite 2H hexagonal perovskite family $A_{1+y}[\text{Mn}_{1-x}\text{Co}x\text{O}_6]_3$. Recently the possibility of extra oxygen incorporation during synthesis has been evidenced leading to a large family aperiodic chain structures [6] expressed by the simple formal formula $\text{Sr}_{1+y}(\text{Mn}_{1-x}\text{Co}x\text{O}_6)_3$; it induces a decrease of the proportion of the number of trigonal prismatic sites ($N_0$) with respect to the octahedral sites ($N_0$) within the chains as $\delta$ increases and concomitantly the formation of cobalt vacancies on the trigonal prismatic sites. Therefore the structural formulae of these oxides must be expressed as $\text{Sr}_{1+y}[\text{Mn}_{1-x}\text{Co}x\text{O}_6]_3$.

The air-synthesized oxide $x = 3/8$-$\text{Sr}_{1+y}(\text{Mn}_{1-x}\text{Co}x\text{O}_6)_3$ is of great interest, since by decreasing the oxygen over stoichiometry to $\delta=0$, one should obtain the oxide “$\text{Sr}_{1+y}\text{Mn}_2\text{Co}_2\text{O}_6$” ($x = y, z = 0$) expected to be built up of trimeric and dimeric polyhedral units according to the sequence $[\text{Sr}_2\text{Mn}_2\text{CoO}_6]_2[\text{Sr}_2\text{CoMnO}_6]$. Such an oxide containing exclusively strontium was never synthesized in air due to the partial oxidation of $\text{Co}^{2+}$ into $\text{Co}^{3+}$, imposing $\delta>0$. We then have investigated the substitution of calcium for strontium in the pure Sr-phase $x = 3/8$ ($\delta=0.09$). The objective was to design composite structures built up of trimeric and dimeric units by decreasing $\delta$ down to zero through Ca for Sr substitution in order to finally obtain the stoichiometric oxide $A_{1+y}\text{Mn}_2\text{Co}_2\text{O}_6$ ($A = \text{Sr,Ca}$). We report herein on a series of $A_{11/8}(\text{Mn}_{1-x}\text{Co}x\text{O}_3)_3$ oxides with composite structures, commensurate or incommensurate, built up of trimeric $\text{M}_2\text{O}_6$ and dimeric $\text{M}_2\text{O}_6$ units ($\text{M} = \text{Mn, Co, } \text{Ca}$) with cationic vacancies on the trigonal prismatic sites. We also show the possibility to synthesize the quasi commensurate stoichiometric composite $\text{Sr}_{1+y}\text{Ca}_6\text{Mn}_2\text{CoO}_6]_2[\text{MnCoO}_6]$ ($\delta = 0.002$).

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