Designing Composite Spin Chain Structures Built up of Dimeric and Trimeric Polyhedral Units: The oxides $A_{1+y}[(Mn_{1-x}Cox)_{1-z}\lozenge_z]O_3$ (A = Ca, 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 $Sr_4Mn_2CoO_9$ consists of chains of face-sharing MnO_6 octahedra and trigonal 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 $A_{1+x}(Mn_{1-}Co_x)O_3$. 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 $Sr_{1+x}(Mn_{1-x}Co_x)O_{3+\delta}$; it induces a decrease of the proportion of the number of trigonal prismatic sites (N_P) with respect to the octahedral sites (N_O) within the chains as δ increases and concomitantly the formation of cobalt vacancies on the trigonal prismatic sites. Therefore the structural formula of these oxides must be expressed as $Sr_{1+y}[(Mn_{1-x}Co_x)_{1-z}\lozenge_z]O_3$.]

The air-synthesized oxide x = 3/8-$Sr_{1+x}(Mn_{1-x}Co_x)O_{3+\delta}$ is of great interest, since by decreasing the oxygen over stoichiometry to δ=0, one should obtain the oxide "$Sr_{11}Mn_5Co_3O_{24}$"(x = y, z = 0) expected to be built up of trimeric and dimeric polyhedral units according to the sequence $[Sr_4Mn_2CoO_9]_2.[Sr_3CoMnO_6]$. Such an oxide containing exclusively strontium was never synthesized in air due to the partial oxidation of Co^{2+} into Co^{3+}, imposing δ>0. We then have investigated the substitution of calcium for strontium in the pure Sr-phase x = 3/8 (δ~0.09). The objective was to design composite structures built up of trimeric and dimeric units by decreasing δ down to zero through Ca for Sr substitution in order to finally obtain the stoichiometric oxide $A_{11}Mn_5Co_3O_{24}$ (*A* = Sr,Ca). We report herein on a series of $A_{11/8}(Mn_{5/8}Co_{3/8})O_{3+\delta}$ oxides with composite structures, commensurate or incommensurate, built up of trimeric M_3O_9 and dimeric M_2O_6 units (M = Mn, Co, $_O$) with cationic vacancies on the trigonal prismatic sites. We also show the possibility to synthesize the quasi commensurate stoichiometric composite $Sr_{4.2}Ca_{6.8}[Mn_2CoO_9]_2.[MnCoO_6]$ (δ = 0.002).

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