Crystal Structure and Magneto-transport Properties of New Cobalt Based Layered Oxides

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The search for new layered cobalt based oxides is very important to discover interesting physical properties as recently illustrated by the discovery of a large thermoelectric power in the metallic phase $Na_{0.5}CoO_2$ [1] and by the report on the superconductivity of the derived hydrated compound $Na_{0.3}CoO_2$,$1.3H_2O$ [2]. Recent investigations in the Sr-Co-M-O systems (M = Ga, Ti….) by means of transmission electron microscopy techniques have allowed to detect new layered cobaltites. Their structure has been obtained by combining high resolution images and powder X-ray/neutron diffraction data.

Firstly, a new oxide, $(Ga_{1/3}Co_{2/3})_2Sr_2CoO_{6+\delta}$, has been isolated [3]. Its complex structure is described from a modulation vector $q^* = q_1a^* + q_2c^*$. For the as-prepared sample ($\delta \approx 0.4$), it can be described in an orthorhombic supercell *Bb2b* (q_1=1/3 and q_2=1) with the unit cell parameters $a=3a_p\sqrt{2}$, $b=a_p\sqrt{2}$ and c=19.2034(4) Å. The layer stacking consists in an intergrowth between a $[SrCoO_3]$ perovskite-type block and a block of triple [AO] layers, $[(SrO)(Co_{2/3}Ga_{1/3}O_{1+\delta/2})(Co_{2/3}Ga_{1/3}O_{1+\delta/2})]$ in which several kinds of GaO_x and CoO_x polyhedra coexist. Low resistivities ($\rho_{300K} \approx 10^{-1}\Omega$.cm) depending on the δ value have been measured whereas a positive thermoelectric power S_{300K} = 30µV/K indicates the presence of holes (Co^{4+}) in the CoO_2 conducting layers. This value can be compared with those observed in the $Na_{0.5}CoO_2$ and the misfit $[(A'_{1-x}Co_y)_{n-2}A_{2+x-y}O_n]^{RS}[CoO_2]_{b1/b2}$ (A'=Bi,Tl.. and A=Ca,Sr..) related cobaltites. Secondly, two hydrated oxyhydroxides have been prepared in air [4]. The structural study coupled to thermal analyses has shown that $Sr_3Co_{1.7}Ti_{0.3}O_5(OH)_2$, xH_2O and $Sr_4Co_{1.6}Ti_{1.4}O_8(OH)_2$, xH_2O are derived from the Ruddlesden-Popper n = 2 and n = 3 members, respectively. The T-dependence of the structure shows upon warming two broad structural transitions from hydrated oxyhydroxides to oxygen deficient RP structures via an anhydrous oxyhydroxide form. The phenomenon of water loss during warming up to 1000°C to obtain the parent RP structures is found to be reversible. The magnetic behavior of these phases is governed by the substituted amount of Ti^{4+} (d^0) for cobalt species : cluster-glass and spin-glass like properties are observed for the hydrated n = 2 and n = 3 members, respectively.

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