Polymorphism of $Ba_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leq x \leq 1$) Perovskites: A Thermal and Structural Study by Neutron Diffraction

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Dedicated to Professor Gérard Demazeau on the occasion of his 65th birthday

The preparation of different hexagonal, orthorhombic and cubic polymorphs of the solid solution $Ba_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leq x \leq 1$) is described. The samples have been studied by thermal analysis (TG and DTA) to identify the phase transitions; the thermal structural evolution and the structural characterization of different phases were analyzed by X-ray and neutron powder diffraction and refined by the Rietveld method. A series of hexagonal perovskites $Ba_{1-x}Sr_xCoO_{3-\delta}$ ($0 \leq x < 0.5$), labelled as "H", were synthesized by thermal treatment of reactive citrate precursors at 900 °C in high oxygen pressure followed by slow cooling to r. t. The hexagonal perovskites with $0.5 \leq x \leq 1$ were obtained from the citrate precursors heated twice at 900 °C in air and slowly cooled in the furnace. Orthorhombic brownmillerite-like structures, labelled "O", were obtained from precursors with composition $0.5 \leq x \leq 1$ by quenching in liquid N_2 from 900 °C. For $x < 0.5$, quenching from high temperatures does not stabilize the "O" phases. The crystal structure for both terms of the solid solution ($x = 0$ and $x = 1$) has been investigated by neutron powder diffraction. DTA and X-ray thermo-diffractometry show that "H" phases experience a reconstructive transition at *ca.* 900 °C to give cubic "C" polymorphs.

Key words: Neutron Powder Diffraction, Reconstructive Phase Transition, Polymorphism of Cobalt Perovskites, Brownmillerite Structure