

15-5-2005

**Synthesis, structures, and magnetic properties of novel
Roddlesden–Popper homologous series $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1,2,3,4$, and
[infinity])**

Xiaolin Wang

University of Wollongong, xiaolin@uow.edu.au

H. Sakurai

National Institute for Materials Science, Japan

E. Takayama-Muromachi

National Institute for Materials Science, Japan

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>



Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/165>

Recommended Citation

Wang, Xiaolin; Sakurai, H.; and Takayama-Muromachi, E.: Synthesis, structures, and magnetic properties of novel Roddlesden–Popper homologous series $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1,2,3,4$, and [infinity]) 2005.
<https://ro.uow.edu.au/engpapers/165>

Synthesis, structures, and magnetic properties of novel Ruddlesden–Popper homologous series $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1, 2, 3, 4$, and ∞)

X. L. Wang^{a)}

Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia and Superconducting Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

H. Sakurai and E. Takayama-Muromachi

Superconducting Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

(Presented on 11 November 2004; published online 16 May 2005)

Ruddlesden–Popper homologous series $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1, 2, 3, 4$, and ∞) compounds were successfully synthesized by a high pressure and high temperature technique. Structure refinement revealed that these compounds crystallize in tetragonal structures, while the compound $n=\infty$ is cubic. These compounds are ferromagnetic with the Curie temperature decreasing from 255 K for $n=1$ to about 200 K for $n=2-4$ and down to 175 K for SrCoO_3 . Co^{4+} ions present as intermediate spin states for $n=1-4$, but in the low spin state in SrCoO_3 . Negative magnetoresistance was observed for Sr_2CoO_4 and found to be larger than that for SrCoO_3 . © 2005 American Institute of Physics. [DOI: 10.1063/1.1855534]

I. INTRODUCTION

Layer structured Ruddlesden–Popper homologous series $\text{Sr}_{n+1}\text{M}_n\text{O}_{3n+1}$ (M =transition metals) compounds with structures built up by regular intergrowth of rock-salt SrO sheets and perovskite $(\text{SrMO}_3)_n$ have always generated great interest in the field of solid state chemistry and physics due to their superior physical properties, such as dielectricity¹ for $M=\text{Ti}$, superconductivity for $M=\text{Ru}$ (Ref. 2) magnetoresistance for $M=\text{Mn}$,³ etc., compared to the $n=\infty$ member, three-dimensional SrMO_3 . However, little is known about the properties and structures for $M=\text{Co}$ due to the extreme difficulty in making samples. So far, only one member with $n=2$ has been synthesized for the layer structured $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$.⁴ However, no physical properties have been reported. In this paper, we report on our successful synthesis of the series of $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1, 2, 3, 4$, and ∞) and present their structures, transport, and magnetic properties.

II. EXPERIMENT

Polycrystalline samples used in this study were prepared as follows. Fine and pure powders of SrO_2 and Co were well mixed in appropriate ratio of $\text{Sr}:\text{Co}$. Approximately 0.2 g of each mixture was placed in a gold capsule and then compressed at 6 GPa in a high pressure apparatus. The samples were then heated at 1000–1500 °C for 1–3 h and quenched to room temperature followed by release of pressure. The high-pressure phases in the samples were identified using powder x-ray diffraction. Structure refinements were carried out by the Rietveld method using the RIETICA program.⁵ Magnetic and electrical transport properties were investigated using a commercial quantum design magnetic property

measurement system and a physical property measurement system between 5 and 330 K in magnetic fields up to 7 T.

III. RESULTS AND DISCUSSIONS

It was found that the phase formation for phases of $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ with $n=1-4$ strictly depended on the sintering temperatures under a fixed 6 GPa. For $n=1$, its x-ray diffraction (XRD) pattern could be indexed when based on a tetragonal unit cell similar to that of Sr_2TiO_4 . Close examination of the diffraction profile revealed the presence of a small amount of SrO_2 in the $n=1$ samples. However, we found that by Y doping we were able to obtain the pure $\text{Sr}_2\text{CoO}_4(214)$ phase. The initial structural model for the refinement was taken from that of Sr_2TiO_4 . The refinement result of the XRD is shown in Fig. 1. It shows an excellent agreement between the calculated pattern and the experimental data. The refined structure of the Y-doped Sr_2CoO_4 was found to be of the K_2NiF_4 type with space group $I4/mmm$. A schematic representation of the structure of Sr_2CoO_4 is shown in the inset in Fig. 1. Refinement results indicated that for $x=0.5$ in $\text{Sr}_{2-x}\text{Y}_x\text{CoO}_4$, the in-plane $\text{Co}-\text{O}(1)$ bond length (1.876 Å) is a bit shorter compared to that for $y=0$ (1.898 Å), while, the $\text{Co}-\text{O}(2)$ bond distance along the c axis is longer (2.030 Å) compared to $x=0$ (1.994 Å). This indicated that the Y^{3+} doping caused the $\text{Co}-\text{O}$ bonds to contract within the ab plane and to elongate along the c axis, yielding more distortion of the CoO_6 octahedron compared with the undoped Sr_2CoO_4 .

XRD peaks for $n=1-4$ samples can be indexed using the lattice parameters for a tetragonal structure with $a=0.375$ nm, $c=1.233$ nm for $n=1$; $a=0.383$ nm, $c=20.22$ nm for $n=2$; $a=0.377$ nm, $c=2.855$ nm for $n=3$; and $a=0.377$ nm, $c=3.624$ nm for $n=4$. The c parameters increased almost linearly with n , similar to the case for

^{a)}Author to whom correspondence should be addressed; electronic mail: xiaolin@uow.edu.au

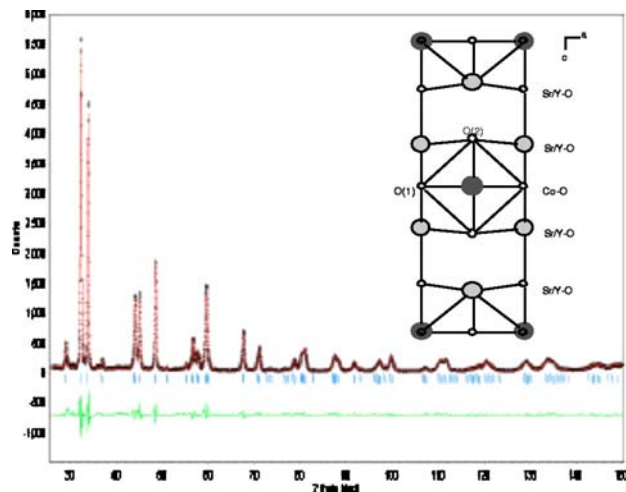


FIG. 1. The observed (crosses), calculated (solid line), and difference diffraction (bottom line) profiles at 300 K for $\text{Sr}_{1.5}\text{Y}_{0.5}\text{O}_4$. The markers relate to Sr_2CoO_4 . Inset is a schematic representation of the structure viewed along (010).

$\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ ($n=1, 2, 3, 4$, and ∞).¹ The XRD patterns for $n=3, 4$, and ∞ are shown in Fig. 2 with peaks indexed using the corresponding lattice parameters.

The temperature dependence of the field cooled (FC) dc magnetization measured in fields of 2 KOe is shown in Fig. 3. All the samples revealed clear ferromagnetic transitions starting from 255 K and decreasing as n increase from one to four, then further decreasing for $n=\infty$. A small upturn of moment around 250 K in the moment vs temperature dependence for $n=2-4$ samples is believed to be due to a small amount of Sr_2CoO_4 inclusion in these samples. The FC inverse molar susceptibility χ^{-1} vs temperature was plotted in the inset in Fig. 3. The data above these ferromagnetic transitions can be well fitted to the Curie-Weiss law, yielding $\mu_{\text{eff}}=3.69\mu_B$, $3.55\mu_B$, and $3.78\mu_B$ for the $n=1, 3$, and 4 samples. We were not able to do a similar fitting for the $n=2$ sample as it contained a large amount of nonmagnetic

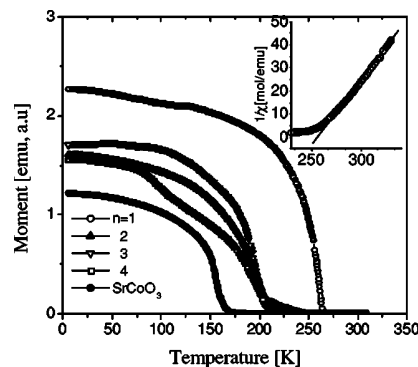


FIG. 3. dc magnetization vs temperature. Inset is Curie-Weiss fitting for $n=1$ sample.

SrO impurity. The deduced values of μ_{eff} indicated that the spin states of Co^{4+} are in an intermediate state, $t_2^4 e_g^1$ ($s=3/2$) which results in a spin only magnetic contribution of $3.87\mu_B/\text{Co}$. However, three dimensional ($n=\infty$) SrCoO_3 made under the same high pressure and high temperature conditions as that of Sr_2CoO_4 also exhibited ferromagnetic behaviors but with much lower T_c of 165 K as shown in Fig. 3, in contrast to that made using a soft chemical method which has a Curie temperature of 300 K.⁶ $\mu_{\text{eff}}=1.92\mu_B$ and $\Theta=200$ K were obtained by fitting to the Curie-Weiss law. This result indicated that the spin state of Co^{4+} should be in the low spin state, $t_2^5 e_g^0$ ($s=1/2$) yielding $1.73\mu_B/\text{Co}$ in agreement with SrCoO_3 prepared by normal pressure and soft chemical methods.⁶

Magnetic hysteresis loops for Sr_2CoO_4 and SrCoO_3 shown in Fig. 4 revealed typical ferromagnetic features for both compounds. However, Sr_2CoO_4 is a hard magnet with a very large coercive field H_c of 2.5 T, five times larger than that for SrCoO_3 . This large H_c is apparently caused by high anisotropy in Sr_2CoO_4 in contrast to three-dimensional (3D) cubic SrCoO_3 . The saturated magnetization from the MH loops is $1\mu_B/\text{Co}$ for SrCoO_3 , corresponding to the low spin state of Co^{4+} in agreement with that deduced from fitting to the Curie-Weiss law.

The temperature dependence of the resistivity ρ for both Sr_2CoO_4 and SrCoO_3 are shown in Fig. 5. It should be noted that there is a kink occurring at 255 K for Sr_2CoO_4 as revealed in the inset of Fig. 5. This kink is believed to be due to a metal-insulator transition at the ferromagnetic transition

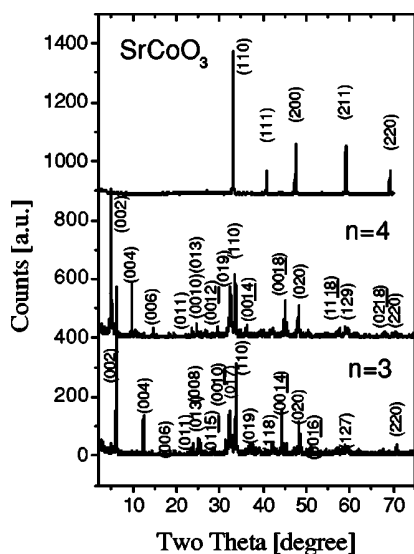


FIG. 2. XRD patterns with indexed peaks for $n=3, 4$, and ∞ .

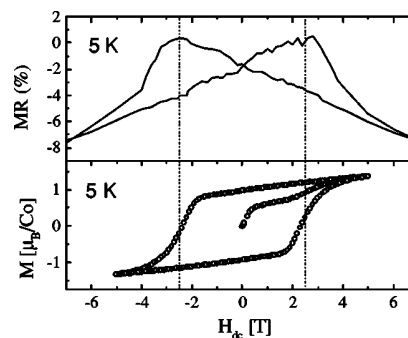


FIG. 4. Magnetic hysteresis loops (lower panel) and field-hysteretic magnetoresistance (upper panel) for Sr_2CoO_4 at 5 K.

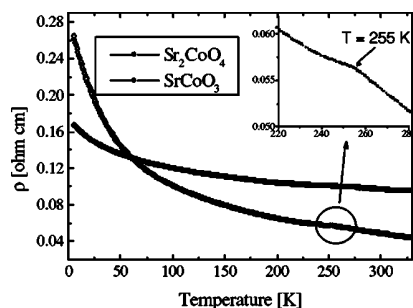


FIG. 5. Temperature dependence of resistivity with details around vicinity of 255 K for $n=1$ sample.

that is seen at 255 K from magnetic measurement. The Sr_2CoO_4 has a lower room temperature resistivity ($0.04 \, \Omega \, \text{cm}$) than that of SrCoO_3 ($0.09 \, \Omega \, \text{cm}$). However, the resistivity of both samples showed a very gradual increase with decreasing of temperature and never tend to reach infinite at low temperature. This indicates that the resistance of both samples is dominated by carrier scattering at grain boundaries as is widely seen for polycrystalline samples. In the field of 5 T, the resistance of both samples dropped and the kink seen in Sr_2CoO_4 at 255 K was totally suppressed. The MR defined as $\text{MR} = (\rho_H - \rho_0) / \rho_0$ vs temperature showed that a sharp peak occurred in the vicinity of the ferromagnetic transition at 255 K followed by a gradual increase of MR with decreasing of temperatures. These results are quite similar to those observed in granular colossal magnetoresistance manganite and cobalates, showing maximum MR values at T_c and an upturn of MR at $T < T_c$ due to electron scattering at grain boundaries. The measurement of MR as a function of magnetic field at 300 K, 255 K where the metal-insulator transition occurs (shown in Fig. 5) revealed that the Sr_2CoO_4 exhibited a room temperature MR value of about 2% in 7 T, which increased up to 5% at the metal-insulator transition. When temperature continued to decrease, field-hysteretic magnetoresistance corresponding to the magnetic hysteresis loop gradually appeared and became much more pronounced at 5 K as shown in Fig. 4. It can be seen that the maximum field-hysteretic MR occurred at a field of 2.5 T, in coincidence with the magnetization process. Such a close correlation between the MR and magnetic domain rotation observed for our Sr_2CoO_4 samples can be well explained in terms of tunneling MR at grain boundaries as has been well established for granular manganite and other MR oxides.⁷ Under the application of magnetic field, the hopping of spin-polarized electron between grains (domains) is predominantly affected by the relative angle of the magnetization directions and controlled by external field through the

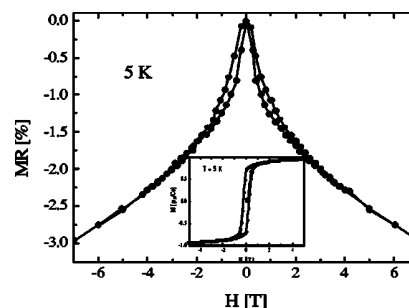


FIG. 6. Field-hysteretic magnetoresistance and magnetic hysteresis loops (inset) for SrCoO_3 at 5 K.

domain-rotation process. Therefore, the observed field-hysteretic MR is ascribed to the field suppression of the spin-dependent scattering at grain (domain) boundaries.⁵

The MR vs field dependence was also measured for 3D SrCoO_3 samples. The SrCoO_3 also exhibited the same trend of MR behavior with field dependence similar to that for Sr_2CoO_4 . Typical field-hysteresis MR behavior at 5 K is shown in Fig. 6. A close correlation between low field MR and magnetization is obvious if the Fig. 6 compared with the MH loop shown as an inset. It can be clearly seen that the MR mechanism in the SrCoO_3 is the same as that in Sr_2CoO_4 as the MR is closely correlated to H_c as well. However, the MR value of the Sr_2CoO_4 is twice as large as that of SrCoO_3 . The large values of MR observed in the layered 2D Sr_2CoO_4 compared to 3D SrCoO_3 indicate that the low dimensionality favours the MR, as we have seen in 2D layered structured $\text{Sr}_3\text{Mn}_2\text{O}_7$ compounds.³

In Summary, the Roddlesden–Popper homologous series $\text{Sr}_{n+1}\text{Co}_n\text{O}_{3n+1}$ ($n=1, 2, 3, 4$, and ∞) compounds crystallize in tetragonal structures for $n \leq 4$ and cubic for $n = \infty$. These compounds are ferromagnetic with the Curie temperatures decreasing as n increases. Co^{4+} present as intermediate spin states for $n \leq 4$ but in the low spin state in SrCoO_3 .

ACKNOWLEDGMENTS

This work was supported partly by the Australian Research Council and National Institute for Materials Science, Japan.

¹J. H. Haeni, C. D. Theis, and D. G. Schlom, Appl. Phys. Lett. **78**, 3292 (2001).

²Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).

³Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature (London) **380**, 141 (1996).

⁴S. E. Dann and M. T. Weller, J. Solid State Chem. **115**, 499 (1995).

⁵B. A. Hunter, Commission Powder Diffraction Newsletter **20**, 21 (1998).

⁶P. Bezdzicka *et al.*, Z. Anorg. Allg. Chem. **619**, 7 (1993).

⁷As a review, M. Ziese, Rep. Prog. Phys. **65**, 143 (2002).