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Study of newly discovered two dimensional cobalt based perovskite compounds doped with various rare earth elements

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Study of newly discovered two dimensional cobalt based perovskite compounds doped with various rare earth elements

A thesis submitted in fulfillment of the requirement for the award of the degree

Doctor of Philosophy (PhD)

from

University of Wollongong

by

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2008
Declaration

I, Qi Wen Yao, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, in the Faculty of Engineering, University of Wollongong, is wholly original work unless otherwise referenced or acknowledged. This thesis has not been submitted for qualifications at any other academic institution.

Qi Wen Yao

Wollongong

November 2008
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ABSTRACT

This thesis focuses on the study of a newly discovered two-dimensional CoO₂ layer structured perovskite compound, Sr₂CoO₄. To explore doping effects on the physical properties of the new compound, a systematic and detailed experimental study has been carried out, relating to the aspects of synthesis, structure, transport and magneto-transport behaviour, magnetism, and dielectricity. Theoretical investigations have also been carried out for both crystal and electronic band structures, using Rietveld refinement and first-principles band structure calculations.

Various rare earth element doped Sr₂CoO₄ polycrystalline compounds (Sr₂₋ₓREₓCoO₄, where x = 0.25 – 1.5 and RE = Pr, La, Gd, Eu, and Nd) were studied systematically. It has been found that the size and valence, as well as the doping level of the rare elements, control the physical properties of the Sr₂CoO₄. Ferromagnetic behaviour is found to exist in some of the doped compounds and to have interesting properties. It was observed that the lattice parameter \( a \) remains relatively stable, with values around 3.7 to 3.8 Å for \( x = 1 \) for various RE doped compounds of Sr₂₋ₓREₓCoO₄. The Co-O(2) in-plane bond lengths were also not sensitive to different RE dopants for the \( x = 1 \) doping level. In contrast, lattice parameter \( c \), as well as the out-of-plane bond length Co-O(1), varies with different RE dopants in the compound for the doping level of \( x = 1 \), and consequently, the unit cell volume also changes, depending on the RE dopant. It was found that Sr₂CoO₄ is the most tolerant to Pr as a dopant. For \( x \) values from 0.5 to 1.5, single phase Sr₂CoO₄ structured samples were achieved. La doping was compatible with single phase compounds for \( x = 1 – 1.25 \), and for Eu doping, single phase compounds
were formed for $x = 0.75 - 1$. For both Gd and Nd doping, near single phases are formed for all the tested $x$ values ($x = 0.5 - 1.25$).

Our results show that some of the Pr-doped and La-doped single phase samples have large coercive fields, and hence, they have good potential industrial applications (permanent magnets in electric motors, magnetic recording media, etc.), while Eu-doped samples can have high magnetoresistance (MR) values, making the Eu-doped compound a good candidate for application as a colossal magnetic resistance (CMR) material.

For the Pr-doped $\text{Sr}_{2-x}\text{Pr}_x\text{CoO}_4$, the lattice parameter $c$ decreased with the Pr doping level $x$. The Curie temperature ($T_C$) was found to be 200 K for $\text{Sr}_{1.5}\text{Pr}_{0.5}\text{CoO}_4$. The resistivities were found to increase with doping level $x$. A large coercive field of about 1 Tesla (T) was found for the sample with $x = 0.75$. The values of the dielectric constant ($\varepsilon$) were over 2000 at low frequencies of less than 1 kHz (not shown here) and gradually decreased with increasing frequencies. The $\varepsilon$ of the $x = 1$ sample is greater than that of the $x = 0.75$ sample, indicating that the charge induced capacitance in the $x = 1$ sample is greater than that of the $x = 0.75$ sample. This is in agreement with the trend of their resistivity measurements.

For the Eu-doped compounds of $\text{Sr}_2\text{CoO}_4$, single 214 phase was achieved for $x = 0.75 - 1$. The lattice parameter $c$ decreased with the Eu doping level. The Curie temperatures were found to be around 160-200 K for samples with $x = 0.75$ and 1. An antiferromagnetic transition is observed at 35 K for the $x = 0.75$ sample. Magnetic
semiconductor characteristics were observed for all the Eu-doped samples. The existence of unusually high magnetoresistance in these compounds makes them stand out from the rest of the RE doped compounds in this regard. For example, the sample with $x = 1.25$ showed a MR value of about 46% at 8 Tesla at 100 K.

For the La-doped $\text{Sr}_2\text{CoO}_4$ compounds, the temperature dependence of the resistivity shows a semiconductor-like behavior over a wide range of temperatures, a metal-insulator transition at 240 K, and an upturn at 160 K for the $x = 1, 1.25$, and 0.75 samples. The coercive field was about 1 T for the sample with $x = 0.75$, while it is about 0.05 T for the $x = 0.75$ and 0.1 T for the $x = 1.25$ sample. A negative field hysteresis in the magnetoresistance in close correlation with the coercive field has been observed and can be explained by the grain boundary tunneling effect. First-principles band structure calculations were carried out for $\text{Sr}_{1.5}\text{La}_{0.5}\text{CoO}_4$, and the results indicate that the system is metallic, with a high spin polarization which is responsible for the observed large magnetoresistance. The phonon density of states (PDOS) reveals that the Co 3d electrons and planar oxygen electrons are responsible for the high spin polarization at the Fermi surface in the compound.

The Gd-doped $\text{Sr}_2\text{CoO}_4$ compounds were found to be paramagnetic semiconductors with MR values of only around 3 to 5%. Their transport properties can be described by the hopping model for semiconductors. Band structure calculations indicate that the spin polarization is high in the Gd-doped $\text{Sr}_2\text{CoO}_4$. 

Nd-doped compounds were found to be ferromagnetic semiconductors at temperatures of about 250 and 170 K for the $x = 1$ and 0.75 samples, respectively. Their MR values were about 5%, similar to those of the Gd-doped samples. The Nd doping raised the Curie temperature of Sr$_2$CoO$_4$, so that it reached 210 K for doping with Nd at levels up to $x = 0.5$. 
Table of Contents

Introduction ............................................. 1

Chapter 1  Fundamentals and Literature Review ...... 11

1. 1 Fundamentals ...................................... 11

1.1.1 Magnetic material category ....................... 11

1.1.2 Colossal magnetoresistance (CMR) ............... 13

1.1.3 Giant Magnetoimpedance (GMI) .................. 14

1.1.4 Interlayer coupling ............................... 17

1.1.5 Tunneling magnetoresistance ...................... 18

1.1.6. Ferromagnetism and its application .............. 19

1.1.7. Curie Weiss Law ................................. 21

1.1.8. Variable Range Hopping (VHR) - - the Mott Theory 22

1.2 Relevant research - K$_2$NiF$_4$-type compounds .... 23

Chapter 2  Experimental procedures and techniques .. 53

2.1. Sample preparation ................................ 53

2.2 Sample characterisation ............................. 56

2.3 The Physical Property Measurement System (PPMS) 56

2.4 The Magnetic Property Measurement System (MPMS) 58

2.5 Dielectric measurements ............................ 59

Chapter 3  Pr doped Sr$_2$CoO$_4$ (Sr$_{2-x}$Pr$_x$CoO$_4$) ... 61
3.1 Introduction 61
3.2 Structural properties 62
3.4 Transport properties 73
3.5 Magnetisation properties 75
3.6 Dielectric properties 79
3.7 Summary 81

Chapter 4  La doped Sr$_2$CoO$_4$ (Sr$_{2-x}$La$_x$CoO$_4$, x = 0.5, 0.75, 1, 1.25) 82
4.1 Introduction 82
4.2 Structural properties 83
4.3 Transport properties 90
4.4 Magnetisation properties 92
4.5 Magnetoresistance 95
4.6 Band structure 97
4.7 Summary 98

Chapter 5  Eu doped Sr$_2$CoO$_4$ (Sr$_{2-x}$Eu$_x$CoO$_4$, x = 0.25, 0.75, 1, 1.25) 100
5.1 Introduction 100
5.2 Structural properties 100
5.3 Transport properties 106
5.4 Magnetisation properties 108
5.5 Magnetoresistance 109
5.6 Summary 111

Chapter 6  Gd doped Sr$_2$CoO$_4$ (Sr$_{2-x}$Gd$_x$CoO$_4$, x = 0.5, 0.75, 1, 1.25) 112
6.1 Introduction 112
6.2 Structural properties 112
6.4 Magnetisation properties 122
6.5 Magnetoresistance 125
6.6 Summary 129

Chapter 7  Nd doped Sr$_2$CoO$_4$ (Sr$_{2-x}$Nd$_x$CoO$_4$, x = 0.5, 0.75, 1, 1.25) 130
7.1 Introduction 130
7.2 Structural properties 130
7.3 Transport properties 138
7.4 Magnetisation properties 140
7.5 Magnetoresistance 143
7.6 Summary. 145

CHAPTER 8  Summary for various doping compounds 146

Publication List 149

References 152

List of Figures

Fig. 1  Structural views of Na$_{0.7}$CoO$_2$ (left) and Na$_x$CoO$_2$$^\cdot$yH$_2$O (right) [32]. 4
Fig. 2  Crystal structure of Sr$_2$CoO$_4$. 6
Fig. 3  Temperature dependence of the resistivity (for the Sr$_{2-y}$Y$_y$CoO$_4$ system. Inset shows the activation energy, $E_a$ (reproduced from [1]). 7
Fig. 4  Temperature dependence of the field cooled dc magnetization, measured at a magnetic field of 20 Oe (reproduced from [1]). 8
Fig. 5  Magnetic hysteresis loops for Sr$_{2-y}$Y$_y$CoO$_4$ (upper panel) and field-hysteretic magnetoresistance (lower panel) for Sr$_2$CoO$_4$ at 5 K (reproduced from [1]). 9

Fig. 1.1  Schematic illustration of the behaviour of the exchange coupling vs distance 17
Fig. 1.2  Illustration of tunneling magnetoresistance (TMR). Two ferromagnetic layers separated by an insulating layer ($i =$ electron current)(reproduced from [41]). 19
Fig. 1.3  Schematic representation of the K$_2$NiF$_4$ structure displayed by the n = 1 RP phases A$_2$BO$_4$. Fig. reproduced from [33] 25
Fig. 1.4  dc magnetization vs temperature for (SrO)(SrCoO$_3$)$_n$ where n = 1, 2, 3, 4 and $\infty$. Inset is Curie–Weiss fitting for n=1 sample [90]. 26
Fig. 1.5  Magnetic hysteresis loops (lower panel) and field-hysteretic magnetoresistance 30
Fig. 1.6  Temperature dependence of the magnetization M for Sr$_2$CoO$_4$ thin films. Inset shows field dependence of the magnetization M measured at 5 K. Fig. reproduced from [92]. 31
Fig. 1.7  The relationship between the reciprocal of the magnetic susceptibility ($1/\chi$) of Ca$_{1+x}$Sm$_{1-x}$CoO$_4$ and temperature (T). Fig. reproduced from [93].

Fig. 1.8  Temperature dependence of magnetoresistance of polycrystalline SrLaCoO$_4$ at 2.5 and 5 T field [21]. Reproduced from [94].

Fig. 1.9  Temperature dependence of field cooled dc magnetization (reproduced from [125]).

Fig. 1.10  Temperature dependence of electric resistivity for the Sr$_{2-x}$Ho$_x$CoO$_4$ system (reproduced from [125]).

Fig. 1.11  Temperature dependence of magnetoresistance (MR) for the Sr$_{2-x}$Ho$_x$CoO$_4$ system under 7 T field (reproduced from [125]).

Fig. 1.12  Magnetoresistance (upper panel) and magnetization M (lower panel) for pure and Y or Gd doped Sr$_2$CoO$_4$.

Fig. 1.13  Temperature dependence of the field-cooled magnetization for both Gd and Y doped Sr$_2$CoO$_4$.

Fig. 1.14  Magnetic hysteresis loops (lower panel) and field-hysteretic magnetoresistance (upper panel) for Sr$_2$CoO$_4$ at 5 K [140].

Fig. 1.15  Temperature dependence of the magnetization M for Sr$_2$CoO$_4$ thin films. Inset shows the field dependence of the magnetization M measured at 5 K [140].

Fig. 1.16  The temperature dependence of the reciprocal of the magnetic susceptibility ($1/\chi$) of Ca$_{1+x}$Sm$_{1-x}$CoO$_4$ [142].

Fig. 1.17  Temperature dependence of the magnetoresistance of polycrystalline SrLaCoO$_4$ for 2.5 T and 5 T fields [21]. Reproduced from [143].
Fig. 1.18  Temperature dependence of the field-cooled dc magnetization of Sr$_2$Ho$_x$CoO$_4$ [144].

Fig. 1.19  Temperature dependence of the electrical resistivity for the Sr$_{2-x}$Ho$_x$CoO$_4$ system [144].

Fig. 1.20  Temperature dependence of the magnetoresistance (MR) for the Sr$_{2-x}$Ho$_x$CoO$_4$ system under a 7 T field [144].

Fig. 1.21  Magnetoresistance (upper panel) and magnetization M (lower panel) for pure and Y or Gd doped Sr$_2$CoO$_4$ [1].

Fig. 1.22  Magnetoresistance (upper panel) and magnetization M (lower panel) for pure and Y or Gd doped Sr$_2$CoO$_4$ [1].

Fig. 2.1  Sample preparation flow chart.

Fig. 3.1  XRD patterns for Sr$_{2-x}$Pr$_x$CoO$_4$ where x = 0.25–1.5.

Fig. 3.2  Crystal structure of Sr$_2$CoO$_4$.

Fig. 3.3  Rietveld refinement for Sr$_{1.5}$Pr$_{0.5}$CoO$_4$.

Fig. 3.4  Rietveld refinement for Sr$_{1.25}$Pr$_{0.75}$CoO$_4$.

Fig. 3.5  Rietveld refinement for SrPrCoO$_4$.

Fig. 3.6  Rietveld refinement for Sr$_{0.75}$Pr$_{1.25}$CoO$_4$.

Fig. 3.7  Rietveld refinement for Sr$_{0.5}$Pr$_{1.5}$CoO$_4$.

Fig. 3.8  The lattice parameter a vs x for Sr$_{2-x}$Pr$_x$CoO$_4$.

Fig. 3.9  The lattice parameter c vs x for Sr$_{2-x}$Pr$_x$CoO$_4$.

Fig. 3.10  The Co-O bond length vs x for Sr$_{2-x}$Pr$_x$CoO$_4$.

Fig. 3.11  The unit cell volume vs x for Sr$_{2-x}$Pr$_x$CoO$_4$.

Fig. 3.12  Resistance vs temperature for Sr$_{1.25}$Pr$_{0.75}$CoO$_4$. 
Fig. 3. 13 $\rho$ vs exp($1/T$)$^{1/3}$ for Sr$_{1.25}$Pr$_{0.75}$CoO$_4$. Straight lines are linear fitting to the 2D VRH model.

Fig. 3. 14 The temperature dependence from 5 K to 300 K of the magnetization of the Sr$_{2-x}$Pr$_x$CoO$_4$ samples with x = 0.25, 0.5, 0.75, 1, 1.25 measured in a magnetic field of 0.2 Tesla.

Fig. 3. 15 Temperature dependence of the Sr$_{2-x}$Pr$_x$CoO$_4$ samples’ magnetization in low temperature range.

Fig. 3. 16 Temperature dependence of the inverse molar susceptibility, ($\chi^{-1}$) for Sr$_{2}$Pr$_x$CoO$_4$, measured at a magnetic field of 2 kOe.

Fig. 3. 17 Magnetic hysteresis loops for Pr$_x$Sr$_{2-x}$CoO$_4$.

Fig. 3. 18 Frequency dependence of dielectric constant for Sr$_{2-x}$Pr$_x$CoO$_4$ (x = 1, 1.25) at room temperature.

Fig. 3. 19 Frequency dependence of dielectric loss for Sr$_{2-x}$Pr$_x$CoO$_4$ (x = 1, 1.25) at room temperature.

Fig. 4. 1 XRD patterns of Sr$_{2-x}$La$_x$CoO$_4$ with x = 0.75, 1, 1.25

Fig. 4. 2 Rietveld refinement for Sr$_{1.25}$La$_{0.75}$CoO$_4$. The observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K for the x=0.75 sample (refinement factors Rp=14.8%, Rb=2.9%; blue-strip range was ignored in refinement).

Fig. 4. 3 Rietveld refinement for SrLaCoO$_4$. The observed (crosses), calculated (solid line), and difference (bottom line) profiles at 300K for the x = 1 sample (refinement factors Rp=12.58%, Rb=7.3%).

Fig. 4. 4 Rietveld refinement for Sr$_{0.75}$La$_{1.25}$CoO$_4$. The observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=12.58%, Rb=7.3% for the x = 1.25 sample).
Fig. 4. 5  Co-O bond lengths vs. doping level x.  

Fig. 4. 6  The temperature dependence of the electrical resistivity ($\rho$) of the Sr$_{2-x}$La$_x$CoO$_4$ samples with $x = 0.75, 1, 1.25$, from 5 K to 350 K, measured in zero field.  

Fig. 4. 7  $\ln(\rho)$ vs. $\exp(1/T)^{1/4}$ for Sr$_{2-x}$La$_x$CoO$_4$. Straight lines are linear fittings to the 2D VRH model.  

Fig. 4. 8  The temperature dependence from 5 K to 350 K of the magnetization of the Sr$_{2-x}$La$_x$CoO$_4$ samples with $x = 0.75, 1, 1.25$, measured in a magnetic field of 0.2 Tesla.  

Fig. 4. 9  Temperature dependence of the inverse susceptibility ($\chi^{-1}$) for the Sr$_{2-x}$La$_x$CoO$_4$ samples, measured at a magnetic field of 2000 Oe.  

Fig. 4. 10  Magnetization hysteresis loops for the Sr$_{2-x}$La$_x$CoO$_4$ samples with $x = 0.75, 1, 1.25$, measured at 10 K.  

Fig. 4. 11  Field hysteretic magnetoresistance for Sr$_{1.25}$La$_{0.75}$CoO$_4$ at 150 K.  

Fig. 4. 12  Magnetoresistance hysteresis for Sr$_{0.75}$La$_{1.25}$CoO$_4$ at 5 K.  

Fig. 4. 13  Rate of change of the resistivity for the sample with $x = 1.25$ at various temperatures in magnetic field.  

Fig. 4. 14  Calculated total density of states of Sr$_{1.5}$La$_{0.5}$CoO$_4$ compound and the partial density of states of Co 3d (upper panel); and the partial density of states of planar and apical oxygen (lower panel), with the Fermi energy set at zero.  

Fig. 5. 1  XRD patterns of the Sr$_{2-x}$Eu$_x$CoO$_4$ samples with $x = 0.25, 0.75, 1, 1.25$, measured at room temperature.
Fig. 5. 2  Rietveld refinement for Sr$_{1.25}$Eu$_{0.75}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=11.4%, Rb=2.9%).

Fig. 5. 3  Rietveld refinement for SrEuCoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=13.4%, Rb=2.1%; blue-strip range was ignored in refinement).

Fig. 5. 4  Rietveld refinement for Sr$_{0.75}$Eu$_{1.25}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=13.8%, Rb=4.6%; blue-strip ranges were ignored in refinement).

Fig. 5. 5  Co-O bond lengths vs. doping level $x$.

Fig. 5. 6  Temperature dependence of the resistivity of Sr$_{2-x}$Eu$_x$CoO$_4$ with $x =$ 0.75, 1, 1.25.

Fig. 5. 7  ln($\rho$) vs. exp(1/T)$^{1/3}$ for Sr$_{2-x}$Eu$_x$CoO$_4$ with $x =$ 0.75, 1, 1.25. Straight lines are linear fittings to the 2D VRH model.

Fig. 5. 8  Field cooled and zero field cooled temperature dependence of magnetization for Sr$_{2-x}$Eu$_x$CoO$_4$ with $x =$ 0.75 and 1.

Fig. 5. 9  Magnetoresistance hysteresis for the Sr$_{1.25}$Eu$_{0.75}$CoO$_4$ sample at 100 K.

Fig. 5. 10 Magnetoresistance hysteresis for the SrEuCoO$_4$ sample at 100 K.

Fig. 5. 11 Magnetoresistance hysteresis for the Sr$_{0.75}$Eu$_{1.25}$CoO$_4$ sample at 100 K.
Fig. 6. 1  XRD patterns of Sr$_{2-x}$Gd$_x$CoO$_4$ with x = 0.5, 0.75, 1, 1.25 (* indicates unknown impurity). 113

Fig. 6. 2  Rietveld refinement for Sr$_{1.5}$Gd$_{0.5}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=14.5%, Rb=5.6%; blue-strip ranges were ignored in refinement). 114

Fig. 6. 3  Rietveld refinement for Sr$_{1.25}$Gd$_{0.75}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=14.3%, Rb=6.2%; blue-strip range was ignored in refinement). 114

Fig. 6. 4  Rietveld refinement for SrGdCoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=12.0%, Rb=3.2%; blue-strip range was ignored in refinement). 115

Fig. 6. 5  Rietveld refinement for Sr$_{0.75}$Gd$_{1.25}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K (refinement factors Rp=16.6%, Rb=7.6%; blue-strip range was ignored in refinement). 115

Fig. 6. 6  Lattice parameters a and c vs. x for Sr$_{2-x}$Gd$_x$CoO$_4$. 119

Fig. 6. 7  Co-O bond lengths vs. doping level x. 120

Fig. 6. 8  Temperature dependence of the resistivity of Sr$_{2-x}$Gd$_x$CoO$_4$ with x = 0.75, 1, 1.25. 121

Fig. 6. 9  ln($\rho$) vs exp(1/T)$^{1/3}$ for Sr$_{2-x}$Gd$_x$CoO$_4$ with x = 0.75, 1, 1.25. Straight lines are linear fittings to the 2D VRH model. 122
Fig. 6.10  Temperature dependence of the magnetization for Sr$_{2-x}$Gd$_x$CoO$_4$ with $x = 0.75$ and 1.

Fig. 6.11  Temperature dependence of the inverse susceptibility ($\chi^{-1}$) for Sr$_{2-x}$Gd$_x$CoO$_4$, measured at a magnetic field of 2000 Oe.

Fig. 6.12  Magnetization hysteresis measurements for Sr$_{2-x}$Gd$_x$CoO$_4$ with $x = 0.75$ and 1, measured at 10 K.

Fig. 6.13  Magnetoresistance hysteresis for Sr$_{1.25}$Gd$_{0.75}$CoO$_4$ at 100 K.

Fig. 6.14  Magnetoresistance hysteresis for SrGdCoO$_4$ at 100 K.

Fig. 6.15  The band structure (upper panel) and density of states (lower panel) of the Sr$_{1.5}$Gd$_{0.5}$CoO$_4$ sample.

Fig. 6.16  Partial density of states of Co in the Sr$_{1.5}$Gd$_{0.5}$CoO$_4$ sample.

Fig. 7.1  XRD patterns of Sr$_{2-x}$Nd$_x$CoO$_4$ with $x = 0.5, 0.75, 1, 1.25$.

Fig. 7.2  Rietveld refinement for Sr$_{1.5}$Nd$_{0.5}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K for the $x = 0.5$ sample (refinement factors Rp=14.9%, Rb=7.4%; blue-strip ranges were ignored in refinement).

Fig. 7.3  Rietveld refinement for Sr$_{1.25}$Nd$_{0.75}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K for the $x = 0.75$ sample (refinement factors Rp=18.4%, Rb=11.5%; blue-strip ranges were ignored in refinement).

Fig. 7.4  Rietveld refinement for SrNdCoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K for the $x = 1$ sample (refinement factors Rp=10.9%, Rb=6.4%; blue-strip range was ignored in refinement).
Fig. 7.5  Rietveld refinement for Sr$_{0.75}$Nd$_{1.25}$CoO$_4$ showing the observed (crosses), calculated (solid line) and difference (bottom line) profiles at 300K for the x = 1 sample (refinement factors Rp=13.9%, Rb=8.4%). 133

Fig. 7.6  Co-O bond lengths v.s doping level x. 137

Fig. 7.7  Lattice parameters a and c vs. x for Sr$_{2-x}$Nd$_x$CoO$_4$. 137

Fig. 7.8  The unit cell volume vs. x for Sr$_{2-x}$Nd$_x$CoO$_4$. 138

Fig. 7.9  Resistance vs. temperature for Sr$_{2-x}$Nd$_x$CoO$_4$ (x = 0.75, 1). 139

Fig. 7.10  ln(ρ) vs. exp(1/T)$^{1/3}$ for Sr$_{2-x}$Nd$_x$CoO$_4$ (x = 0.75, 1). Straight lines are linear fittings to the 2D VRH model. 140

Fig. 7.11  The temperature dependence from 10 K to 340 K of the magnetization of the Sr$_{2-x}$Nd$_x$CoO$_4$ samples with x = 0.75, 1, measured in a magnetic field of 0.2 Tesla. 141

Fig. 7.12  Temperature dependence of the inverse susceptibility ($\chi^{-1}$) for Sr$_{2-x}$Nd$_x$CoO$_4$, measured at a magnetic field of 2000 Oe. 142

Fig. 7.13  Magnetic hysteresis loops for Sr$_{2-x}$Nd$_x$CoO$_4$ with x = 0.75, 1. 143

Fig. 7.14  Magnetoresistance hysteresis for SrGdCoO$_4$ at 100 K. 144

Fig. 7.15  Magnetoresistance hysteresis for Sr$_{1.25}$Nd$_{0.75}$CoO$_4$ at 100 K. 144
List of Tables

<table>
<thead>
<tr>
<th>Table 1.1</th>
<th>Summary of different types of magnetic behaviour (Source: University of Birmingham website).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>Single phase polycrystalline samples Sr_{2-x}RE_xCoO_4 that have been attempted to produce.</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Crystal data of Sr_{2-x}Pr_xCoO_4 (x=0.5, 0.75, 1, 1.25) - Space group: I4/mmm.</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Crystal data of Sr_{2-x}La_xCoO_4 (0.75, 1, 1.25) - Space group: I4/mmm.</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Structural parameters of Sr_{2-x}La_xCoO_4 with x = 0.75, 1 &amp; 1.25 from the Rietveld refinement (space group I4/mmm) results.</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Crystal data of Sr_{2-x}Eu_xCoO_4 (x = 0.75, 1, 1.25) - Space group: I4/mmm.</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Structural parameters of Sr_{2-x}Eu_xCoO_4 with x = 0.75, 1 &amp; 1.25 from the Rietveld refinement (space group I4/mmm) results.</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>Crystal data of Sr_{2-x}Gd_xCoO_4 (x = 0.5, 0.75, 1, 1.25) - Space group: I4/mmm.</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Structural parameters of Sr_{2-x}Gd_xCoO_4 with x = 0.5, 0.75, 1, 1.25 from the Rietveld refinement (space group I4/mmm) results.</td>
</tr>
<tr>
<td>Table 7.1</td>
<td>Crystal data of Sr_{2-x}Nd_xCoO_4 (x = 0.5, 0.75, 1, 1.25) - Space group: I4/mmm.</td>
</tr>
<tr>
<td>Table 7.2</td>
<td>Structural parameters of Sr_{2-x}Nd_xCoO_4 with x = 0.5, 0.75, 1, 1.25 from the Rietveld refinement (space group I4/mmm) results.</td>
</tr>
</tbody>
</table>
Table 8.1 Summarization of the properties for different doped compounds.