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

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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.

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ABSTRACT

This thesis focuses on the study of a newly discovered two-dimensional CoO_2 layer structured peroskite compound, Sr_2CoO_4. 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 Sr_2CoO_4 polycrystalline compounds ($Sr_{2-x}RE_xCoO_4$, 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 Sr_2CoO_4. 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* reminds relatively stable, with values around 3.7 to 3.8 Å for x = 1 for various RE doped compounds of $Sr_{2-x}RE_xCoO_4$. 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 Sr_2CoO_4 is the most tolerant to Pr as a dopant. For x values from 0.5 to 1.5, single phase Sr_2CoO_4 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 $Sr_{2-x}Pr_xCoO_4$, the lattice parameter *c* decreased with the Pr doping level x. The Curie temperature (T_C) was found to be 200 K for $Sr_{1.5}Pr_{0.5}CoO_4$. 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 (ε) were over 2000 at low frequencies of less than 1 kHz (not shown here) and gradually decreased with increasing frequencies. The ε 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 Sr_2CoO_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 stands 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 Sr_2CoO_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 $Sr_{1.5}La_{0.5}CoO_4$, 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 Sr_2CoO_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 Sr_2CoO_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 valves were about 5 %, similar to those of the Gd-doped samples. The Nd doping raised the Curie temperature of Sr_2CoO_4, so that it reached 210 K for doping with Nd at levels up to x = 0.5.

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