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Structure and magnetism in the oxygen-deficient perovskites $Ce_{1-x}Sr_xCoO_{3-\delta}$ ($x \geq 0.90$)

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Abstract

We have examined the structure and phase behaviour of strontium-doped $Ce_{1-x}Sr_xCoO_{3-\delta}$ and found that the perovskite form is stabilised over a relatively narrow solid solution range ($x > 0.85$). A combination of electron, powder X-ray and neutron diffraction has revealed tetragonal superstructures of the basic perovskite unit; (*I4/mmm*) $2a_p \times 2a_p \times 4a_p$ ($x = 0.90$) and (*P4/mmm*) $a_p \times a_p \times 2a_p$ ($x = 0.95$). Magnetisation measurements show ferromagnetic behaviour under applied magnetic fields. Low temperature neutron diffraction of $Ce_{0.10}Sr_{0.90}CoO_{2.80}$ in zero field reveals a magnetic cell of dimension $2a_p \times 2a_p \times 4a_p$ with an ordered cobalt moment of 1.7 B.M. at 25 K.

Keywords: A. Oxides; B. Sol–gel chemistry; C. Electron diffraction; D. Magnetic properties

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1. Introduction

There has been substantial recent interest in strontium-doped rare earth perovskites ($Ln_{1-x}Sr_xCoO_{3-\delta}$) as cathode materials for solid oxide fuels cells [1–4] and as high temperature ceramic membranes [5,6]. These phases also display novel magnetic behaviour, including glassiness [7–10] and room temperature ferromagnetism [11–16]. We have lately explored structural variation within the $Ln_{1-x}Sr_xCoO_{3-\delta}$ perovskite phase diagram and demonstrated that an extensive range of solid solution is present for the larger rare earth ions (La^{3+}, Pr^{3+}, Nd^{3+}, and Sm^{3+}). For Y^{3+} and the smaller lanthanide ions, the range of solid solution becomes increasingly restricted with decreasing ionic radii. Furthermore we have shown that combinations of cation and oxygen vacancy ordering lead to different tetragonal superstructures for the highly doped $Ln_{1-x}Sr_xCoO_{3-\delta}$ ($x > 0.60$) perovskites [10,17]. These phases show a variety of magnetic behaviours with mixed $Co^{3+/4+}$ oxidation states ranging up to more than 50% Co(IV). This current study explores the phase relationships, structural and magnetic properties of the related $Ce_{1-x}Sr_xCoO_{3-\delta}$ series of perovskite compounds.

2. Experimental

2.1. Synthesis

Polycrystalline samples of $Ce_{1-x}Sr_xCoO_{3-\delta}$ were prepared from spectroscopic grade powders of $SrCO_3$ (98+%), $Co(NO_3)_2{\cdot}6H_2O$ (98%) and $Ce(NO_3)_3{\cdot}5H_2O$ (99.9%). The powders were dissolved in dilute nitric acid and an intimate mixture of the metal oxides was formed via the decomposition of a citric acid/ethylene glycol sol-gel. The residues were pelleted and sintered in a tube furnace at 1100 °C under flowing oxygen for up to 3 days with intermediate re-grinding and re-pelleting until no further reaction was evident by powder X-ray diffraction. The samples were cooled from 1100 °C to room temperature at a rate of 2 °C per minute.

2.2. Thermogravimetry

Thermogravimetry of ca. 70 mg of single-phase samples of the $Ce_{1-x}Sr_xCoO_{3-\delta}$ were carried out with a SETARAM TAG24 Simultaneous Thermogravimetric and Differential Thermal Analyser. The samples were reduced under a mixture of 3.5% hydrogen in nitrogen over a temperature range of 25–950 °C at a heating rate of 5 °C/min. Each of the samples studied were reduced under hydrogen to give the component oxides CeO_2 and SrO as well as Co metal. As has been shown for other rare earth perovskite cobaltates [17], the observed mass loss is therefore apportioned to the change in oxygen content as Co^{n+} in the as-synthesized sample is reduced to Co metal.

2.3. Electron energy loss spectroscopy (EELS)

Transmission electron microscope (TEM) samples were prepared by crushing powdered samples in a mortar and pestle in AR grade ethanol. A drop of the resulting suspension was pipetted onto a holey carbon-covered copper grid (200 mesh) and allowed to dry. Electron energy loss spectroscopy (EELS) measurements were conducted with a Gatan Imaging Filter (GIF 2000) attached to a JEOL 2010F field