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Oxygen vacancy ordering in strontium doped rare earth cobaltate perovskites $Ln_{1-x}Sr_xCoO_{3-\delta}$ (Ln = La, Pr and Nd; $x > 0.60$)

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Abstract

A family of Sr-doped perovskite compounds $Ln_{1-x}Sr_xCoO_{3-\delta}$ (Ln = La^{3+}, Pr^{3+} and Nd^{3+}; $x > 0.60$), were prepared by sol–gel chemistry and reaction at 1100 °C under 1 atm of oxygen. This structural family has been shown to be present only for rare earth ions larger than Sm^{3+} and an upper limit of Sr^{2+} solubility in these phases was found to exist between $x = 0.90$ and 0.95. X-ray diffraction shows oxygen-deficient, simple cubic (*Pm*-3*m*) perovskite crystal structures. The combination of electron and powder neutron diffraction reveals that oxygen vacancy ordering occurs, leading to a tetragonal (*P*4/*mmm*) superstructure and a doubling of the basic perovskite unit along the crystallographic *c*-axis. No additional Ln^{3+}/Sr^{2+} cation ordering was observed.

Keywords: A. Oxides; C. Electron diffraction; C. Thermogravimetric analysis (TGA); D. Crystal structure

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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 [7–9] and room temperature

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ferromagnetism [10–15]. We have lately explored structural variation within the $Ln_{1-x}Sr_xCoO_{3-\delta}$ perovskite phase diagram [16,17]. For the largest rare earth elements (La^{3+}–Sm^{3+}) an extended range of Sr-doping has previously been observed by a number of authors [3,18–21]. Prior to our own work, the upper solubility limit for these phases has been shown to be $x = 0.80$ for La [3,18], and $x = 0.50$ for Nd and Pr [19,20]. In this study we demonstrate that the upper solubility limits for each of these $Ln_{1-x}Sr_xCoO_{3-\delta}$ (Ln = La, Pr and Nd) phases are between $x = 0.90$ and 0.95 and in particular we show oxygen vacancy ordering to be present for $x \geq 0.67$.

2. Experimental

2.1. Synthesis

Polycrystalline samples of $Ln_{1-x}Sr_xCoO_{3-\delta}$ were prepared from spectroscopic grade powders of $SrCO_3$ (+98%), $Co(NO_3)_2{\cdot}6H_2O$ (98%) and either Ln_2O_3 (Ln = La and Nd) (≥99.9%) or Pr_6O_{11} (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/min.

2.2. Thermogravimetry

Thermogravimetry of ca. 70 mg of each of the $Ln_{1-x}Sr_xCoO_{3-\delta}$ samples were carried out with the use of 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 decomposed under hydrogen reduction to give the component oxides Ln_2O_3 and SrO as well as Co metal. The measured mass-loss was then used to determine the number of oxygen vacancies present in phase, as well as the average oxidation state of the cobalt ions.

2.3. Electron diffraction

Electron diffraction (ED) was carried out on a Philips EM 430 Transmission Electron Microscope operating at 300 kV. Samples suitable for TEM work were prepared by the dispersion of finely ground material onto a holey carbon film.

2.4. Powder diffraction measurements

Powder X-ray diffraction measurements were made on a Scintag Inc. XGEN 4000 X-ray diffractometer at ambient temperature using Cu Kα radiation and a flat-plate sample holder. Data of sufficient quality for structural refinement were collected, over $5° < 2\theta < 105°$, in 0.02° steps, with 10 s acquisition times per step. Powder neutron diffraction data were collected on the MRPD instrument ($\lambda = 1.6661$ Å) at the HIFAR facility, Sydney, Australia. Structure refinements were carried out by the