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Structural, electrochemical and magnetic characterization of the layered-type $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ perovskite

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ABSTRACT

Structural, electrical and magnetic properties of the layered cobaltite $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ have been investigated by means of neutron diffraction, electron diffraction, thermogravimetric analysis and SQUID magnetometry. Rietveld analysis of neutron diffraction data shows the ordered distribution of oxygen vacancies in $[PrO_\delta]$ planes which doubles the lattice parameters from the simple perovskite cell parameter as $a \approx 2a_p$ and $c \approx 2a_p$ (a_p is the cell parameter of the simple Perovskite) yielding tetragonal symmetry in the *P4/mmm* space group. On heating, above 573 K in air, structural rearrangement takes place and the structure can be defined as $a \approx a_p$ and $c \approx 2a_p$ in the same space group. Oxygen occupancies have been determined as a function of temperature from neutron diffraction results. Initially ($\geq$373 K), oxygen occupancy was increased and then decreased with increasing temperature. It was found that at 973 K the total oxygen loss is calculated about 0.265 oxygen/formula unit. Oxygen vacancy ordering was observed below 573 K, and the oxygen occupancy decreases as cell volume increases with increasing temperature. Area specific resistance (ASR) measurements show a resistance of 0.153 Ωcm^2 and 0.286 Ωcm^2 at 973 K and 923 K, respectively. On cooling, paramagnetic to ferromagnetic and an incomplete ferromagnetic to antiferromagnetic transition takes place. Different behaviours in field cooled and zero-field-cooled measurements leads to a coexistence of ferromagnetic and antiferromagnetic order.

1. Introduction

Cobalt containing perovskite oxides have superior oxygen activation kinetics and show unique electronic and magnetic properties as a consequence of the ability of Co to adopt 2+, 3+ and 4+ oxidation states [1–3]. In addition to the spin, charge and orbital degrees of freedom found in the manganite perovskites, the cobaltates are expected to exhibit a degree of freedom in the electronic configuration of the cobalt ion. Layered cobaltites with general formula $LnBaCo_2O_{5+\delta}$ (*Ln*=lanthanides, $0<\delta<1$) have been the subject of several studies during the last years due to their giant magnetoresistance (the highest found in cobalt oxides), the spin-state transitions, the interplay of the spin-state with the charge, orbital and metal-insulator transitions [4–9]. More recently, these materials have been found to be good cathode materials for solid oxide fuel cells [10–12]. The oxygen content and mobility plays the major role for their electronic, magnetic and transport properties. The oxygen content also controls the mean valence of Co ions, the coordination of Co (pyramidal or octahedral) and has a strong influence on the spin state of cobalt. So far, most of the investigations have concentrated on two particular compositions, namely δ=0.0 and 0.5, for which an ordering of oxygen vacancies possibly exists. In $LnBaCo_2O_5$ (δ=0) the pyramidal positions are occupied by the same amount of Co^{2+} and Co^{3+} ions. In contrast, in $LnBaCo_2O_{5.5}$ (δ=0.5) only Co^{3+} ions are present which coexist in ideally alternating octahedral CoO_6 and pyramidal CoO_5 environments. For low δ, there is a strong tendency to form charge-ordered structures which has been reported for $YBaCo_2O_5$ [4] and $TbBaCo_2O_5$ [5]. Defect equilibrium in $PrBaCo_2O_{5+d}$ at elevated temperatures has been studied by Suntsov et al. [13]. Neutron diffraction measurements show that $LnBaCo_2O_5$ (δ=0) compounds are antiferromagnetic (AFM) with $T_N \sim$350 K (for *Y*) [14], ~380 K (*Ln*=Nd) [15]. Metal-insulator and spin-state transitions as well as successive magnetic transitions due to competing ferromagnetic (FM)–AFM interactions are present in compounds with δ=0.5 for a wide variety of rare earths [1,6,9,16]. The metal-insulator transition mainly takes place in the

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temperature range from room temperature to 373 K (depending on *Ln*), which seems to be related to a spin-state transition of the Co^{3+} ions [1,6,7,9,16–19].

Depending on the oxygen content, δ, several kinds of superstructures have been reported in the literature along with the various possible models of oxygen ordering [1–3,20,21]. The crystal structure adopted by $LnBaCo_2O_{5+\delta}$ has been reported to be tetragonal *P*4/*mmm* ($a_p \times a_p \times 2a_p$), orthorhombic *Pmmm* ($a_p \times 2a_p \times 2a_p$ or $a_p \times a_p \times 2a_p$), or orthorhombic *Pmmb* ($a_p \times 2a_p \times 2a_p$); where a_p refers to the simple cubic perovskite in the *Pm*-3*m* space group ($a_p \approx 3.9$ Å). The doubling of *c* is due to the ordering of *Ln* and Ba into layers perpendicular to *z*. The doubling of *b*, and the transition from tetragonal to orthorhombic, have been suggested to arise from an ordering of the oxide ion vacancies into channels at a value of $\delta = 0.5$ [1,3,6,21,22]. Due to the wide range of oxygen non-stoichiometry and a strong tendency of the oxygen ions and vacancies to order, the extra oxygen which is known to fill LnO_δ layers, can create complex crystal structures with mixed octahedral and pyramidal cobalt environments.

Several research groups have reported excellent properties of $LnBaCo_2O_{5+\delta}$ as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) [23–25]. Our recent studies on $LnBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (*Ln*=Pr and Nd) show that the electrical conductivity decreases with temperature, and at 873 K the conductivity is 493 S/cm. Area specific resistance (ASR) decreases with increasing temperature, at 873 K the ASR is 0.286 Ωcm^2 [26].

The main objective of this work is to investigate the temperature dependent structural and magnetic properties in $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$. The concise structural information was presented in our earlier publication [26]. Here we have explained structural data from Neutron Powder Diffraction (NPD) in detail and compared with the information from Specific Area Electron Diffraction (SAED). From the structural data, we have explored the oxygen content and mean valence states of Co at different temperatures (from RT to 973 K). We have also made the conductivity, thermogravimetric and magnetic measurements related with the structural data.

2. Experimental

Polycrystalline samples of $PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (PBSCO) were prepared by standard solid state reactions, starting with high purity oxides and carbonates (Pr_6O_{11}, Co_3O_4, $BaCO_3$, $SrCO_3$). The sample was fired in two steps. In the first step, the powders were mixed, pressed into pellets and heated in air at 1273 K for 8 h. The temperature was increased in 4 steps i.e. 423, 573, 773 and 973 K before reaching 1273 K. The duration of heating at each step was 2 h. The sample was then cooled down to room temperature, ground and ball milled for 24 h. In the second step, the sample was heated at 1373 K for 36 h. The heating and cooling rate was 5°/min for all cycles.

Phase purity, identity and homogeneity were confirmed by X-ray powder diffraction (XRD) experiments using a STOE Stadi P transmission diffractometer (Cu$K\alpha_1$, $\lambda = 0.15406$ nm). High resolution and high intensity time-of-flight NPD data were collected as a function of temperature using a GEM diffractometer at the ISIS spallation source at Rutherford Appleton Laboratory, UK. The sample (ca. 5 g) was loaded into a thin-walled, cylindrical vanadium can and placed in the sample chamber in ambient conditions. Neutron diffraction data was collected at 295, 373, 473, 573, 673, 773, 873 and 973 K using a furnace designed for the diffractometer. Rietveld analysis of the diffraction data sets were carried out using GSAS software [27]. The background was fitted using an empirical Chebyshev polynomial and peak shapes were considered as a pseudo-Voigt function. SAED patterns were collected on a Jeol JEM-2011 electron microscope operated at 200 kV. The powder sample was ground using a mortar and pestle, and suspended in acetone. One drop of suspension was deposited on a copper grid with a holey carbon film. Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209 instrument to evaluate the oxygen content (weight loss) at different temperatures and to compare with neutron diffraction results. The initial weight of the sample was about 40 mg. The effect of buoyancy was corrected by using pre-empty crucible runs under the corresponding gas atmosphere and flow rates. The samples were heated up to 1073 K in the TG furnace at a heating rate of 5 K/min in air. The temperature dependent DC magnetization measurements were carried out in both field-cooled (FC) and zero-field-cooled (ZFC) modes, using a Quantum design PPMS in the temperature range 5 K to 300 K using magnetic fields 100 Oe, 500 Oe and 1000 Oe. Field dependent magnetisation data were collected from 0 Oe to 5000 Oe at 5 K.

3. Results and discussion

Rietveld refinement of room temperature (RT) XRD and NPD data shows that the structure can be refined using an average tetragonal symmetry with the unit cell parameters $a = b \approx a_p$ and $c \approx 2a_p$ and space group *P*4/*mmm* (No. 123). Careful investigation of the refined diffraction profile shows that in addition to this average structure a set of smaller unindexed peaks are present which is related to a superstructure. The most intense superstructure peak was observed at the *d*-spacing 4.468 Å and can be indexed as (1 1 1). These superstructure peaks are attributed to a particular order of oxygen vacancies in the structure and can be indexed by doubling both *a* and *b* lattice parameters. Different models and oxygen orderings were considered to explore the possible order arrangements of the oxygen vacancies. The first model corresponds to the orthorhombic symmetry in the space group *Pmmm* (No. 47) where *a, b* and *c* cell parameters are related as $a_p \times a_p \times 2a_p$. The second model was considered in the same space group with the relation $a_p \times 2a_p \times 2a_p$. Both the models were examined for different possibilities of oxygen ordering but no one of these were appropriate to explain the superstructure reflections. The third possibility corresponds to the *P*4/*mmm* space group in the setting $2a_p \times 2a_p \times 2a_p$ and with the perfect order in a $2a_p \times 2a_p$ supercell in the [PrO_δ] planes, with vacancies located in 1*b* (0 0 1/2), 1*d* (1/2 1/2 1/2) and 2*f* (0 1/2 0) Wyckoff positions. This model can also index superstructure reflections corresponding to the reflection condition HHL and HLL (H and L are odd numbers and $H \neq L$). The refinement of oxygen occupancies for other oxygen sites improved the peak intensity matching. It was observed from the refinement that the oxygen position at 1*d* (1/2 1/2 1/2) were completely vacant and 1*b* (0 0 1/2) and 2*f* (0 1/2 0) were partially vacant. Fig. 1a shows the Rietveld refinement profile and Table 1 shows the main crystallographic information of the room temperature NPD. The refinement of the structural parameters shows the possible ordering of oxygen vacancies and cations. The ordering of the oxygen vacancies in the perovskite matrix is responsible for the superstructure (also observed in the SAED pattern). The oxygen vacancies order within the [PrO_δ] layers, result in oxygen-rich and oxygen deficient *a*–*c* layers and consequently in a doubling of the unit cell along *a* and *b* directions [3]. The location of oxygen vacancies in [PrO_δ] planes does not correspond with the ordering into channels as reported for $LnBaCo_2O_{5.5}$ compounds [1]. Rietveld refinement of room temperature data shows the composition as $PrBa_{0.5}Sr_{0.5}Co_2O_{5.243}$. In this composition we have observed an imperfect order of the vacancies consisting in the preferential occupation of the 1*b* position. Partial disorder is restricted to a solution with atoms in 1*b* and 2*f* Wyckoff positions of the *P*4/*mmm* space group. In order