Electrical Conductivity and Oxygen Nonstoichiometry of \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \)

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Received February 1, 1999

Abstract—The oxygen stoichiometry and defect structure of \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) were studied by solid-electrolyte coulometry, thermogravimetry, and conductivity measurements at temperatures from 20 to 1000°C and oxygen partial pressures from 1 to \( 10^5 \) Pa. The results were used to construct the \( p-T-x \) and \( p-T-\sigma \) phase diagrams and identify the sequence of phase transformations in the Co-substituted strontium ferrate (low-temperature perovskite \( \rightarrow \) brownmillerite \( \rightarrow \) high-temperature perovskite). \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) was shown to be \( p \)-type throughout the \( p_{O_2} \) and temperature ranges studied. Cooling in flowing oxygen or air was found to give rise to sharp changes in the resistivity of \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \).

INTRODUCTION

\( \text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \) mixed oxides exhibit high oxygen-ionic and electronic conductivity and are potentially attractive as electrode materials for solid-electrolyte devices [1–6] and materials for oxygen-permeable ceramic membranes and membrane reactors for partial oxidation of hydrocarbons [1, 6–8].

The structure and physicochemical properties of the constituent oxides \( \text{SrCoO}_{3-\delta} \) and \( \text{SrFeO}_{3-\delta} \) have been studied in great detail [9–13]. The \( p-T-x \) diagrams of these compounds and \( \text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) [14] were reported in the literature. Above 900°C, \( \text{SrCoO}_{3-\delta} \) undergoes a phase transition from a rhombohedral structure containing ordered oxygen vacancies to a cubic perovskite structure with a disordered oxygen sublattice and high oxygen-ion mobility [10–12, 15]. \( \text{SrFeO}_{3-\delta} (\delta \leq 0.27) \) has a cubic perovskite structure at \( p_{O_2} > 100 \) Pa [9, 13, 16]. The preparation of dense, gas-tight ceramics from \( \text{SrFeO}_{3-\delta} \) involves a number of series difficulties [17].

The structure and properties of \( \text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \) (0.1 \( \leq x \leq 0.9 \)) materials have been studied in only a few works [1, 3, 17]. In a previous study [17], we found that the unit-cell volume of \( \text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta} \) (0.25 \( \leq x \leq 1.0 \)) passes through a maximum at \( x = 0.75 \), and that the corresponding material, \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{2.69} \), has a cubic perovskite structure.

In this paper, we report the electrical conductivity and oxygen nonstoichiometry of \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) and the stability limits of its polymorphic forms.

EXPERIMENTAL

Polycrystalline \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) was prepared by the conventional ceramic route from analytical-grade \( \text{Sr(NO}_3)_2 \) and extra-pure-grade \( \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) and \( \text{Fe}_2\text{O}_3 \). The synthesis and x-ray characterization procedures were described in detail earlier [17].

The oxygen stoichiometry of the as-prepared material was determined with an accuracy of \( \pm 0.01 \) by reduction to \( \text{Co} \) and \( \text{Fe} \) metals and \( \text{SrO} \) in flowing hydrogen at 950°C in the thermogravimetric (TG) unit described in [18].

The equilibrium oxygen stoichiometry as a function of temperature was determined on powder \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) during steplike heating and cooling, using the TG unit for measurements at high \( p_{O_2} \) and an \text{OXYLYT} coulometric system (SensoTech, Germany) at low \( p_{O_2} \) [19]. To characterize the processes induced in \( \text{SrCo}_{0.25}\text{Fe}_{0.75}\text{O}_{3-\delta} \) by heating and cooling, powder samples were heated in the \text{OXYLYT} system from room temperature to 1000°C at 8°C/min in a flowing gas stream of oxygen (\( p_{O_2} = 1.5–286 \) Pa) in argon, held under these conditions until equilibrium was reached, and then cooled. The relative error in oxygen content was estimated to be no greater than 1% at a 98% confidence level.

In dc conductivity measurements between 20 and 1020°C in a flowing gas stream with \( p_{O_2} = 1–10^5 \) Pa, we used the four-probe technique and rectangular samples \( 10 \times 3 \times 1 \) mm in dimensions with platinum contacts. The equilibrium conductivity was determined during both heating and cooling at constant partial pressure and also by raising and reducing \( p_{O_2} \) at fixed
temperature. Resistivity was also measured in different environments during cooling at 0.8–8°C/min from different temperatures after equilibration. In the resistivity range 10^{-3} to 10 \Omega cm, the systematic error in our electrical measurements was no greater than 1%.

In all experiments, the temperature was maintained with a stability of ±0.5°C.

Measurements were made in flowing oxygen, air, or argon (P_{O_2} = 1.5 Pa). Oxygen was introduced into the argon flow from air or an oxygen container through the wall of a silicone rubber tube placed in a thermostat. The oxygen concentration in the gas flow was measured with the OXYLYT of a TslIRKON-M instrument.

RESULTS AND DISCUSSION

Oxygen stoichiometry of SrCo_{0.25}Fe_{0.75}O_{3-\delta}. The oxygen stoichiometry of the as-prepared SrCo_{0.25}Fe_{0.75}O_{3-\delta} was determined to be 2.69 ± 0.01. The variation of the titration current during heating and cooling is illustrated in Fig. 1a, and the corresponding oxygen stoichiometry data are displayed in Fig. 1b.

It can be seen that the oxygen loss during heating depends little on P_{O_2} and begins at 300 ± 20°C. After equilibration at 1000°C, the oxygen stoichiometry is 2.39 at P_{O_2} = 1.5–10 Pa and 2.42 at P_{O_2} = 100–286 Pa.

Each of the titration curves shows two minima around 450 and 850°C, close in temperature to the maxima in the rate of oxygen loss. These minima are attributable to either phase transformations [10] or oxygen removal from different crystallographic sites, without drastic structural changes [20].

To elucidate the origin of the minima, two samples were held at 745 and 1000°C (P_{O_2} = 1.5 Pa) for 5 h and then, after quenching to room temperature, characterized by x-ray diffraction. The sample heated at 745°C was found to have a rhombohedral structure of the brownmillerite type, and that heated at 1000°C consisted of a mixture of brownmillerite and cubic perovskite phases, the latter being prevalent. Since the as-prepared material had the cubic perovskite structure, the lower temperature minimum is likely to be related to the cubic–brownmillerite phase transition, and the higher temperature minimum to the transformation of

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**Fig. 1.** Variation of the (a) titration current and (b) oxygen stoichiometry during heat treatment of SrCo_{0.25}Fe_{0.75}O_{3-\delta} at different oxygen pressures.