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Structure and oxygen stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

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Abstract

High temperature X-ray diffraction (HT-XRD), temperature programmed desorption (TPD), thermogravimetric analysis–differential thermal analysis (TGA/DTA) and neutron diffraction were combined to determine the structure and oxygen stoichiometry of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) up to 1273 K in the pO_2 range of 1 to 10^{-5} atm. Formation of the vacancy-ordered brownmillerite phase, $SrCo_{0.8}Fe_{0.2}O_{2.5}$, was observed as a region of zero oxygen release in the TPD measurements and confirmed by HT-XRD and TGA/DTA. No ordering was observed in the BSCF system by any of the techniques utilized in this work. The oxygen vacancy concentration of BSCF was found to be considerably higher than that of SCF and always higher than that of the ordered brownmillerite phase of SCF, $\delta = 0.5$. The combination of a high vacancy concentration and absence of ordering leads to higher oxygen permeation fluxes through BSCF membranes in comparison to SCF.

Keywords: Perovskite-type oxides; Membranes; Oxygen non-stoichiometry; Order-disorder transitions; Neutron scattering

1. Introduction

Mixed ionic and electronic conducting (MIEC) perovskite-structured oxides are of interest as ceramic membranes for oxygen production and electrode materials for solid oxide fuel cells (SOFC). The crystal structure and oxygen defect concentration are both critical parameters influencing ionic and electronic transport, surface kinetics and mechanical properties of these materials. Oxygen separating MIEC membranes are typically subjected to oxygen partial pressures in the range 1 to 10^{-5} atm at temperatures between 973 and 1273 K. $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) is reported to provide one of the largest membrane oxygen fluxes in the series $La_{1-y}Sr_yCo_xFe_{1-x}O_{3-\delta}$ [1–3]. However, undesirable ordering of SCF into a brownmillerite-type structure, $Sr_2Co_{1.6}Fe_{0.4}O_5$, has been reported to occur below 1073 K at pO_2 lower than around 0.1 atm [1,3–6]. This ordered state reduces the oxygen flux, while the associated lattice expansion of the membrane surface exposed to the low pO_2 side leads to large mechanical stresses across the membrane [3,7]. Recent work by Shao et al. [8,9] has demonstrated an increase in oxygen flux and an apparent increase in the stability of the cubic perovskite phase upon 50% substitution of Ba for Sr, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF). In addition, BSCF has recently been proposed as a cathode material for intermediate temperature SOFC [10].

The oxygen defect concentration of perovskites is typically tuned by substituting B-site cations with more or less reducible cations or by substituting A-site cations with cations of different charge. For example, increasing substitution of Sr^{2+} for La^{3+} on the A-site of $LaCo_{0.8}Fe_{0.2}O_{3-\delta}$ leads to increased oxygen non-stoichiometry and, subsequently, increased ionic conductivity at the expense of stability of the cubic perovskite phase [2,11]. However, the impact on defect chemistry and vacancy ordering

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of doping the A-site with cations of the same charge is not well understood.

Various parameters have been suggested to influence the ionic conductivity in perovskite oxides. Mogensen et al. [12] suggested that lattice distortion, that is the stress caused by distortion of the perfect cubic lattice, leads to a reduction in ionic conductivity. They suggested that the A-site cation should have a radius [13] close to that of the oxide ion, 1.40 Å, implying that La^{2+} (1.36 Å) and Sr^{2+} (1.44 Å) will result in the largest ionic conductivities and that Ba^{2+} (1.61 Å) substitution will result in a reduced conductivity. However, this is in contrast with the increased membrane performance reported when Ba^{2+} is substituted for Sr^{2+} on the A-site of SCF [8]. Further factors suggested to influence the ionic conductivity of the material include the average metal–oxygen bond enthalpy and lattice free volume [14]. In comparing SCF and BSCF less than 1% difference was found in the average metal–oxygen bond energy, while the lattice free volume of both materials is below the suggested optimum of 30–35 $Å^3$. It should be noted that both of these last parameters were suggested for solid electrolytes. Geometric influence on the ionic conductivity of the perovskite phase has also been related to the tolerance factor, t, with $t = 0.96$ as an optimum [15]. Assuming all of the B cations in the 3+ oxidation state, $\delta = 0.5$, the tolerance factors for SCF and BSCF are 0.977 and 1.00, respectively. If we assume all of the Co in the Co^{2+} state the tolerance factors are 0.93 and 0.957, suggesting that reduction of Co^{3+} to Co^{2+} is desirable in BSCF but undesirable in SCF.

In this paper, the structure and defect chemistry of SCF and BSCF are investigated in the pO_2 range of 1 to 10^{-5} atm and between 573 and 1273 K.

2. Experimental

Phase pure commercial $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) powders (Praxair specialty ceramics,

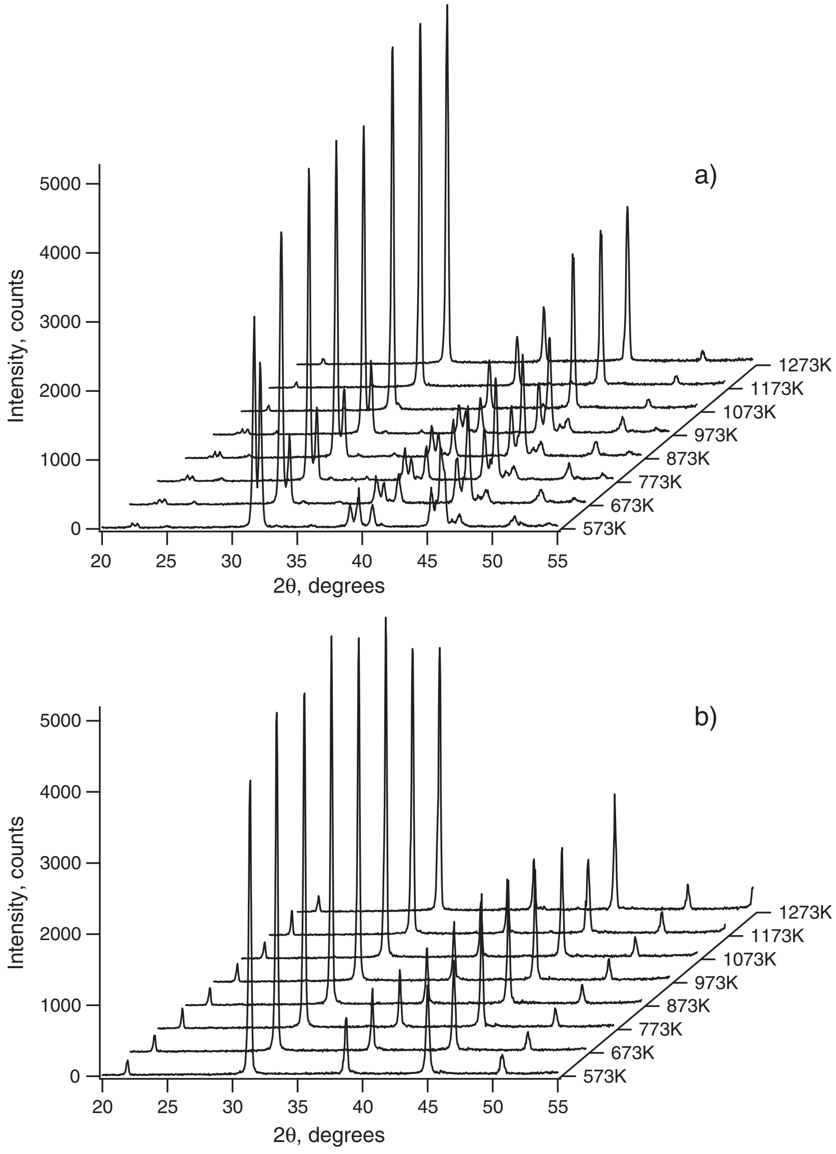

Fig. 1. HT-XRD patterns of a) $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and b) $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ measured under flowing nitrogen, $pO_2 = 1 \times 10^{-3}$ atm. Higher angles are not shown for clarity.