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Synthesis and characterization of the K_2NiF_4 phases $La_{1+x}Sr_{1-x}Co_{0.5}Fe_{0.5}O_{4-\delta}$ ($x = 0$, 0.2)

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ABSTRACT

The K_2NiF_4 phases $LaSrCo_{0.5}Fe_{0.5}O_4$ and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_4$, and their reduced forms $LaSrCo_{0.5}Fe_{0.5}O_{3.75}$ and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_{3.85}$, have been successfully prepared by solid-state reactions, followed by reduction in 10% H_2/N_2 in order to produce oxygen-deficient materials. All materials crystallize in a tetragonal K_2NiF_4 structure (space group $I4/mmm$) with Co and Fe randomly distributed over the B-sites of the structure. Mössbauer spectra have confirmed the trivalent state of Fe in these materials. In the reduced materials, oxide ion vacancies are confined to the equatorial planes of the K_2NiF_4 structure and the Co is present almost entirely as Co^{2+} ions; low-temperature neutron powder diffraction data reveal that these reduced phases are antiferromagnetically ordered with a tetragonal noncollinear arrangement of the moments. The Co^{3+} ions, present in stoichiometric $LaSrCo_{0.5}Fe_{0.5}O_4$ and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_4$, inhibit magnetic order and are assumed to be in the low-spin state.

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1. Introduction

Perovskite-type oxides which are able to support both mobile oxygen ions and electronic conductivity over a wide range of oxygen partial pressures are of great interest as electrode materials in solid oxide fuel cells (SOFCs), oxygen separation membranes and catalysts. For this reason, the mixed conducting perovskites $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ have been widely studied [1–3]. Recently, some interest has been focused on related Ruddlesden Popper phases $(La/Sr)_{n+1}(Co/Fe)_nO_{3n+1}$ which exhibit variable oxygen nonstoichiometry along with structural stability at high temperatures in reducing conditions; this has been linked to the flexibility of the cations to accommodate a range of transition metal coordination environments. Of these systems, the parent material $Sr_3Fe_2O_{7-\delta}$ has a tetragonal structure (space group $I4/mmm$) and exhibits oxygen deficiency $\delta \leqslant 1$. The sample with $\delta = 1$ was prepared in 5% H_2/N_2 atmosphere at 700 °C and showed no variation in the crystal structure symmetry [4]. Manthiram et al. [5] have studied structural stability and oxygen permeation properties of $Sr_{3-x}La_xFe_{2-y}Co_yO_{7-\delta}$, which retains tetragonal symmetry with temperatures up to 1000 °C in the oxygen partial pressure range 10^{-5}–0.21 atm. Other related systems which showed high ability to sustain low oxygen content without change in crystal structure symmetry are $Sr_3FeCoO_{7-\delta}$ ($\delta \leqslant 1.55$) [6], $Sr_3LaFe_{1.5}Co_{1.5}O_{8.25}$ and $Sr_3LaFe_{1.5}Co_{1.5}O_{7.5}$ [7].

The stoichiometric materials $LaSrCo_{1-x}Fe_xO_4$ have been synthesized by Tabuchi et al. [8]. The study involved detailed structural and magnetic characterization, although the half-doped member $LaSrCo_{0.5}Fe_{0.5}O_4$ has not been characterized. We report here the synthesis and characterization of the $n = 1$ Ruddlesden Popper phases $LaSrCo_{0.5}Fe_{0.5}O_4$ and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_4$ and their reduced forms $LaSrCo_{0.5}Fe_{0.5}O_{3.75}$ and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_{3.85}$; the reduction has been achieved in 10% H_2/N_2 at 800 °C with no variation in the crystal structure symmetry; moreover, TG data indicate structural stability of these materials in this atmosphere up to 1000 °C. The present study involves structural and magnetic characterization of these materials.

2. Experimental

$LaSrCo_{0.5}Fe_{0.5}O_{4-\delta}$ (LA1) and $La_{1.2}Sr_{0.8}Co_{0.5}Fe_{0.5}O_{4-\delta}$ (LA12) were prepared using conventional solid-state reactions involving analytical grade $SrCO_3$, La_2O_3, Co_3O_4 and Fe_2O_3 (all previously heated in air at 800 °C for 12 h to remove residual water hydroxide or carbonate). Attempts to effect the reaction in air were unsuccessful, since some perovskite impurities were produced, and a two-step synthesis procedure was therefore adopted. Stoichiometric amounts of starting materials were initially intimately mixed, pressed into pellets and calcined at 1350 °C for 30 h under a N_2 atmosphere. After grinding, the samples were

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subsequently heated in air (at 800 °C for 12 h) or flowing 10% H_2/N_2 gas (at 800 °C for 12 h) in order to prepare the "oxidized" samples (LA1-ox and LA12-ox) and the "reduced" samples (LA1-red and LA12-red), respectively.

X-ray powder diffraction (XRD) data were collected using a Siemens D5000 diffractometer in transmission mode, employing Cu$K\alpha_1$ radiation from a germanium monochromator. Neutron powder diffraction (NPD) data were collected at room temperature and 5 K on the D2B diffractometer at the Institute Laue Langevin, Grenoble, using a wavelength of 1.594 Å. Rietveld refinement was performed on the powder diffraction data using the GSAS suite of programs [9] employing a pseudo-Voigt peak shape for the oxidized materials and a combination of pseudo-Voigt and Finger–Cox–Jephcoat functions for the reduced samples. This function was necessary to obtain a good fit to the experimental data and indicates significant anisotropic peak broadening in these materials. A small correction for preferred orientation was also allowed in the refinement. Magnetic data were collected using a Quantum Design PPMS magnetometer in the temperature range 5–300 K. Zero-field-cooled (ZFC) and field-cooled (FC) data were collected on warming using an applied field of 0.3 T. ^{57}Fe Mössbauer spectra were recorded at 298 K with a microprocessor-controlled Mössbauer spectrometer using a 25 mCi ^{57}Co/Rh source. The spectra were computer fitted and isomer shifts are reported relative to metallic iron at room temperature.

3. Results

3.1. Structural characterization

XRD patterns indicated that all samples were single-phase with no evidence of product impurities or starting materials. The patterns were readily indexed on a body-centred tetragonal unit cell, consistent with a structure related to that of K_2NiF_4. Although structural refinements based on XRD data confirmed the structure ($I4/mmm$ space group), the refinements were insensitive to oxygen stoichiometry and the oxide ion sites could be fixed at full occupancy.

NPD data collected at room temperature were used to probe more reliably the oxygen content and defect structure of these phases. Rietveld profile refinement of the high-intensity powder diffraction (HIPD) data was performed and the profile-fit and difference patterns of the Rietveld analysis of different samples are shown in Fig. 1; structural data and some selected bond lengths are given in Tables 1 and 2, respectively.

The O2 apical (axial) oxygen sites (0,0,z) were allowed to vibrate anisotropically and all samples had higher displacements perpendicular to the (Co/Fe)–O bond (Table 1). This is quite normal for this layered structure, but might also be augmented by the different bond requirements of Co and Fe in this mixed oxide. Split oxide ion sites have previously been invoked in the analysis of $LaSrCoO_{3.5-x}$ [10]. Oxide ion vacancies created in

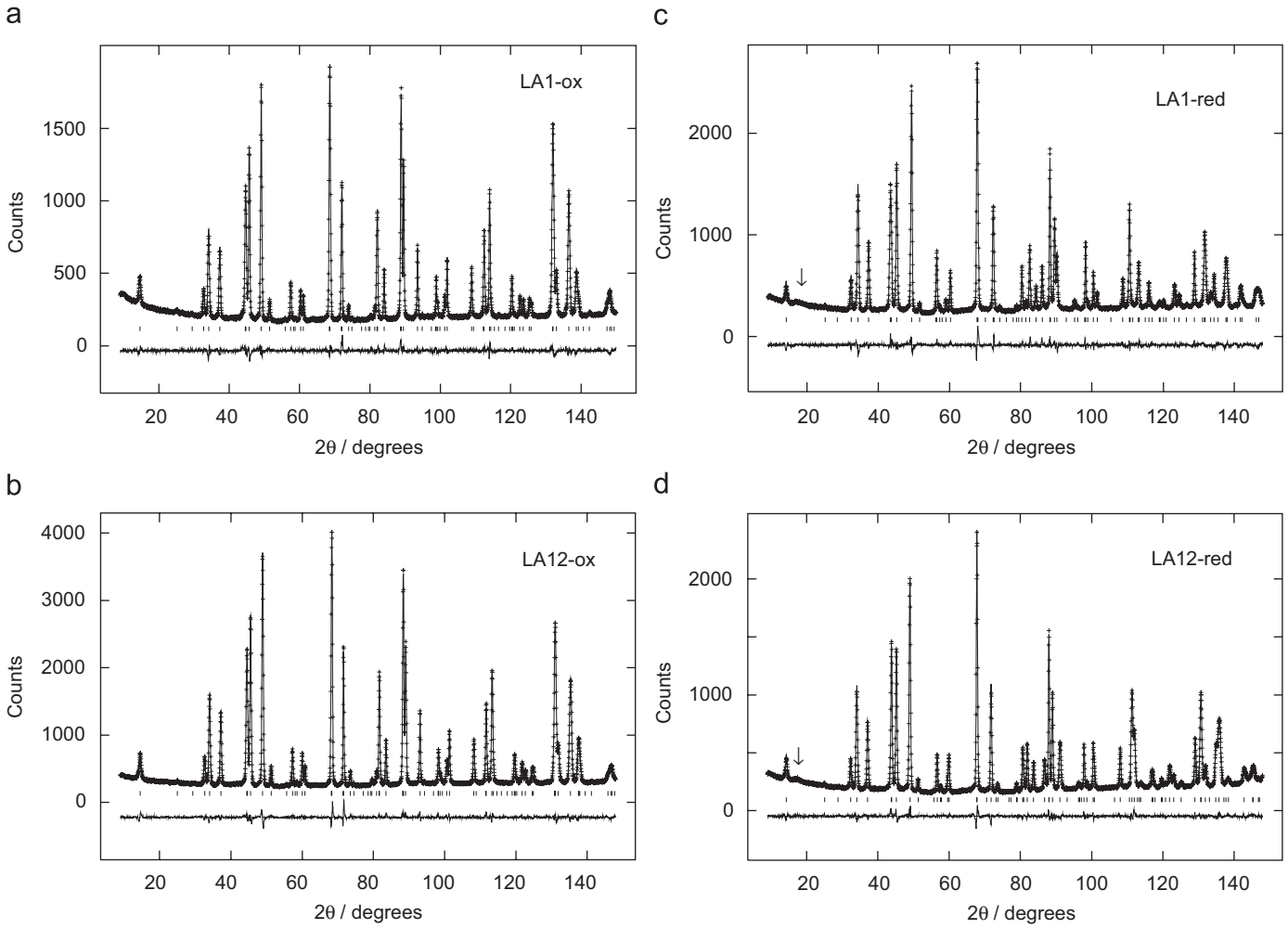

Fig. 1. Observed, calculated and difference profiles for NPD data collected at room temperature: (a) LA1-ox, (b) LA12-ox, (c) LA1-red and (d) LA12-red. The arrows in (c) and (d) show diffuse peaks that may indicate short-range magnetic ordering.

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