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CRYSTAL STRUCTURES OF MIXED-CONDUCTING OXIDES PRESENT IN THE Sr-Fe-Co-O SYSTEM

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ABSTRACT

The potential applications of mixed-conducting ceramic oxides include solid-oxide fuel cells, rechargeable batteries, gas sensors and oxygen-permeable membranes. Several perovskite-derived mixed Sr-Fe-Co oxides show not only high electrical-conductivity but also appreciable oxygen-permeability at elevated temperatures. For example, dense ceramic membranes of $SrFeCo_{0.5}O_{3-\delta}$ can be used to separate oxygen from air without the need for external electrical circuitry. The separated oxygen can be directly used for the partial oxidation of methane to produce syngas. Quantitative phase analysis of the $SrFeCo_{0.5}O_{3-\delta}$ material has revealed that it is predominantly composed of two Sr-Fe-Co-O systems, $Sr_4Fe_{6-x}Co_xO_{13}$ and $SrFe_{1-x}Co_xO_{3-\delta}$. Here we report preliminary structural findings on the $SrFe_{1-x}Co_xO_{3-\delta}$ ($0 \le x \le 0.3$) system.

INTRODUCTION

Mixed-conducting ceramic oxides are of great interest because of their technological importance in high-temperature electrochemical applications. The mixed Sr-Fe-Co oxide systems possess high electronic (σ_e) and oxygen ionic (σ_i) conductivities, together with structural stability over a wide range of oxygen partial pressures [1-4]. These materials have found applications in high-temperature electrodes, solid-oxide fuel cells, gas sensors and also hold particular promise as oxygen-permeable ceramic membranes. Teraoka et al. [2] have investigated the mixed electronic-ionic conductivity of the $Sr_{1-x}La_xFe_{1-y}Co_yO_{3-\delta}$ perovskite system and have shown that $SrFe_{0.2}Co_{0.8}O_{3-\delta}$, with $\sigma_e \approx 100$ and $\sigma_i \approx 1$ S.cm^{-1} at 800°C in air, has a particularly high oxygen-permeability. Recently, Balachandran et al. [4] have demonstrated that a material of nominal composition $SrFeCo_{0.5}O_{3-\delta}$ possesses a significantly higher oxygen-permeability ($\sigma_e \approx 10$ and $\sigma_i \approx 7$ S.cm^{-1} at 800°C in air). Unlike most of the known mixed conductors, which generally have much higher electronic than ionic conduction, $SrFeCo_{0.5}O_{3-\delta}$ has comparable conductivities. This combination of high electronic and oxide ion conductivities in $SrFeCo_{0.5}O_{3-\delta}$, means that it can act as an selective oxygen-permeable membrane without the need for external electrical circuitry. A promising application of $SrFeCo_{0.5}O_{3-\delta}$ oxygen permeable membranes, is in reactors that directly convert methane to syngas [5].

When used as a ceramic membrane in gas separation, $SrFeCo_{0.5}O_{3-\delta}$ is exposed to a large oxygen partial pressure (pO_2) difference (the resulting chemical potential gradient drives the transport of oxygen from the high to low pO_2 sides of the membrane). Under such a range of pO_2 and at typical operational temperatures of 600-800°C, the oxygen stoichiometry and crystal structure may vary significantly through the membrane.

In order to develop and understand an oxygen permeation mechanism for $SrFeCo_{0.5}O_{3-\delta}$ precise information concerning the crystal structures formed and oxygen nonstoichiometry at various temperatures and oxygen partial pressures is required. We have therefore initiated a wide ranging crystallographic study of the $SrFeCo_{0.5}O_{3-\delta}$ material and related phases.

Quantitative analysis of powder X-ray and neutron diffraction data from $SrFeCo_{0.5}O_{3-\delta}$, performed at Argonne, has revealed its multiphase nature. The major phase, present at a wt. fraction of ~ 70%, is of the form $Sr_4(Fe,Co)_6O_{13}$ and is isotypic in crystal structure to $Sr_4Fe_6O_{13}$ [6,7]. Present also are, an oxygen deficient perovskite of the form $Sr(Fe,Co)O_{3-\delta}$ with a wt. fraction of ~ 25% and CoO as a minor phase at ~ 5% wt. fraction. We have therefore undertaken a study of the two Sr-Fe-Co oxide systems present in the $SrFeCo_{0.5}O_{3-\delta}$ material. In this paper we report preliminary structural findings on the $SrFe_{1-x}Co_xO_{3-\delta}$ ($0 \leq x \leq 0.3$) system.

EXPERIMENTAL

Synthesis

Polycrystalline samples of $SrFe_{1-x}Co_xO_{3-\delta}$ (x = 0, 0.1, 0.2 and 0.3) were prepared by solid-state reaction of $SrCO_3$, Fe_2O_3 and Co_3O_4. The starting materials were mixed under n-amyl alcohol in a ball-mill for 3 hr. After drying, these mixtures were initially fired at 900°C for 12 hr., cooled to room temperature and reground in an agate mortar. Further firings at 1050°C, 1100°C and 1150°C for 12 hr. durations were carried out to complete the reaction. Subsequently, each $SrFe_{1-x}Co_xO_{3-\delta}$ sample was split into three and annealed under the following conditions, flowing Ar at 1050°C, air at 550°C or flowing O_2 at 350°C, all for 8 hr. periods. Overall twelve samples in the $SrFe_{1-x}Co_xO_{3-\delta}$ system were prepared with x = 0, 0.1, 0.2 and 0.3 combined with $\delta \approx 0.12$, 0.25 and $\delta = 0.5$ from the O_2, air, and Ar annealing stages, respectively.
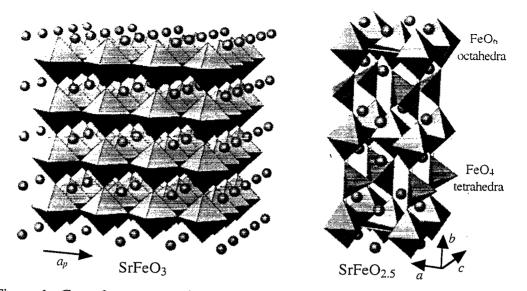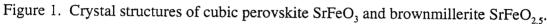
Characterization

Powder X-ray and time-of-flight neutron diffraction data were collected on all samples using a Scintag diffractometer and the Special Environment Powder Diffractometer at Argonne National Laboratory's Intense Pulsed Neutron Source. Rietveld profile analysis of the powder neutron diffraction data was performed using the GSAS suite of programs [8].

RESULTS AND DISCUSSION

For the end member $SrFeO_{3-\delta}$, Takeda et al. [9] have determined that four distinct phases, with differing crystal structures, exist. The phases are defined by the ideal compositions $SrFeO_{3-1/n}$, where n = ∞, 8, 4 and 2. The n = ∞ and 2 members, $SrFeO_3$ and $SrFeO_{2.5}$, possess simple primitive cubic perovskite and brownmillerite crystal structures respectively see Figure 1. In the brownmillerite structure, oxygen vacancies are ordered into lines along the c-axis, which is the $[110]_p$ direction of the parent cubic perovskite. These lines of vacancies are located in every other $(001)_p$ plane, giving rise to alternate layers of FeO_4 tetrahedra and FeO_6 octahedra.

Electron diffraction measurements performed on the n = 8 and 4 members, $SrFeO_{2.88}$ and $SrFeO_{2.75}$, have revealed oxygen vacancy ordering to give perovskite based superstructures [9,10], however the precise crystal structures were unknown. Takano et al. [10] proposed that $SrFeO_{2.88}$ and $SrFeO_{2.75}$ possessed body centred tetragonal (a = 10.934Å and c = 7.705Å) and C-face centred orthorhombic (a = 10.972Å, b = 7.700Å and c = 5.471Å) unit cells, respectively. Furthermore, the volume of these unit cells are related to the parent cubic perovskite, where $a_p \approx 3.85$Å. by $(2\sqrt{2}a_p)^2 \times 2a_p$ and $2\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$.

Figure 1. Crystal structures of cubic perovskite $SrFeO_3$ and brownmillerite $SrFeO_{2.5}$.

In this study we have prepared $SrFe_{1-x}Co_xO_{2.88}$, $SrFe_{1-x}Co_xO_{2.75}$ and $SrFe_{1-x}Co_xO_{2.5}$ systems via annealing of $SrFe_{1-x}Co_xO_{3-\delta}$ samples under O_2, air, and Ar, respectively. Powder X-ray diffraction revealed that for all the $SrFe_{1-x}Co_xO_{3-1/n}$ samples, the desired superstructures were formed in single phase. From a consideration of the proposed vacancy ordering schemes and resulting atomic relaxations, we have determined that the crystal structures of $SrFe_{1-x}Co_xO_{2.88}$ and $SrFe_{1-x}Co_xO_{2.75}$ may be described with orthorhombic Fmmm ($a \approx b \approx 4a_p$ and $c \approx \sqrt{2}a_p$) and monoclinic C2/m ($a \approx 2\sqrt{2}a_p$, $b \approx 2a_p$, $c \approx \sqrt{2}a_p$ and $\beta \approx 90°$) cell symmetries, respectively. Schematic representations of these crystal structures are shown in Figure 2. In $SrFe_{1-x}Co_xO_{2.88}$ the oxygen vacancies are located at the vertices and face centres of the unit cell, giving rise to adjacent $(Fe,Co)O_5$ square pyramids. Like brownmillerite, the vacancies are located in every other $(001)_p$ plane such that a layered structure, with $a \neq b$, results.
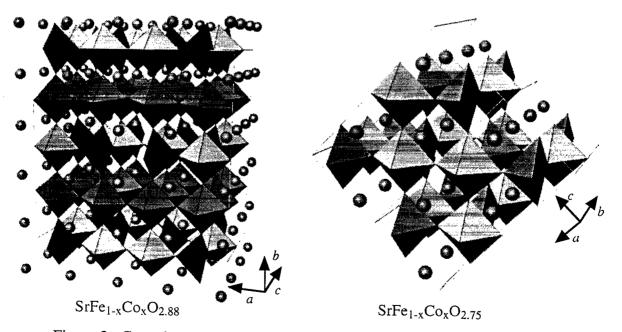

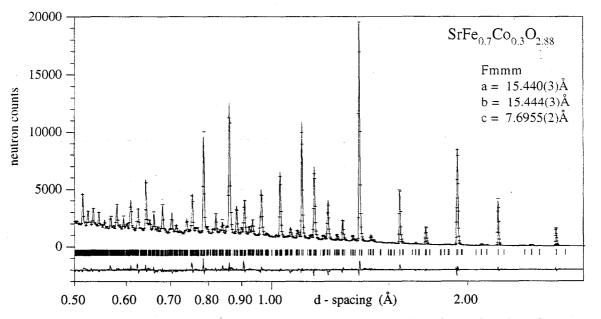Figure 2. Crystal structures of the $SrFe_{1-x}Co_xO_{2.88}$ and $SrFe_{1-x}Co_xO_{2.75}$ systems.

Figure 3. Final observed, calculated and difference profiles for $SrFe_{0.7}Co_{0.3}O_{2.88}$.

Table I. Refined crystallographic parameters for $SrFe_{0.7}Co_{0.3}O_{2.88}$.
Space group Fmmm $a = 15.440(3)$Å, $b = 15.444(3)$Å and $c = 7.6955(2)$Å
$R_{wp} = 0.061$, $R_p = 0.043$, $R_e = 0.019$ and $R_I = 0.067$.

Atom	Site	x	y	z	B_{iso}	$Occ.$
Sr (1)	16(k)	0.25	0.1278(5)	0.25	0.4(1)	1.0
Sr (2)	16(m)	0	0.1249(5)	0.2341(6)	0.6(1)	1.0
Fe/Co (1)	8(g)	0.1261(5)	0	0	0.4(1)	0.74(2)
Fe/Co (2)	8(g)	0.3755(5)	0	0	0.5(1)	0.68(2)
Fe/Co (2)	16(o)	0.1250(3)	0.2501(3)	0	0.4(1)	0.71(2)
O (1)	16(o)	0.1298(5)	0.1278(8)	0	1.7(2)	1.0
O (2)	8(e)	0.25	0.25	0	1.1(2)	1.0
O (3)	16(o)	0.3742(4)	0.1230(6)	0	0.6(1)	1.0
O (4)	8(g)	0.2533(8)	0	0	2.2(3)	1.0
O (5)	4(b)	0	0	0.5	0.8(2)	1.0
O (6)	16(l)	0.1233(4)	0.25	0.25	0.3(1)	1.0
O (7)	16(n)	0.1132(4)	0	0.2283(7)	1.4(1)	1.0
O (8)	8(h)	0	0.2660(5)	0	0.3(1)	1.0

In $SrFe_{1-x}Co_xO_{2.75}$ the vacancies are located at the vertices and centre of the c faces of the unit cell. Furthermore, this structure can be derived from $SrFe_{1-x}Co_xO_{2.88}$ simply by removing the layers composed only of $(Fe,Co)O_6$ octahedra. For the $SrFe_{1-x}Co_xO_{2.88}$ and $SrFe_{1-x}Co_xO_{2.75}$ systems there exists three and two distinct Fe/Co sites, respectively. Rietveld analysis of powder neutron diffraction data has successfully refined these crystal structures. In Figure 3, a Rietveld profile fit to the $SrFe_{0.7}Co_{0.3}O_{2.88}$ powder neutron diffraction data is shown, with the associated crystal structure data presented in Table I. While in Table II, the refined crystallographic parameters for $SrFe_{0.8}Co_{0.2}O_{2.75}$ are given. For these two vacancy ordered perovskite systems no appreciable site preference by Co and no magnetic Bragg reflections in the neutron diffraction profiles (at room temperature) were detected.

Table II. Refined crystallographic parameters for $SrFe_{0.8}Co_{0.2}O_{2.75}$.
Space group C2/m $a = 10.9762(9)$Å, $b = 7.6729(3)$Å, $c = 5.4736(5)$Å & $\beta = 90.06(2)°$
$R_{wp} = 0.101$, $R_p = 0.068$, $R_e = 0.021$ and $R_I = 0.084$.

Atom	Site	x	y	z	B_{iso}	$Occ.$
Sr (1)	8(j)	0.1212(6)	0.2369(3)	0.756(2)	0.4(1)	1.0
Fe/Co (1)	4(i)	0.1231(5)	0	0.245(2)	0.4(1)	0.81(1)
Fe/Co (2)	4(i)	0.3735(5)	0	0.744(2)	0.4(1)	0.80(1)
O (1)	8(j)	0.1140(6)	0.2267(4)	0.237(2)	0.9(1)	1.0
O (2)	4(i)	0.2614(8)	0	0.006(3)	0.9(2)	1.0
O (3)	2(b)	0	0.5	0	0.7(3)	1.0
O (4)	2(d)	0	0.5	0.5	2.9(3)	1.0
O (5)	2(c)	0	0	0.5	1.0(2)	1.0
O (6)	4(i)	0.2648(8)	0	0.493(3)	0.4(1)	1.0

The brownmillerite $SrFe_{1-x}Co_xO_{2.5}$ system was refined in the magnetic space group $Icm'm'$ using initial starting parameters reported by Battle *et al.* [11]. In Figure 4, a Rietveld profile fit to the $SrFe_{0.8}Co_{0.2}O_{2.5}$ neutron diffraction data is shown ($R_{wp} = 0.054$, $R_p = 0.038$, $R_e = 0.019$ and $R_I = 0.040$). In $SrFe_{1-x}Co_xO_{2.5}$ the magnetic moments were found to remain ordered in an antiferromagnetic fashion directed along the c-axis for x = 0 to 0.3. Differing from the $SrFe_{1-x}Co_xO_{2.88}$ and $SrFe_{1-x}Co_xO_{2.75}$ systems, Co was consistently found to show a degree of selectivity between the available Fe/Co sites. To illustrate, in $SrFe_{0.7}Co_{0.3}O_{2.5}$ the layer composed of $(Fe,Co)O_4$ tetrahedra was found to contain 36(1)% Co, this is greater than the 30% expected from a random distribution.
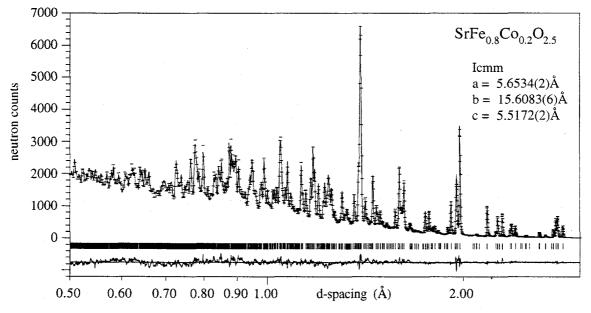

Figure 4. Final observed, calculated and difference profiles for $SrFe_{0.8}Co_{0.2}O_{2.5}$.

For ceramic membranes to operate for long periods under changing temperatures and large pO_2 gradients, they must be structurally stable. If the crystal structure of the membrane material changes significantly between different operating conditions, then this may lead to structural instability, for example, cracking. Large changes in unit cell volume as one varies the pO_2 are particularly undesirable in ceramic membrane materials . In Figure 6, we have plotted the primitive perovskite unit cell volumes for the $SrFe_{1-x}Co_xO_{3-1/n}$ systems as a function of x. It can be seen that Co doping has only a small effect on the unit cell volumes, however the oxygen

content has a much greater influence. In moving from the oxygen rich $SrFe_{1-x}Co_xO_{2.88}$ to the $SrFe_{1-x}Co_xO_{2.75}$ system, the average unit cell volume increases by ~ 1%. The situation is clearly different on moving to the $SrFe_{1-x}Co_xO_{2.5}$ system where the unit cell volume increases by ~ 6%. This relatively huge volume increase is a consequence of significant changes in crystal structure and bonding. For the n = ∞, 8, and 4 members of $SrFe_{1-x}Co_xO_{3-1/n}$, there exists significant bonding in all 3-directions. In the n = 2 brownmillerite system, however, the alternate layers composed of $(Fe,Co)O_4$ tetrahedra can be considered to be without bonding in the a direction, and this results in a large relative expansion of the unit cell. These unit cell volume considerations, in part suggest that oxygen-permeable ceramic membranes composed only of $SrFe_{1-x}Co_xO_{3-\delta}$ may not possess the structural stability required in high-temperature reactors.
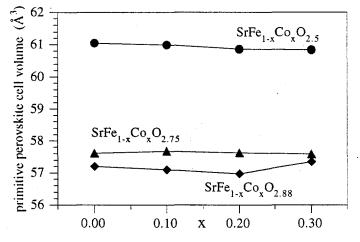

Figure 6. Primitive unit cell volumes plotted as a function of x for the $SrFe_{1-x}Co_xO_{3-1/n}$ systems.

ACKNOWLEDGMENTS

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