

ANW/ET/CP-97895

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Sr-Fe-Co-O System*

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April 1999

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SEP 28 1999
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Paper to be published in proceedings of the American Ceramic Society
101st Annual Meeting & Exposition, Indianapolis, April 25-28, 1999.

*Work supported by U.S. Department of Energy, Federal Energy
Technology Center, under Contract W-31-109-Eng-38.

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THERMODYNAMICS AND STABILITY OF THE MIXED-CONDUCTING Sr-Fe-Co-O SYSTEM

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ABSTRACT

Mixed-conducting Sr-Fe-Co oxides have potential applications in dense ceramic membranes for high-purity oxygen separation and/or methane conversion to produce syngas ($\text{CO} + \text{H}_2$), because of their combined high electronic/ionic conductivity and significant oxygen permeability. We studied the crystal structure and microstructure of the system in X-ray diffraction experiments and by using scanning electron microscopy, respectively. Thermogravimetric analysis was conducted on the $\text{SrFeCo}_{0.5}\text{O}_x$ sample in environments of various oxygen partial pressures (p_{O_2}). Conductivity increased while weight decreased with increasing temperature. Activation energy decreased while conductivity increased with increasing p_{O_2} . The p_{O_2} -dependent conducting behavior of the $\text{SrFeCo}_{0.5}\text{O}_x$ system can be understood by considering the trivalent-to-divalent transition of transition-metal ions.

INTRODUCTION

In recent years, mixed-conducting oxides, in which both electronic and ionic charge carriers exist, have received increased attention because of their technological importance in high-temperature applications such as solid oxide fuel cells, batteries, and sensors [1-5]. They are also good candidate materials as ceramic membranes for gas separation if their oxygen permeation flux rates are high enough. Recently, Balachandran [6-8] et al. showed that $\text{SrFeCo}_{0.5}\text{O}_x$ exhibits not only high combined electronic and oxygen ionic conductivities but also appreciable oxygen permeability. Dense membranes made of $\text{SrFeCo}_{0.5}\text{O}_x$ can be used to separate oxygen from air without the need for external electrical circuitry. Extruded tube membranes made of this material have been evaluated in a reactor operating at $\approx 850^\circ\text{C}$ that converts methane to syngas ($\text{CO} + \text{H}_2$) in the

presence of a reforming catalyst. Methane conversion coefficients >98% were observed [8,9], and some of the reactor tubes have been operated for more than 1000 h.

When used as a ceramic membrane in gas separation, the material is exposed to large oxygen gradients. Oxygen transport from the high- pO_2 side to the low- pO_2 side occurs when the pO_2 difference between two side of the membrane can build up a substantial oxygen flux. Therefore, an understanding of the oxygen stoichiometry is extremely important. In this paper, we report the results of conductivity testing and the thermogravimetric analysis (TGA) on $SrFeCo_{0.5}O_x$ in various pO_2 environments. A simplified defect model is proposed to explain the experimental results.

EXPERIMENT

$SrFeCo_{0.5}O_x$ samples were prepared by a solid-state reaction method; $SrCO_3$, Fe_2O_3 , and $Co(NO_3)_2 \cdot 6H_2O$ were the starting materials. Mixing and grinding were performed in isopropanol with zirconia media. After drying, the mixtures were calcined at $\approx 850^\circ C$ for 16 h in air, with intermittent grinding.

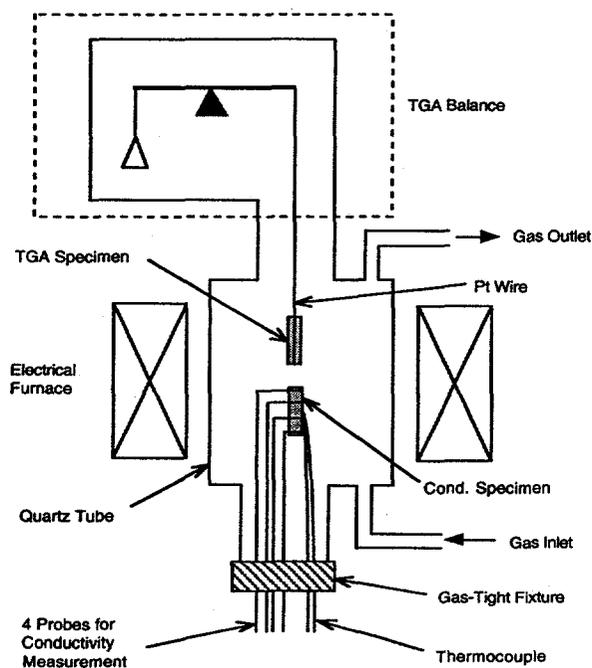


Figure 1. Schematic drawing of experimental setup.

Phase purity was confirmed by X-ray diffraction (XRD). The resulting powders were then pressed into pellets and sintered in air at 1200°C for 5 h, after which the sintered pellets were cut into thin bars for conductivity testing and TGA. The true density of SrFeCo_{0.5}O_x was measured on powder with an AccuPyc 1330 pycnometer. The bulk density of the sintered sample was determined by the Archimedes method, and was ≈95% of the true value. A scanning electron microscopy (SEM) observation showed dense and uniform structure.

Figure 1 illustrates our experimental setup. Environments of various pO₂ values were established with premixed gases. Weight change of a specimen was measured with a CAHN TG-121 TGA apparatus. Conductivity was determined by the four-probe method and is related to the measured resistance, R (in Ω), in

$$\sigma = \frac{d_{vw}}{R \cdot A} \quad (1)$$

where d_{vw} is the distance between two potential leads (in cm), and A is the cross-sectional area of the specimen (in cm²). The activation energy was calculated by fitting the temperature-dependent conductivity data to

$$\sigma \cdot T = A_0 \exp(-E_a / k_B T) \quad (2)$$

where A_0 is a constant, E_a is the activation energy, k_B is the Boltzmann constant, and T is the absolute temperature. A K-type thermocouple was attached to the conductivity sample to measure and control the temperature. During our experiment, specimen temperature was controlled within 1°C.

RESULTS AND DISCUSSION

The sintered SrFeCo_{0.5}O_x sample displayed a dense uniform structure with no open pores or cracks. X-ray powder diffraction indicates that this sample consists of multiple phases, a layered Sr₄(Fe_{6-x}Co_x)O_{6±δ} phase and a perovskite Sr(Fe_{1-x}Co_x)O_{3-δ} phase. Detailed discussion on its crystal structures can be found in Ref. 10. Figure 2 shows Arrhenius plots of conductivity in various pO₂ environments. The activation energy of SrFeCo_{0.5}O_x can be calculated according to Eq. 2, and the result is plotted in Fig. 3 as a function of pO₂. Activation energy increases with decreasing pO₂ in the low-pO₂ range.

The log(σ) as a function of pO₂ measured in various different atmospheres at 950°C is shown in Fig. 4. Our earlier results obtained with a gas-tight electrochemical cell [11] are replotted in Fig. 4. Conductivity decreases with decreasing pO₂ with a slope of ≈1/6. At 950°C, the conductivity of SrFeCo_{0.5}O_x is ≈21 and

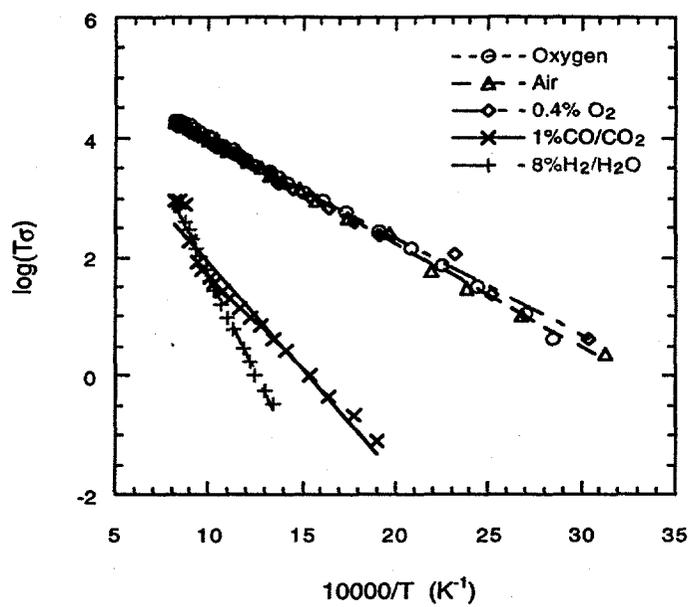


Figure 2. Temperature-dependent conductivity of SrFeCo_{0.5}O_x in various pO₂ environments.

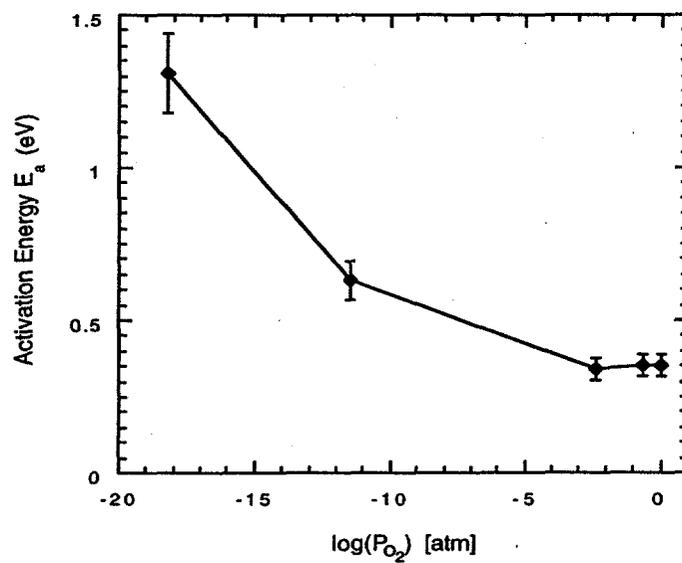


Figure 3. Activation energy as a function of pO₂.

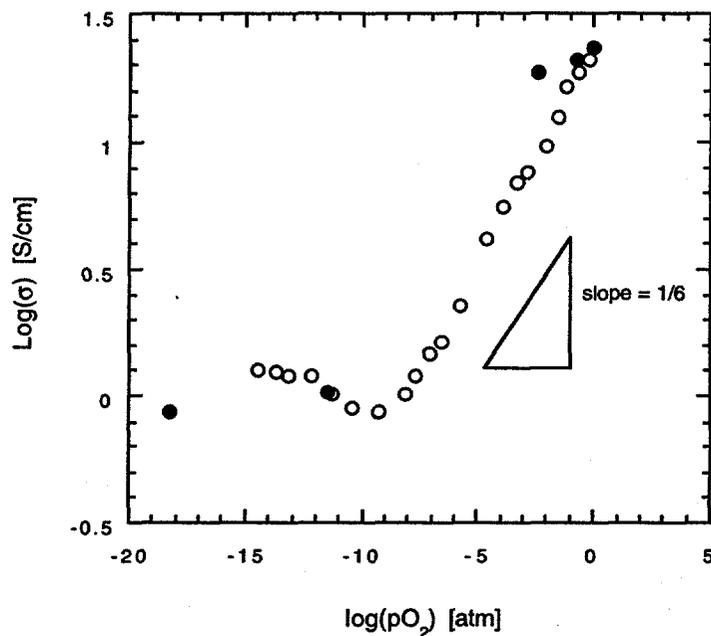
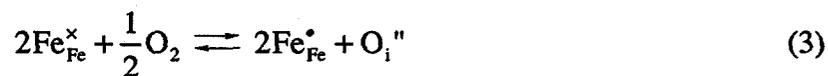


Figure 4. Conductivity of SrFeCo_{0.5}O_x as a function of pO₂ at 950°C.

≈0.8 S·cm⁻¹ in air and in 8% H₂/H₂O environments, respectively. The results from the two different experimental techniques are in good agreement. To understand the pO₂ dependence of this material in the intermediate-pO₂ region, a simplified defect model is proposed below.

Interaction between transition-metal ions and oxygen in the surrounding atmosphere can be represented as



Considering the case where the concentration of free holes (h[•]) is much lower than the concentration of trapped holes (Fe_{Fe}[•]), the electroneutrality equation can be written as

$$2[\text{O}_i^{\prime\prime}] = [\text{Fe}_{\text{Fe}}^{\bullet}] \quad (4)$$

and the mass-balance relationship of transition-metal ions gives

$$[\text{Fe}_{\text{Fe}}^{\bullet}] + [\text{Fe}_{\text{Fe}}^{\times}] = 1 \quad (5)$$

Here, we use Fe to represent both transition-metal (Fe and Co) ions. Equation 3 leads to the equilibrium relationship of

$$K = \frac{[\text{Fe}_{\text{Fe}}^{\bullet}]^2 [\text{O}_i^{\prime\prime}]}{[\text{Fe}_{\text{Fe}}^{\times}]^2 (p\text{O}_2)^{1/2}} \quad (6)$$

where K is the temperature-dependent equilibrium constant. Let $x = [\text{Fe}_{\text{Fe}}^{\bullet}]$, and using Eqs. 4 and 5, we have

$$[\text{O}_i^{\prime\prime}] = \frac{x}{2} \quad (7)$$

and

$$[\text{Fe}_{\text{Fe}}^{\times}] = 1 - x \quad (8)$$

Substituting Eqs. 7 and 8 into Eq. 9, we have

$$K = \frac{x^3}{2(1-x)^2 (p\text{O}_2)^{1/2}} \quad (9)$$

Under the condition of $x \ll 1$, i.e., the concentration of trivalent transition-metal ions is much lower than the concentration of divalent transition-metal ions, Eq. 9 leads to

$$x = (2K)^{1/3} \cdot (p\text{O}_2)^{1/6} \quad (10)$$

or

$$[\text{O}_i^{\prime\prime}] \propto (p\text{O}_2)^{1/6} \quad (11)$$

Because conductivity is proportional to concentrations of charge carriers, we have

$$\sigma \propto (p\text{O}_2)^{1/6} \quad (12)$$

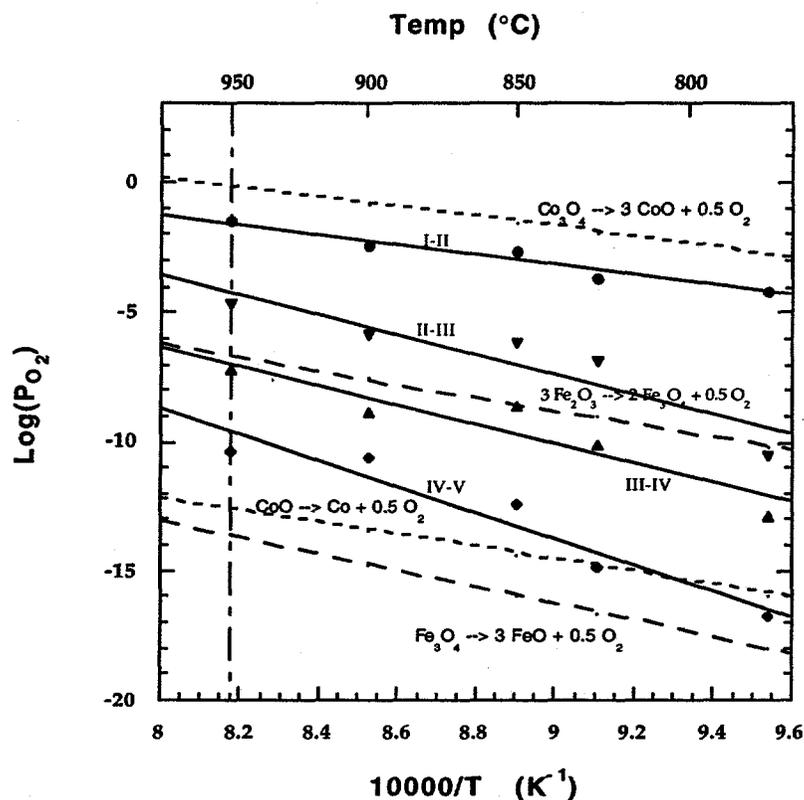


Figure 5. Transition boundaries of $\text{SrFeCo}_{0.5}\text{O}_x$, along with phase transitions of cobalt and iron oxides.

The $1/6$ dependent slope in Fig. 4 is an indication that change in valence of the transition-metal ions plays an important role in the interaction between the $\text{SrFeCo}_{0.5}\text{O}_x$ sample and oxygen in the surrounding atmosphere.

Table 1. Weight and corresponding oxygen content change of $\text{SrFeCo}_{0.5}\text{O}_x$ with changed $p\text{O}_2$ at 950°C^a .

Atmosphere Change	$\Delta\log(p\text{O}_2)$	ΔW	Δx
100% O_2 to air	-0.678	0.2366	0.0211
Air to 0.4% O_2/Ar	-1.695	0.1503	0.0134
0.4% O_2/Ar to 1% CO/CO_2	-9.127	1.7153	0.1529
1% CO/CO_2 to 8% $\text{H}_2/\text{H}_2\text{O}$	-6.700	8.2115	0.7321

^aInitial weight of specimen (in air) was 0.1549 g.

Table 1 lists the weight change measured in TGA experiments, and the corresponding change in oxygen content of $\text{SrFeCo}_{0.5}\text{O}_x$ with changed $p\text{O}_2$ at 950°C . And Fig. 5 shows the phase transition boundaries of $\text{SrFeCo}_{0.5}\text{O}_x$, along with those of cobalt and iron oxides. Based on the conductivity data [11], we noticed that at 950°C , a transition that is likely related to the transition from hematite (Fe_2O_3) to magnetite (Fe_3O_4) of iron oxide occurred after switching the surrounding atmosphere from 0.4% O_2/Ar to 1% CO/CO_2 . From Table 1, we observe that the change of oxygen content for $\text{SrFeCo}_{0.5}\text{O}_x$ is 0.1663 ($0.0134 + 0.1529$) after the surrounding atmosphere changed from air to 1% CO/CO_2 . This value of oxygen content change is in very good agreement with the value that corresponds to the hematite-to-magnetite transition of iron. Hence, we have good reason to believe that Fe ions exist in the 3+ state, and that Sr and Co ions exist in 2+ states at 950°C in air. From another point of view, $\text{SrFeCo}_{0.5}\text{O}_x$ can be considered as a solid solution of SrO , Fe_2O_3 , and CoO with the appropriate mole ratio. This leads to $x = 3$ in the chemical formula of the material at 950°C in air. Oxygen content as a function of $p\text{O}_2$ for $\text{SrFeCo}_{0.5}\text{O}_x$ at 950°C is shown in Fig. 6.

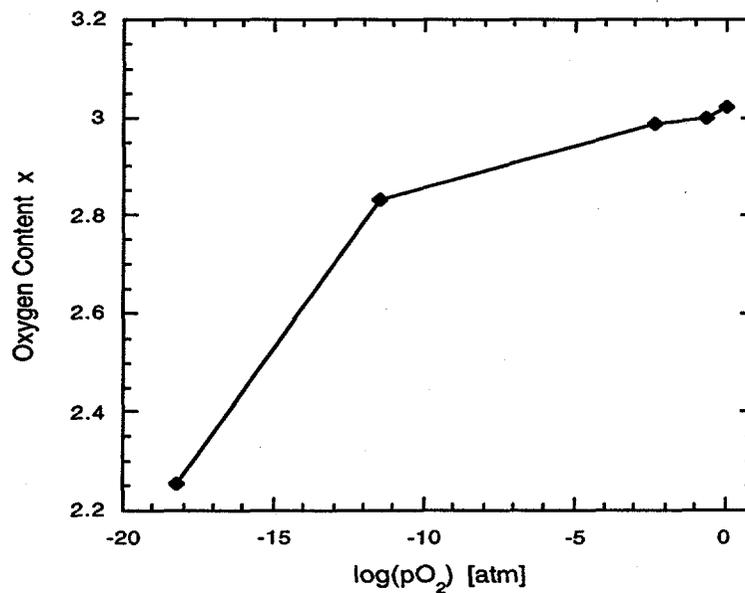


Figure 6. Oxygen content as a function of $p\text{O}_2$ for $\text{SrFeCo}_{0.5}\text{O}_x$ at 950°C .

Redox experiments on the $\text{SrFeCo}_{0.5}\text{O}_x$ sample were conducted at high temperature and in various atmospheres to investigate its phase stability [12]. Figure 7 shows SEM images of polished samples before and after several heating and cooling cycles. The sample became less dense after several thermal shocks. However, its phase integrity was retained [12].

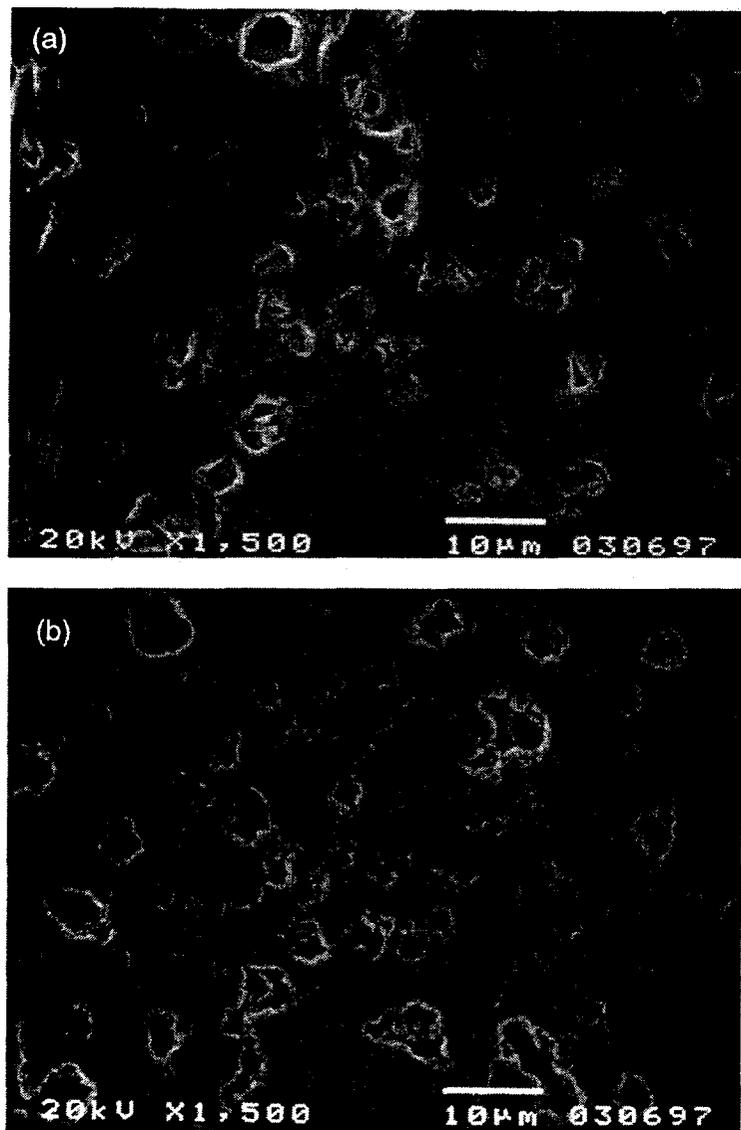


Figure 7. SEM images of $\text{SrFeCo}_{0.5}\text{O}_x$ (a) before and (b) after several thermal shocks.

CONCLUSIONS

The sintered $\text{SrFeCo}_{0.5}\text{O}_x$ sample has a dense and uniform structure with no open pores or cracks. It is a multiple-phase material consisting of $\text{Sr}_4(\text{Fe}_{6-x}\text{Co}_x)\text{O}_{6+8}$ phase and perovskite $\text{Sr}(\text{Fe}_{1-x}\text{Co}_x)\text{O}_{3-8}$ phase. Conductivity of $\text{SrFeCo}_{0.5}\text{O}_x$ increases with increasing temperature and increasing oxygen partial pressure. At 950°C , the conductivity of $\text{SrFeCo}_{0.5}\text{O}_x$ is ≈ 21 and $\approx 0.8 \text{ S}\cdot\text{cm}^{-1}$ in air and in 8% $\text{H}_2/\text{H}_2\text{O}$ environments, respectively. A simple defect model was proposed to explain the $1/6$ dependence in the conductivity vs. $p\text{O}_2$ curve. Changes in valence states of the transition-metal ions play an important role in the interaction between the $\text{SrFeCo}_{0.5}\text{O}_x$ sample and oxygen in the surrounding atmosphere. TGA results suggested that Fe ions exist in 3+ state, and that Sr and Co ions exist in 2+ states in the solid solution, at 950°C in air.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Federal Energy Technology Center, under Contract W-31-109-Eng-38.

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