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Studies of Nonstoichiometry and Physical Properties of the Perovskite $Sm_{1-x}Sr_xCoO_{3-y}$ System

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A series of samples in the $Sm_{1-x}Sr_xCoO_{3-y}$ ($x=0.00$, 0.25, 0.50, 0.75 and 1.00) system has been prepared at 1200 ℃ under ambient atmosphere. The X-ray diffraction patterns of the samples with $x=0.00$ and 0.25 are indexed with orthorhombic symmetry like $GdFeO_3$ and $x=0.50$ appears to be perfectly cubic. In the tetragonal system ($x=0.75$), the structure is similar to that of $SrCoO_{2.80}$. The composition of $x=1.00$, $SrCoO_{2.52}$, shows the brownmillerite-type structure. The reduced lattice volume is increased with x value in this system. The chemical analysis shows the τ value (the amount of the Co^{4+} ions in the system) is maximized at the composition of $x=0.50$. Nonstoichiometric chemical formulas are determined by the x, τ and y values. The electrical conductivity has been measured in the temperature range of 78 to 1000 K. The activation energy is minimum for those of $x=0.25$ and $x=0.50$ with metallic behavior. First-order semiconductor-to-metal transition of $SmCoO_3$ is not observed. Instead, a broad, high-order semiconductor-to-metal transition is observed. In general, the effective magnetic moment is increased with increasing τ values at low temperature. At high temperature, the magnetic moment is maximum for that of $x=0.00$. The 3d-electrons are collective and give ferromagnetism in $x=0.50$.

Introduction

Preparations and characterizations of oxides containing appreciable quantities of cobalt in a rare valence state $+4$ have been reported by several research groups. In perovskite-type ABO_3 compounds, the higher valence state of the transition metal is generally stabilized with larger A-site ion.[1~7]

Raccah and Goodenough[8] and Bhide *et al.*[9] have investigated a $LaCoO_3$ system in which cobalt ions predominantly exist in the diamagnetic, low spin state $Co^{3+}(t_{2g}^6 e_g^0)$ at low temperature. According to these studies, the low-spin $^1A_1$ state of trivalent cobalt ion is only 0.08 eV more stable than the high-spin $^5T_2$ state. Therefore, the equilibrium between the states can be changed with temperature. They have also suggested that $LaCoO_3$ exhibits a first-order transition due to the delocalization of the eg electrons forming a σ* band states. So beyond 1200 K, $LaCoO_3$ becomes metallic.

Thornton *et al.*,[10] however, have suggested that the $LnCoO_3$ (Ln : La, Nd, Gd, Ho, and Y) system show broad, high order semiconductor-to-metal transitions over the approximate temperature ranges (La : 385-570 K, Nd : 400-590 K, Gd : 490-770 K). These transitions involve gradual delocalization of eg electron to form a collective σ* band.

The $SrCoO_{2.5}$ has brownmillerite or hexagonally deficient perovskite structure depending on annealing temperature and oxygen pressure during the sample preparation.[11~13] The high temperature phase of $SrCoO_{2.5}$ is brownmillerite-type,

orthorhombic structure, and has the Néel temperature of 550 K.[11]

Substitution of La^{3+} in $LaCoO_3$ by Sr^{2+} (creating Co^{4+} holes) brings about remarkable changes.[13,14] Thus, the system $La_{1-x}Sr_xCoO_3$ becomes ferromagnetic at low temperatures when $x>0.125$, the ferromagnetism arising from the positive Co^{4+}-O-Co^{3+} interaction; the d electrons show itinerant behavior (both above and below T_c) in these compositions.

In this present study, the $Sm_{1-x}Sr_xCoO_{3-y}(0.00 \leq x \leq 1.00)$ system has been prepared and their structures are analyzed by X-ray diffraction and a thermal analysis method. The amount of Co^{4+} ions to the total cobalt ions is determined by an iodometric titration. The magnetic and other physical properties of this system with the nonstoichiometry are discussed.

Experimental

Samples of $Sm_{1-x}Sr_xCoO_3$ with various values of x ($x=0.00$, 0.25, 0.50, 0.75, and 1.00) were prepared by coprecipitating the starting materials in the required proportions, essentially following the method described earlier.[16] The starting materials were Sm_2O_3, $SrCO_3$, and $Co(NO_3)_2 \cdot 6H_2O$. Appropriate amounts of the mixtures were dissolved in dilute nitric acid. The solution was evaporated over a burner flame and then fired at 800 ℃ for 4 hr. After being ground, the samples were heated at 1200 ℃ under an ambient atmosphere for

Table 1. Lattice Parameters, Reduced Lattice Volume, and Crystal System of the $Sm_{1-x}Sr_xCoO_{3-y}$ System

x	Lattice parameter (Å) (± 0.001 Å)			Reduced lattice volume (Å³)	Crystal system
	a	b	c		
0.00	5.297	5.357	7.500	53.20	Orthorhombic
0.25	5.363	5.353	7.592	54.49	Orthorhombic
0.50	3.795			54.66	Cubic
0.75	10.877		7.716	57.06	Tetragonal
1.00	5.454	15.702	5.559	59.51	Orthorhombic

48 hr. The weighing, grinding, and heating processes were repeated in order to produce homogeneous solid solutions. In order to minimize oxygen vacancies, the samples have been annealed at 1000 ℃ for 3 days. Especially the $SrCoO_{2.5}$ ($x=1.00$) was fired at 1150 ℃ in air and was subsequently quenched to prevent it from changing into the low temperature phase and absorbing oxygen. Each powdered sample was shaped into a pellet, then sintered under the same conditions.

X-ray diffraction patterns were taken at each stage to monitor the completion of the reaction. By the X-ray diffraction analysis with monochromatized CuKα ($\lambda = 1.5418$ Å) radiation, the lattice parameter, the reduced lattice volume of the unit cell, and the crystal structure of the prepared samples were determined. DTA and TGA were carried out in the range specified by the chemical analysis in which the samples were dissolved in an acidified KI solution and followed by redox titration.

The electrical conductivity (employing the four probe method) measurements of the samples were made in the temperature range 78-1000 K. The electrical conductivities were calculated using Laplume's equation. Magnetic susceptibility measurements were made in the temperature range 300-800 K employing a Faraday balance.

Result and Discussion

The X-ray diffraction patterns of the compositions of $x=$ 0.00 and 0.25 are indexed on the basis of a distorted perovskite-type structure with orthorhombic symmetry like Gd-FeO₃.[16] According to the spectra of the compositions of $x=$ 0.50 and 0.75, the symmetries of these compositions are cubic and tetragonal, respectively. The orthoferrite-type distortion decreases with increasing Sr content, and the composition of $x=0.50$ appears to be perfectly cubic. In the tetragonal system ($x=0.75$), the structure is similar to that of $SrCoO_{2.80}$. The composition of $x=1.00$, $SrCoO_{2.52}$, shows the brownmillerite-type structure which is similar to the $SrCoO_{2.50}$ suggested by Grenier *et al.*.[11,12,17] They suggested that $SrCoO_{2.50}$, the brownmillerite-type structure, contains oxygen vacancies which are ordered along [101] rows.[17] The lattice parameters of the crystal system of $SrCoO_{2.52}$ are similar to that of $SrCoO_{2.50}$.

The lattice parameters, the reduced lattice volume of the unit cell, and the crystal system of the compositions are listed in Table 1. The ionic radius effect of the substituted
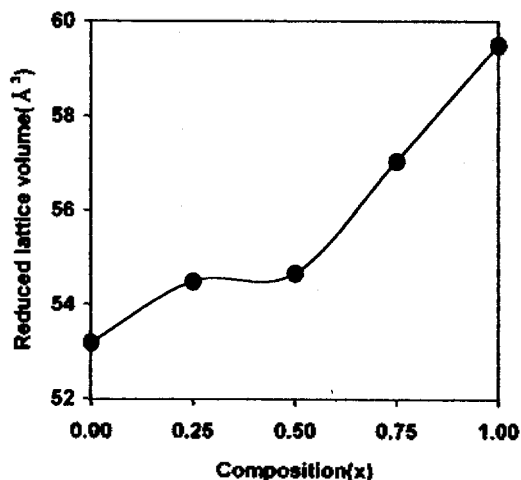
Figure 1. Plot of reduced lattice volume *vs.* composition (x) for the $Sm_{1-x}Sr_xCoO_{3-y}$ system.

Table 2. x, τ, y Values, and Nonstoichiometric Chemical Formulas for the $Sm_{1-x}Sr_xCoO_{3-y}$ System

x	τ (± 0.005)	y	Chemical formula
0.00	0.00	0.00	$Sm_{1.00}Co^{3+}_{1.00}O_3$
0.25	0.21	0.02	$Sm_{0.75}Sr_{0.25}Co^{3+}_{0.79}Co^{4+}_{0.21}O_{2.98}$
0.50	0.50	0.00	$Sm_{0.50}Sr_{0.50}Co^{3+}_{0.50}Co^{4+}_{0.50}O_3$
0.75	0.18	0.29	$Sm_{0.25}Sr_{0.75}Co^{3+}_{0.82}Co^{4+}_{0.18}O_{2.71}$
1.00	0.04	0.48	$Sr_{1.00}Co^{3+}_{0.96}Co^{4+}_{0.04}O_{2.52}$
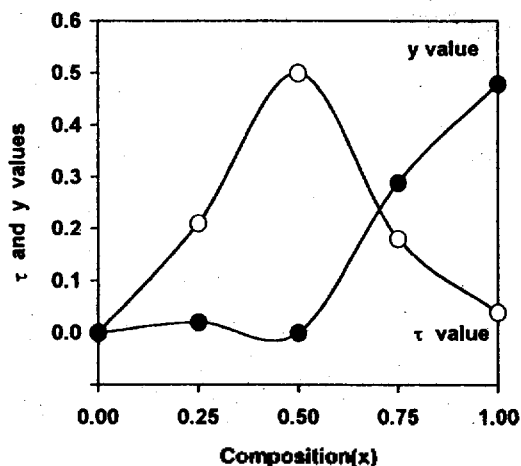
Figure 2. Plot of τ and y-values *vs.* composition for the $Sm_{1-x}Sr_xCoO_{3-y}$ system.

ions in the system is predominant.[5] Therefore, The reduced lattice volume increases with the substitution of Sr^{2+}(1.58 Å) for Sm^{3+}(1.38 Å) as shown in Figure 1.

The τ value (the mole ratio of the Co^{4+} ion), y value, and nonstoichiometric formula corresponding to each composition are listed in Table 2. The compositions of $x=0.00$ and 0.50 are stoichiometric compounds and the others are nonstoichiometric ones. As shown in Figure 2, the τ value increases as the x value increases within the range of 0.00

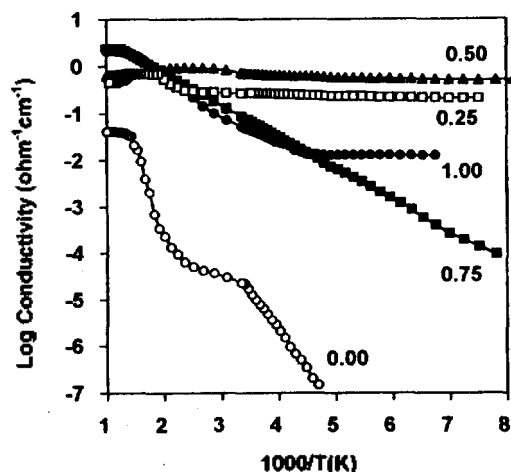**Figure 3.** Plot of log conductivity *vs.* 1000/T for the $Sm_{1-x}Sr_x$-CoO_{3-y} system.

Figure 4. Plot of $1/\chi_M$ *vs.* temperature for the $SmCoO_{3.00}$.

Table 3. Activation Energies of the $Sm_{1-x}Sr_xCoO_{3-y}$ System

x-value	Temperature range (K)	Activation energy (eV)
	$80 \leq T \leq 290$	0.34
0.00	$290 \leq T \leq 500$	0.08
	$500 \leq T \leq 720$	0.89
0.25	$80 \leq T \leq 430$	0.006
0.50	$80 \leq T \leq 360$	0.008
0.75	$80 \leq T \leq 800$	0.134
1.00	$80 \leq T \leq 220$	0.001
	$240 \leq T \leq 450$	0.132

Figure 5. Plot of $1/\chi_M$ *vs.* temperature for the $Sm_{1-x}Sr_xCoO_{3-y}$ ($x=0.25$, 0.50, and 0.75) system.

$\leq x \leq 0.50$ and the τ value is maximized at the composition of $x=0.50$. However, the τ value decreases as the x value increases for the compositions of $x>0.50$, in which the formation of oxygen vacancies might be easier than the formation of the Co^{4+} ion.

The experimental data of DTA and TGA for the compositions of $x=0.00-1.00$ show that there is neither weight loss nor phase transition in the temperature range of 300-1000 K. These compositions, therefore, are thermally stable in this temperature range. The electrical conductivity measurements have been carried out in the temperature range 78-1000 K under an atmospheric condition. These conductivity data are shown in Figure 3. The activation energies of electrical conduction are listed in Table 3 for all the compositions in the given temperature ranges. In $SmCoO_{3.00}$, the activation energy for $T<290$ K corresponds to the excitation from a localized t_{2g} band to a conduction σ^* band in the trivalent cobalt ion. The short range ordering is established between low and high spins of the trivalent cobalt ions in the temperature range of 290 to 500 K. $SmCoO_{3.00}$ shows high conductivity as well as metallic behavior above 720 K because of overlapping of π^* and σ^* band.[18] The electrical conductivity rises from $10^{-4}\Omega^{-1}cm^{-1}$ at 500 K to $10^{-1}\Omega^{-1}cm^{-1}$ at 730 K. And $SmCoO_{3.00}$ shows no first-order transition at about 1200 K in DTA spectra. These facts suggest a mechanism for the semiconductor-to-metal transition which borrows much from the band broadening and overlap model. The mechanism
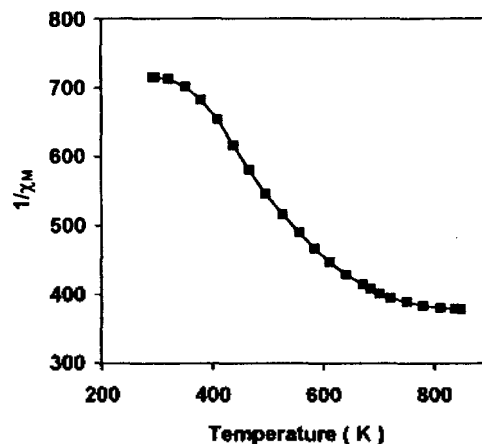
proposed by Thornton *et al.*[18] deduced for Ti_2O_3 involves thermal population of the e_π band from the a_1 band. It involves collective d-electron states, with thermal population of the highly antibonding σ^* band from the π^* band, which would result in an increase in Co-O bond length and hence the lattice parameters. In turn, this would result in a stabilization of both π^* and σ^* bands due to a reduction in Δ^σ_{cal} and Δ^π_{cal} overlap integrals. However, because $\Delta^\sigma_{cal}>\Delta^\pi_{cal}$, the σ^* bands would be stabilized with respect to π^*, the π^*-σ^* band gap decreased, and the π^*-σ^* excitation made easier.

In the $Sm_{1-x}Sr_xCoO_{3-y}$ ($x=0.25$, 0.50, 0.75, and 1.00) system, there exists the low spin state of the Co^{4+} ion ($t_{2g}^5e_g^0$) by replacing the Sm^{3+} ion with the Sr^{2+} one. The activation energy is minimum for those of $x=0.25$ and 0.50 with metallic behavior. The activation energy of the $x=0.75$ composition is considerably larger than that of $x=0.25$ even though they have similar τ values. The oxygen vacancies formed by the replacement of the Sm^{3+} ion with the Sr^{2+} one interrupt the ferromagnetic Co^{3+}-O^{2-}-Co^{IV} interaction. The $SrCoO_{2.52}$ sample contains a small amount of the Co^{4+} ion and many oxygen vacancies. Therefore it has a higher activation energy than those of the $x=0.25$ and 0.50 in the temperature range $T>200$ K. Both the activation energy and the resistivity are
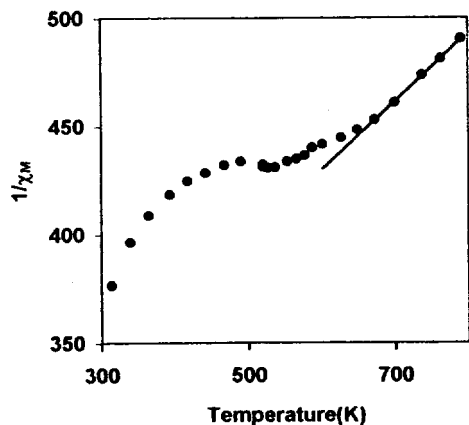
Perovskite $Sm_{1-x}Sr_xCoO_{3-y}$ *System*

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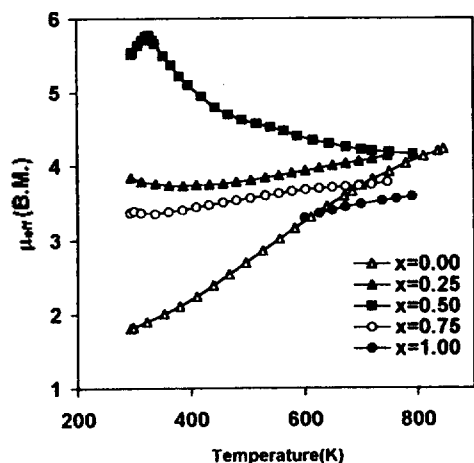**Figure 6.** Plot of $1/\chi_M$ *vs.* temperature for the $SrCoO_{2.52}$.

Figure 7. Plot of effective magnetic moment *vs.* temperatures for the $Sm_{1-x}Sr_xCoO_{3-y}$ system.

decreased in proportion to the amount of ferromagnetic Co^{3+} -O^{2-}-Co^{IV} interaction.

The reciprocal magnetic susceptibilities as a function of temperature are shown in Figures 4-6 within the temperature range of 300-800 K. The Sm^{3+} ion($4f^5$), with a $^6H_{5/2}$ ground state, does not follow a simple Curie-Weiss law.[19] Furthermore, the |7/2> state are at a low enough energy to mix strongly with the components of the |5/2> ground state, and thereby modify substantially the g-values. So, the compositions of $x=0.00$-0.75 show no good linearity in plots of $1/\chi_M$ *vs* T. In $SmCoO_{3.00}$, a plot of $1/\chi_M$ *vs* T is similar to $YCoO_3$. Demazeau *et al.*[20] assigned the increase in $YCoO_3$ cell parameters and magnetic susceptibility to a rapid increase in the concentration of high-spin cobalt species. The total effective magnetic moments as a function of temperature are shown in Figure 7. In general, the effective magnetic moment is increased with increasing τ values at low temperature. It has been reported that Co^{3+} ion is stabilized with low spin states ($t_{2g}^6 e_g^0$) at low temperature and the μ_{eff} of the Sm^{3+} ion is very small (0.84 μ_B).[6] Therefore, the effective magnetic moment of the Co^{4+} ions is predominant in the

system and the total effective magnetic moments is proportional to τ value. At high temperature, the magnetic moment becomes maximum for the sample with $x=0.00$. As the temperature increases, the Co^{III} low spin states transfer to Co^{3+} high spin states ($t_{2g}^4 e_g^2$). The $SrCoO_{2.52}$ sample has the lowest effective magnetic moment ($\simeq 2$ μ_B) due to substituting paramagnetic Sm^{3+} ions with diamagnetic Sr^{2+} ions. The composition $Sm_{0.5}Sr_{0.5}CoO_3$ is a metallic ferromagnet ($T_c \simeq 325$ K). The ferromagnetism arising from the positive Co^{3+}-O^{2-}-Co^{IV} interaction; the d electrons show itinerant behavior in this composition.

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