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BRIEF COMMUNICATION

Studies on the Synthetic, Structural, Electrical, and Magnetic Properties of the New Layered Oxides $Ln_2MCo_2O_7$ (Ln = Sm, Gd; M = Sr, Ba)

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Three new oxides $Ln_2MCo_2O_7$ (Ln = Sm, Gd; M = Sr, Ba) have been synthesized in solid state reaction method. The powder X-ray diffraction spectra show that they are all isostructural with $Sr_3Ti_2O_7$. The electrical resistivities in the temperature range 300–1100 K show that they are all semiconductors, and a transition to metals is observed at 1053, 1053, and 573 K for $Sm_2SrCo_2O_7$, $Gd_2SrCo_2O_7$, and $Sm_2BaCo_2O_7$, respectively. The magnetic suspectivities of $Gd_2SrCo_2O_7$ in the temperature range 300–673 K fit the Curie–Weiss law well. A plateau is observed in the curves of $Sm_2MCo_2O_7$ (M = Sr, Ba) which is attributed to the configuration state change of Co(III) from low spin to high spin. © 1995 Academic Press, Inc.

INTRODUCTION

Since the discovery of high-Tc superconducting cuprates, much attention has been focused on the intergrowth structures based on perovskite blockes. Ruddlesden and Poper have described the intergrowth structures with the general formula $Sr_{n+1}Ti_nO_{3n+1}$, where n is the number of perovskite layers separated by SrO halite layers (1). In fact, La_2CuO_4 corresponds to the n = 1 phase, and $La_{2-x}Sr_xCuO_4$, which initiated the revolutionary discovery of high-Tc superconducting cuprates, has this structure as well (2). By the replacement of Ti^{+4} with lower valent transition metals and charge compensation with higher valent ions on the alkaline earth site, many new oxides have been synthesized, such as $Ln_2AB_2O_7$ (Ln = la, Nd, Sm, Eu, Gd, or Tb; A = Sr, Ba; M = Fe, Mn or Sc) (3–6). The replacement of Ti^{+4} by Cu^{+2} to form $La_2SrCu_2O_6$ needs the removal of an oxygen ion for overall charge neutrality, and the apical oxygen joining the two octahetral is missing, resulting in the layers of copper pyramids whose bases face each other (7–9). In this report, three new oxides with intergrowth structures $Ln_2MCo_2O_7$ (Ln = Sm, Gd; M = Sr, Ba) were synthesized successfully. This is the first time that $Sr_3Ti_2O_7$-type oxides with Co were obtained and their structural, electrical, and magnetic properties were studied.

EXPERIMENTAL

A mixture of reagent grade oxides Sm_2O_3, Gd_2O_3, $SrCO_3$, and Co_2O_3 was ground in an appropriate metal ratio, pressed into pellets under 25 MPa atmosphere, and then placed in crucibles. Finally, the pellets were fired at 1450 K for three days in O_2 flow. Using this method, $Ln_2SrCo_2O_7$ (Ln = Sm or Gd) was obtained. $Sm_2BaCo_2O_7$ was synthesized by the firing of reagent grade oxides Sm_2O_3, $BaCO_3$, and Co_2O_3 at 1300 K for two weeks in O_2 flow.

X-ray powder diffraction analysis was made with a Rigaku Denki 2028 D/max = II B diffractometer using Cu$K\alpha$ (λ = 0.1542 nm) radiation. The sillion powder was used as the internal standard. XPS measurement was carried out with a VG scientific, Ltd. ESCALAB-MK II using Al$K\alpha$ (1486.6 ev) as the internal standard under 1×10^{-6} mbar atmosphere. A Shimadzu MB-II magnetic balance was used to measure the magnetic suspectivities of the samples between 300 and 1051 K in an applied field of 448 mT. The electrical resistivities were measured in the range 300–1100 K by four-probe techniques with In point contacts and copper wires.

RESULTS AND DISCUSSION

The X-ray diffraction spectra of $Ln_2SrCo_2O_7$ (Ln = Sm and Gd) and $Sm_2BaCo_2O_7$ are shown in Fig. 1 and their lattice parameters are listed in Table 1. All three samples have isostructures with $Sr_3Ti_2O_7$. The X-ray diffraction coordination of $Gd_2SrCo_2O_7$ is shown in Table 2.

The XPS of the three new oxides shows that the peaks

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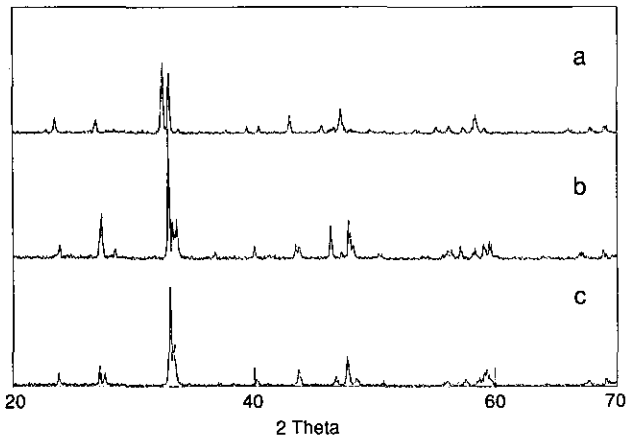

FIG. 1. The XDS of (a) $Sm_2BaCo_2O_7$ (b) $Sm_2SrCo_2O_7$, and (c) $Gd_2SrCo_2O_7$.

for Co $2p_{3/2}$ are 780.6, 780.8, and 779.7 ev for $Sm_2SrCo_2O_7$, $Gd_2SrCo_2O_7$, and $Sm_2BaCo_2O_7$, respectively, and the peak for Co_2O_3 is 780.5 ev. It is certain that the valence of Co in $Ln_2MCo_2O_7$ is +3 and the oxygen content is 7.

The resistivities of $Sm_2SrCo_2O_7$, $Gd_2SrCo_2O_7$, and $Sm_2BaCo_2O_7$ are 6.02, 8.09, and 1.27 $\Omega \cdot$ cm, respectively, at room temperature. $Ln_2SrCo_2O_7$ (Ln = Sm and Gd) are n-type semiconductors, and $Sm_2BaCo_2O_7$ is a p-type semiconductor at 300 K. It is shown that the excitation energies of the three samples are changing with the temperature from 300 to 1100 K (see Fig. 2). This is characteristic of weakly localized systems (10). Similar to $LaCoO_3$ (11), the transition from semiconductors to metals is observed in all the three samples and the transition temperatures are 1053, 1053, and 593 K for $Sm_2SrCo_2O_7$, $Gd_2SrCo_2O_7$, and $Sm_2BaCo_2O_7$, respectively.

Figure 3 shows the variations of magnetic suspectivities of $Sm_2SrCo_2O_7$, $Gd_2SrCo_2O_7$, and $Sm_2BaCo_2O_7$ as a function of temperature from 300 to 1100 K. In the temperature range 300–673 K, the magnetic suspectivities of $Gd_2SrCo_2O_7$ can be represented by the Curie–Weiss Law, i.e., $\chi = C/(T - \theta p)$, θp = 47.18 K, showing high-temperature paramagnetic behavior. In the suspectivity curves of $Sm_2SrCo_2O_7$ and $Sm_2BaCo_2O_7$, plateaus are observed in the temperature ranges 823–1013 K and 723–1023 K, respectively, similar to those of $LaCoO_3$ and $NdCoO_3$ (11). This perhaps indicates that low-spin Co(III) transforms to a high-spin state.

In conclusion, we have synthesized three new Sr_3

TABLE 1
The Lattice Parameters for $Ln_2MCo_2O_7$

Compounds	Systems	a (nm)	b (nm)	c (nm)	c/a
$Sm_2SrCo_2O_7$	Tetra.	0.3801		1.9562	5.1464
$Gd_2SrCo_2O_7$	Tetra.	0.3801		1.9356	5.0924
$Sm_2BaCo_2O_7$	Ortho.	0.3821	0.3776	1.9426	5.0840

TABLE 2
The X-Ray Diffraction Coordination of $Gd_2SrCo_2O_7$

h	k	l	$d_{obs.}$ (nm)	$d_{cal.}$ (nm)	I/I_0
0	1	1	0.3735	0.3730	8
0	1	3	0.3276	0.3275	15
0	0	6	0.3227	0.3226	10
1	0	5	0.2713	0.2712	100
1	1	0	0.2689	0.2688	41
0	0	8	0.2419	0.2420	2
1	0	7	0.2236	0.2236	8
1	1	5	0.2193	0.2208	2
1	1	6	0.2065	0.2065	17
0	0	10	0.1936	0.1936	9
0	2	0	0.1901	0.1901	32
1	0	9	0.1871	0.1872	9
1	1	8	0.1800	0.1798	5
0	2	6	0.1639	0.1638	8
1	0	11	0.1598	0.1597	7
1	1	10	0.1571	0.1571	8
2	0	7	0.1559	0.1566	15
1	2	5	0.1550	0.1556	9
1	1	12	0.1383	0.1383	5
2	0	10	0.1357	0.1356	7

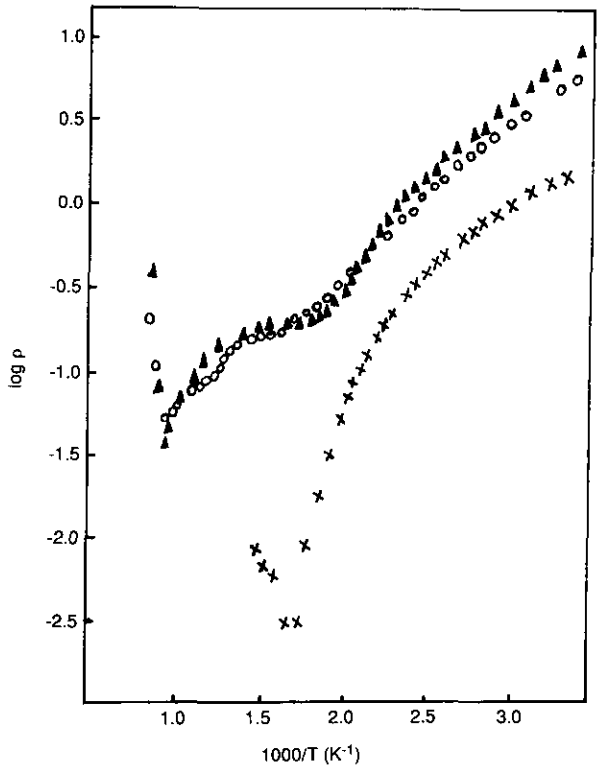

FIG. 2. The resistivities vs temperature of (○) $Sm_2SrCo_2O_7$, (▲) $Gd_2SrCo_2O_7$, and (×) $Sm_2BaCo_2O_7$.

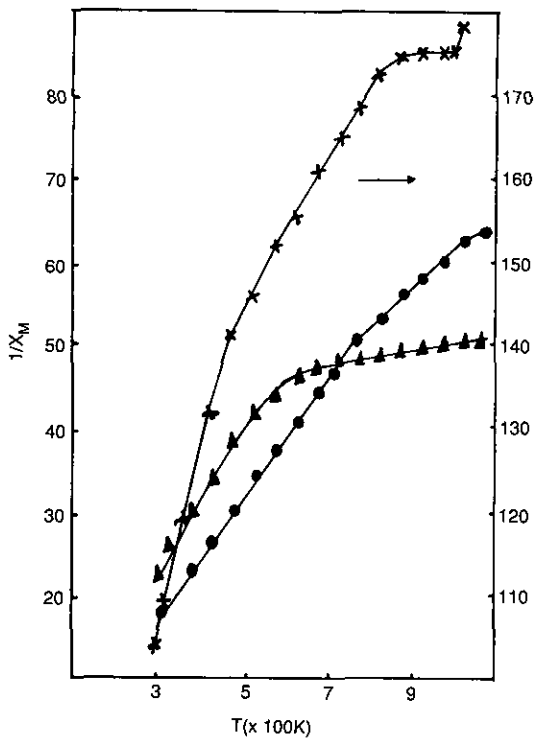

FIG. 3. The magnetic suspectivities vs temperature of (×) $Sm_2SrCo_2O_7$, (○) $Gd_2SrCo_2O_7$, and (▲) $Sm_2BaCo_2O_7$.

Ti_2O_7-type oxides, $Sm_2SrCo_2O_7$, $Sm_2BaCo_2O_7$, and $Gd_2SrCo_2O_7$, and have studied their structural, electrical, and magnetic properties. We are now studying their IR spectra and comparing them with K_2NiF_4-type $SmSrCoO_4$ and $GdSrCoO_4$ to investigate the effect of structural dimension on the electrical and magnetic properties.

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