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Preparation and Characterization of Lanthanum Lead Cobalt Titanium Oxide, $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$ $(0 < x < 1)$

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Attempts have been made to prepare the solid-solution $La_{1-x}Pb_xCo_{1-x}O_3$ for $0 < x < 1$. X-ray diffraction indicates the formation of single-phase materials over the entire range. Compositions with $0 < x \leq 0.20$ are rhombohedral, those with x in the range 0.2 to 0.8 are cubic, and those with $x \geq 0.9$ are tetragonal. Chemical analysis shows that all these samples are lead deficient. This is due to volatilization of PbO during preparation. Conduction is mainly due to $3d$ electrons of cobalt ions. All the samples except $x = 0.05$ show p-type conduction at and above 300 K. Samples with $x \geq 0.5$ exhibit dielectric anomaly at a particular temperature which increases with increasing x. © 1987 Academic Press, Inc.

Introduction

Lanthanum cobaltate, $LaCoO_3$, exhibits interesting electrical and magnetic properties due to coexistence of low-spin and high-spin cobalt ions in it (*1*, *2*). The population of low-spin and high-spin states changes with temperature and it undergoes localized $\rightleftharpoons$ collective d electron transition around 1210 K (*2*). Properties of $LaCoO_3$ can be widely modified due to varieties of substitutions possible at La^{3+} and/or Co^{3+} sites (*3–5*). In this communication we present the preliminary results of our efforts to investigate the possibility of formation of solid-solution $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$ in the system $LaCoO_3$–$PbTiO_3$, where Pb^{2+} and Ti^{4+} are expected to replace La^{3+} and Co^{3+}, respectively, due to size considerations. This, therefore, represents an example of compensated valence substitutions in either $LaCoO_3$ or $PbTiO_3$ (*6*). $PbTiO_3$ is a well-known ferroelectric with a Curie temperature of 768 K (*6*). $LaCoO_3$ is a semiconductor at moderate temperatures. It was, therefore, considered worthwhile to investigate the properties of this solid solution.

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TABLE I

STRUCTURE AND LATTICE PARAMETERS FOR VARIOUS SAMPLES IN THE SYSTEM $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$

x	Structure	Lattice parameters (Å)
0.05	Rhombohedral	$a = 5.373$; $\alpha = 60.4°$
0.1	Rhombohedral	$a = 5.373$; $\alpha = 60.4°$
0.2	Rhombohedral	$a = 5.429$; $\alpha = 60.6°$
0.3	Cubic	$a = 3.903$
0.4	Cubic	$a = 3.925$
0.5	Cubic	$a = 3.920$
0.6	Cubic	$a = 3.938$
0.7	Cubic	$a = 3.938$
0.8	Cubic	$a = 3.937$
0.9	Tetragonal	$a = 3.896$; $c = 4.086$
0.95	Tetragonal	$a = 3.908$; $c = 4.068$
0.99	Tetragonal	$a = 3.902$; $c = 4.128$

Experimental

Samples with various values of x in the range $0 < x < 1$ were prepared starting with lanthanum oxalate, lead monoxide, cobalt oxalate, and titanium dioxide, all having purity better than 99%. Stoichiometric quantities of these salts were mixed, ground, and calcined at 973 K for 2 hr in platinum crucibles. The calcined powders were again mixed, ground, and pressed into cylindrical pellets. The pellets surrounded by calcined powders of same composition were fired in platinum crucibles at 1323 K for 24 hr. Formation of single-phase materials was confirmed by X-ray diffraction. Chemical analysis was carried out using a Perkin–Elmer atomic absorption spectrophotometer. Electrical resistance was measured using the two-probe method with a Keithley 616 electrometer. Seebeck coefficients were measured relative to platinum. Dielectric constant and dielectric loss were measured on pellets coated with Au–Pd alloy using a HP-4192 LF impedance analyzer as a function of temperature at different frequencies.

Results and Discussion

Results of chemical analysis indicate that there has been loss of lead from all the samples due to volatilization of PbO during preparation. For lead-rich samples ($x \geq 0.5$), the loss is significant. Detailed results will be published shortly. X-ray data indicate the presence of single phase in all the samples. X-ray diffraction data of the compositions with $x \leq 0.2$ could be indexed on the basis of a rhombohedral unit cell similar to $LaCoO_3$, while compositions with $0.3 \leq x \leq 0.8$ are cubic and those with $x > 0.8$ are tetragonal similar to $PbTiO_3$. Lattice parameters of all these compositions are given in Table I.

Plots of log ρ vs $1000/T$ for all the samples exhibit two distinct regions: (i) Region I (300–500 K) of high activation energy in which resistivity decreases very sharply and (ii) Region II (above ~500 K) of very low or zero energy of activation where the resistivity changes very little with temperature. These two regions are also observed in the case of $LaCoO_3$ (*4*). Typical plots of two compositions with $x = 0.2$ and 0.9 are shown in Fig. 1. Values of activation energies of conduction (in Region I) are given in Table II along with values of specific resis-

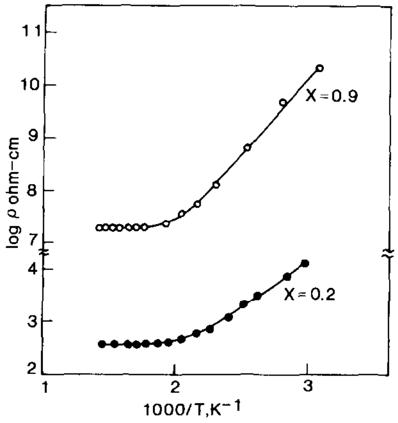

FIG. 1. Plots of log ρ vs $1000/T$ for the samples with $x = 0.2$ and 0.9 in the system $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$.

TABLE II

VALUES OF RESISTIVITY AT 400 K, ρ_{400}, THE SEEBECK COEFFICIENT AT 500 K, α_{500}, AND ACTIVATION ENERGY, E_a, IN REGION I OF THE SYSTEM $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$

x	ρ_{400} (ohm cm)	α_{500} (μV/K)	E_a (eV)
0.05	—	58	—
0.1	—	85	—
0.2	2.0×10^3	206	0.38
0.3	3.9×10^4	411	0.44
0.4	8.5×10^5	500	0.50
0.5	8.7×10^5	520	0.50
0.6	2.0×10^6	680	0.50
0.7	4.3×10^6	780	0.58
0.9	6.2×10^8	928	0.62

tivity at 400 K for various samples. Resistivity increases with x, indicating that conduction is mainly due to 3d electrons of cobalt. Measurements of the Seebeck coefficient in the temperature range 300–700 K show that all the samples except $x = 0.05$ are p-type semiconductors at and above room temperature. The value of the Seebeck coefficient, α, increases with increasing x. This is in accordance with increasing value of resistivity with increasing x. The Seebeck coefficient for sample $x = 0.05$ changes sign from negative to positive at 425 K. Values of the Seebeck coefficient at 500 K for various samples are given in Table II. Constant values of α are obtained in Region II. Behavior of the Seebeck coefficient and resistivity in Region II indicate saturation of charge carriers in this temperature range.

Preliminary measurements of the dielectric constant, ε, and the dielectric loss, tan δ, as a function of temperature for samples with $x = 0.50$–0.90 at various frequencies indicate that ε vs T plots exhibit a peak characteristic of ferroelectric–paraelectric transition at a particular temperature which increases with increasing x. The peak observed in ε vs T plots becomes diffuse with increasing frequency. Also the position of the peak shifts to higher temperature with increasing frequency. Moreover, the dielectric constant decreases with increasing frequency. All these features indicate that these materials exhibit relaxor behavior. Detailed studies are in progress and the results will be published elsewhere in the near future.

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