

Preparation and Properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($0.2 \leq x \leq 0.6$)

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The preparatory conditions for the oxide compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ have been determined along with their crystallographic, thermochemical, and electrical properties. Single phase solid solutions of the perovskite structure form at $x < 0.6$. It has been established that the compounds obtained in the open air atmosphere are oxygen deficient, the deficit increasing with x and temperature. The specific resistivity at $x = 0.2-0.6$ is $(1-2) \cdot 10^{-3}$ ohm \cdot cm; it increases with the concentration of oxygen vacancies. At $0.3 \leq x \leq 0.6$ the p -type conductivity is metallic in character with low temperature resistivity coefficients of the order $(1-5) \cdot 10^{-4}$ K $^{-1}$ in the interval 20-700°C.

Introduction

The substitution of trivalent lanthanum in LaCoO_3 by divalent ions of strontium (1, 2, 3), barium (4), and calcium (5, 6) is known to yield high conductivity solid solutions $\text{La}_{1-x}\text{M}_x\text{CoO}_3$ with x up to 0.9, 0.5, and 0.6, respectively ($M = \text{Sr, Ba, Ca}$). Many of these are oxygen deficient. Therefore, in Refs. (5, 6), the crystallographic, magnetic, and electrical properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ have been investigated using the samples obtained at high oxygen pressures. The electrical conductivity has been measured over a low temperature range from 80 to 300 K, with only a few measurements taken at higher temperatures (7).

In the present experiments the possibility and the conditions for preparing single-phase solid solutions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ in

the open air atmosphere have been examined. Also, the crystallographic parameters and thermal stability range for the oxygen deficient perovskite phases have been determined. The thermochemical properties have been observed over a temperature range from 300 to 1500 K, and the electrical properties from 300 to 1000 K. Such investigations, in our opinion, are of both theoretical and practical importance.

Experimental

The compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x = 0.2-0.6$) were obtained from the corresponding nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (chemically pure), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (chemically pure), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (pure for analyses). The content of crystallization water was checked by the gravimetric method. The initial salts were used in predetermined ratios and heated to melting in the crystallization water, then evaporated and decom-

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posed at temperatures up to 900°C. The resulting oxide mixtures were then ground and subjected to additional firing in the 1000–1300°C temperature range for 2–3 hr. Samples of $0.03 \times 0.005 \times 0.005$ -m size were formed from the synthesized powders and pressed by a hydraulic method to 400–600 Pa/m². The samples were calcined in the open air atmosphere at 1100–1300°C for 1–10 hr. Their density was evaluated from mass and geometrical size as well as by hydrostatic weighing. The conductivity was measured in the open air atmosphere by the four-probe method using direct current in the cells, with uni- and bilateral location of Pt probes over a temperature range from room temperature to 700–800°C. A correction for porosity was not introduced. The thermo-emf coefficients were determined under the temperature differences at the sample ends equal to 15–30°C. The spread in conductivity values and the Seebeck coefficients did not exceed ± 10 –15%. The X-ray phase analysis was performed on the DRON-2 diffractometer at room temperature using $\text{CuK}\alpha$ and $\text{CoK}\alpha$ radiation. The standard deviation is estimated to be $\pm 0,001$ Å. The thermal expansion coefficients (TEC) were measured with the quartz dilatometer. The differential thermal analysis (DTA), with simultaneous recording of the mass loss curves (TG) and a differential mass loss curves (DTG), was performed on a Derivatograph OD-103 of F. Paulik, I. Paulik, and L. Erday in the open air atmosphere, the heating rates of the powders being 7.5°/min in the interval from room temperature to 1200°C. Finally, 0.6 to 0.8 g of the substance were taken for analysis.

Results and Discussion

The X-ray phase analysis data show that, upon firing in the open air atmosphere at 1200°C for several hours with subsequent slow cooling in the switched off furnace,

the compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ at $0.2 \leq x \leq 0.5$ become monophasic and have a perovskite structure. Already, at $x = 0.6$, a most strong CaO reflection can be seen in the diffractogram that disappears upon additional firing in oxygen at 900°C. The temperature range of 1100–1200°C is found to be most suitable for the short-time (2–3 hr) syntheses of compounds $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$. At 1000°C, the synthesis is not completed within the time interval mentioned above. Either the presence of oxide phases of the initial compounds or distortion of the unit cell (baseline splitting) have been observed. Firing at 1300°C does not essentially alter the diffractogram with $x = 0.2$, but does lead to a partial decomposition of compounds with $x \geq 0.5$ and to a partial fusion of the samples.

Characteristically, the perovskite lattice $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ exhibits a slight rhombohedral distortion. In analogy with (5), the observed distortion decreases with increasing x , and the structure of the compounds approaches the cubic lattice (Table I). In the range of $x = 0$ –0.3, a change in a_H , c_H , and a_R is of the nature described in (5). However, at high x values ($x \geq 0.5$) an insignificant increase in a_H , c_H , and the unit cell volume has been observed (Table I).

The results of the X-ray investigations agree with those of differential thermal (DTA) and thermogravimetric (TG) analyses. The derivatograms were taken from the samples equilibrated with oxygen by

TABLE I
CELL CONSTANTS VS COMPOSITION IN THE SYSTEM
 $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$

x	a_H (Å)	c_H (Å)	V_H (Å ³)	a_R (Å)	α_R
0	5.450	13.10	336.96	5.382	60°50'
0.2	5.427	13.18	336.16	5.396	60°24'
0.3	5.409	13.14	332.90	5.379	60°22'
0.5	5.413	13.17	334.18	5.389	60°16'

continuous firing in oxygen flow successively at 1100, 800, and 600°C up to a constant weight. It is noteworthy that compositions with x equal to 0.2 and 0.6 equilibrated with oxygen did not reveal any thermal effects up to 900°C (Fig. 1a,b). Heating of these in the open air atmosphere to the mentioned temperature level is accompanied by a weight decrease of 0.45 and 0.56%, respectively, i.e., 0.06 g/atom oxygen per g/mole of each solid solution. For the compositions with $x = 0.5-0.6$, several distinct endothermal effects have been observed in the temperature range about 910, 950, and 1120°C, followed by a stepwise process of oxygen release. On heating the materials with $x = 0.2$ and 0.6 up to 1200°C in the open air atmosphere, the mass decrease reaches 1.5 and 3.0%, i.e., 0.18 and 0.35 g/atoms of oxygen per g/mole of the initial compositions, respectively.

The X-ray phase analysis of the samples synthesized in the open air atmosphere and cooled rapidly from 1200°C to room temperature showed that at low values of x the compositions are single phases, and at $x \geq 0.5$, the strongest calcium reflections appeared. The loss in weight observed during the derivatographic analysis may have resulted both from the formation of anion va-

cancies and from partial decomposition of solid solutions at high x values at temperatures above 1100°C. A stepwise character of weight decrease and the accompanying endothermal effects are likely to be due to the ordering process in anion vacancies and to the formation of superstructures in analogy with LaNiO_3 (8). It is a peculiar fact that upon heating of the strontium- and barium-substituted lanthanum cobaltites at $x = 0.2-0.8$ and $x = 0.2-0.5$, respectively, no thermal effects are observed and the loss in weight evenly increases with rising temperature.

The electrical properties of compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ have been examined using ceramic samples generally sintered at 1200°C in the open air atmosphere for a few hours, and then slowly cooled within 10-15 hr to room temperature. These samples were essentially equilibrated with air oxygen. Their density was 85-90% of the theoretical value. After sintering at 1100°C, the samples became less dense and possessed higher resistivity. The dependence of the specific resistivity on composition at room temperature is presented in Fig. 2, and the temperature dependence of specific resistivity, in Fig. 3. As seen from these figures, in the range of formation of solid solutions

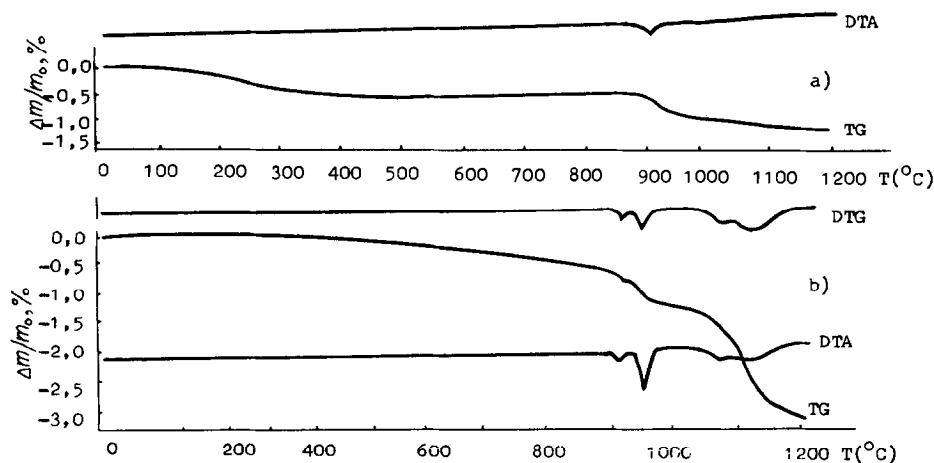


FIG. 1. DTA, TG, and DTG curves for compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ at x : a) 0.2; b) 0.6.

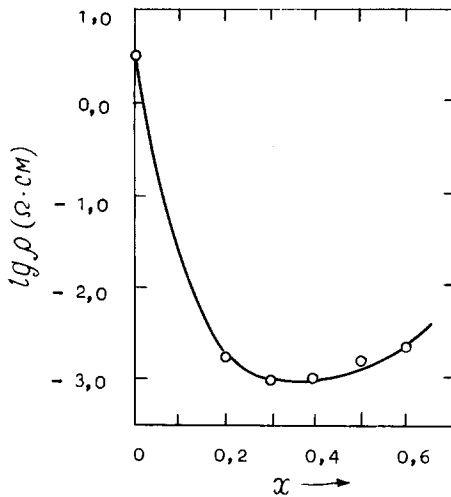


FIG. 2. Specific resistivity of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ vs composition.

$\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ at $x = 0.2-0.6$, the values of specific resistivity differ insignificantly. The compositions $\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$ possess the lowest resistivity. Over the range from room temperature to 200°C , the solid solution $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ shows semiconductive behavior (Fig. 3, curve 2), the activation energy of electrical conductivity being of the order of 0.01 eV . At $0.3 \leq x \leq 0.6$ the compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ reveal metallic-type conductivity with low values of temperature coefficients of resistivity (TCR) of the order of $(1-5) \cdot 10^{-4}\text{ K}^{-1}$. No drastic increase in resistivity at temperatures above $400-600^\circ\text{C}$ (as with composi-

tions $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$) (1, 3) has been observed. An additional firing in oxygen at $900-1000^\circ\text{C}$ for 5–8 hr does not lead to any noticeable change in resistivity. Moreover, the indicated resistivity values (Fig. 2) are close to those in (6), obtained from samples continuously kept at high oxygen pressures. It can be claimed, therefore, that the presence of oxygen vacancies within the definite concentration range does not markedly affect the electrical conductivity of solid solutions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$.

The resistivity of samples with $x = 0.2-0.6$ sintered at 1200°C and hardened in the open air atmosphere increases two orders compared with that found for the same compositions slowly cooled in the switched off furnace. Subsequent measurement of the temperature resistivity dependence showed that the heating and cooling curves for the hardened samples did not coincide. Heating of such samples in the open air atmosphere at $600-700^\circ\text{C}$ for several hours results in a resistivity decrease to values almost as low as those presented in Figs. 2 and 3. A sharp resistivity increase in the hardened samples may be caused by retention of an essentially oxygen deficient structure or by a partial decomposition of the perovskite phase into less conductive components. Since the appearance of new phases in the hardened samples at $x = 0.2-0.5$ is not registered in the X-ray analysis, it may be assumed that these were present in

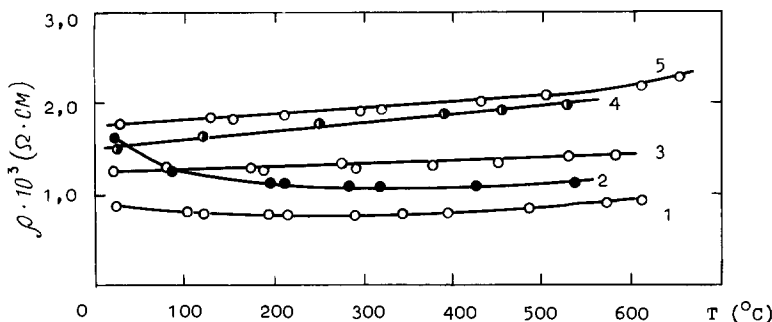


FIG. 3. Temperature dependence of electrical conductivity for samples of the composition $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ with x : 1 = 0.3; 2 = 0.2; 3 = 0.4; 4 = 0.5; 5 = 0.6.

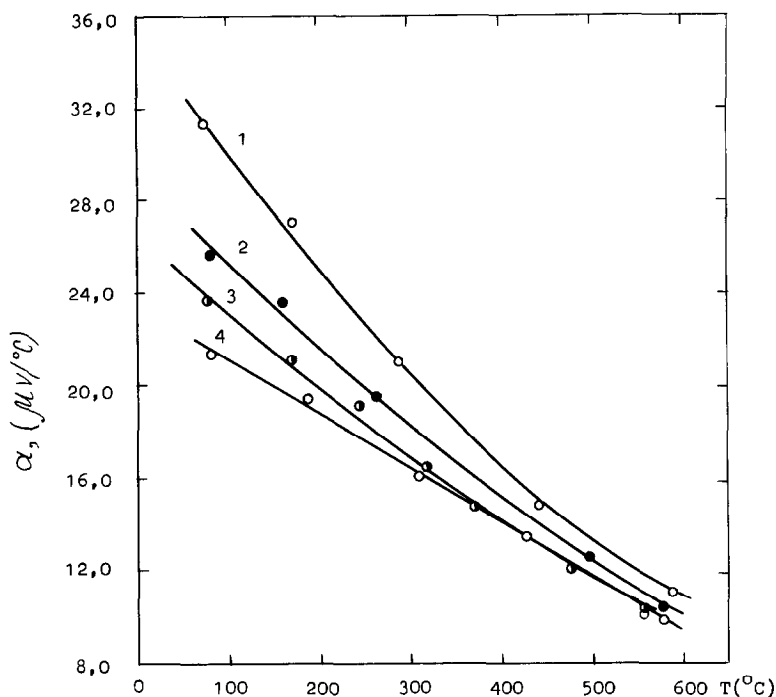


FIG. 4. Temperature dependence of the thermo-emf coefficient for the compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ for x : 1 = 0.2; 2 = 0.3; 3 = 0.4; 4 = 0.5.

insignificant amounts. However, if the low conductivity microphases are located between grain boundaries, they block the highly conductive grains in the perovskite phase and drastically increase the total resistivity of samples. The rapid growth of conductivity upon slow cooling, as well as in the process of firing of the hardened samples in the open air, points to high diffusion rates of the oxygen ions (9).

The temperature dependencies of the thermo-emf coefficients for $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ at $x = 0.2-0.5$ are given in Fig. 4. With increasing x , the slope in the temperature dependence curves of thermo-emf lowers. The positive sign of the thermo-emf coefficient as well as an approximate evaluation of the Hall constant show that the calcium-substituted lanthanum cobaltites at $x = 0.2-0.6$ are predominantly degenerate hole semiconductors with the charge carrier concentrations of the order of 10^{22} cm^{-3} .

In analogy with the strontium- and barium-substituted lanthanum cobaltites (1-4), electrical neutrality of solid solutions of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ may also be achieved either via the formation of Co^{4+} ions or by oxygen vacancies, V_{O}'' , or both, following the equations



The above results from the study of electrical behavior prove that the substitution of the La^{3+} ion by Ca^{2+} in LaCoO_3 leads to a resistivity decrease and to their transformation from semiconductive to metallic conductivity. According to (10-12), the transition may have resulted from the positive type interactions of $\text{Co}^{3+}-\text{O}-\text{Co}^{4+}$ chains. A preferential formation of Co^{4+} ions is further substantiated by a specific decrease of the unit cell volume at low x values (Table I), since in the high-spin state the radius of Co^{4+} ion (0.54 Å) is markedly lower than

that of Co^{3+} (0.61 Å) (13). At higher calcium concentration ($x \geq 0.5$), the electrical neutrality is largely achieved via the formation anion vacancies; the concentration of Co^{4+} drops, which is manifested by a certain increase in electrical resistivity (Fig. 1) and in unit cell volume (Table I). The mechanism of electrical conductivity of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ may be interpreted (as in (5, 6)) by the models of Goodenough (11) or Zener (12).

The thermal expansion coefficient for the compositions $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ decreases with an increase in x . At $x = 0.2-0.5$ in the temperature range from room temperature to 600°C , its values are found to be equal to $18 \cdot 10^{-6}$ and $15 \cdot 10^{-6} \text{ K}^{-1}$, respectively.

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