Inorg. Chem. **1992**, *31*, 738-741

Contribution from the Department of Applied Chemistry,
Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan

A New Preparation Method of $LaCoO_3$ Perovskite Using Electrochemical Oxidation

Yasumichi Matsumoto,* Takeshi Sasaki, and Jukichi Hombo

Received July 26, 1991

$LaCoO_3$ perovskite film was prepared by electrochemical oxidation in solutions containing both La^{3+} and Co^{2+} ions. Heat treatment at a temperature higher than about 500 °C was necessary for crystallization, because the as-deposited oxide films were amorphous. The composition of the deposited oxide film was strongly dependent on the temperature and the applied potential during the electrolysis. It was judged from the range of the applied potential producing the $LaCoO_3$ precursor and an XPS measurement that the production of Co^{3+} was necessary for the incorporation of La^{3+} ion into the oxide during the electrolysis. La^{3+} ion existed as a nitrate in the as-deposited oxide according to an IR measurement. Consequently, the bond strength between the $La(NO_3)_3$ and the Co oxide is relatively strong in the $LaCoO_3$ precursor. The mechanisms of the deposition of the $LaCoO_3$ precursor and the crystallization of perovskite by heat treatment are discussed.

Introduction

It is well-known that an oxide film can be anodically prepared on a metal substrate, where the metal cation with lower valence is electrochemically oxidized in a solution, followed by some chemical reactions with OH^- and/or H_2O in the solution. In this case, a complex oxide film can be synthesized if the solution contains other metal cations. From this point of view, we have electrochemically synthesized $La_{1-x}Sr_xMnO_3$ perovskite oxides, where the solutions contain Mn^{2+}, La^{3+}, and Sr^{2+} ions.[1-3] The electrochemical synthesis of a complex oxide film has the following two advantages compared with other methods such as CVD, sputtering, etc. One is that the film can be easily prepared using a simple apparatus and under simple conditions. The other is that the film thickness and the composition of the oxide can be controlled by the quantity of electricity and the applied potential, respectively.

$LaCoO_3$ is an important material, being used as an oxidation catalyst[4] and an electrocatalyst.[5] $LaCoO_3$ is especially suitable as an air electrode material for high-temperature solid oxide fuel cells (SOFC) because of its chemical stability at high temperature and its superior electrocatalytic property.[6] Therefore, some preparation methods for thin films of $LaCoO_3$ have been studied.[7]

Cobalt oxides can be directly synthesized on an electrode by anodic oxidation in a solution containing Co^{2+}.[8,9] Therefore, it will be possible to form $LaCoO_3$ films by anodic oxidation, if the solution contains both metal cations, Co^{2+} and La^{3+}, as in the case of $La_{1-x}Sr_xMnO_3$.[1-3] In this paper, a new preparation method for the $LaCoO_3$ film using electrochemical oxidation is demonstrated and its mechanism is discussed.

Experimental Section

Pt plates (99.9%, 10 × 10 mm) were used as the working and counter electrodes, and a Ag/AgCl electrode was used as the reference. Electrode potential was referred to Ag/AgCl unless otherwise stated. The electrolytes were $Co(CH_3COO)_2$, $Co(NO_3)_2$, $CoSO_4$, and $La(NO_3)_3$ in aqueous solutions, in which the $La(NO_3)_3$ concentration was fixed at 2 M and the concentration of the cobalt salts were changed from 2×10^{-3} to 2 M. A mixed solution consisting of $Co(CH_3COO)_2$ and $La(NO_3)_3$ was usually used as the electrolyte because of the good adherence of the oxide film deposited in this solution. The pH of the solution was maintained at 6 by 0.1 M NaOH titration, since no deposition of oxide occurred when the pH was <3. Temperature during the electrolysis was very important for the incorporation of La^{3+} ion into the deposited oxide film as a temperature higher than about 50 °C was necessary for this incorporation. Therefore, both galvanostatic and potentiostatic electrolyses were carried out for 2 h at 50 °C. In the case of the galvanostatic electrolysis, the current density was kept constant at 0.5 mA/cm^2. The oxide films prepared on the electrode were washed with distilled water, followed by drying at room temperature. The as-deposited films were examined by infrared absorption spectroscopy (IR), thermal gravimetry (TG), and X-ray photoelectron spectroscopy (XPS). All the samples were heated in air at various temperatures for 4 h for the purpose of crystallization, since the as-deposited oxide films were always amorphous. The structures of the oxide films after the heat treatment were examined by X-ray diffraction analysis (XRD) using monochromatic Cu Kα radiation. Morphological observations of the oxide films were carried out with a scanning electron microscope (SEM). The oxide films were dissolved in HCl and then analyzed by inductively coupled plasma (ICP) spectroscopy to determine the atomic La/Co ratios in the oxide films.

Results and Discussion

Figure 1A shows the voltammograms of the Pt electrode at 50 °C in 1 M Co^{2+} solution with pH = 6, where the equilibrium potentials of Co_2O_3/Co^{2+} (0.50 V) and CoO_2/Co_2O_3 (0.90 V) are also shown. In the case of the $Co(NO_3)_2$ solution, a current due to the formation of Co_2O_3 is clearly observed at about 0.6 V, but not for the case using the $Co(CH_3COO)_2$ solution. The formation of Co_2O_3 has been already reported by Chen et al.,[9] although a distinction between Co_2O_3 and CoOOH, which have Co^{3+} ions in their lattices, has been ambiguous until now. In the present paper, Co_2O_3 is used as a Co oxide with Co^{3+} ion formed during the electrolysis. In the case of $Co(CH_3COO)_2$ solution, an oxidation current which may be based on the other electrochemical reactions, such as the oxidation of acetate ion, was observed at about 0.75 V, and an oxide film was formed at a potential more positive than 0.90 V. The formation of Co_2O_3 is very important for the incorporation of La^{3+} ion into the as-deposited oxide film, as stated in a later section. Parts B and C of Figure 1 show the potential under a constant current density of 0.5 mA/cm^2 and the current density under a constant applied potential of 0.95 V as a function of electrolytic time in a 0.02 M $Co(CH_3COO)_2$ and 2.0 M $La(NO_3)_3$ mixed solution, respectively. The oxide films were deposited in both cases. A decrease in the current density shown in Figure 1C is based on the growth of a deposited oxide film with high resistivity.

Since all the as-deposited oxide films were amorphous, a heat treatment was necessary for crystallization. Figure 2 shows typical X-ray diffraction patterns of the heat-treated oxide films at 1000 °C. Samples A and B in this figure were prepared in the 0.02 M $Co(CH_3COO)_2$ and 2.0 M $La(NO_3)_3$ mixed solution at 1.2 and 0.95 V, respectively. As can be seen, sample B consisted of a single phase of $LaCoO_3$, while sample A consisted of a mixture of Co_3O_4 and $LaCoO_3$. For the intensities in Figure 2, eq 1 was

$$I_{\mathrm{LaCoO_3}} = I_{\mathrm{LaCoO_3(104)}}/(I_{\mathrm{LaCoO_3(104)}} + I_{\mathrm{Co_3O_4(311)}}) \tag{1}$$

used for the purpose of qualitative evaluation of the degree of $LaCoO_3$ formation in the oxide film, where $I_{\mathrm{LaCoO_3(104)}}$ and

---

(1) Sasaki, T.; Morikawa, J.; Hombo, J.; Matsumoto, Y. *Denki Kagaku* **1990**, *58*, 567.

(2) Sasaki, T.; Matsumoto, Y.; Hombo, J. *J. Solid State Chem.* **1991**, *91*, 61.

(3) Matsumoto, Y.; Sasaki, T.; Hombo, J. *J. Electrochem. Soc.* **1991**, *138*, 1259.

(4) Chien, M. W.; Pearson, I. M.; Nobe, K. *Ind. Eng. Chem. Prod. Res. Div.* **1975**, *14*, 131.

(5) Tsueng, A. C. C.; Bevan, H. L. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *45*, 429.

(6) Goodenough, J. B.; Raccah, R. C. *J. Appl. Phys.* **1963**, *36*, 1031.

(7) Michibata, H.; Namikawa, T.; Yamazaki, Y. *Denki Kagaku* **1984**, *57*, 255.

(8) Tench, D.; Warren, L. F. *J. Electrochem. Soc.* **1983**, *130*, 869.

(9) Chen, Y. D.; Noufi, R. N. *J. Electrochem. Soc.* **1984**, *131*, 1447.

0020-1669/92/1331-0738$03.00/0

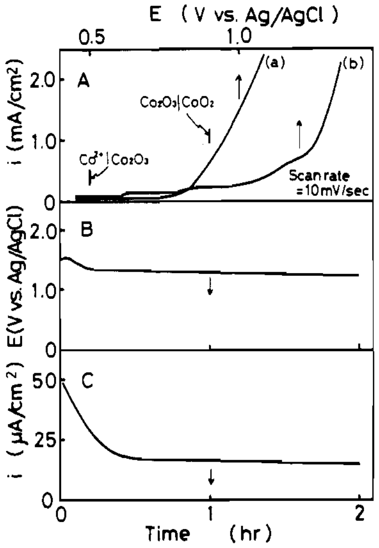

Figure 1. Current-potential-time relationships of Pt electrode at 50 °C in 1 M Co^{2+} solutions with pH = 6. Part A shows voltammograms in 1 M $Co(CH_3COO)_2$ (a) and $Co(NO_3)_2$ (b). Part B shows potential under 0.5 mA/cm^2 as a function of time in a 0.02 M $Co(CH_3COO)_2$ and 2.0 M $La(NO_3)_3$ mixed solution. Part C shows current density under 0.95 V as a function of time in the same solution as in part B.

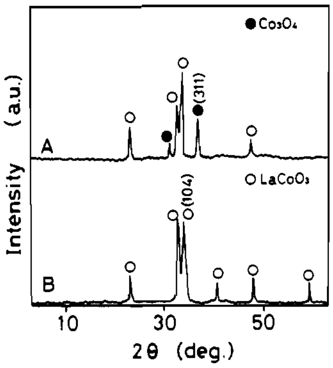

Figure 2. Typical X-ray diffraction patterns of the heat-treated oxide films at 1000 °C. Sample A was prepared at 1.2 V in a 0.02 M $Co(CH_3COO)_2$ and 2.0 M $La(NO_3)_3$ mixed solution, while sample B was prepared at 0.95 V under the same conditions as sample A.

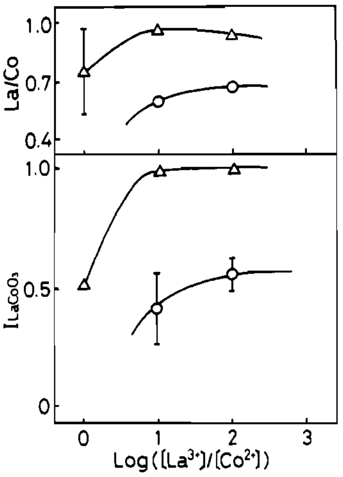

Figure 3. I_{LaCoO_3} and La/Co ratio as a function of $[La^{3+}]/[Co^{2+}]$ ratio in the solution with $Co(CH_3COO)_2$ and $La(NO_3)_3$. Triangle and circle symbols denote the oxides prepared at 0.95 V and under 0.5 mA/cm^2, respectively.

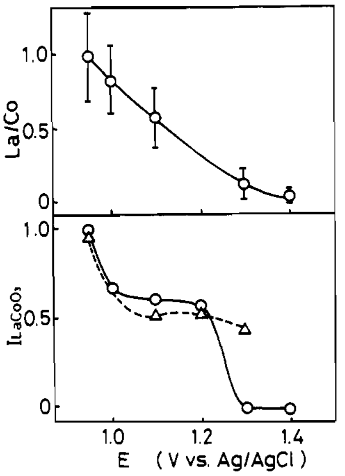

Figure 4. Potential dependences of I_{LaCoO_3} and La/Co ratio in the oxides prepared potentiostatically in solutions with 0.02 M Co^{2+} and 2.0 M La^{3+} ions. Circle and triangle symbols denote the oxides prepared in the solutions containing $Co(CH_3COO)_2$ and $CoSO_4$, respectively.

Table I. I_{LaCoO_3} and La/Co Ratios of the Oxides Prepared Potentiostatically under Various Conditions with Heat Treatment Performed at 1000 °C

electrolyte[a]	applied potential, V	immersion time in water, min	I_{LaCoO_3}	La/Co ratio
$Co(CH_3COO)_2$ $La(NO_3)_3$	0.95	30	0.9	1.0
$Co(CH_3COO)_2$ $La(NO_3)_3$	0.95	1	1.0	1.1
$Co(NO_3)_2$ $La(NO_3)_3$	0.70–0.95	1	1.0	1.1
$CoSO_4$ $La(NO_3)_3$	0.70–0.95	1	1.0	0.9

[a] Ratio of $[Co^{2+}]/[La^{3+}]$ is fixed to be 0.02 M/2.0 M.

$I_{Co_3O_4(311)}$ are the intensities of the (104) diffraction peak of $LaCoO_3$ perovskite and of the (311) diffraction peak of Co_3O_4, respectively. I_{LaCoO_3} and the La/Co atomic ratio in the oxide film as a function of the $[La^{3+}]/[Co^{2+}]$ ratio in the solution during the electrolysis are shown in Figure 3. Both parameters, I_{LaCoO_3} and the La/Co ratio, increase with an increase in the $[La^{3+}]/[Co^{2+}]$ ratio of the solution for both cases of galvanostatic (0.5 mA/cm^2) and potentiostatic (0.95 V) electrolysis, although their parameters almost saturate in the range of more than about 10 for the $[La^{3+}]/[Co^{2+}]$ ratio of the solution. This phenomenon is similar to the case of $LaMnO_3$, where the above parameters were more strongly dependent on the cationic ratio in the solution.[2] Thus, a large amount of La^{3+} ion in the solution is preferable for the incorporation of La^{3+} into the oxide film during the electrolysis. No oxide film was deposited on the Pt electrode, when the $[La^{3+}]/[Co^{2+}]$ ratio was higher than 1000. Therefore, the cationic ratio of $[La^{3+}]/[Co^{2+}]$ in the solution was fixed to be 100 in all the subsequent experiments.

Figure 4 shows the potential dependences of I_{LaCoO_3} and La/Co ratios, where $Co(CH_3COO)_2$ and $CoSO_4$ salts were used for the preparation of solution containing Co^{2+} ion. The incorporation of La^{3+} ion into the oxide strongly depends on the applied potential with a more negative potential preferable for this incorporation, although no oxide film was deposited in the potential region more negative than 0.9 V for the $Co(CH_3COO)_2$ solution, and 0.7 V for the $CoSO_4$ and $Co(NO_3)_2$ solutions. Table I also lists the I_{LaCoO_3} and La/Co ratios of the oxide films prepared under various conditions. Consequently, a single phase of $LaCoO_3$, whose La/Co ratio is about 1, is obtained at the potential of 0.95 V for the case of the $Co(CH_3COO)_2$ solution and in the potential region from 0.7 to 0.95 V for the $CoSO_4$ and $Co(NO_3)_2$ solutions. These potential regions correspond to the formation of Co_2O_3, while the potential region more positive than about 0.9 V corresponds to the formation of CoO_2 with Co^{4+} ion. Therefore, the presence of Co^{3+} ion in the deposited oxide will be very important for the incorporation of the La^{3+} ion in the solution so as to have a La/Co atomic ratio of 1 in the oxide ($LaCoO_3$ precursor).

Figure 5 shows the XPS spectrum of Co $2P_{3/2}$ in the as-deposited oxide film ($LaCoO_3$ precursor), which was prepared at

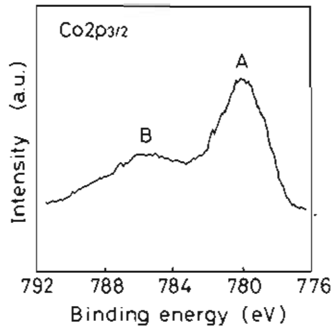

Figure 5. XPS spectrum of Co $2P_{3/2}$ in the $LaCoO_3$ precursor prepared at 0.95 V in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M.

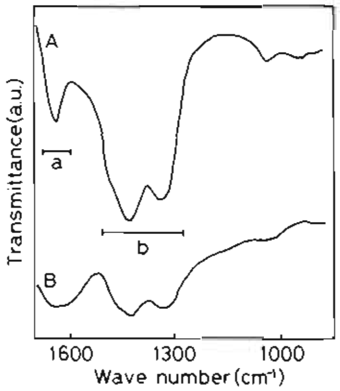

Figure 6. Infrared absorption spectra of the as-deposited oxide films, which were prepared at 0.95 V (curve A, $LaCoO_3$ precursor) and 1.3 V (curve B) in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M.

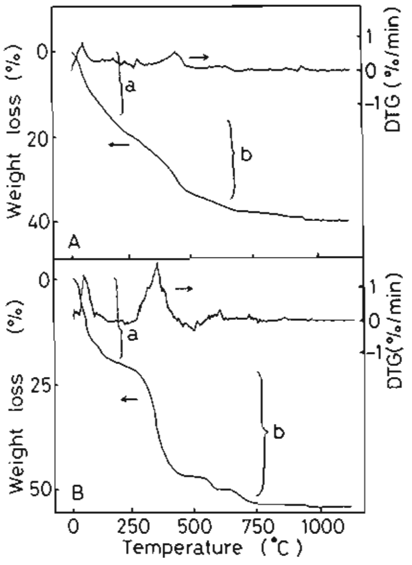

Figure 7. TG-DTG curves of the $LaCoO_3$ precursors, which were prepared at 0.95 V in the solutions with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M (curve A) and $[Co(NO_3)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M (curve B).

0.95 V in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M. The binding energy of the main peak (A) was 780.2 eV, suggesting that Co in the deposited oxide film exists as the Co^{3+} ion.[10] However, the presence of a small shake-up satellite peak (B) will indicate that a small amount of Co^{2+} also coexists in this sample such as in the case of CoO.[11] Co^{2+} ion may be

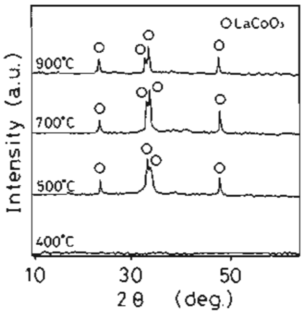

Figure 8. X-ray diffraction patterns of the oxide films prepared by heat treatment of the $LaCoO_3$ precursor at various temperatures. The $LaCoO_3$ precursor was prepared in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M at 0.95 V.

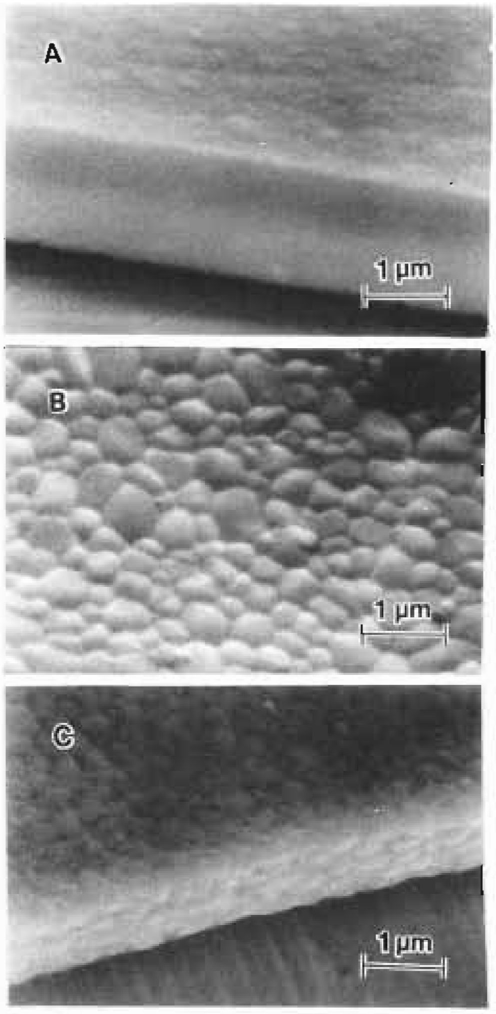

Figure 9. SEM micrographs of the $LaCoO_3$ precursor (A) and $LaCoO_3$ perovskite (B, C) prepared by heat treatment of the $LaCoO_3$ precursor at 1000 °C. The $LaCoO_3$ was prepared in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3]$ = 0.02 M/2.0 M at 0.95 V.

produced by a reduction of Co^{3+} ion in the as-deposited oxide film under a vacuum in the XPS measurement, because the deposited potential of 0.95 V corresponds to the formation potential of Co_2O_3, as previously stated.

Figure 6 shows a typical infrared absorption spectra of the as-deposited oxide films which were prepared at 0.95 V (curve A) and 1.3 V (curve B). The absorption peaks of a and b in curve A correspond to the vibrations of OH in H_2O and NO_3^- in $La(NO_3)_3$, respectively.[12] Absorption peaks b decreased with a

---

(10) Johnson, O. *Chem. Scr.* **1975**, *8*, 162.

(11) Grimblot, J.; d'Huysser, A.; Bouelle, J. P.; Beaufilts, J. P. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *6*, 71.

(12) Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds*; Academic Press: New York, 1971.

decrease in the concentration of La^{3+} ion in the oxide (atomic ratio of La/Co is shown in Figure 4) as shown in curve B and were never observed for the as-deposited oxides containing no La^{3+} ion. These results indicate that La^{3+} ion in the $LaCoO_3$ precursor exists in a state similar to that in $La(NO_3)_3$.[12] Consequently, the $LaCoO_3$ precursor will be electrochemically deposited by the following two steps.

$$2Co^{2+} + 6H_2O \rightarrow Co_2O_3{\cdot}3H_2O + 6H^+ + 2e^- \quad (2)$$

$$Co_2O_3{\cdot}3H_2O + 2La(NO_3)_3 \rightarrow Co_2O_3{\cdot}2La(NO_3)_3{\cdot}3H_2O \text{ (LaCoO}_3\text{ precursor)} \quad (3)$$

Reaction 3 proceeds at a temperature higher than about 50 °C, because no incorporation of La^{3+} occurred at a temperature lower than 50 °C as already stated.

TG-DTG curves shown in Figure 7 quantitatively give the amount of water and NO_3^- in the $LaCoO_3$ precursors which were prepared at 0.95 V in the solutions with $[Co(CH_3COO)_2]/[La(NO_3)_3] = 0.02$ M/2.0 M (A) and with $[Co(NO_3)_2]/[La(NO_3)_3] = 0.02$ M/2.0 M (B). The weight loss below about 200 °C (part a) is based on the release of water in the oxides, while that in the temperature range from 250 to 500 °C (part b) is based on the release of NO_2. In the IR measurements, no absorption peaks due to NO_3^- (b in Figure 6) were observed for the sample prepared by heat treatment of the $LaCoO_3$ precursor at 500 °C, while those peaks were observed for the sample heated at 200 °C. All of the weight loss in Figure 7 was in harmony with the composition of the $LaCoO_3$ precursor in eq 3.

It should be noted that no La^{3+} ion had dissolved in the water from the $LaCoO_3$ precursor after an immersion for 30 min, as shown in Table I. This result is very different from the case of the $LaMnO_3$ precursor, where almost all the La^{3+} ion dissolved in the water from the $LaMnO_3$ precursor after immersion.[2] Probably, Co^{2+}, La^{3+}, NO_3^- and O^{2-} ions in the $LaCoO_3$ precursor will strongly combine with each other, although its structure is ambiguous because of its amorphous state.

Figure 8 shows the X-ray diffraction patterns of the oxide films heated at various temperatures, where the $LaCoO_3$ precursor was prepared at 0.95 V in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3] = 0.02$ M/2.0 M. Only some $LaCoO_3$ perovskite diffraction peaks appeared with heat treatment at temperatures higher than about 500 °C, while no diffraction peak was observed when the temperature of the heat treatment was lower than 400 °C. It is worth noting that $LaCoO_3$ perovskite is formed by heat treatment even at temperatures as low as 500 °C (Figure 8), since a temperature higher than about 900 °C for heat treatment, in general, is necessary for the crystallization of $LaCoO_3$ perovskite using a ceramic technique. Consequently, the $LaCoO_3$ precursor with a composition of $Co_2O_3{\cdot}2La(NO_3)_3{\cdot}3H_2O$, is very suitable as a starting material in the preparation of $LaCoO_3$ perovskite. The reactions 4–6 will proceed during the heat-treatment, where

$$Co_2O_3{\cdot}2La(NO_3)_3{\cdot}3H_2O \xrightarrow{<200\ ^\circ C} Co_2O_3{\cdot}2La(NO_3)_3 + 3H_2O \quad (4)$$

$$Co_2O_3{\cdot}2La(NO_3)_3 \xrightarrow{250\text{–}500\ ^\circ C} 2LaCoO_3 + 6NO_2 + 1.5O_2 \quad (5)$$

$$LaCoO_3 \xrightarrow{>500\ ^\circ C} LaCoO_3 \text{ perovskite (crystallization)} \quad (6)$$

$LaCoO_3$, produced by eq 5, is amorphous. Figure 9 shows SEM micrographs of the $LaCoO_3$ precursor (A) prepared at 0.95 V in the solution with $[Co(CH_3COO)_2]/[La(NO_3)_3] = 0.02$ M/2.0 M and $LaCoO_3$ perovskite (B) prepared by heat treatment at 1000 °C. The film thickness was about 1.5 μm and the grain size of the $LaCoO_3$ perovskite was in the range from 0.2 to 0.8 μm. Thus, a thin film of the $LaCoO_3$ perovskite was easily prepared by the present method, and its composition can be easily controlled by the applied potential. Therefore, the present method will be very useful for the preparation of the $LaCoO_3$ electrode in SOFC.

Registry No. $LaCoO_3$, 12016-86-3; $Co(CH_3COO)_2$, 71-48-7; $La(NO_3)_3$, 10099-59-9; $Co(NO_3)_2$, 10141-05-6; $CoSO_4$, 10124-43-3; $Co_2O_3{\cdot}2La(NO_3)_3{\cdot}3H_2O$, 138540-39-3; Co, 7440-48-4.

Contribution from the Department of Chemistry,
University of Florence, Florence, Italy

Gadolinium(III) Complexes with Pyridine-Substituted Nitronyl Nitroxide Radicals

Cristiano Benelli, Andrea Caneschi, Dante Gatteschi,* and Luca Pardi

Received July 24, 1991

Two compounds of formula $Gd(hfac)_3(NIToPy){\cdot}0.5C_7H_{16}$ (I) and $Gd(hfac)_3(NITpPy)$ (II), respectively, where hfac = hexafluoroacetylacetonate, NIToPy = 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl 3-oxide, and NITpPy = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl 3-oxide, have been synthesized. Compound I crystallizes in the monoclinic space group $P2_1/n$ with $a = 1642.4$ (4) pm, $b = 1300.8$ (8) pm, $c = 2089.4$ (4) pm, $\beta = 109.85$ (2)°, $Z = 4$, $R = 0.0668$, and $R_w = 0.0711$. The structure consists of isolated molecules where the nitronyl nitroxide radical acts as a bidentate ligand toward gadolinium(III) through the nitrogen atom of the pyridine ring and the oxygen atom of the N–O group. Compound II crystallizes in the monoclinic space group $P2_1/n$ with $a = 1709.9$ (4) pm, $b = 1222.2$ (6) pm, $c = 1850.2$ (5) pm, $\beta = 93.01$ (2)°, $Z = 4$, $R = 0.0432$, and $R_w = 0.0464$. In the solid state a NITpPy molecule is bound through the pyridine nitrogen to a $Gd(hfac)_3$ molecule and through the oxygen of the N–O group to gadolinium(III) of another asymmetric unit. In this way molecules are formed where two gadolinium(III) and two nitronyl nitroxide radicals are present. The magnetic properties of both the complexes were studied by measuring their magnetic susceptibilities at various temperatures in the 1.6–300 K range. The analysis of these data showed that a ferromagnetic coupling between the lanthanide ion and the radical is always present. This result is discussed on the basis of magnetic exchange through a spin polarization mechanism.

Introduction

Recently several compounds in which gadolinium(III) is bound to paramagnetic ligands have been reported. These can be either nitronyl nitroxide radicals[1–5] or copper(II) complexes,[6–9] but in every case a weak ferromagnetic coupling between gadolinium(III) and the other paramagnetic center has been observed. The model which has been suggested in order to justify the preferred parallel

---

(1) Benelli, C.; Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 913.
(2) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P.; Shum, D. P.; Carlin, R. L. *Inorg. Chem.* **1989**, *28*, 272.
(3) Benelli, C.; Caneschi, A. Gatteschi, D.; Guillou, O.; Pardi, L.; Rey, P. *Inorg. Chim. Acta* **1989**, *160*, 1.
(4) Benelli, C.; Caneschi, A.; Fabretti, A. C.; Gatteschi, D.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 4153.
(5) Benelli, C.; Caneschi, A.; Gatteschi, D.; Pardi, L.; Rey, P. *Inorg. Chem.* **1990**, *29*, 4223.
(6) Bencini, A.; Benelli, C.; Caneschi, A.; Carlin, R. L.; Dei, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 8128.
(7) Bencini, A.; Benelli, C.; Caneschi, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 572.
(8) Carlin, R. L.; Vaziri, M.; Benelli, C.; Gatteschi, D. *Solid State Commun.* **1988**, *66*, 79.
(9) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750.

0020-1669/92/1331-0741$03.00/0